DECEMBER, 1929. Vol. LIV., No. 645.

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. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—Noel Lionel Allport, A.I.C., James Gilbert Lunt, B.Sc., A.I.C., Fred Morris, F.I.C., Albert William Peters, Juda Hirsch Quastel, D.Sc., Ph.D., A.R.C.S., A.I.C., and Joseph Harold Totton, B.A., B.Sc., F.I.C.

Certificates were read for the second time in favour of:—Alfred George Avent, A.I.C., William Rhys Davies, F.I.C., Ernest Roadley Dovey, A.R.C.Sc., F.I.C., James Gray, F.I.C., James Henderson, B.Sc., A.I.C., Claude Alexander Scarlett, B.Sc., A.K.C., A.I.C., Percy Arthur William Self, B.Sc., F.I.C., Thomas Brooks Smith, B.Sc., A.R.C.S.

The following were elected Members of the Society:—John William Haigh Johnson, M.Sc., F.I.C., Mamie Olliver, B.Sc., A.I.C., and George Edw. Shaw, B.Sc.

The following papers were read and discussed:—"The Grouping of Fatty Oils with Special Reference to Olive Oil," by E. R. Bolton, F.I.C., and K. A. Williams, B.Sc., A.I.C.; "The Heat-Resistance Curve: A New Bacteriological Test for Pasteurised Food," by Cuthbert Dukes, M.D., M.Sc., D.P.H.; and "A New Borax Solubility Test for Lactic Acid or Natural Sour Casein," by W. R. Mummery, F.I.C., and F. Bishop.

Death.

WITH deep regret we record the death, on November 13th, of Dr. Samuel Rideal, a Past-President of the Society. An obituary notice will be published in a subsequent issue.

The Chemical Examination of Furs in Relation to Dermatitis.

BY H. E. COX, M.Sc., Ph.D., F.I.C.

(*Read at the Meeting, October* 2, 1929.)

CASES of dermatitis, attributed to the wearing of dyed furs, have occurred with increasing frequency during the last few years; many, perhaps most, have been well authenticated, and the clinical diagnosis certain, but in others, although the dermatitis may be beyond question, it is open to doubt whether it has originated from the action of anything toxic in the fur. There is now quite a considerable literature on fur dermatitis, but, so far as I am aware, there is little published information on the analytical side; and some of the statements bearing on this aspect of the matter are not in agreement with my observations, which are based on the examination of quite a large number of furs alleged to have caused the disease.

Two medical papers dealing with the causes and symptoms of fur dermatitis are of particular interest: Dr. Prosser White's (*Trans. Lond. Dermat. Soc.*, 1923, p. 41), and Dr. Parson's Report to the Minister of Health (No. 27 of 1924); the latter has a bibliography up to the year 1924. Briefly put, the cause of dermatitis with which we are concerned is the presence in or on the fur of active chemical substances used in the dyeing process; these may remain as the result of incomplete oxidation in the dye-forming stage or incomplete washing afterwards. Arsenic, lime and various inorganic substances used in preparing the skins have been known to occasion disease to workers in the factories, although there appear to be no recorded cases in which dermatitis to the wearer has been traced to such substances. The possibility of such action needs to be borne in mind in the examination of a fur if it is found not to have been dyed, or is one which yields no reaction for the organic compounds usually concerned.

DYEING PROCESSES.—These organic compounds are the irritant dyes or intermediates used in dyeing fur by oxidation or developing processes in which the

pigment is produced in or on the fur by immersion in a bath containing the intermediates, with hydrogen peroxide, potassium chlorate, dichromate or vanadium compounds as oxidising agents. Alternatively, the colouring may be effected by brushing the ends of the fibres with the appropriate solutions; this method is useful where it is desired to tint the hair rather than dye the whole skin. More recently all kinds of finished dyes, acid, basic and chrome, have been employed, and the use of vat dyes has lately been advocated. Such dyes are not so likely to be irritant to the skin as are those dependent on development by oxidation on the fur. It is not always easy to say whether a fur has been dyed, and careful examination must be made of the hairs and of the skin as a whole, for it sometimes happens that only part of the fur on a collar or other garment has been dyed, or that it has been dyed in stripes with different substances; and sometimes in a coat made up from pieces of small skins, some of the pieces are heavily dyed and contain the irritant substances, whilst other pieces do not. Clearly, one is mainly interested in those parts of the fur which would come in contact with the face, neck or wrists of the wearer.

CHARACTERISTICS OF FURS.—It is useful to examine the specimen both macroscopically and microscopically to determine if possible what kind of fur it really is, and whether it has been dyed. The most common is the rabbit, which appears under a variety of names which do not suggest the genus Lepus. Illustrations of a few types are to be found in Mitchell and Prideaux's book, *Fibres Used in Textile and Allied Industries*, and in an article by the same authors in *Knowledge* (1910, **36**, 283). Verbal descriptions and even photographs are of limited utility for the identification of hairs of different mammals, but the following account may be given of some of those most frequently met.

The long fully-developed hairs of the fur are of the greatest diagnostic interest. It is curious that in nearly all furs there is a sort of substratum of short wool-like hair having but little medulla; these hairs do not present any marked differences in the different animals; so the long, fully developed, fibres should be examined, or an erroneous deduction may be made. The descriptions given apply to the fully developed hairs. It is possible that other animal hairs may present similar features, but I have not observed any, other than the rabbit and hare, which show the characteristic longitudinal marks found in rabbit fur.

Rabbit.—These are mainly small fibres about 2 cm. in length and 30–40 μ diameter. Some are as wide as 80 μ, and show 3, 4, 5, or 6 rows of medullary cells with well-defined longitudinal lines; the medullary cells in the larger hairs occupy almost the whole thickness. (Fig. 1.)

Hare.—These are similar to the rabbit hairs, but are longer and thicker. The hairs may be 3 cm. or more in length and 100 μ diameter, but show the characteristic medulla.

Cat.—These hairs are generally smaller than those of the rabbit; length about 2·5 cm. and width 15–35 μ. The medullary cells are rectangular and some

distance apart; they do not occupy the whole width as in the rabbit. The edge shows scales distinctly. (Fig. 2.)

Peschianiki (*Russian Cat*).—This fur differs materially from that of the ordinary cat. The fibres, though short and soft, are much thicker (about 100 μ in the largest), and the medulla occupies most of the width, and is composed of thin-walled cells compressed in concertina fashion; the appearance is not unlike the scales of a fish in the wider hairs. (Fig. 3.)

Opossum.—Large thick hairs, 3–5 cm. long and 50 to 80 μ wide. They are fairly uniform, and have a thick medullary layer occupying about half the width. The medullary cells are thick and distinct in outline. (Fig. 4.)

Skunk.—This shows hairs wider than the opossum, and with a very wide, ill-defined medulla, not showing definite cell walls; length 5 or 6 cm. The smaller hairs are much scaled, and generally there is more woolly hair at the base of the fur than with the opossum. (Fig. 5.)

Nutria (*Coypou or Otter*).—Short woolly fibres about 2 cm. long and 20–30 μ diameter, showing large scales but no medulla; fairly uniform. (Fig. 6.)

Sable (*Weasel*).—These are rather delicate hairs, though large. The width is up to 80 μ, with a wide dense medulla interlocked with cells showing scale-like markings. The small hairs show barbed scales at the edge. (Fig. 7.)

Fox.—The fur has long hairs (6 or 8 cm.) with bearded edges; the width is about 50 μ, and there is a dense thick-walled medulla occupying 80 per cent. of the width. (Fig. 8.)

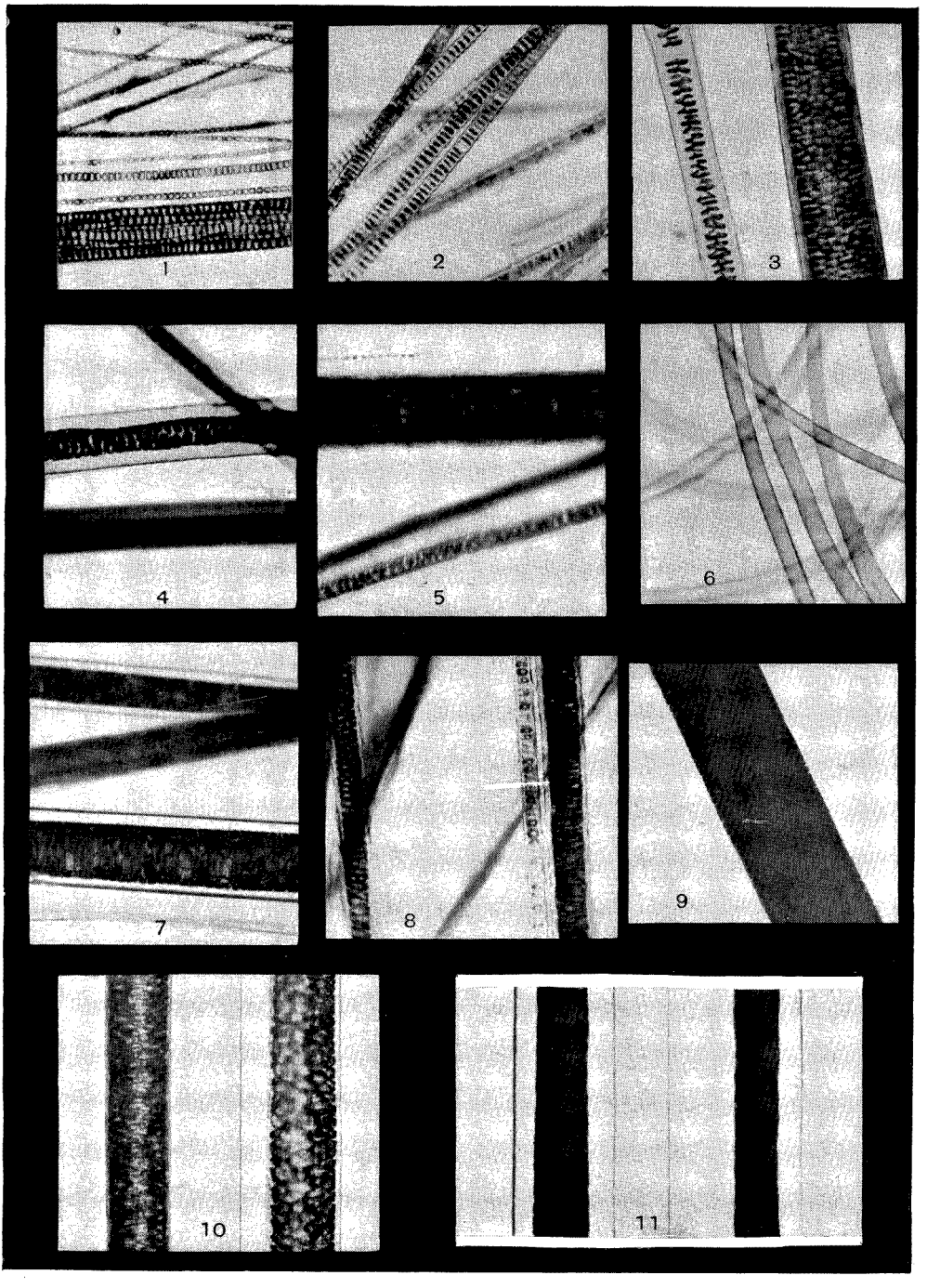
Goat.—The hairs are long and coarse and very dense; length up to 6 cm., and width 120 to 130 μ. The medulla is thick, occupying 75 per cent. of the width, and has a fishscale-like structure. (Fig. 9.)

Wallaby.—The hairs are about 3 cm. in length and 80 μ in diameter; well defined, dense medulla occupying nearly the whole width, irregularly arranged cells not overlapping, as do those of the weasel; smooth edges. (Fig. 10.)

Racoon.—The fur has long coarse hairs, 5 or 6 cm. by 120 μ; very dense medulla, 50 μ wide, with smooth edge and indefinite structure; the sheath of the hair is smooth and transparent, showing no scales. (Fig. 11.)

COMMON IRRITANT DYESTUFFS.—While the number of dyestuffs or intermediates which may be applied to furs is quite large, the following is a list of the more common and possibly irritant ones:—(1) meta-phenylene diamine; (2) para-phenylene-diamine; (3) toluylene-diamine 1:2:4; (4) toluylene-diamine 1:3:4; (5) toluidine *o*-, *m*- and *p*-; (6) pyrogallol; (7) quinone; (8) hydroquinone; (9) para-aminophenol (ursol P.); (10) di-aminophenol (amidol); (11) para-methyl-aminophenol (metol); (12) di-amino-diphenylamine. It is my purpose to describe tests which are available for these substances in dilute solution. The list is not

TYPES OF FIBRES IN FURS.



1 Rabbit. 2 Cat. 3 Russian Cat. 4 Opossum. 5 Skunk.
6 Coypou. 7 Sable 8 Fox. 9 Goat.
10 Wallaby (two parts of the same fibre).
11 Racoon (two parts of the same fibre).
(*All multiplied 120 diameters.*)

exhaustive but it is readily demonstrable by physiological experiment that all, except No. 5, are definitely irritant to the skin. Nos. 1, 2, 3 and 6 are, in my experience, the most common, and, of these, para-phenylene-diamine is perhaps the most frequently met with, and the most toxic. With regard to toluidine, I do not think it likely that it is irritant in small quantity to the normal skin, and certainly, when applied to my own arm, it did not produce any inflammation in 24 hours, although para-phenylene-diamine does so in an hour or two, and diamino-phenol raises blisters which persist for days. It sometimes happens that two of these substances may be present in the same fur, as in the case of one (exhibit) showing stripes of brown and black, due to pyrogallol and *m*-phenylene respectively. Methoxy and ethoxy groups may be associated with para-phenylene-diamine, and naphthalene-diamines are a possibility.

All these substances are strong reducing agents and reduce silver nitrate; several are known as photographic developers, some of which cause irritation and blisters on the fingers of persons with sensitive skins. They also reduce Fehling's solution, with the production of various colours, but these colours are not sufficiently constant for diagnostic purposes, being much influenced by concentration and by other substances which may be extracted from the fur.

IDENTIFICATION REACTIONS.—The following reactions all apply to aqueous solutions in concentration 1 in 10,000; they are distinctly visible at this concentration, and many of them at 1 in 100,000, some even at greater dilutions, especially if viewed in column in Nessler glasses. They are sufficient for the identification of the substances named, though I cannot state definitely that the colours are absolutely specific in all cases. It is needful to confirm the reactions and not take one test as conclusive; thus the yellow colour with sodium nitrite is given by several other substances besides the commonest one—meta-phenylene-diamine; and, of course, there may be a mixture of two or more substances which will complicate the reactions. Care must be taken not to add too much reagent, especially when testing very dilute solutions. In the case of test (4) it is important that the solution should not contain any free acid, or chlorine may be liberated and a different reaction obtained; the solution should be neutral or very slightly alkaline, and large excess of hypochlorite must be avoided, or the colour may be bleached. This test is not equally valuable in all cases; for example, the difference between the brownish-pink given by meta-phenylene-diamine or 1:2:4 *m*-toluylene diamine and the violet-blue of para-phenylene-diamine and 1:3:4 meta-toluylene diamine is distinctive, but, though the three toluidines give different colours when pure, it is not practicable to distinguish them in very dilute solution as extracted from fur.

In test (5) the solution should be distinctly acid with hydrochloric acid; this reagent, which is the familiar indole reagent of the bacteriologist, serves to distinguish *p*-phenylene-diamine from meta-toluene-diamine. In No. 6 about 2 drops of ferric chloride solution should be added to the neutral or faintly acid

liquor, then hydrogen sulphide water, 1 c.c. at a time; a large excess may mask the colour or liberate sulphur.

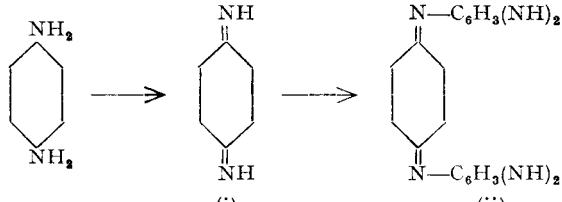
The reduction of Fehling's solution in the cold refers to the effect observed on adding 3 or 4 drops of mixed Fehling solution to 5 c.c. of the solution to be tested, not to the reverse addition of a little of the solution to be tested to a relatively large volume of the Fehling solution. It is generally advisable to use boiled cooled distilled water to eliminate oxidation as far as possible, and the solutions should be fairly fresh.

	Meta-phenylene-diamine.	Para-phenylene-diamine.	1:2:4-Meta-toluylene-diamine.	1:3:4-Meta-toluylene-diamine.	Para-amino-phenol.	Para-amino-diphenyla-mine.
	—	—	—	—	—	—
1. Dilute sodium nitrite added to cold acidified solution.	Intense brownish yellow	Slight* brown colour (fades)	Orange colour	Brownish pink	Slightly yellow	Red
2. Excess of alkaline solution of β-naphthol added to (1).	Reddish-brown colour	Brownish colour	Intense red	Dirty yellow or brown	Fluorescent green afterwards turning brown	Yellow or brown
3. Bromine water.	Slight white ppt.	Nil	Nil	Very faint ppt.	Nil	Brownish precipitat
4. Phenol (5 per cent. solution) and 2 drops of sodium hypochlorite added to neutral solution.	Pink	Violet blue	Pink	Violet	Blue	Yellow colour
5. Alcoholic solution of *p*-dimethyl-amino-benzaldehyde added to acidified solution.	Bright yellow	Red	Yellow	Yellow	Yellow	Faint yellow
6. Ferric chloride.	Nil	Violet	Nil	Violet	Nil	Reddish violet
7. Hydrogen sulphide water added to (6).	Nil	Intense violet	Nil	Claret colour	Violet	Brick-red colour
		The dimethyl compound gives similar reactions but a blue colour with $FeCl_3$ and H_2S. Both give a pink colour with potassium cyanide.	Reduces Fehling's solution in the cold			Violet colour with quinone

* As this cannot be a real diazo compound, it is probably an oxidation reaction.

	o-, *m*-, *p*-toluidine.	2:4 Diamino-phenol.	Methyl-*p*-amino-phenol.	Quinone.	Hydro-quinone.	Pyro-gallol.
	—	—	—	—	—	—
1. Dilute sodium nitrite added to acidified solution.	Nil	Bright red	Faint yellow	Nil[1]	Faint yellow	Nil
2. Excess of alkaline naphthol added to (1).	Bright red colour or ppt.	Brown colour	Slightly brown	Slight reddish colour	Red colour	Nil
3. Bromine water.	White ppt.	White ppt.	Nil	Nil	Nil	Nil
4. Phenol (5 per cent. solution) and 2 drops of sodium hypochlorite added to neutral solution.	Brown at first, *o*- and *m*- subsequently become blue	Red colour	Blue-violet develops slowly	Nil	Nil	Brownish
5. Alcoholic solution of *p*-dimethyl-amino-benzaldehyde (acidified).	Greenish yellow	Yellow	Nil	Slight yellow	Slight yellow	Slight yellow
6. Ferric chloride.	Nil	Nil	Nil, but turns green on adding H_2S	Nil	Nil	Reddish, turning greenish-black
7. Mercuric acetate solution.	Nil	Purple colour	No colour (very slight pink on standing)	Pale yellow with mercuric sulphate	Nil	Yellowish
8. Potassium cyanide solution.	Nil	Greenish blue	Yellow slowly develops	Brownish Reduces Fehling's solution cold. Gives purple-black colour with ammoniacal copper chloride, also violet colour with *p*-amino-diphenylamine	Yellow	Pink Gallic acid gives bright red with mercuric acetate

OXIDATION PRODUCTS.—The chemistry of the oxidation of these substances is obscure, and the composition of the final products appears to be unknown. Para-phenylene-diamine is of particular interest in this connection, because of the intermediate compounds formed during its oxidation and their possible toxicity. It seems certain that the first stage (according to Prof. Perkin) is the formation of quinone di-imide (i), and the second Bandrowski's base (ii) thus:



(i) (ii)

Some controversy centres round this substance. Gordon (*Trans. Med.-Legal Soc.*, **1926, 20, 73**) shows that it is non-irritant and expresses the opinion that it is the proper end-product in fur dyeing. This seems to be open to question, as, although the constitution of finished black or brown (in its many forms) is not settled, it is clear that it has at least 8 rings, and that Bandrowski's base is not the final product, nor is it a fast colour. Gordon attributes the irritant properties of fur dyed with para-phenylene-diamine to a substance which he calls "A", the constitution of which is not stated, but which gives a coloured solution with water, whereas the base B. is insoluble; it would appear that A. is the di-imide. He identifies A. by spectroscopic comparison. In my observation of these dyes and their intermediate products there is only a general absorption visible spectroscopically, not a specific one, so that one cannot differentiate with certainty the colour due to A. from that of other (possibly similar) bodies, or even some finished dyes. It may further be remarked that Bandrowski's base is easily reduced to the form of a leuco compound (*Ber.*, 1894, **27**, 482), so that it may, in appropriate circumstances, be an indirect cause of irritation. In my experience, Bandrowski's base is always associated with some partially oxidised para-phenylene-diamine, which can be detected by the reactions given.

EXTRACTION OF THE FUR FOR THE TESTS.—For the application of these tests extracts from the fur must be prepared; this may be done by cutting the fur from the skin as closely as possible (sometimes it is desirable to soak the skin also), de-fatting with petroleum spirit, then extracting with (1) cooled boiled water, (2) dilute (1 per cent.) acetic acid for at least 24 hours. All the solutions should be preserved from atmospheric oxidation as much as possible. The petroleum spirit should be shaken with acidified water to extract from it any bases. The object of using weak acetic acid is to simulate the action of perspiration, which in contact with the fur may be an agency in setting up the irritation. Some furs which are easily wetted may be soaked without de-fatting.

The extract so prepared should be tested for inorganic substances and for acids, as well as for dyestuffs or intermediates. Well-dyed furs yield no colour when so treated, other than a trace of dirt; those containing diamines are usually of a distinct brown or pink colour, which is an unfavourable sign. Decolorisation of the extract with charcoal is inadvisable, as it may remove traces of the important substances.

It is interesting to make an approximate estimate of the amount of any substance detected in the extract; this can be done colorimetrically by comparison with known solutions, using the same volumes of reagents. The question of what quantity is deleterious is beyond the scope of this paper. The worst case in my observation contained about 20 mgrms. of para-phenylene-diamine in 1 grm. of fur (including the skin), which was equivalent to an area of about 6 square inches: usually very much less is found, and sometimes a trace so small that it is open to doubt whether it could possibly cause dermatitis to a normal person, and in such

cases practical physiological test, in the manner described by Dr. Gordon, is particularly valuable.

I wish to thank Mr. T. J. Ward for kindly preparing the photo-micrographs for me.

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11, BILLITER SQUARE,
LONDON, E.C.3.

DISCUSSION.

The PRESIDENT said that this matter had been before chemists for a good many years, and this was the first systematic attempt they had had to deal with the problem (and, he thought, the first mention in THE ANALYST). The Society was very much indebted to Dr. Cox for the work and the information he had given them. It was a strange thing, seeing how largely articles of clothing were dyed, that this trouble occurred only with fur; he presumed there were particular difficulties in the dyeing of fur. He was sorry that Dr. Gordon could not be present, as he was particularly interested in this subject. He thought that Dr. Gordon's spectroscopic tests had been done on what he (Dr. Gordon) described as "Material A," and not on "Material B."

Dr. ROCHE LYNCH referred to a case he had seen of a substance for tinting eyebrows and eyelashes, which had caused intense dermatitis. He regarded the main issue as being the fact that one could prove that any one of this group of substances was present (not necessarily identify it); to be able to extract it was practically to condemn a fur in a case of dermatitis. Dr. Cox had suggested that possibly the size of the individual fibres might cause irritation, and Dr. Roche Lynch would suggest that the one most likely to produce that effect was fox; it had been clearly pointed out that these hairs had very large natural spines. He asked whether the same group of substances was used in dyeing serges and cloth, and, if so, whether the author had come across any cases of irritation caused through black serge or black cloth. If not, there must be two factors—one dye and one the actual fibre of the fur.

Mr. W. PARTRIDGE pointed out that references to papers on the subject by Semon, Roxburgh and Castle had appeared in THE ANALYST for 1923 (pages 282, 283 and 284, respectively). He referred to cases where mineral substances, notably chromium compounds and also salt, had been the causes of dermatitis from furs.

Mr. F. W. F. ARNAUD said that the paper was of very great importance, because, from time to time, chemists were called upon to examine furs alleged to have caused dermatitis. It was probably well known that some people suffered from severe irritation from the mere presence of flannel next to the skin. He enquired whether Dr. Cox had tried any method of concentrating the intermediates, because, if this were possible, the reactions would be more marked and differentiation of injurious substances would be easier. He referred to a case where a dog suffered from dermatitis round the neck, which was found to have been caused by a collar made of chrome leather.

Mr. R. L. COLLETT said that it was possible to identify a number of animals by the surface of the skin and the arrangement of the hair follicles in it—he instanced goat. It would be very interesting to see whether these fur-bearing animals had any particular arrangement of the follicles. Dr. Roche Lynch had

pointed out the possibility of the fibre itself being an irritant. The hairs, for instance, of the wild boar which was used in brush-making had a distinct serrated surface. Hair was not an absolutely inert substance, and he thought that in all these examinations of hair one should bear in mind that it was possible that substances were being extracted from the hair itself which might have an important bearing on the results.

Dr. C. A. MITCHELL agreed with the caution given by Dr. Cox, when he pointed out that more than one type of hair might occur in a fur. Fibres ranging from the woolly type to the characteristic hair type were common in the fur of most animals, and good examples of both types could be found in the coat of the Bedlington terrier. He suggested that the osmium tetroxide reaction for pyrogallol, which he (the speaker) had devised and adapted to quantitative purposes (ANALYST, 1924, **49**, 162) might be of service in determining pyrogallol in the very dilute extracts from dyed furs. In one instance where a claim had been made he had found that the extract from the fur gave a coloration which corresponded with 1 part of *m*-phenylene-diamine in 20,000 parts of the pelt. This claim was settled out of court.

Dr. J. T. DUNN congratulated Dr. Cox. He said that he had had very little experience himself of fur dermatitis. In one or two cases, however, he had found that dermatitis was not due to dye at all, but to potassium chromate.

Mr. C. E. SAGE said that these analytical tests required very careful consideration. With regard to the cause of dermatitis, he did not know that chemists had anything more to do than to express personal opinions. He then referred to the fact that some people possessed exceedingly sensitive skins which were affected where others were not, and illustrated this with examples from his own experience.

Prof. J. T. HEWITT (in a written communication) said that it seemed that there was no case for the actual dyeing of fur by Bandrowski's base; the oxidation was carried out on the fibre, and there was nothing to show that the fur itself did not also take part in the reaction. He thought that a pigment of the aniline-black type was probably present, and referred to papers by Erdmann (*Ber.*, 1904, **37**, 2776, 2906) and by Heiduschka (*Arch Pharm.*, 1916, **254**, 584), showing that the oxidation of *p*-phenylene-diamine gave different results according to the oxidising agent employed.

Dr. Cox, replying, said that, having no experience of the practice of dyeing cloth, he could not answer the questions on this point. With regard to irritation due to non-dyed furs, he thought that when these cases come to the analyst they were usually in relation to a claim for money; if there was nothing improper or irritant on the fur, it did not seem reasonable that the vendor or merchant should be called upon to pay because a wearer happened to have super-sensitive skin. If, however, a known toxic substance could be identified it would be difficult to avoid liability.

It appeared to be necessary to dye furs in alkaline or half-alkaline* solution, because acid or acid liberated from hydrochlorides tended to rot the fibres. He had tried to concentrate the solutions of extract from the fur, but found that oxidation took place, which might spoil the tests. In reply to Mr. Hinks, he found that the absorption spectrum (at least in the visible region) of the substance A and of most of the intermediates was general not specific, and was not of much diagnostic value.

* *I.e.*, with one of the HCl groups of the hydrochloride neutralised.)

ADDENDUM BY DR. KNYVETT GORDON.

My own contributions to the subject are summarised in a paper read before the Medico-Legal Society in March, 1926. Prior to this, I had described in March, 1924 (*Medical Press and Circular*, March 26th, 1924) some experimental work on the effect of certain dyes on human skin, and the report of the Ministry of Health was issued in September of the same year, but contained no reference to these experiments.

The Ministry attributed the deleterious effects of certain furs in regard to dermatitis to Bandrowski's base, but I had previously shown, by cutaneous tests (in the papers referred to), that this substance was neither poisonous nor irritating. I have frequently applied it in the fresh state to scarified human skin without any visible or sensory effect whatever.

On the other hand, the soluble intermediate oxidation products of para- and meta-phenylene-diamine are highly irritating, and I think there can be no doubt that it is to them, and not to the insoluble Bandrowski's base, that fur dermatitis is due. Inasmuch as careful washing of the fur suffices to remove these intermediate products, their presence is rightly held by the Courts to justify a claim for negligence.

I regard this contribution to our knowledge of microscopy of the various furs and the chemical tests for dyes therein as of great value; but when one is asked to decide as to whether a claim against a fur, for having given rise to dermatitis in the human subject, is justified or not, it is mainly to tests on the skin that one should turn. These, however, require careful control on the lines which I endeavoured to indicate in my paper to the Medico-Legal Society.

Dr. Cox has done much service in enlarging the list of dyes which might be incriminated in any given case, and it will now be advisable to apply the physiological test to these; but, from the practical point of view, the points that come into Court are:

(1) Whether the patient is suffering from true fur dermatitis or one of the diseases which closely simulate it;

(2) Whether the patient has a natural idiosyncrasy with regard to rabbit or whatever the natural fur may be;

(3) Whether the incriminated fur does, or does not, cause irritation or inflammation of a normal human skin when tested by the appropriate methods.

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates.

XVI. Observations on Tartaric Hydrolysis.

XVII. The Quantitative Precipitation of the Earth Acids and certain other Oxides from Tartrate Solution.

By W. R. SCHOELLER, Ph.D., and H. W. WEBB.

(*Work done under the Analytical Investigation Scheme.*)

(*Read at the Meeting, October* 2, 1929.)

XVI. OBSERVATIONS ON TARTARIC HYDROLYSIS.

This Section continues the work recorded in Section I (Analyst, 1922, **47**, 93) and IX, Part II (*id.* 1927, **52**, 633). In the former, a forecast is given of a scheme for the analysis of earth-acid minerals, in which the initial hydrolysis is avoided by solution of the pyrosulphate melt in tartaric acid solution; in the latter, it is shown that the tartaric solution of the earth acids undergoes hydrolytic precipitation when boiled with excess of nitric or hydrochloric acid ("tartaric hydrolysis"). The precipitate is purer than that formed in the customary pyrosulphate hydrolysis (XII, Analyst, 1928, **53**, 474), an approximate separation of the earth acids from titania being the most obvious advantage of the new process. In this Section, we submit a study of the quantitative course of the tartaric hydrolysis of the earth acids in presence of some of their mineral associates, the data being considered necessary in view of the likely application of the procedure in the proposed scheme of mineral analysis. When this is carried out as planned in Section I, the tartaric solution of the earth acids, freed from certain elements, may still contain "tungsten, titanium, and zirconium; rare-earth metals and thorium; aluminium, glucinum, manganese, calcium, and magnesium." The deportment of most of these elements in the tartaric hydrolysis is described below.

A. Earth-Acid Recovery not quite Quantitative.—The recovery of the earth acids from tartrate solutions has already been illustrated in Table V, Section IX (*loc. cit.*); a small positive error, for which we have no satisfactory explanation, was observed in the two tantalum experiments Nos. 1 and 3. Such positive errors have never recurred in subsequent work; in a typical experiment, 0·2003 grm. of Ta_2O_5 gave a precipitate weighing 0·1985 grm. We are satisfied that the recovery of the earth acids is never quite complete.

Two additional tests were made with small amounts of the pentoxides, which were fused with bisulphate and precipitated from tartrate solution by 15 minutes' boiling with 30 c.c. of hydrochloric acid in a bulk of 200 c.c.:

Exp.	Taken.	*HP.*	Error.	Ppt. formed:
2	Ta_2O_5 0·0110 grm.	0·0100	−0·0010	after 1 minute's boiling
3	Nb_2O_5 0·0111 grm.	0·0104	−0·0007	at once

It may be stated here, in view of our contemplated work on the separation of the earth acids from the rare earths (*cf.* Pied, ANALYST, 1925, **50**, 36), that hydrolytic precipitation of the earth acids from oxalo-tartaric solution is quite incomplete; hence tartaric hydrolysis cannot be applied to solutions containing also oxalic acid. In Exps. 4 and 5, one grm. of ammonium oxalate was added, and the tartaric solutions boiled as usual with 30 c.c. of nitric acid:

Exp.	Taken.	*HP.*	Ppt. formed:
	Grm.	Grm.	
4	M_2O_5 0·2025	0·1117	very
5	do. 0·2060	0·1289	gradually

The use of hydrochloric (instead of nitric) acid as an alternative precipitating agent was tried in practically all the tests here recorded, because hydrochloric acid may be almost completely removed from the hydrolysis filtrate by evaporation, without destruction of the tartaric acid; with nitric acid this is not feasible. Nitric acid has the disadvantage that it destroys cupferron, a reagent likely to be used in subsequent work (*vide infra*, Sect. XVII).

B. TUNGSTEN AND EARTH ACIDS.—The similarity in the behaviour of tartaric solutions of tungsten, tantalum, and niobium towards nitric acid is brought out in Exps. 6 to 9. The tungsten precipitate is yellow and filters well. When hydrochloric acid is used, the precipitation is incomplete at higher, and may not take place at all at lower, concentrations (Exps. 10 and 11):

Exp.	Taken.	Precipitant.	*HP.*
	Grm.		Grm.
6	WO_3 0·1000	30 c.c. HNO_3	0·0952
7	,, 0·1000	do. do.	0·0958
8	,, 0·1000	do. do.	0·0934
9	,, 0·1036 + M_2O_5 0·2045	do. do.	0·3000
10	WO_3 0·1000	30 c.c. HCl	no ppt.
11[1]	,, 0·3218	35 c.c. do.	0·2808

[1] 0·5 grm. of wolframite (64·36 per cent. WO_3 by *aqua regia* method) fused with bisulphate; melt dissolved in tartaric acid; boiled with HCl.

C. TITANIA AND EARTH ACIDS.—As stated in the preamble, an approximate separation from titania is achieved by the procedure. Nitric acid having been used as the precipitant in the earlier investigation (IX, *loc. cit.*, Table VI), two supplementary experiments were carried out in which precipitation was effected by 5 minutes' boiling with 30 c.c. of hydrochloric acid in a total bulk of 300 c.c. When the combined filtrates from P^1 and P^2 are boiled down sufficiently, a small additional earth-acid precipitate, P^3, is formed; this is filtered off before

the complete expulsion of the hydrochloric acid; otherwise it re-dissolves in the residual strong tartaric acid solution:

Exp.	M_2O_5 taken. Grm.	TiO_2 added. Grm.	HP^1. Grm.	HP^1 re-treated. Grm.	TiO_2 in. Grm.	M_2O_5 by difference. Grm.
Ta 12	0·1114	0·1128	0·1241	P^2: 0·1076 P^3: 0·0067	P^2: 0·0052 P^3: 0·0006	P^2: 0·1024 P^3: 0·0061
Nb 13	0·1110	0·1141	0·1381	P^2: 0·1151 P^3: 0·0028	P^2: 0·0145 P^3: 0·0002	P^2: 0·1006 P^3: 0·0026

It is seen that the separation of titanium from tantalum is more satisfactory than that from niobium; in Exp. 12, re-treatment of P^{2+3} yielded P^4, weighing 0·0928 grm. and containing only 0·0010 grm. TiO_2.

D. ZIRCONIA AND EARTH ACIDS.—Mixtures of the pentoxides and zirconia, after bisulphate fusion, were hydrolysed in solutions containing 3 grms. of tartaric acid, both by nitric and by hydrochloric acid; the precipitate, *HP*, was collected, washed with acidulated water, ignited, and weighed:

	Precipitant: 30 c.c. HNO_3.					Precipitant: 30 c.c. HCl.			
Exp.	Taken Ta_2O_5. Grm.	Added ZrO_2. Grm.	*HP*. Grm.	Error. Grm.	Exp.	Taken Ta_2O_5. Grm.	Added ZrO_2. Grm.	*HP*. Grm.	Error. Grm.
14	0·1009	0·0117	0·1034	+0·0025	28	0·1026	0·0123	0·1013	−0·0013
15	0·1017	0·0216	0·1040	+0·0023	29	0·1008	0·0211	0·0954	−0·0054
16	0·1008	0·0312	0·0955	−0·0053	30	0·1012	0·0314	0·0843	−0·0169
17	0·1012	0·0428	0·0856	−0·0156	31	0·1009	0·0408	0·0701	−0·0308
18	0·1030	0·0520	0·0775	−0·0255	32	0·1023	0·0519	0·0540	−0·0483
19	0·1006	0·0753	0·0584	−0·0422	33	0·1022	0·0753	0·0367	−0·0655
	Nb_2O_5					Nb_2O_5			
20	0·1020	0·0121	0·1008	−0·0012	34	0·1028	0·0109	0·0984	−0·0044
21	0·1014	0·0209	0·1018	+0·0004	35	0·1018	0·0211	0·0982	−0·0036
22	0·1014	0·0322	0·0996	−0·0018	36	0·1010	0·0331	0·0967	−0·0043
23	0·1028	0·0429	0·0984	−0·0044	37	0·1025	0·0440	0·0966	−0·0059
24	0·1016	0·0531	0·0980	−0·0036	38	0·1018	0·0590	0·0947	−0·0071
					39	0·1016	0·0750	0·0985	−0·0031
	M_2O_5					M_2O_5			
25	0·1037	0·0152	0·1072	+0·0035	40	0·1032	0·0142	0·1066	+0·0034
26	0·1009	0·0419	0·1070	+0·0061	41	0·1052	0·0453	0·1098	+0·0046
27	0·1018	0·0732	0·1018	0·0000	42	0·1056	0·0727	0·1002	−0·0054

The figures make it evident that the recovery of the tantalum decreases with an increase in the zirconia, whereas, curiously enough, the precipitation of the niobium is hardly thus affected; again, the mixed pentoxides used (61·4 Ta_2O_5: 38·6 Nb_2O_5) behaved like niobic oxide. The probability of the occlusion of zirconia in *HP* was next investigated; four of the precipitates, taken at random, were analysed by Method B, Section XIII (ANALYST, 1928, **53**, 518):

Exp.	Pentoxide taken. Grm.	Zirconia added. Grm.	*HP*. Grm.	ZrO_2 in *HP*. Grm.
15	Ta_2O_5 0·1017	0·0216	0·1040	0·0090
18	Ta_2O_5 0·1030	0·0520	0·0775	0·0112
23	Nb_2O_5 0·1028	0·0429	0·0984	0·0104
27	M_2O_5 0·1018	0·0732	0·1018	0·0206

These results leave no doubt in our mind that all the precipitates obtained must contain zirconia; hence the net earth-acid recovery errors are much larger than the apparent errors shown in the above Table. We conclude that zirconia creates a marked disturbance in the quantitative course of the reaction by inducing less complete earth-acid precipitation and by contaminating the hydrolysis precipitate.

E. Thoria (Rare Earths) and Earth Acids.—The very slight interference of thoria in tartaric hydrolysis, as compared to that of titania and zirconia, reflects the progressive change in chemical behaviour of the elements of Group IV. We conducted 8 tests with 1:1 mixtures of mixed pentoxides and thoria. It was observed in all cases that precipitation proceeded normally, but that a slight, permanent mistiness pervaded the solution after the precipitate had settled. The weighed *HP* was fused with bisulphate, the product dissolved in tartaric acid solution, and the unfiltered solution treated with oxalic acid. After several days' standing, the small precipitate was collected and weighed; being obviously impure, the precipitates from two tests were combined and re-treated, the thorium oxalate being re-precipitated from a very small bulk of filtered solution. For a confirmatory test, the purified thorium fractions were dissolved and tested with tannin in acetic solution, when they gave white (not orange) precipitates. Hence thoria is co-precipitated, but to a much smaller extent than titania and zirconia (see Exps. 43 to 46).

Two further tests (47 and 48) were made in exactly the same manner with a mixture of pentoxides and a preparation of ceria earths of unknown purity:

Exp.	M_2O_5 taken.	ThO_2 added.	Precipitant: 30 c.c. of	*HP*.	ThO_2 in *HP*: Impure.	Purified.
	Grm.	Grm.		Grm.	Grm.	
43	0·0988	0·0980	HNO_3	0·1022	0·0049	0·0047
44	0·1008	0·1024	HCl	0·0978	0·0018	
45	0·1023	0·1024	HNO_3	0·1046	0·0010	0·0013
46	0·1032	0·1016	HCl	0·0976	0·0023	
		Ce_2O_3			Ce_2O_3 in *HP*:	
47	0·0974	0·100	HNO_3	0·0966	0·0009	doubtful
48	0·0954	0·100	HCl	0·0936	0·0014	

As far as the evidence goes, the rare earths do not appear to interfere in tartaric hydrolysis. When a supply of pure rare-earth preparations has been secured, it is intended to devote a special section to a study of the behaviour of the rare earths in the contemplated analytical scheme, and of their separation from the earth acids.

F. Alumina, Beryllia, Ferric and Manganous Oxides, and Earth Acids.—Alumina and beryllia could not be detected with certainty in *HP*, produced as described under E (Exps. 49 to 52). In Exps. 53 and 54, ferric oxide was traced in very small quantity in *HP* by means of sulphide precipitation from ammoniacal tartrate solution; it is quite likely, however, that part, at least, of this small amount was not present in the precipitate as weighed, but got introduced during the subsequent operations. Finally, the hydrolysis precipitates

obtained in presence of manganous oxide (Exps. 55 and 56) were tested by fusion with potassium carbonate and a little nitrate: no greenish tint, indicative of manganate, was observed.

Exp.	M_2O_5 taken.	Added.	Precipitant: 30 c.c. of	*HP*.	Purity of *HP*.
	Grm.	Grm.		Grm.	Grm.
49	0·1044	0·100 Al_2O_3	HNO_3	0·0988	0·0010[1] Al_2O_3
50	0·1048	0·100 do.	HCl	0·1020	0·0012[1] doubtful
51	0·1024	0·107 BeO	HNO_3	0·0986	0·0011[1] BeO
52	0·1010	0·107 do.	HCl	0·0982	0·0010[1] doubtful
53	0·2008	0·050 Fe_2O_3	HNO_3	0·1956	0·0010 Fe_2O_3
54	0·2016	0·050 do.	HCl	0·1972	0·0006 do.
55	0·0982	0·100 MnO	HNO_3	0·0958	MnO nil
56	0·0974	0·100 do.	HCl	0·0952	

[1] Weight of small ammonia precipitate obtained in filtrate from hydrolysis of pyrosulphate melt.

CONCLUSIONS.—The great value of the tartaric hydrolysis reaction in qualitative analysis has been proved in Section XV (ANALYST, 1929, **54**, 456). In the present paper, the quantitative course of the reaction has been elucidated.

(1) Towards nitric acid, tantalic, niobic, and tungstic acids react alike; their precipitation is complete but for a few mgrms., which remain dissolved as the result of what must be regarded as a balanced reaction.

(2) The separation of the earth acids from titania is far from perfect; but, used in conjunction with the oxalate and salicylate method (XIV, ANALYST, 1929, **54**, 322), tartaric hydrolysis forms the first step of the most reliable separation procedure known to us.

(3) The presence of zirconia in substantial amounts is a complicating factor. The fact that tantalic, unaccompanied by niobic, acid is very incompletely precipitated when much zirconia is present is not to be regarded as a very serious matter, because the two earth acids almost invariably occur together; rather is it the contamination of the tartaric hydrolysis precipitate with zirconia that will have to be borne in mind when the method is applied. Fortunately the new pyrosulphate and tannin method (XV, *loc. cit.*) promises to become an effective and simple means for purifying the earth-acid precipitate from zirconia and titania; the question will be investigated at an early date.

(4) Thoria contaminates the hydrolysis precipitate to such a small extent that its complete removal, by any process achieving that of zirconia and titania, may be regarded as a foregone conclusion.

(5) Still less than thoria do the common metals and beryllium interfere. Iron can, in any case, be removed, previous to tartaric hydrolysis, by precipitation of ferrous sulphide from ammoniacal solution. The influence of the rare earths is yet to be studied.

(6) Nitric or hydrochloric acid may be used as the precipitant; in presence of oxalic acid, the earth-acid recovery is incomplete.

(7) The greatest weakness of the method lies in incomplete earth-acid precipitation (mentioned under 1), and this can be overcome, as will be shown in Section XVII below, by the application of one of two methods, neither of which necessitates the previous destruction of the tartaric acid.

SUMMARY.—Precipitation of the earth acids from tartrate solution by mineral acid, previously shown to be a sensitive and specific earth-acid reaction, has now been investigated as a quantitative method. Precipitation of tantalic and niobic, also tungstic, acids is never quite quantitative; a few mgrms. escape precipitation. Of all the other mineral associates of the earth acids, only titanium and zirconium interfere to a certain extent with the normal course of the reaction. Means for obviating this interference will be studied; the recovery of the small fraction of non-precipitated earth acid from the tartrate solution will be discussed in the next Section.

XVII. THE QUANTITATIVE PRECIPITATION OF THE EARTH ACIDS AND CERTAIN OTHER OXIDES FROM TARTRATE SOLUTION.

In the preceding Section, the quantitative course of the tartaric hydrolysis reaction has been investigated, it being shown, *inter alia*, that a few mgrms. of the earth acids escape precipitation. In this Section it will be proved that two reagents ensure quantitative recovery of the earth acids from tartrate solution, namely, tannin and cupferron. That being so, it may be asked why one of the reagents should not be applied at once to the quantitative precipitation of the earth acids without an intervening hydrolytic precipitation of the main fraction. Our answer is, that we favour tartaric hydrolysis, supplemented by tannin or cupferron precipitation, because the tartaric hydrolysis reaction, being more specific, permits of a more selective precipitation, yielding a main earth-acid fraction containing practically the whole of the tungstic acid, with other oxides, if any, as impurities. The next step—tannin or cupferron precipitation—furnishes the balance of the earth acids, together with other oxides that are quantitatively precipitated, but neither reagent precipitates the tartaric complex of tungsten. In view of the indefiniteness of the precipitation reactions of the more important constituents of earth-acid minerals, it is quite clear that their analysis is bound to include processes of fractional enrichment leading up to the final precipitation of the purified oxides. Another advantage of the procedure we advocate is this, that the tartaric hydrolysis precipitates are compact compared with the cupferron and, still more, with the bulky tannin precipitates. The latter are very suitable for micro-work.

A. TANNIN PRECIPITATION.

This new method is a practical application of an observation recorded in Section XI (ANALYST, 1928, **53**, 265), namely, the precipitability of titania by tannin from neutralised tartrate solutions. In this paper the process is investigated at greater length, and extended to tantalum, niobium, zirconium, thorium, and aluminium.

EARTH ACIDS.—The quantitative precipitation of tantalum and niobium as tannin complexes from tartrate solutions presents no difficulties, as it takes place either in the neutralised solution or in moderately acid solution treated with alkali acetate. We proceed as follows: (1) The tartrate solution, containing 30 c.c. of hydrochloric acid (*i.e.* the filtrate from the tartaric hydrolysis) is titrated with ammonia (1:1), a bit of litmus paper in the liquid serving as indicator; the acid reaction is restored with a drop or two of dilute acid. The liquid is then boiled, and a fresh, strong solution of 0·5 grm. of tannin added; flocculation occurs after short boiling. (2) The same solution as in (1) is approximately neutralised with ammonia so as to remain slightly acid, boiled, and treated with excess of ammonium acetate and 0·5 grm. tannin, as before.

The precipitate from either procedure is collected, well washed with 2 per cent. ammonium chloride solution containing a little tannin, and ignited wet, finally at high temperature. The niobium precipitate is orange- to brownish-red, whilst the tantalum complex (which should be gale yellow) generally has a mauve hue, due to the presence of traces of iron.

RESULTS OF TEST ANALYSES.—The following remarks apply to all those tabulations below in which the weight of precipitate obtained (*P*) is given as "*gross*" and "*net*"; when the precipitation was quantitative, the result always gave a positive error, due to adsorption or, more probably, slightly incomplete washing out of alkali, and inclusion of a little silica and ferric oxide as unavoidable impurities. The weighed precipitates were therefore digested hot with acidulated water which was rendered ammoniacal, then filtered off, ignited, and again weighed; the precipitates were then fused with bisulphate, the product dissolved in tartaric acid, and the unfiltered solution made ammoniacal and treated with hydrogen sulphide. The small precipitate was collected, ignited, and weighed as (Fe_2O_3+SiO_2), and its weight subtracted from that of the leached precipitate, the difference giving the "*net*" weight.

The following results were obtained by working with "unknown" quantities; in Exps. 1 to 5 the precipitation was done in the neutralised liquid, in 6 to 8 in slightly acid acetate solution:

Exp.	Taken M_2O_5.	*P* Gross.	*P* Net.	Error.	Exp.	Taken.	*P* Gross.	*P* Net.	Error.
	Grm.	Grm.	Grm.	Grm.		Grm.	Grm.	Grm.	Grm.
Ta 1	0·0104	0·0107	0·0100	−0·0004	EA 9	ZrO_2 0·0257	0·0274	0·0255	−0·0002
Ta 2	0·0052	0·0061	0·0054	+0·0002	,, 10	,, 0·0257	0·0272	0·0255	−0·0002
Nb 3	0·0073	0·0084	0·0071	−0·0002	,, 11	,, 0·0263	0·0283	0·0265	+0·0002
EA 4	0·0038	0·0046	0·0033	−0·0005	,, 12	,, 0·0208	0·0234	0·0211	+0·0003
,, 5	0·0068	0·0087	0·0072	+0·0004	,, 13	TiO_2 0·0258	0·0280	0·0249	−0·0009
,, 6	0·0178	0·0205	0·0175	−0·0003	,, 14	,, 0·0228	0·0242	0·0221	−0·0007
,, 7	0·0054	0·0073	0·0052	−0·0002	,, 15	ThO_2 0·0210	0·0227	0·0209	−0·0001
,, 8	0·0102	0·0130	0·0099	−0·0003	,, 16	,, 0·0231	0·0246	0·0229	−0·0002
17	(0·0212 ZrO_2+0·0133 M_2O_5+0·0123 ThO_2)				=	0·0468	0·0492	0·0467	−0·0001
18	(0·0236 ZrO_2+0·0131 M_2O_5+0·0123 TiO_2)				=	0·0490	0·0518	0·0484	−0·0006

ZIRCONIA AND TITANIA.—When investigating the quantitative precipitation of zirconia by tannin, we at first obtained low and erratic results, which were

traced to incomplete precipitation even at low acid concentrations, as for titania (XI, *loc. cit.*). In oxalate solution the zirconium-tannin complex is likewise very sensitive to acid (XIII, ANALYST, 1928, **53**, 516). In the course of further work we elaborated the following procedure, which not only secures a quantitative precipitation of zirconia, but answers equally well for the earth acids, titania, thoria, and mixtures of these oxides.

PROCEDURE.—The filtrate from the tartaric hydrolysis precipitate (acidity, 30 c.c. of hydrochloric acid) is treated with 1 grm. of tannin in strong solution, cooled, and carefully titrated with ammonia (1:1). A long strip of wet litmus paper is made to adhere to the side of the beaker so that the lower extremity is immersed in the liquid; in this manner the progress of neutralisation is easily observed in spite of the formation of a voluminous precipitate. The liquid is barely re-acidified, *i.e.* to the violet tint of the indicator, and boiled for two minutes. The neutralisation must be carried out with precision; if this is done, the precipitation is quantitative, even though no acetate is added; but we include treatment of the solution with 5 grms. of ammonium acetate at this point, so as to provide for the possible formation of soluble complex beryllium acetate (*cf.* Moser and Niessner, ANALYST, 1928, **53**, 403). The precipitate is left to settle, collected, and treated and purified exactly as the earth-acid precipitates in Exps. 1 to 8. The results (Exps. 9 to 14) show that quantitative precipitation is achieved by the above procedure, the distinctive feature of which is addition of tannin before neutralisation. An excess of ammonia must be avoided, as it would lead to co-precipitation of divalent metals (*e.g.* beryllium, manganese); double precipitation may be required in the analysis of minerals.

THORIA; MIXED OXIDES.—The precautions required for the quantitative precipitation of zirconia can, apparently, be relaxed in the case of thoria, as this oxide is precipitated by tannin from approximately neutralised, boiling tartrate solutions on addition of ammonium acetate, as in the case of the earth acids; however, we used the procedure just described under zirconia, as it should be applied systematically to all unknown mixtures. The results for thoria and two ternary oxide mixtures are tabulated as Exps. 15 to 18.

ALUMINA.—The co-precipitation of the minute quantities of iron accidentally present in the above tests led us to infer that alumina also might be precipitated from tartrate solutions by the tannin reaction. Such is actually the case, alumina being quantitatively recovered by partial neutralisation and boiling with ammonium acetate and tannin, as described under Earth Acids; it is unnecessary to neutralise as closely as for zirconia.

This observation seems to us of analytical importance beyond the special subject of earth-acid analysis. The separation of small quantities of alumina from much iron is quite frequently required in ore analysis. Precipitation of the alumina by thiosulphate, or its conversion into soluble alkali aluminate, are processes of questionable value. Determination by difference, after volumetric determination of the iron in the weighed mixed oxides, is wrong in principle,

because the subordinate constituent should actually be determined. Precipitation of ferrous sulphide from ammoniacal tartrate solution is an accurate separation process, but the determination of the alumina in the filtrate by the usual methods necessitates destruction of the tartaric acid. Now the tannin method renders that manipulation unnecessary; after precipitating the iron as sulphide, we dilute the ammoniacal tartrate solution to a definite volume, and filter an aliquot portion. This saves time, as the washing of bulky ferrous sulphide precipitates is tedious; and, even if the amount of alumina is very small, part of the solution suffices, because the aluminium-tannin complex is exceedingly bulky; hence it is well suited for micro-work, but inconveniently large for more than 0·02 grm. of Al_2O_3.

The ammoniacal tartrate filtrate is acidified with acetic acid, and boiled till hydrogen sulphide is expelled; 5 to 10 grms. of ammonium acetate chloride, if not already present, and a fresh solution of tannin (1 grm.) are then added, and boiling is continued for a few minutes. After settling, the buff-coloured precipitate is collected, washed with dilute ammonium nitrate solution containing a little tannin, ignited wet, and weighed. If more than a few mgrms., it should be digested with hot water and a drop of nitric acid, which is neutralised by ammonia before filtration; the precipitate is again collected, washed, ignited strongly, and weighed as Al_2O_3. Four test separations of "unknown" mixtures gave the following results:

	Fe_2O_3.			Al_2O_3.		
Exp.	Taken.	Found.	Error.	Taken.	Found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
19	0·1131	0·1140	+0·0009	0·0066	0·0074	+0·0008
20	0·0954	0·0956	+0·0002	0·0114	0·0116	+0·0002
21	0·0764	0·0768	+0·0004	0·0079	0·0081	+0·0002
22	0·1108	0·1103	−0·0005	0·0024	0·0025	+0·0001

REACTION FOR ALUMINIUM.—We have discovered another reaction of aluminium not described in the literature. Aluminium solutions containing free tartaric acid are not precipitated by phosphate in the cold, but boiling causes precipitation (zirconium gives the same reaction: I, *J. Chem. Soc.*, 1921, **120**, 1931); an ammoniacal tartrate solution, on the other hand, is not precipitated, ammonia re-dissolving the precipitate obtained in the hot acid liquid. When alumina is precipitated by tannin from tartrate solutions containing phosphate, the precipitate is free from phosphate.

Gallium reacts like aluminium, being precipitated by tannin from tartrate solution (Moser and Brukl, *Monatsh. Chem.*, 1929, **51**, 79).

B. CUPFERRON PRECIPITATION.

Cupferron precipitation of the earth acids has been studied by Pied (ANALYST, 1925, **50**, 36), who finds that they are recovered quantitatively from solutions containing oxalic, tartaric, and sulphuric acid. The reagent is added to the cold solution during vigorous agitation; the precipitate is filtered off at once, washed with dilute sulphuric acid, and ignited gradually. Titania also is precipitated.

PRECIPITATION FROM TARTRATE SOLUTION.—We desired to do some further tests on cupferron precipitation from tartrate solution so as to be able to apply the procedure, if necessary, to the recovery of the small quantities of earth acid not precipitated in the tartaric hydrolysis. In this investigation we were fortunate to have the co-operation of Messrs. G. E. F. Lundell and H. B. Knowles, of the U.S. Bureau of Standards, who have made a special study of cupferron precipitation methods (ANALYST, 1920, **45**, 237). Dr. Lundell kindly gave us the following account of the work: The oxide was fused with potassium carbonate, and the melt dissolved in sulphuric and tartaric acids. A preliminary precipitation with cupferron was made, and the precipitate ignited and weighed. The object of this operation was, to remove any possible impurities not precipitated by cupferron. The weighed precipitate, P^1, was brought into solution (200 c.c.) as before, and the cupferron precipitation repeated at acid concentrations given below. A large excess of cupferron (50 c.c. of 6 per cent. solution) and addition of macerated paper were thought advisable, and the solutions cooled in ice-water for 30 minutes before filtration; the precipitates, P^2, were washed with 10 per cent. hydrochloric acid containing a little cupferron, and ignited:

Exp.	P^1.	P^2.	Error.	Acidity per cent.	
	Grm.	Grm.	Grm.	$C_4H_6O_6$.	H_2SO_4.
1	0·1936 Nb_2O_5	0·1930	−0·0006	5	5
2	0·1947 ,,	0·1942	−0·0005	5	10
3	0·1962 Ta_2O_5	0·1961	−0·0001	5	5
4	0·1955 ,,	0·1946	−0·0009	5	10

The results show a very slight negative error, though no earth acid could be detected in the filtrates. Messrs. Lundell and Knowles are of the opinion that the precipitation may be regarded as complete within the limits of experimental error. They find the niobium precipitate to be bulkier than that of tantalum, and to coagulate more readily; we confirm this observation.

Our own tests were conducted with small, "unknown" amounts of pentoxides in solutions (250 to 300 c.c.) containing 30 c.c. of strong hydrochloric acid partly neutralised with 10 c.c. of strong ammonia, in view of a possible future application under these conditions. The bisulphate melt was brought into solution with 3 grms. of tartaric acid; the liquid, after addition of acid and ammonia, was left to cool, and treated during agitation with a filtered cupferron solution; nearly one grm. of reagent proved to be required for satisfactory flocculation. The precipitates were filtered off after less than an hour, washed with 10 per cent. hydrochloric acid, ignited, and weighed. Positive errors were recorded, due to contamination with ferric oxide and silica, as before; these impurities were determined and deducted, the difference giving the "*net*" weight:

Exp.	Taken.	P Gross.	P Net.	Error.
	Grm.	Grm.	Grm.	Grm.
23	Ta_2O_5 0·0210	0·0224	0·0210	0·0000
24	,, 0·0283	0·0296	0·0278	−0·0005
25	Nb_2O_5 0·0251	0·0260	0·0249	−0·0002
26	,, 0·0285	0·0298	0·0285	0·0000
27	ZrO_2 0·0257	0·0260	—	+0·0003

Two further tests were made along the same lines with 0·02 grm. portions of tungstic oxide: no precipitation took place.

The earth-acid recovery is satisfactory, with a slight tendency towards a negative error. From the practical point of view we are inclined to favour precipitation with tannin, this being the more easily procurable and stabler reagent; the precipitates produced by it flocculate much more readily; hence for very small quantities of pentoxides the tannin method appears more reliable. Alumina is precipitated by tannin, but not by cupferron under these conditions. As regards the rare earths, Lundell and Knowles (*loc. cit.*) state that cerium is not without influence on the cupferron precipitation of titanium and zirconium. The action of tannin on tartrate solutions of the rare earths will be investigated.

C. Analytical Application.

Precipitation of small quantities of earth acid from tartrate solution by tannin or cupferron supplements tartaric hydrolysis; a combination of the two processes enables us to precipitate large or small amounts quantitatively without having to destroy the tartaric acid. In Exps. 28 and 29, the tartrate solution was hydrolysed with 30 c.c. of hydrochloric acid, which gave *HP*; the filtrate was precipitated with tannin after approximate neutralisation and addition of ammonium acetate, yielding *TP*:

Exp.	Taken.	*HP*.	*TP*.	ΣP.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.
28	Ta_2O_5 0·1065	0·1052	0·0013	0·1065	0·0000
29	Nb_2O_5 0·1014	0·0927	0·0084	0·1011	−0·0003

Precipitation Reactions for Earth-Acid Minerals.—We now dispose of a number of precipitation reactions from tartrate solution capable of being applied to the analysis of earth-acid minerals, namely: (1) Hydrogen sulphide in acid tartrate solution precipitates tin, antimony, etc. (2) Tantalum, niobium (major fraction), and tungsten are precipitated by tartaric hydrolysis. (3) The sulphides of iron and uranium (manganese partly) are precipitated from ammoniacal solution. (4) Oxalic acid precipitates thorium and the rare earths from acid solution (Pied, *loc. cit.*). (5) Cupferron precipitates the earth acids (minor fraction), titania, and zirconia. (6) The oxides enumerated under (5) are precipitated by tannin from the neutralised solution, together with thoria and alumina. (7) The metals still left in the tartrate solution are manganese (major fraction), beryllium, calcium, and magnesium; they are recovered after the destruction of the organic compounds, though this may not prove obligatory: beryllium and manganese give a tannin, calcium an oxalate, magnesium a phosphate, precipitate in ammoniacal solution. The order in which some of the above reactions will be applied, and other details of procedure, remain to be investigated.

Summary.—The earth acids are quantitatively precipitated from tartrate solution by tannin after neutralisation or addition of excess of ammonium acetate; we utilise this reaction for the recovery of the earth acid fraction not precipitated

by tartaric hydrolysis. Zirconia and titania are likewise precipitated, but accurate neutralisation after addition of the tannin is required. Thoria and alumina are precipitated like the earth acids. The reaction is useful and convenient for the direct determination of small quantities of alumina after precipitation of iron as sulphide. Cupferron is available for the quantitative recovery of the earth acids from tartrate solutions in presence of mineral acid. The earth acids and their mineral associates are classed into analytical groups according to their precipitability from tartrate solution.

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A Study of the Methods of Determining Boron Compounds in Food and Drugs.

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(Work done under the Analytical Investigation Scheme.)

PART II. EXPERIMENTAL: EFFECT OF FATS AND OTHER ORGANIC SUBSTANCES ON THE DETERMINATION.

PRACTICAL experience has shown that substances containing large percentages of fat cannot be ignited, even in presence of excess of alkali, without considerable loss of boron compounds resulting. Special methods, such as that of Richmond and Harrison (ANALYST, 1902, **27**, 179) have been devised to get over the difficulty, but their application is limited to substances like butter, margarine, or egg melanges, which can readily be transformed into a homogeneous fluid condition. Substances such as ham, sausages, cakes and fruits, however, apparently cause considerable difficulty, as none of these can be rendered homogeneous by means of ordinary solvents. Since the presence of fat or oil is the chief source of trouble, the following series of experiments was tried with a view to discovering if, under any condition, the fat can readily be removed without any loss of boric acid.

SOLUBILITY OF BORIC ACID IN ORGANIC SOLVENTS AT 60° F.—Weighed quantities of pure dry boric acid were stirred for 5 minutes in a dry beaker with 20 c.c. of methylated ether, petroleum spirit, benzene, chloroform and carbon tetrachloride, respectively, the temperature being maintained at 60° F. In a second series of experiments 5 c.c. of pure olive oil were added in each case. The contents of the beaker were then filtered through a Swedish filter paper into a dry beaker, and 10 c.c. of each filtrate were evaporated to dryness in a porcelain basin (care being taken to keep the solvent below its boiling point during the evaporation), the residue was taken up with 10 to 15 c.c. of distilled water, and

the solution titrated after the addition of 0·5 grm. of mannitol and phenolphthalein. (In each case the solution was tested and found to be neutral before the mannitol was added.)

The remaining portion of the filtrates was tested qualitatively with turmeric paper for the presence of boric acid.

In the case of the filtrates containing oil, 10 c.c. were extracted with 5 c.c. of 0·5 *N* sodium hydroxide solution and about 30 c.c. of water. The extracts (about 50 c.c. in volume) were acidified, boiled for 5 minutes, cooled, neutralised with sodium hydroxide solution (with Sofnol Indicator No. 1), and finally titrated after the addition of 0·5 grm. of mannitol and six drops of phenolphthalein solution.

TABLE I.

Solvent 20 c.c.	Quantity of boric acid taken. Grms.	Final titration. 0·1 *N* NaOH c.c.	Final titration. $=H_3BO_3$ (actual). Grm.	Reaction.
Ether (dry)	0·051	0·64	0·0040	Very distinct
,, ,,	0·052	0·40	0·0025	,, ,,
Petroleum spirit	0·051	<0·01	—	Practically nil
Chloroform	0·052	0·01	0·0006	Distinct trace
Benzene	0·049	<0·01	—	Practically nil
Benzene+trace of alcohol	0·050	0·01	—	Distinct trace
Carbon tetrachloride	0·051	<0·01	—	Practically nil
15 c.c. ether+5 c.c. oil	0·052	0·75	0·0047	Very distinct
15 c.c. ether+5 c.c. oil	0·051	1·00	0·0062	,, ,,
Petroleum spirit+5 c.c. oil	0·053	<0·01	—	Practically nil
Chloroform+5 c.c. oil	0·050	0·07	0·0043	Very distinct
Benzene+5 c.c. oil	0·052	<0·01	—	Practically nil
Carbon tetrachloride+5 c.c. oil	0·051	0·28	0·0017	Very distinct

The above results show that solvents, such as petroleum spirit, benzene and carbon tetrachloride, which do not readily mix with water, dissolve practically no boric acid. Ether and chloroform, on the other hand, dissolve a small quantity at 60° F. In the above experiments the solubility, except with ether, was found to be less than 1 part in 10,000 of solvent, but the proportion in all cases probably depends upon the amount of moisture the solvent has taken up during the course of the test. The presence of a minute trace of alcohol mixed with benzene was found to render boric acid more soluble than in the pure dry benzene.

The solubility of boric acid in mixtures of oil and benzene or petroleum spirit at 60° F. is practically negligible. Mixtures of pure olive oil and methylated ether, chloroform or carbon tetrachloride, on the other hand, dissolve small, but quite appreciable, quantities of boric acid. It is, however, quite possible that different oils and fats might behave differently from olive oil, but this may readily be verified by subsequent tests.

In view of the fact that some products are more or less acid, and that some of their boric acid content may be lost if they are dried without previous neutralising with caustic soda, another series of experiments was tried, in which about 0·5 grm. of boric acid and 10 c.c. of *N* sodium hydroxide solution were evaporated to dryness before stirring up with the solvents. The results are shown below:

TABLE II.

SOLUBILITY OF SODIUM BORATE IN ORGANIC SOLVENTS AT 60° F.

Oil or fat.	Solvent.	Boric acid reaction of filtrate.
Olive oil	Ether	Distinct
,, ,,	Petroleum spirit	Practically nil
,, ,,	Benzene	Practically nil
,, ,,	Chloroform	Distinct
,, ,,	Carbon tetrachloride	Distinct trace
Cocoa butter	Ether	Distinct
,, ,,	Petroleum spirit	Practically nil
,, ,,	Benzene	Practically nil
,, ,,	Chloroform	Distinct
,, ,,	Carbon tetrachloride	Distinct trace

As shown by the foregoing experimental results, benzene and petroleum spirit can be used to eliminate fats and oils from vegetable products by merely washing out at room temperature and rejecting. The quantity of boric acid dissolved thereby is practically negligible if the product is first dried, either alone or after being rendered slightly alkaline with caustic soda. This has an important practical bearing, as much time might thus be saved. Perfect dryness, however, is essential, and it is safer to determine the quantity of boric acid in the extract as shown below.

The following experiment was tried to ascertain whether, instead of rejecting the filtrate containing the excess of fat, the quantity of boric acid could be directly titrated and allowed for:

TABLE III.

Fat or oil.	Solvent.	Boric acid added.	Titration.	
			0·1 *N* NaOH	$=H_3BO_3$.
		Grm.	c.c.	Grm.
Olive oil	Ether	0·0195	3·14	0·0195
,, ,,	Petroleum spirit	0·0195	3·14	0·0195
,, ,,	Benzene	0·0195	3·14	0·0195
,, ,,	Chloroform	0·0195	3·14	0·0195
,, ,,	Carbon tetrachloride	0·0195	3·14	0·0195

As shown in Table III, the presence of oil, together with methylated ether, petroleum spirit, benzene, chloroform or carbon tetrachloride, does not affect the accuracy with which boric acid solutions can be titrated. In these experiments a known quantity (3 c.c.) of boric acid solution was titrated direct, with the use of 0·5 grm. of mannitol and phenolphthalein. Similar quantities were placed in a porcelain basin, together with 5 c.c. of olive oil and 15 c.c. of the above organic solvents, in turn. About 30 c.c. of water were added, and the contents of the basin were heated for 5 minutes on a water-bath, with constant stirring, and then cooled. The contents were then titrated with 0·1 *N* sodium hydroxide solution, after the addition of 0·5 grm. of mannitol and phenolphthalein, and the results were recorded as shown in the Table.

These results are of importance in so far as they show how the usual lengthy determination of boric acid in products containing a large percentage of fat may be

shortened considerably. Now that it is known that the determination of boric acid may be made direct on the fat-solvent portion without first extracting with alkali, the product under examination can be dried, washed with a solvent into a titrating basin, and the extracted boric acid determined and added to the result obtained in the main determination.

One would, however, require to select a solvent and carry out the extraction of the oil or fat under such conditions as would prevent the extraction of any phosphates along with the boric acid. A further investigation would, therefore, require to be made to ascertain under what conditions the phosphates would be excluded.

Effect of Concentration of Fat on Loss of Boric Acid when Ignited with Excess of Alkali.—Three different quantities of boric acid solution containing 0·0124 grm., 0·0186 grm., and 0·0310 grm. of boric acid, respectively, were placed in a platinum basin together with 3 c.c. of *N*-sodium hydroxide solution. The contents of the basin were evaporated to dryness on a water-bath, and different weights of olive oil were added. The oil, borate and excess of alkali were then heated gradually, ignited and burned off at a dull red temperature. The ash was boiled with water containing a slight excess of *N*-sulphuric acid, filtered, and washed into a flat titrating basin. The contents of the basin were boiled for 5 minutes to ensure the complete expulsion of carbonic anhydride and then cooled. One drop of Sofnol Indicator No. 1 was added, and 0·1 *N* sodium hydroxide solution was carefully run in from a burette until the liquid was just neutral. The burette was now filled up and carefully adjusted for the final titration of the boric acid. Then 0·1 grm. of mannitol and about 6 to 8 drops of phenolphthalein solution were added, and the contents were titrated.

In order to determine more accurately the loss due to the oil the following experiment was tried:—Three platinum basins, each containing 0·0186 grm. of boric acid and 3 c.c. of *N*-sodium hydroxide solution, were heated on a water-bath until complete evaporation of the contents had taken place. Two were then heated alone, one at a dull red heat, and the other at a high temperature. The former was found to contain 0·0183 grm. of boric acid, and the latter 0·0174 grm. That is, the ignition of 0·0186 grm. of boric acid in the presence of excess of alkali caused a loss of 0·0003 grm. of boric acid at a dull red heat, and of 0·0012 grm. of boric acid at a high temperature.

The contents of the third platinum basin were ignited with 10 grm. of stearic acid and treated as in the experiments with the olive oil. The ash, when finally titrated, was found to contain 0·0178 grm. of boric acid.

This experiment showed that if one took into account the difficulty of igniting a highly carbonaceous substance like stearic acid, the loss due to the presence of the stearic acid was very similar to that of the borate when ignited alone. In other words, the presence of a fatty acid causes little loss of boric acid when ignited with excess of alkali.

The following table shows the losses of boric acid which occurred on igniting olive oil with borate and excess of alkali:

TABLE IV.

EFFECT OF CONCENTRATION OF FAT ON LOSS OF BORIC ACID WHEN IGNITED WITH EXCESS OF ALKALI.

Quantity of fat taken. Grms.	Quantity of boric acid added. Grms.	Quantity of boric acid added. Percentage in fat.	Final titration. 0·1 *N* NaOH c.c.	Final titration. $=H_3BO_3$ Grm.
1	0·0124	1·24	1·60	0·0099
1	0·0186	1·86	2·22	0·0138
1	0·0310	3·10	4·42	0·0274
5	0·0124	0·248	0·63	0·0039
5	0·0186	0·372	0·94	0·0058
5	0·0310	0·620	1·50	0·0093
10	0·0124	0·124	0·45	0·0028
10	0·0186	0·186	0·72	0·0045
10	0·0310	0·310	1·40	0·0087
15	0·0124	0·083	0·65	0·0040
			0·63	0·0039
15	0·0186	0·124	0·68	0·0042
15	0·0310	0·207	1·30	0·0081
20	0·0124	0·062	0·50	0·0031
20	0·0186	0·093	0·75	0·0046
20	0·0310	0·155	1·40	0·0087

In each test 3 c.c. of *N* sodium hydroxide were used for fixing the boric acid during ignition.

These results show that when 1 grm. of oil was used the loss, though considerable, was distinctly irregular. Greater regularity was observed when 5 grms. and upwards of oil were used. This is shown by the following tabulated results, which were calculated from the figures found in Table IV.:

TABLE V.

H_3BO_3 present. Per Cent.	H_3BO_3 found. Per Cent.	H_3BO_3 lost. Per Cent.	Percentage of total H_3BO_3 lost.
0·062	0·016	0·046	74·2
0·083	0·026	0·057	69·4
0·083	0·027	0·056	68·7
0·093	0·023	0·070	75·3
0·124	0·028	0·096	77·4
0·124	0·028	0·096	77·4
0·155	0·044	0·111	71·6
0·186	0·045	0·141	75·7
0·207	0·054	0·153	73·9
0·248	0·085	0·163	69·4
0·310	0·087	0·223	71·9
0·372	0·116	0·256	68·8
0·620	0·186	0·434	70·0

It will be observed that the percentage of boric acid lost under the above conditions is very large, and, although not very constant, yet possesses a degree of constancy which suggests that if the conditions of ignition were more uniform a fairly constant percentage loss would result.

The losses shown in Table V fluctuate between 68·7 and 77·4 per cent., and have a mean value of 72·6 per cent.

In view of the fact that a very small percentage only of boric acid is lost when ignited, either with alkali alone or with alkali and a fatty acid, it is evident that

the loss must be due to the glyceride present when an oil is used. The apparent constancy of loss appears to suggest that, when excess of oil and caustic alkali is present, a complex consisting of a sodium salt, borate and glycerol is formed in course of ignition, and that this complex splits up into sodium borate and glyceroborate. This contains about 70 per cent. of the original borate, and is volatilised in the course of ignition, leaving sodium borate.

In order to ascertain whether the amount of alkali in excess of that required to neutralise the boric acid was an important factor, different quantities of caustic soda were added to the same quantities of boric acid and olive oil prior to ignition. It was found, however, that the results obtained were so similar as to admit of the conclusion being drawn that, so long as the sodium hydroxide was in excess, the amount was immaterial.

It is also quite evident from the above experiments that, so long as there is sufficient oil or fat present to provide the necessary glycerol for the boric acid present, the quantity of oil or fat is also immaterial.

VARIATION IN THE LOSS OF BORIC ACID CAUSED BY IGNITING DIFFERENT OILS IN PRESENCE OF BORIC ACID AND EXCESS OF ALKALI.—Similar weights (5 grms.) of different fats and oils were ignited with known weights of boric acid and excess of sodium hydroxide at a dull red heat. The ash was digested with water and 6 drops of concentrated hydrochloric acid, and filtered into a titrating basin. The filter paper and contents were returned to the platinum basin and fully ignited, and then washed into the basin. The contents of the basin were boiled for 5 minutes, with constant stirring, to expel the carbonic anhydride, cooled, neutralised, and then titrated after the addition of 0·5 grm. of mannitol. The results obtained are given in the following Table:

TABLE VI.

			Final titration.		
Kind of oil 5 grms.	N-NaOH added. c.c.	Loss of H_3BO_3. Per Cent.	Boric acid H_3BO_3 added. Grm.	0·1 *N* NaOH. c.c.	$=H_3BO_3$. Grm.
Coconut butter	3·0	73·0	0·0189	0·83	0·0051
,, ,,	3·0	73·5	0·0189	0·81	0·0050
Olive oil	3·0	69·0	0·0186	0·94	0·0058
,, ,,	3·0	70·0	0·0186	0·90	0·0056
Almond oil	3·0	58·6	0·0189	1·25	0·0078
,, ,,	3·0	58·2	0·0189	1·28	0·0079
Cacao butter	3·0	61·4	0·0189	1·18	0·0073
,, ,,	3·0	60·3	0·0189	1·21	0·0075
Linseed oil	3·0	56·4	0·0186	1·30	0·0081
,, ,,	3·0	46·4	0·0186	1·30	0·0081
Castor oil	3·0	56·1	0·0189	1·34	0·0083
,, ,,	3·0	54·5	0·0189	1·38	0·0086
Sesame oil	3·0	54·0	0·0199	1·40	0·0087
,, ,,	3·0	54·5	0·0189	1·38	0·0086
Rape oil	3·0	50·8	0·0189	1·50	0·0093
,, ,,	3·0	50·3	0·0189	1·51	0·0094
Cottonseed oil	3·0	49·2	0·0186	1·65	0·0102
,, ,,	3·0	44·0	0·0186	1·70	0·0105
,, ,,	3·0	51·1	0·0186	1·47	0·0091

From these results it will be observed that different kinds of fat or oil give rise to variations in the percentage of boric acid volatilised and lost during the process of ignition. The proportion of loss is fairly constant for the same kind of oil, and appears to have some bearing on the constitution of the oil. As already mentioned, the glycerol content of an oil plays an important part in rendering boric acid volatile, so that there appears to be some possibility of utilising the ignition of boric acid in presence of excess of alkali as a means of identifying a glyceride (fat or oil), and also of determining the amount of glycerol contained in compounds or mixtures. The above results were obtained under ordinary laboratory conditions, but, so far as they go, they afford reason for the belief that, if special precautions were taken, which would keep the conditions constant and exclude any disturbing factors, characteristic results would be found for individual oils and fats.

Effect of the Presence of Organic Matter on the Loss of Boric Acid when Ignited with Excess of Alkali.—Twenty grms. each of different organic substances which were free from boric acid, were ignited at a dull red heat in a platinum basin with a known quantity of boric acid and excess of alkali (3 c.c. of 0·1 *N* H_3BO_3 + 3 c.c. of *N*-NaOH). The boric acid was then determined in the usual way after lixiviating and eliminating carbonic anhydride and phosphates, if present. When the substance (*e.g.* sugar) contained no phosphates, the ash was boiled with water and a slight excess of hydrochloric acid until most of the carbonic anhydride was expelled, and the solution was then transferred to a 100 c.c. flask, made up to the mark, shaken and filtered. Fifty c.c. of the filtrate were placed in a porcelain titrating basin and boiled for 5 minutes, with constant stirring, to ensure the complete expulsion of carbonic anhydride. After rapid cooling, the contents were neutralised with 0·1 *N* sodium hydroxide solution, Sofnol Indicator No. 1 being used. The final titration was effected after adding 0·5 grm. of mannitol and phenolphthalein solution. For convenience, these results are shown in the following Table doubled to equal the entire quantity.

The starch was found to contain a small percentage of phosphates, which rendered the above shortened method inapplicable. The boric acid in the ashes obtained from mixtures containing starch was therefore determined by the usual long method.

The following Table, No. VII (see p. 722), shows the results obtained.

These results indicate that substances of the nature of carbohydrates and fatty acids do not have any considerable effect on the loss of boric acid, when ignited in presence of excess of alkali. It will be observed that a slight loss does take place, but it is insignificant when compared with that produced by the ignition of an oil or fat, and is, in reality, not much more than is caused by the ignition of boric acid and excess of alkali alone. There are certainly slight differences with different substances, but these appear to be mainly due to the variation in the inflammability of these substances. The loss of boric acid in these cases would therefore be mechanical rather than chemical, as in the case of substances containing glycerol.

TABLE VII.

EFFECT OF THE PRESENCE OF ORGANIC MATTER ON THE LOSS OF BORIC ACID WHEN IGNITED WITH EXCESS OF ALKALI.

Substance, 20 Grms.	Boric acid taken.		Final titration.	
		Percentage of substance.	0·1 *N* NaOH.	$=H_3BO_3$
	Grm.		c.c.	Grm.
Olive oil	0·0186	0·093	0·76	0·0047
Sugar	0·0186	0·093	2·98	0·0185
Starch	0·0186	0·093	2·96	0·0184
Stearic acid	0·0186	0·093	2·84	0·0176
19 sugar and 1 oil	0·0186	0·093	2·96	0·0184
18 sugar and 2 oil	0·0186	0·093	2·40	0·0149
15 sugar and 5 oil	0·0186	0·093	1·68	0·0104
			1·80	0·0112
19 starch and 1 oil	0·0186	0·093	2·90	0·0180
18 starch and 2 oil	0·0186	0·093	2·38	0·0148
			2·46	0·0153
15 starch and 5 oil	0·0186	0·093	2·38	0·0148
19 starch and sugar and 1 oil ..	0·0186	0·093	2·94	0·0182
18·8 starch and sugar and 1·2 oil	0·0186	0·093	2·78	0·0172
18·6 starch and sugar and 1·4 oil	0·0186	0·093	2·30	0·0143
18·4 starch and sugar and 1·6 oil	0·0186	0·093	2·00	0·0124
18·2 starch and sugar and 1·8 oil	0·0186	0·093	2·04	0·0126
18 starch and sugar and 2 oil ..	0·0186	0·093	1·88	0·0117

A comparison of the results shown in Table VII with those in Table IV shows that the presence of carbohydrates with fat tends to diminish the loss of boric acid which would have been caused by the presence of the same amount of fat by itself. Thus, for example, 1 grm. of olive oil ignited with 0·0186 grm. of boric acid and 3 c.c. of *N* sodium hydroxide causes an actual loss of 0·0048 grm. of boric acid, whilst 1 grm. of olive oil, together with 19 grms. of sugar, ignited with 0·0186 grm. of boric acid and 3 c.c. of *N* sodium hydroxide solution causes an actual loss of merely 0·0002 grm. of boric acid. Also, 5 grms. of olive oil under the above conditions causes an actual loss of 0·0128 grm. of boric acid, whereas 5 grms. of olive oil and 15 grms. of sugar causes a loss of 0·0069 grm. of boric acid; and 5 grms. of olive oil and 15 grms. of starch causes a loss of only 0·004 grm. of boric acid. The difference in these last two results is probably due to the dry nature of the starch affording a better protecting medium between the oil and the sodium borate than sugar, as a mixture of oil and sugar allows a quantity of the oil to come into direct contact with the sodium borate, thereby causing greater loss when the mass is ignited. In some instances the experiments were repeated several times before concordant results were obtained. This difficulty appeared to be caused by the variations in the degree of contact between the oil and the sodium borate.

The conditions of the foregoing experiments are to a large extent artificial, and the oil and the boric acid are by no means as homogeneously mixed with the starch, etc., as they would be in natural vegetable substances. The protective properties of the non-fatty constituents would, therefore, tend to be more variable. So far as the above results go, it would appear that comparatively little loss of boric acid occurred during direct ignition if the percentage of oil or fat in the

sample did not exceed 5 per cent. If that were absolutely correct for all substances, then Thomson's process could be curtailed by directly igniting in presence of excess of alkali any substance which was known to contain less than 5 per cent. of oil.

The following table shows some results obtained by the use of natural vegetable substances in place of artificial mixtures of starch, sugar and oil:

TABLE VIII.

EFFECT OF THE PERCENTAGE OF FAT OR OIL IN VEGETABLE PRODUCTS ON THE LOSS OF BORIC ACID ON IGNITION.

Article, 20 grms.	Containing in 20 grms.		Boric acid added.	Final Titration.	
	H_3BO_3.	Oil.		For ½ quantity.	$=H_3BO_3$.
	Grm.	Grm.	Grm.	c.c.	Grm.
Dairy meal ..	0·0001	1·30	0·0188	1·45	0·0090
,, ,,	0·0001	1·30	0·0310	2·43	0·0151
Soya meal ..	0·0005	0·14	0·0188	1·46	0·0091
,, ,,	0·0005	0·14	0·0310	2·41	0·0149
Dried grains ..	Nil	1·43	0·0188	1·48	0·0092
,, ,,	—	1·43	0·0310	2·43	0·0151
Kardi seed cake	0·0003	1·73	0·0189	1·48	0·0092
,, ,,	0·0003	1·73	0·0313	2·48	0·0154
Calf meal ..	0·0003	1·69	0·0310	2·45	0·0152

The loss of boric acid is shown in the following table:

TABLE VIII*a*.

Article, 20 grms.	Oil.	Loss of boric acid H_3BO_3.	
			Percentage of total boric acid.
	Per Cent.	Grm.	
Dairy meal ..	6·50	0·0009	4·75
,, ,,	6·50	0·0009	2·90
Soya meal ..	0·70	0·0011	5·70
,, ,,	0·70	0·0017	5·08
Dried grains ..	7·15	0·0004	2·13
,, ,,	7·15	0·0008	2·58
Kardi seed cake ..	8·65	0·0008	4·16
,, ,, ,,	8·65	0·0008	2·53
Calf meal ..	8·45	0·0009	2·88

From the above results it will be observed that a slight loss of boric acid has taken place in each determination. It is apparent, however, that the loss bears no relationship to the percentage of oil or fat present in the sample, and is, in fact, greater in the case of the extracted soya meal, which contained little oil, than in any of the other samples. The comparatively low results with this sample may be attributed to losses other than those caused by ignition, as the large percentage of phosphates and other mineral matter rendered the separation of the boric acid extremely difficult. The other actual quantities of boric acid lost are more constant, and are comparable with the loss due to the ignition of fat-free organic matter and boric acid together with excess of alkali. It would appear, therefore, that there is a tendency towards slightly low results. The deficiency may amount to about 0·0008 grm. of boric acid (H_3BO_3), but should be considerably less in the case of substances which do not contain high percentages of phosphates and other mineral constituents.

As already mentioned, the loss of boric acid, due to the oil in a sample, depends upon the degree of contact between the oil and the boric acid. The samples used in this experiment did not appear oily, and, apparently, the contact of the oil and the boric acid is very slight, as even 8·65 per cent. of oil causes no definite loss. In all probability the percentage of oil in some natural vegetable products could be increased still further without causing any appreciable loss of boric acid. As, however, the constitution of some vegetable products may give rise to greater contact between the oil and boric acid present, it would be inadvisable to take too high a percentage of oil as the general margin of safety.

Taking everything into consideration, it would appear that any vegetable substances which contains less than 8 per cent. of oil, may be safely ignited directly without previous extraction of the oil, and that no appreciable loss of boric acid will result therefrom.

By taking 8 per cent. of oil as a general margin of safety, and omitting the preliminary extraction of oil in all samples containing 8 per cent. of oil and under, considerable time and trouble will be saved. It is, however, imperative to mix such samples with a solution of alkali, and to dry them thoroughly at water-bath temperature before attempting to ignite them, as the presence of moisture causes a loss of boric acid if an attempt is made to ignite a moist sample.

Loss of Boric Acid resulting from Boiling Acidified Boric Acid Solutions.—In keeping with the practice of boiling 50 c.c. of solution to eliminate carbonic anhydride, 50 c.c. of liquid containing sulphuric acid and a known weight of boric acid were boiled for various lengths of time. One series was carried out in a beaker flask covered with a watch glass; the other series was carried out by boiling the solution in an open shallow titrating basin, with constant stirring. The solutions were cooled, neutralised with 0·1 *N* sodium hydroxide solution, with Sofnol Indicator No. 1, and finally titrated after adding 0·5 grm. of mannitol and phenolphthalein. The volume to which the original solution was evaporated during the boiling was ascertained by pouring into a burette and measuring the contents of the vessel after titrating, and deducting the known volume of the solutions added during the neutralising and titrating.

Table IX.

Boric acid taken. Grm.	Time of boiling. Minutes.	Final volume. c.c.	Final titration. 0·1 *N* NaOH. c.c.	Final titration. $=H_3BO_3$. Grm.
Open Basin.				
0·0329	5	24·7	5·30	0·0329
0·0329	10	12·2	5·20	0·0322
0·0329	15	2·0	4·58	0·0284
0·0329	to dryness	—	4·28	0·0266
Beaker Flask and Watch Glass.				
0·0329	5	47·3	5·30	0·0329
0·0329	10	43·F	5·30	0·0329
0·0329	15	33·1	5·30	0·0329

N.B.—In each of these tests the volume of the original solution was 50 c.c., and the acidity equal to 5 c.c. of 0·1 *N* H_2SO_4.

From the above results it will be observed that a fair amount of liberty can with safety be taken in the process of expelling carbon dioxide from acidified dilute boric acid solutions. The boiling was found to be done most expeditiously in an open basin; 5 minutes, or even less with constant stirring, expels the carbon dioxide completely. The only likely causes of loss arise from too rapid boiling, which may cause spurting or over-drying at the edges, but this is easily remedied if constant attention is given. It was found that an appreciable loss occurred only when the solution was concentrated to about one-fifth of its original bulk, but such a condition is unlikely to occur in practice.

(*To be concluded.*)

The Determination of Small Quantities of Lead, with Special Reference to Urine and Biological Materials.

By A. G. FRANCIS, B.Sc., F.I.C., C. O. HARVEY, B.Sc., A.I.C., and J. L. BUCHAN, M.Sc., A.I.C.

I. Introduction.—For the purpose of the experimental investigation that the Committee of Enquiry on Lead Ethyl Petrol decided to carry out, a method was needed to determine small quantities of lead in a variety of substances, including urine and biological materials. It was thought that a method of determining lead giving satisfactory results with urine could be applied, with suitable modifications, to the other substances likely to be met in the course of the Committee's programme of work. The method to be described has been in use for a year, and has given satisfactory results with urine and other materials containing organic matter; and, as the details of the method are of interest to chemists, the Committee has now given permission for it to be published.

When the work was begun the only valuable method of determining lead in urine was the modified Fairhall process (*J. Biol. Chem.*, 1924, **60**, 485)* adopted by the American investigators on the health hazards associated with the distribution and use of lead ethyl petrol; but, after the method to be described had been in use for several months, there came to our notice the methods of Taylor (*J. Proc. Roy. Soc., New South Wales*, 1927, **61**, 315), Cooksey and Walton (Analyst, 1929, 97), and Millet (*J. Biol. Chem.*, 1929, **82**, 265). Taylor's method depends on the absorption of the lead in urine by calcium oxalate precipitated directly therein, but no evidence is produced to show that

* See also: "A Study of the Health Hazards Associated with the Distribution and Use of Ethyl Gasoline," 1925, p. 16, by Kehoe and co-workers, Richberg Laboratory, University of Cincinnati, Ohio, U.S.A.

the filtrate from the calcium oxalate is free from lead. The method also involves the conversion of the oxalate into carbonate by gentle ignition, a process best avoided. Cooksey and Walton's method depends on the direct electrolysis of urine, but it is not known that the whole of the lead in urine is in a form capable of carrying the electric current. Beyond repeating the electrolysis, no evidence is afforded that the electrolyte finally discarded is free from lead. Millet's method in its earlier stages is the same as that of Fairhall and, therefore, some objections to Fairhall's method would apply to it. For these reasons, and also, because the method to be described was satisfactory in practice, the three processes mentioned above were not investigated.

FAIRHALL'S METHOD.— Fairhall's method, however, as it has been so largely used, requires fuller consideration. It depends in the first place on the precipitation of the lead, together with calcium phosphate, when the urine is made ammoniacal. The precipitate is filtered on paper, dried and ashed in a muffle at 500° C., the residue being extracted with nitric acid to remove the lead. The lead is subsequently precipitated under carefully controlled conditions, first, as lead sulphide; secondly, as lead sulphate; thirdly, as lead sulphide; and, finally, as lead chromate, the precipitate in each case being allowed to stand overnight before being filtered from its solution. Finally, the lead is determined colorimetrically by making use of the reaction between lead chromate and di-phenyl carbazide, which is oxidised by the chromate radicle, giving a pink colour. The process is long, taking about six days to complete.

A consideration of the Fairhall method suggested the following points for investigation or modification:

(1) It seemed improbable in a biological fluid, such as urine, that the whole of the lead would be in a form precipitable by ammonia. Moreover, Fairhall states that precipitation of the lead is complete only if the urine is fresh. This condition cannot always be satisfied.

(2) It seemed desirable to avoid the risk of loss of lead by ashing at any stage in the method.

(3) When the final lead solution is determined colorimetrically it seemed preferable to make use of a reaction dependent on the lead ion rather than on the chromate ion.

(4) The process was too long, and a shorter method consistent with the requisite degree of accuracy was desirable.

(5) No figures are given showing the magnitude of the error due to the presence of lead in the reagents used in the analysis, but it is stated on page 362 of "Experimental Studies on the Effect of Ethyl Gasoline and its Combustion Products" (*Bureau of Mines*, Washington, 1927) that "blank determinations should be made frequently on lead free material as a check against contamination from apparatus or reagents." Kehoe and Edgar, in *A Study of the Hazards Associated with the Sale and Distribution of Ethyl Gasoline*, 1925, p. 20, state that "lead-free reagents were employed throughout," but no mention of blank determinations is made.

The method to be described was devised, having regard to these five points. It has been tested, with satisfactory results, with urine, to which known proportions of lead in the form of lead hippurate have been added. The method was also used to show that lead is not always precipitated completely by ammonia from normal urine, even when the urine is quite fresh. This has also been shown by Taylor (*loc. cit.*).

II. Outline of the New Method.—An outline of the method indicates how the five considerations stated above were met. The stages of the method are:

(1) The whole of the urine is reduced to the state of a solution of inorganic salts by a process of wet combustion. This avoids the precipitation of the lead in a solution containing organic matter. Since approximately 90 per cent. of the organic matter in urine is urea, and as the salts of urea are comparatively stable, it was realised that this substance should be destroyed before attempting to remove the other organic matter by hot strong acids. This can be done by nitrous acid or an alkali nitrite, but the use of these substances was attended by some experimental inconveniences, such as an excessive volume of solution or difficulty in procuring alkali nitrites free from lead. We are indebted to Dr. Fox, Deputy Government Chemist, for the suggestion to use for this purpose, nitrosyl-sulphuric acid. The suggestion was adopted and proved entirely satisfactory in practice.

(2) After the volatilisation of silica, separated by the process of wet combustion, the lead is precipitated from the solution as lead sulphide, together with copper sulphide, the copper having been added to aid the precipitation of the lead.

(3) After the mixed sulphides have been washed with a solution of sodium sulphide, they are dissolved in nitric and sulphuric acids and the solution is evaporated to dryness. The mixed sulphates are dissolved in dilute nitric acid, and the solution is electrolysed, the lead being deposited on the anode as lead peroxide. This process shortens the duration of the analysis.

(4) The lead peroxide is dissolved from the anode, and the lead is precipitated from the solution as lead sulphate, leaving behind traces of bismuth, manganese and platinum.

(5) The lead sulphate is dissolved in a solution of ammonium acetate, and the lead in solution is determined colorimetrically as lead sulphide. This reaction depends on the lead ion.

(6) Blank determinations were made with the actual quantities of the reagents used in each set of experiments. The magnitude of the very small "blanks" obtained is given later.

At no stage in the process is there any "ashing" of a precipitate or filter paper, these being invariably destroyed by wet combustion. Normally, the process takes three and a half days to complete.

III. TESTING OF THE METHOD.—The method has been tested and found satisfactory, both as regards its individual stages and as a whole. Experiment has shown that no loss of lead occurs at those stages in the method involving filtration, washing of precipitates or electrolysis. These stages comprise:

(1) The precipitation of lead sulphide and the washing of it with water saturated with hydrogen sulphide. When the filtrate and wash water, to which a further quantity of copper nitrate has been added, is again saturated with hydrogen sulphide, no further precipitate of lead sulphide is obtained.

(2) Washing of the mixed sulphides with sodium sulphide. When the sodium sulphide washings are heated with sulphuric acid and the acid solution is subsequently electrolysed, no lead peroxide is deposited on the anode.

(3) The electrolysis. When small quantities of lead, varying from 0·015 to 1·1 mgrm., are electrolysed under the conditions to be described, the whole quantity of the lead is deposited on the anode and no lead is found on the cathode. A second electrolysis does not yield any further lead, and no lead can be detected in the electrolyte.

(4) The precipitation of the lead as lead sulphate. The filtrate from the lead sulphate obtained from normal urines gives a coloration with sodium sulphide corresponding with quantities of lead varying from 0·003 to 0·007 mgrm. But this coloration is, in part, due to traces of platinum, and possibly also to bismuth. The possible loss of lead at this stage is, on the average, less than 0·005 mgrm.—a negligible quantity. That no lead sulphate remains on the filter paper after it has been washed with ammonium acetate, has been shown by the destruction of the filter paper by means of sulphuric acid and the examination of the resulting solution by the sulphide colorimetric process.

The whole process has been tested by the addition of known quantities of lead hippurate to urine, with the following result:

Lead (Pb) added to one litre of urine.	Lead (Pb) found.
Mgrm.	Mgrm.
0·021	0·024
0·021	0·015
0·042	0·040
0·063	0·067
0·106	0·116
0·265	0·255
0·530	0·535

Since the lead is determined finally by means of the colour produced in alkaline solution on the addition of sodium sulphide, it is essential that the solution to be

examined shall be free from all metals that give coloured sulphides. This condition is met in the following manner. All these metals, except traces of bismuth, are removed by the sulphide precipitation or by electrolysis. The lead is separated from the last traces of bismuth by precipitation as lead sulphate. Under the conditions to be described the lead can be completely separated from 1·0 mgrm. of bismuth, but this quantity of bismuth will never be present at that stage of the process, since most of it has been removed during electrolysis. The greatest quantity of bismuth found on the electrode with the lead during the progress of the work was 0·03 mgrm.

As the proportion of lead in urine is very small, it is essential to avoid, as far as possible, any adventitious gain of lead during the procedure, and, as this cannot be avoided altogether, it becomes necessary to know exactly how much lead is gained. The work was carried out in new silica vessels, and special precautions were adopted to prevent the access of dust during the process. All the reagents were specially prepared, and, wherever possible, from materials purifiable by volatilisation. A "blank" determination was made on all the reagents used for the process with each set of determinations, these being usually four in number, sometimes two, and occasionally six. Normally these "blanks" have varied from 0·002 to 0·005 mgrm. of lead (Pb), and averaged 0·004 mgrm.; in the early stages of the work three "blanks" of greater magnitude were obtained. These were 0·012, 0·013 and 0·010 mgrm., bringing the average for all the 24 "blanks" to 0·005 mgrm.

IV. Preparation of the Reagents.—*Water.*—The distilled water was tested periodically in portions of 1 litre, and found to be free from lead. If a metal condenser is used, care should be taken to avoid soldered joints, otherwise lead will be found in the distillate.

Hydrochloric Acid.
Nitric Acid.
Sulphuric Acid.

These were redistilled from a still made completely of clear silica ware and were stored in stoppered flasks of clear silica.

Hydrofluoric Acid.—This was redistilled from a still made completely of platinum and stored in a platinum bottle.

Nitrosyl Sulphuric Acid.—This reagent was prepared as follows:—Four hundred ml. of redistilled nitric acid (sp. gr. 1·4) were placed in a silica beaker of 800 ml. capacity and cooled in a bath of crushed ice. Gaseous sulphur dioxide from a syphon of the liquid substance was led into the cooled acid through a large trap consisting of an empty flask of 1500 ml. capacity, the tube dipping into the nitric acid being made of silica. The gas was bubbled slowly into the acid at such a rate that it was absorbed completely. When crystals began to form at the bottom of the beaker, the silica tube was progressively raised to prevent the incoming sulphur dioxide from coming into contact with them, since they react with sulphur dioxide to form sulphuric acid. The reaction is complete in 16–24 hours, when the liquid becomes pale green in colour. The liquor and crystals

were well mixed and divided into 5 equal portions, each of which was sufficient to destroy the urea of 1 litre of urine.

Ethyl and Amyl Alcohols.—These were redistilled from a glass still, the first and last runnings being rejected.

Citric Acid Solution.—A 10 per cent. solution of citric acid in water was made from citric acid that had been tested and found free from lead.

Ammonia (Selected).—Fifty ml. of ammonia (sp. gr., 0·88) must show no coloration on the addition of 2 drops of 10 per cent. sodium sulphide solution. It must also be free from sulphide.

Copper Nitrate Solution.—Electrolytic copper containing 0·02 per cent. of lead was dissolved in nitric acid and re-electrolysed. The deposited copper was dissolved in the minimum quantity of nitric acid, and the solution diluted until 1 ml. contained approximately 2 mgrm. of copper (Cu).

Sodium Sulphide Solution.—A 20 per cent. solution in water was made, allowed to stand for some days and then filtered. This strong solution was diluted with four volumes of water to make a 4 per cent. solution.

Ammonium Acetate Solution.—A 10 per cent. solution was made from selected specimens of the crystallised solid that were free from lead, copper, iron, and sulphide.

"Masked" Methyl Orange Indicator. (Hickman and Linstead, *J. Chem. Soc.*, 1922, p. 2502.)—One grm. of methyl orange and 1·4 grms. of Xylene Cyanol F.F. were dissolved in 500 ml. of 50 per cent. alcohol (by vol.).

Potassium Cyanide (Selected).—Ten ml. of a 10 per cent. solution must give no reaction for lead and sulphide.

Ten Per Cent. Sodium Sulphide Solution, for the colorimetric determination of lead:

Strong solution for stock: { Pure Na_2S crystals, 50 grms. / Pure glycerin, 50 grms. / Water to 250 ml. }

This stock solution, which keeps well, was diluted with an equal volume of water before use.

V. METHOD OF SAMPLING.—The urine was collected in selected Winchester quart bottles. Seventy-two bottles, all of the same make and delivery, were chosen after tests had been made on three of them, selected at random from the 72. The tests were:—(1) In each of the three bottles were placed 50 ml. of hydrochloric acid of sp. gr. 1·1, the bottles and their contents were heated for 8 hours in a boiling water-bath and agitated at half-hour intervals. The lead dissolved by the hot acid was found to be 0·004 mgrm. (2) Fifty ml. of ammonia, of sp. gr. 0·88, was allowed to remain in each of the bottles for 8 hours, the bottles being agitated at half-hour intervals. At the end of that time no lead was detected in the ammonia.

A similar number of glass funnels, 4½ inches in diameter, were tested in the same manner by having hot acid and concentrated ammonia poured through them repeatedly over a period of 1 hour, but no lead was detected in the acid or alkaline solutions.

The bottles and funnels were thoroughly cleansed before use by rinsing first with 250 ml. of hot dilute nitric acid (1 to 10), next with a copious stream of tap-water, and finally with distilled water. The clean, well-drained bottles and funnels were placed in padded baskets and dispatched from time to time to the source of origin of the samples.

The urine from males only was examined. It was collected directly into the bottles, transference of the urine from one vessel to another being thus avoided. A full 24-hour supply was collected in each case, usually from 3 p.m. on one day to 3 p.m. the next.

VI. Details of the Method of Analysis.—(1) *For Urine.*—The total volume of the sample is measured. The drained bottle is washed with 50 ml. of hot dilute nitric acid (1 vol. of acid, sp. gr. 1·4 diluted with 9 vols. of water) until every trace of deposit has been removed from the sides and bottom of the bottle. Whenever possible, 1000 ml. of urine are taken for analysis, and to it is added its appropriate fraction of the nitric acid washings of the bottle.

(*a*) *Destruction of the Organic Matter.*—To 1 litre of the urine and its appropriate fraction of washings contained in a two-litre silica beaker, nitrosyl sulphuric acid, prepared from 80 ml. of concentrated nitric acid, is added gradually (*i.e.* one of the five portions obtained as described above). Repeated addition of small quantities (10 drops) of redistilled amyl alcohol is necessary to prevent frothing caused by the gaseous products of the reaction between the nitrous acid and urea. To minimise local action and consequent loss of nitrous acid, the nitrosyl sulphuric acid should be stirred frequently during its addition. The urine must, of course, be stirred constantly during the addition of the nitrosyl sulphuric acid.

When the vigorous reaction is complete, a few more drops of amyl alcohol are added, and the mixture is boiled down to about one-third of its original volume. After cautious addition of 20 ml. of redistilled conc. nitric acid (sp. gr. 1·4), the beaker is covered and the boiling continued until charring occurs, when a further 3 ml. of nitric acid are added. The heating is continued, with further additions of small quantities of nitric acid, as may be necessary, until the liquid is in a sufficiently clean state for transference to a 600 ml. beaker (any silica adhering to the large beaker should be removed by means of dilute hydrofluoric acid, as described later). After transference, a little more nitric acid is added to the diluted solution, and the boiling down is continued until sulphuric acid fumes are again evolved.

The final destruction of traces of organic matter is completed by boiling the concentrated acid solution vigorously for some time in the covered beaker, adding a few drops of concentrated nitric acid to the hot mixture, if necessary.

To ensure decomposition of residual traces of nitrosyl sulphuric acid, the warm, almost colourless, sulphuric acid solution is diluted, and again boiled

down until fumes of sulphuric acid appear. If this final dilution is omitted, the residual nitrous and nitric acids will interfere with the indicator used in neutralisation, and may prevent the complete precipitation of the lead as sulphide.

The excess of sulphuric acid is now expelled by heating until crystallisation of calcium sulphate just commences. Heating must not be continued beyond this stage, or the calcium sulphate will be rendered insoluble in water.

(*b*) *Removal of the Separated Silica.*—Before actual solidification takes place, the warm syrupy acid solution is diluted cautiously, first with a little cold water, and then with hot water to a volume of about 400 ml. At this stage all the calcium sulphate should be in solution, but it may be necessary to add a little hydrochloric acid and to continue heating for a short time.

The silica is now filtered off on an 11 cm. acid-washed filter paper, and washed once or twice with hot water. Any silica that remains adhering to the silica beaker is removed by means of hot water containing a few drops of hydrofluoric acid, and this solution is transferred to a platinum dish, which is covered and set aside.

The filter paper containing the silica is now transferred to a 250 ml. tall silica beaker and treated with a mixture containing 10 ml. of concentrated nitric acid, 10 ml. of water, and 3 ml. of concentrated sulphuric acid. The covered beaker is heated on the hot plate until copious fumes of sulphuric acid are evolved, when the cover is removed for two or three minutes. (*Note.*—If charring occurs, a few drops of concentrated nitric acid are added and heating continued.) The contents of the beaker are now transferred to the platinum dish, previously mentioned, a few drops of hydrofluoric acid again being used, if necessary, to ensure complete transference of silica. After the addition of 1–2 ml. of hydrofluoric acid to the solution in the platinum dish, the silica is volatilised by evaporation of the solution on the hot plate to the fuming stage. (*Note.*—In cases where difficulty has occurred in bringing about complete solution of calcium sulphate, some of which may have been filtered off with the silica, the heating with concentrated sulphuric acid in the dish must be continued until all the sulphate passes into solution in the hot concentrated acid.) Upon transference to the beaker containing the original solution, there should be no further difficulty in obtaining a perfectly clear solution.

(*c*) *Precipitation of the Lead Sulphide.*—To the clear colourless solution 5 ml. of a 10 per cent. solution of citric acid and 5 ml. of a solution containing approximately 2 mgrms. of pure copper per ml. are added, followed by a few drops of "masked methyl orange" indicator. Concentrated ammonia (sp. gr. 0·880) is now run in, with constant stirring, when the colour of the solution will gradually change from red to purple, and finally to a neutral greyish tint. At this point the addition of one or two more drops of ammonia will cause a change to green (P_H about 4–5), the solution being now only slightly acid to litmus. This is the degree of acidity which has been found to be suitable for the precipitation of the sulphides. Hydrogen sulphide is now passed through the solution for one hour.

After the precipitated sulphides have been allowed to settle (15–30 minutes—not longer), the supernatant liquid is decanted through an 11 cm. acid-washed

filter paper, which must be free from pinholes. Finally, the sulphides are transferred to the paper and washed twice with hydrogen sulphide water, and then with 10–15 ml. of warm (40–50° C.) 4 per cent. sodium sulphide solution to remove sulphides of arsenic, antimony and tin. If the filtrate is not quite bright, it must again be passed through the filter.

The paper containing the sulphides is now destroyed by wet combustion in a tall 250 ml. silica beaker, as described previously for the silica separation, and, when all organic matter is destroyed, the excess of sulphuric acid is expelled, the beaker being removed from the hot plate when practically all the acid has evaporated, and the remaining acid being driven off by gentle blowing, while the beaker is still hot. The lead and copper are now in the form of sulphates.

(*d*) *Electrolytic Deposition of Lead Peroxide.*—To the tall 250 ml. silica beaker containing the dry sulphates, 10 ml. of water are added and then concentrated (0·88) ammonia, drop by drop, until any free sulphuric acid is neutralised, this being shown by the appearance of the blue colour due to copper. Fifteen ml. of water containing 1 ml. of concentrated redistilled nitric acid are then added, and the resulting solution electrolysed, under the following conditions:—Temperature, 70–80° C.; voltage, 1½–2 volts; current density, 0·3–0·4 amps./100 sq. cm.; speed of rotation of anode, 1500-2000 revolutions per minute.

The anode is a cylinder of platinum iridium (25 per cent. of iridium) foil, 1 cm. deep and 1 cm. diameter, joined centrally to a platinum iridium wire, about 12 cm. long, and is rotated at the above-mentioned speed. The cathode is a plate of platinum iridium foil, 1½ cm. square, also joined to a wire. Before electrolysis the cathode has a thin coating of copper deposited on it electrolytically. The beaker is fitted through the lid of a water bath so that it remains suspended by the rim, the temperature of the bath being kept between 70° and 80° C. By means of a sliding resistance the voltage from a 4 V accumulator is cut down until the current through the electrolyte is 20 milliamps, this giving the correct current density. The dimensions of the beaker are such that when the electrodes are at opposite sides and this current passes, the voltage drop between the electrodes is 1·6 volts. The distance between the electrodes is then about 4 cm. The beaker is covered with a split clock-glass, and the electrolysis continued for 1 hour, after which the motor rotating the anode is stopped, and the anode removed from the solution and washed.

(*e*) *Precipitation of Lead Sulphate.*—The lead peroxide is dissolved from the anode in a 100 ml. tall silica beaker by heating for 30 minutes in a boiling water-bath with a mixture containing 25 ml. of water, 0·5 ml. of concentrated nitric acid, and 5–10 drops of alcohol. The anode should now be visibly free from lead peroxide, and should give no coloration when tested with Trillat's reagent (*Compt. rend.*, 1903, **136**, 1205). Redistilled concentrated sulphuric acid (0·5 ml.) is now added to the solution, and the mixture evaporated on the hot plate to complete dryness (to remove all nitric acid). A further 0·5 ml. of concentrated sulphuric acid is now added, and the beaker is covered and again heated to the fuming point for a few seconds. After cooling, 15 ml. of a mixture containing 1 vol. of alcohol (about 94 per cent. by

volume) to two volumes of water are added, and *thoroughly mixed with the acid.* The mixture is allowed to stand overnight, when the lead sulphate is filtered off on a 5 cm. acid-washed, close filter paper, and washed twice with a mixture containing alcohol, water, and concentrated sulphuric acid in the respective proportions by volume 10, 20 and 1. Ten ml. of 10 per cent. ammonium acetate solution are now boiled in the beaker in which the sulphate precipitation was carried out, and the hot solution is passed through the filter into a similar beaker. This operation is repeated, the same 10 ml. of ammonium acetate being again raised to boiling, passed through the filter, and collected in the first beaker. The filter is finally washed three times with about 5 ml. of hot water containing a little ammonium acetate.

(*f*) *Colorimetric Determination as Lead Sulphide.*—An opinion as to the approximate quantity of lead present having been formed by inspection of the electrode after electrolysis, the whole, or a suitable proportion of the ammonium acetate solution, is transferred to a tall 50 ml. Nessler cylinder. The best quantity to be used for the matching as lead sulphide under these conditions has been found to be 0·05 mgrm. of lead. An exactly similar cylinder is used for the solution with which it is to be compared, and 10 ml. of the ammonium acetate reagent are placed in this cylinder. To each cylinder are added 2 ml. of 10 per cent. potassium cyanide solution, 5 ml. of approximately 6 *N* ammonia, water to the 50 ml. graduation, and, finally, with constant stirring, 2 drops of the special 10 per cent. sodium sulphide solution. A solution containing 0·01 mgrm. of lead per ml. is now run from a burette into the cylinder containing the control solution, until a match is obtained.

The solution in the cylinder containing the control is now rejected, and a fresh control prepared containing all the reagents (except the sulphide) and a volume of the standard lead solution which is less by 1 ml. than that added in the first comparison. The sulphide is added last, followed by a little more lead solution as may be necessary to produce a perfect match. The burette reading may then be recorded. The cylinders should be viewed both with the cylinder containing the control on the left and also on the right of the cylinder containing the solution to be examined.

By working with 0·05–0·10 mgrm. of lead, the results obtained colorimetrically are within 5 per cent. of the exact amount present.

(2) For Biological Materials.—The method has been applied, with slight modification, to biological materials, the essential difference being the omission of the nitrosyl sulphuric acid. The material is first heated in a covered silica beaker with dilute nitric acid, containing 10 per cent. by volume of nitric acid (sp. gr. 1·4) until most of the solid matter has been disintegrated. The destruction of the organic matter is then completed by the action of concentrated sulphuric and nitric acids, and the process is then continued as described above.

(3) For Miscellaneous Materials.—Organic matter, if present, is first destroyed by wet combustion with strong nitric and sulphuric acids, the method

then being continued as described in VI (1) (*b*) above. It should be noted, however, that the presence in the electrolyte of relatively large quantities of iron salts causes an incomplete deposition of the lead during electrolysis. If, on neutralisation of the electrolyte during the process of adjusting the acidity of the solution prior to electrolysis, a red precipitate of ferric hydroxide should be observed, it is advisable to reverse the sequence of the electrolysis and the separation of the deposited lead as lead sulphate.

VII. RESULTS.—Fifty-five samples of normal urine from persons residing in London and the surrounding country districts gave quantities of lead varying from nil to 0·133 mgrm. of lead (Pb) per litre, the average value being 0·040 mgrm. of lead per litre.

We wish to thank Sir Frederick Willis, K.B.E., C.B., Chairman of the Committee of Enquiry on Lead Ethyl Petrol, for permission to publish the work described in this paper, and also Sir Robert Robertson, K.B.E., M.A., F.R.S., the Government Chemist, for constructive criticism and advice.

THE GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE, LONDON, W.C.2.

Official Appointment.

THE Minister of Health has confirmed the following appointment :

MR. A. E. JOHNSON, B.Sc., F.I.C., as Public Analyst for the County Borough of Wolverhampton (November 11, 1929).

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.

STEROLS IN BUTTER.

DR. VAN SILLEVOLDT, Director of the Dutch Dairy Station at Leiden, has kindly given me permission to publish the following process for separating the sterols from butter and similar fats. The process, which was devised by the Director, in association with the members of the staff of the Dairy Station, was given to me in April, 1928, and, since then, I have found it to be of great use in the examination of butter, especially of small samples.

Process.—Saponify, with reflux condenser, 15 grms. of filtered fat with 9·5 ml. of potassium hydroxide solution (1000 grms. of KOH in 1400 ml. of water) and 20 ml. of alcohol (96 per cent.) in a 300 ml. conical flask. Shake while warm until the fat is dissolved, and heat further for half-an-hour.

Cool, add 60 ml. of water and 180 ml. of alcohol (96 per cent.), mix, and add 10 to 20 ml. of digitonin solution (1 per cent. of Merck's digitonin in 96 per cent. alcohol). Allow the mixture to stand for 24 hours in a cool place and filter on Buchner funnel with a closely-fitting paper. Wash with a small amount of alcohol to remove soap. The digitonin-sterol compound flakes off on drying. Weigh the steride and acetylate it with ten times its weight of acetic anhydride, and proceed with the crystallisation from alcohol (about 95 per cent.) as in the Bömer method.

A. MORE.

THE FALL IN REICHERT–MEISSL VALUES ON KEEPING BUTTER SAMPLES.

THE following figures may be of interest as showing how the Reichert–Meissl values of five samples of butter decreased after having been kept for nearly six years in bottles fitted with metal screw caps and cork discs. From the condition of the caps it appeared possible that a slow renewal of the air in the bottles might have taken place by diffusion, and, owing to temperature changes, over a prolonged period. The original samples were genuine butters with abnormally low Reichert–Meissl values, and moisture percentages ranging from 12·4 to 14·7.

It will be noted that there is a parallel between the amounts of free fatty acids formed, and the corresponding losses in volatile acids, suggesting that the former might possibly be taken as an index of the latter.

Sample No.	R.M. values of the fresh samples.	The same samples nearly 6 years old.				
		Free fatty acids. Per Cent.	R.M. value.	Polenske value.	Kirschner value.	Saponification value.
1	20·7	27·0	8·0	1·3	7·1	211
2	21·8	14·5	16·5	1·6	11·9	224
3	20·7	14·0	15·8	1·3	12·4	224
4	21·1	7·5	19·5	2·2	14·4	231
5	21·5	6·0	20·8	2·0	15·2	230

PAUL ARUP.

BUTTER TESTING STATION,
DUBLIN.

FURFURAL IN HEATED HONEY.

IN the paper entitled "Furfural and Diastase in Heated Honey" (ANALYST, 1929, 381), we stated that the tests on the possible development of furfural in heated honey due to storage were being continued. These tests have now been completed. In the case of the samples cited on page 387:—

Samples described under (*a*) still gave negative aniline acetate and Fiehe tests after storing for 12 months.

Samples described under (*b*) still gave negative aniline acetate and Fiehe tests after storing for 8 months.

Samples described under (*c*) still gave, after continued storing for 9½ months, the same results in the aniline acetate and Fiehe tests as directly after heating.

Moreover, in all cases, samples of the same honey, unheated, were kept side by side with the heated samples; these also produced no furfural.

CONCLUSION.—These further results indicate that no furfural or furfural derivatives are developed when heated honey is stored for periods up to 12 months.

L. H. LAMPITT.
E. B. HUGHES.
H. S. ROOKE.

FURTHER EXPERIMENTS ON THE ACTION OF AIR ON FLOWERS OF SULPHUR AND GROUND SULPHUR.

IN view of the suggestion that the results previously recorded (ANALYST, 1929, 590) might have been due to the ground sulphur being coarser than the corresponding samples of flowers of sulphur, the following further estimations were carried out on a sample of ground sulphur which was finer than the flowers of sulphur originally employed.

The sample of flowers of sulphur used in the previous estimations showed 98·5 per cent. passing a 300-mesh sieve, and the one used in the following estimations showed 100 per cent. passing a 300-mesh sieve.

The results obtained were as follows:

Class of sulphur.	Weight of sulphur taken. Grm.	Temperature. °C.	Vol. of air. Cb. ft.	*N*/100 iodine. c.c.	Equivalent to SO_2 on weight of sulphur taken. Per Cent.
Ground	1	60	1	Nil	Nil
Ground	1	80	1	Nil	Nil
Ground	1	90	1	0·2	0·0064
Ground	1	100	1	1·3	0·0416

These results are practically identical with those previously recorded, and confirm the inactivity of ground sulphur at lower temperatures in comparison with flowers of sulphur.

J. E. STEPHENSON.
S. W. BRIDGE.

AUTOMATIC PIPETTE.

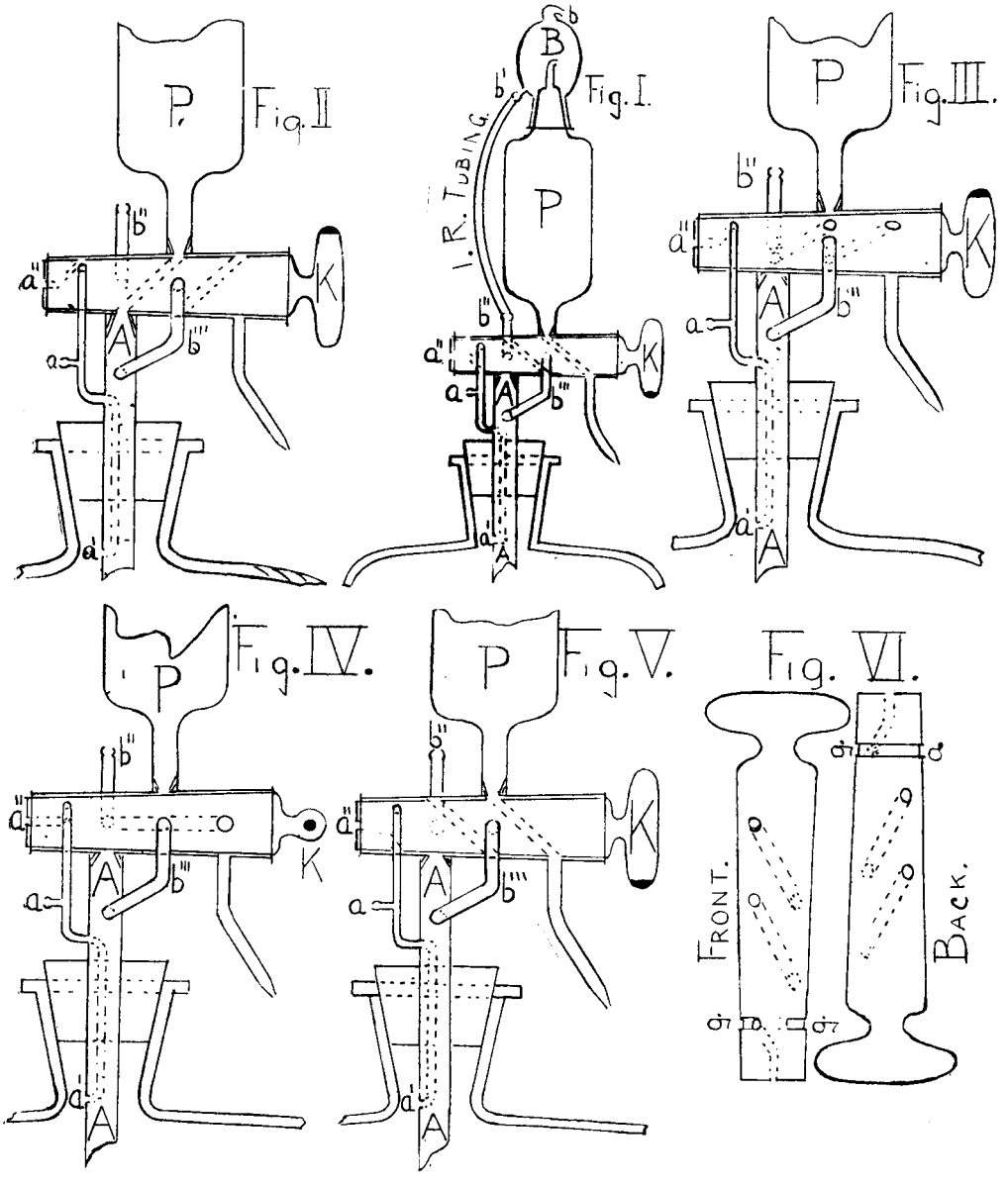
THIS form of automatic pipette is intended for filling by means of air-pressure and for fitting on to large storage-bottles, as shown. Ordinarily, the necessary pressure is obtained by the use of a small hand-bellows. If desired, however, a slight additional transverse surface-grooving of the key will permit the using of a small-power mechanical blower (g. Fig. VI).

From the diagrams it will be seen that:

(i) All the movements involved in the use of the pipette are under the control of a single key, and

(ii) single-necked storage bottles and one-hole stoppers suffice.

MANIPULATION.—A one-hole stopper having been fitted (as shown) on the stem A of the pipette and fastened securely in position in the neck of the storage-bottle, the bellows is joined up at *a*, and the pressure inside the bottle is increased by way of *a* and *a'* (Fig. I).



(1) The key K being set as in Fig. II, the liquid rises in A, then through the key and the pipette-body P, to overflow into the bulb B (Fig. I). Should B overflow, excess of liquid will run off through *b*, fitted with a suitable length of rubber-tubing, into a beaker or a sink. *The free end of this tubing must not dip under liquid.*

(2) P being filled to overflowing into B (Fig. I) the key is turned forward (the end marked black in the diagram towards the operator) into the position shewn in Fig. III. This

(i) disconnects P from the storage-bottle, and

(ii) connects the bellows and storage-bottle with the external air by means of *a*, *a'* and *a''*.

(3) Air-pressure inside the storage-bottle being again normal, K is continued forward into the position shown in Fig. IV:

(i) The overflow in B (Fig. I) runs back into the bottle by way of *b'* (Fig. I), rubber-tubing, *b''*, the key, and *b'''*.

(ii) The tip of the pipette-body is left clear of overflow.

(4) K is again continued forward into the position shown in Fig. V, and P is thus connected with the receiving vessel into which it discharges.

On turning back the key into the position in Fig. II, the operator is again ready to begin a measurement.

Should the operator consider that attaching a bellows at *a* might lead to fracture of this part of the pipette through an accidental jerk, *a* may be closed and the bellows connected with the air-space of the store-bottle by means of a glass elbow of small-bore tubing which is fitted into a second hole in the stopper.

The apparatus is made by McCulloch Bros. and Wilson, 46A, West Princes Street, Glasgow, C.4.

A. HENDERSON.
J. ROBERTS.

UNIVERSITY OF GLASGOW.

Notes from the Reports of Public Analysts.

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

CITY OF LEEDS.

REPORT OF THE CITY ANALYST FOR THE SECOND AND THIRD QUARTERS, 1929.

THE total numbers of samples examined in the two quarters were 731 and 713, of which 523 and 494, respectively, were samples taken under the Food and Drugs Acts. Of these, the percentages adulterated were 14·3 and 14·8.

MILK.—One hundred and thirty-seven of the 724 samples of milk were adulterated or below standard. It is significant that one of the worst cases of fat deficiency (19 per cent.) was a Grade A milk. Fat deficiency in Grade A milk is partly due to the practice of bottling milk from individual cows instead of bottling

the mixed product of the whole herd. Where the herd is a Friesian one, the fat deficiency is liable to be more pronounced than in the case of other herds. In these instances the public are paying an increased price for milk which, though it has to conform to a bacteriological standard not demanded of ordinary milk, is nevertheless inferior to the latter as regards its chemical composition.

CREAM BUNS.—Of 5 samples submitted, 4 contained imitation cream filling. In one case this consisted of a mixture of 75 per cent. of cane sugar and water with 25 per cent. of fat, which was composed of 97 per cent. of palm-kernel oil and 3 per cent. of butter fat.

In a second case coconut oil was the predominant oil, but in this case, as in the remaining two, the quantity of fat available for examination was insufficient for a full analysis. In the remaining two cases fats with low Reichert and Polenske values had been employed. In the case where butter fat only had been used in conjunction with cane sugar and water, the proportions were as follows:—Water, 9·6; cane sugar, 17·9; butter fat, 72·5 per cent.

Legal advice has been taken concerning imitation cream used as a filling, and is to the effect that the Artificial Cream Act, 1929, does not cover this. Hence, as none of the buns in question contained boric acid, they have been returned as genuine. (*Cf.* ANALYST, 1928, **53**, 383.)

C. H. MANLEY.

CITY OF SALFORD.

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1928.

THE total number of samples (1484) is greater than that for any previous year, with the exception of 1924, and represents a purchase of 593 samples per 100,000 of the population, which is a greater number than that taken by most other local authorities. Of the total samples, 70, or 4·72 per cent., were returned as adulterated. The number of informal samples was 751.

MILK.—During the year 1103 samples were examined, of which 43 (3·9 per cent.) were returned as adulterated.

Abnormal Milk.—During the first quarter a number of samples from different farms gave a percentage of solids-not-fat below the legal standard. These samples came from so large a number of different farms that it was evident that it was not so much a question of adulteration as of natural variation. No action was, of course, taken, since it was obvious that these samples were as they came from the cow. No reason can be assigned for this unusual state of affairs, but there is a possibility that it may be connected in some way with the extraordinary rise in the percentage of fat during the last four months of 1927, which continued into the first three months of 1928. The average fat figures for all milk samples during these seven months were as follows:

September	4·21
October	4·25
November	4·14
December	4·05
January	3·92
February	3·68
March	3·81

These figures are very seldom equalled either in Salford or anywhere else, and our knowledge of the cow's physiology is not so complete as to be able to

assign a reason for this phenomenon. There is at least a possibility that there may be some sort of relation between it and the, quite as unusual, drop in solids-not-fat. At least two other Public Analysts in this district experienced the same sort of thing, and no reason could be assigned in these cases.

CHEESE.—Eighteen samples of Cheshire cheese contained from 49 to 60·3 per cent. of fat (calculated on the dry substance). Cheshire cheese should contain at least 45 per cent. of fat (on the dry substance).

Bondon Cheese.—One sample of "Bondon" cheese contained only 0·8 per cent. of fat and 72·1 per cent. water. There is, however, no standard for this type of cheese, although it seems originally to have been a whole-milk cheese. A large section of the dairy industry are now making it from skimmed milk, and consider the practice perfectly legitimate.

Full-Cream Cheese.—A sample labelled "full cream" cheese was bought by the inspector as cream cheese, but, on analysis, it was found to be an ordinary whole milk cheese. A representative of the firm, when interviewed, said that he thought that it was a cream cheese. It was pointed out to him that, although the term "full cream" might, in the trade, signify whole milk cheese, it would be taken by the ordinary purchaser to signify a better article, particularly as the price was higher than that of other cheeses sold in the shop. The firm agreed to substitute the words "pure rich" for "full cream" on the labels of this cheese.

Standards for Cheese.—Although power is given under the Food and Drugs Act to make regulations as to the composition of cheese, this power has, as yet, not been exercised. A fairly definite standard has now been adopted for Cheshire cheese, but this is only one variety out of many.

Home-made Lemon Cheese.—Fines were imposed on the vendor and makers of an article described as "Home-made Lemon Cheese," the Stipendiary remarking that home-made articles should be made from ingredients such as the house-wife would use. (*See* ANALYST, 1929, 105.)

WHISKY.—A sample was found to be 43·6 degrees under proof, and proceedings were instituted against the vendor, who was fined £5. It was discovered that this whisky had been bought from a wholesale spirit merchant and invoiced to the retailer as 40 degrees under proof. The wholesaler was interviewed, and in conversation admitted that he was responsible for the labelling of the bottles, and also that the spirit was nominally 45 degrees under proof. A summons was thereupon taken out against him under Sec. 27 of the 1875 Food and Drugs Act, the relevant part of which states that "Every person who shall wilfully give a label with any article sold by him which shall falsely describe the article sold shall be guilty of an offence, etc." In this case it was possible to prove both that the actual composition of the article was known to the person giving the label and that the label was wilfully given by him. It is not often that this can be done in such cases.

The case was adjourned by the Stipendiary for the attendance of either the actual proprietress or her legal representative, and at the adjourned hearing it was submitted that the label was false, inasmuch as it described as whisky, without any qualification, spirit which had been diluted below the strength of 35 degrees under proof. This rather novel submission was upheld by the Stipendiary, and the defendant was fined £15 and 30s. costs.

COD-LIVER OIL TABLETS.—In addition to the case in which the defendants were fined £30 and 75 guineas costs (ANALYST, 1928, **53**, 336), there have been several instances of misdescription of cod-liver oil tablets. A sample of one brand was advertised as containing the "active principle of the liver in a palatable form," and it was also stated that each tablet was equivalent to a tablespoonful of cod-liver oil. Examined by the colour test, five tablets were found to contain less vitamin *A* than one drop of ordinary commercial cod-liver oil. The firm, when interviewed, agreed to discontinue the sale of these tablets.

Another brand, which contained vitamins *A* and *D* in good proportion, bore on the label the statement: "Each tablet is equal to a spoonful of the finest cod-liver oil." Since to state that a tablet which contains merely a vitamin-containing portion of the oil is equal in value to the oil itself, is obviously untrue, the firm was communicated with and agreed to substitute the phrase: "These tablets contain vitamins *A* and *D* extracted from the finest cod-liver oil."

Another sample represented a brand which was advertised to be "250 times as rich in vitamins as the best butter." Vitamin *A* was found to be practically absent, five tablets containing less than does one drop of cod-liver oil. The firm promised that the article would no longer be manufactured.

PROPRIETARY MEDICINES.—Under existing law the sale of worthless proprietary medicines cannot be prevented. Under Sec. 2 of the Food and Drugs (Adulteration) Act, 1928, proprietary medicines are specifically exempted from the Act; the prosecution for the sale of cod-liver oil tablets is probably the first case of its kind, taken under the Food and Drugs Acts, which has succeeded. Had the article been asked for under the proprietary name of "——'s Cod-Liver Extract Tablets," there would have been no case, since the purchaser would have got precisely what he demanded. But inasmuch as cod-liver oil tablets, which are not proprietary, were asked for, and the proprietary article was supplied, a case could be brought, though the question whether the sub-section, dealing with proprietary medicines, was still operative, was not raised by the defendant.

This country is practically the only civilised country in the world which has no means of controlling these articles; and, in view of the immense amount of harm that may be caused by them, this lack of control is a national disgrace. As an example of the state of British, as compared with foreign, law on the subject, it may be of interest to mention that one person is said to have made a profit of £60,000 in this country by advertising and selling an alleged vibratory cure for many diseases, whereas, for the same procedure in France, he was fined £120 and sentenced to three years' imprisonment.

H. H. BAGNALL.

Legal Notes.

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

PRESERVATIVE IN MEAT. REFUSAL OF WARRANTY BY WHOLESALER.

ON August 28, a firm of butchers was summoned at Wimbledon for selling beef which contained 0·022 per cent. of sulphur dioxide, contrary to Sec. 2 of the Food and Drugs Act, 1928.

Mr. Beck, for the defence, submitted that there was no case to answer, since there was no evidence of fraudulent intent. The meat was sold in exactly the same condition as when it was received from the Smithfield market. The Smithfield dealers refused to give a guarantee that the meat sold complied with the Preservatives Regulations. Since the regulations came into force no preservatives had been purchased or used in the shop at Wimbledon. A modern meat safe had been installed, and only sufficient meat for the daily trade was bought.

The Chairman said that the Bench was agreed that there had been no fraudulent intent, and had decided to dismiss the case.

Mr. Hart, for the Surrey County Council, asked if the Bench would be prepared to state a case for appeal on the point of law that had been raised.

OBLITERATION OF ORIGIN MARKS FROM EGGS.

ON October 21, the adjourned summons under the Merchandise Marks Act against an egg dealer was heard before the Hull Stipendiary magistrate.

An inspector of the Hull Corporation gave evidence that, on visiting the defendant's premises, he had found one of the rooms partitioned off and provided with means for washing eggs. Three employees were there, and he noticed two receptacles, one of which contained sulphuric acid. Witness asked the employees if they were engaged in rubbing the marks off the eggs. One girl replied "Yes," another "No," and the boy did not answer the question. Witness later purchased some marked eggs at 1s. 4d. per dozen, and others marked "Guaranteed English eggs," at 1s. 8d. per dozen, which was 2d. per dozen below the wholesale price, and these eggs had obviously been washed.

Mr. A. R. Tankard, F.I.C., Public Analyst, said that he had examined a number of eggs which had been purchased from the defendant. Some of them which were unmarked gave abundant evidence of sulphate, and showed traces of purple spots and smears. Three eggs of another batch (from the shop) had originally been marked in purple, and, in his opinion, had been treated with sulphuric acid. The two bottles of liquid submitted consisted of dilute sulphuric acid of 0·17 and 0·84 per cent. strength, and both contained a deposit of calcium sulphate.

The defendant said that the eggs were often dirty, and his employees were provided with materials for washing them; after washing they were re-stamped. He had a stamp marked "Holland."

In reply to the Magistrate, he said that, although he also bought eggs from Russia, France and Belgium, he stamped all of them, after washing, with the "Holland" stamp.

The Stipendiary Magistrate said that the defendant had not discharged the onus of proof that the cause for the removal of the marking had not been for the purpose of concealing the origin of the eggs at the time of their sale.

He inflicted a fine of £5, with ten guineas costs.

Department of Scientific and Industrial Research.

FOOD INVESTIGATION. Special Report No. 35.

HEAT INSULATORS.*

THE function of insulating materials such as granulated cork, charcoal or slag wool is to subdivide the air space into such small cells that convection is reduced to the maximum extent and transmission of heat through a wall of granulated material is the composite effect of conduction, radiation and convection.

Experiments described consist in a quantitative measurement of the thermal conductivity of various materials, which is defined on the British system as the quantity of heat in B.Th. Units which flows per sq. ft. per hour through 1 in. thickness of material for a difference of temperature of 1° F. between the faces. This number is 2903 times that which would express the same conductivity on the C.G.S. system.

* Obtainable from H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 2s. 6d. net.

The apparatus used consists essentially of a central hot plate and a guard ring round it of an outer plate in the form of a ring in the same plane with the central part, but separate, and maintained at the same temperature. The hot plate is fixed centrally between two cold plates, and the material under investigation is packed between. The heat transmitted is measured as watts dissipated in the hot place, and the temperature difference is observed by means of a number of thermocouples attached to various points on the hot and cold faces. Several sets of this apparatus were used, 5 ft. 20 in. and 12 in. The apparatus is filled with the material which, if compressible, is adjusted to the density of packing desired, the heat supply switched on and adjusted till the specified temperature of the hot plate is obtained. The temperature of the guard ring is equalised and the apparatus left undisturbed with a constant energy supply from battery to hot plate, and observations of temperature are made about every 12 hours until a steady state is obtained. The temperature difference, average temperature of faces, and the calories per sq. cm. per second per 1 cm. thickness are worked out.

A study of convection currents shows that the phenomenon of the transfer of heat from a vertical hot wall is more complicated than has been supposed, and, in estimating effects of convection, account must be taken of the altered character of the flow of air along the surface.

Details of experiments on some 40 different materials tested include the following figures for B.Th.U. per sq. ft. per hour for 1 in. thickness and 1° F. difference in temperature, and the mean temperature of the insulating material:— Slab cork, 0·28, 46°; granulated cork, $0{\cdot}29_8$, 32°; sample baked, $0{\cdot}25_3$, 177°; coarsely granulated cork, packed, 5·4 lb. per cu. ft., 0·32 to 0·35, 23°; cork wool, treated with paraffin, 0·22, 48°; charcoal, $0{\cdot}34_8$, 63°; fibre from bark of eucalyptus tree, 0·32 to 0·38, 32°; rubber sponge sheet (24 lb. per cu. ft.), 0·37, 95°; teak, 0·81, 81°; eel grass, $0{\cdot}31_3$, 86°; concrete block, 8·1, 88°.

The value 0·29 B.Th.U. per sq. ft. per hour per 1 in. thickness for 1° F. difference of temperature between the faces is regarded as representing the thermal conductivity of an insulating material of good quality. Finely granulated cork after baking to a dark brown colour is a better insulator than the raw material, and coarsely granulated cork is not so good; cork wool or cork shavings are very good insulators, but, in practice, the material would have to be protected from access of moisture. Dry charcoal is good, but the moisture-absorbing powers are a great drawback. Of timbers, the light wood "balsa" combines efficiency with some facility for being cut into shape, but it is soft; crude diatomaceous earth and granular pumice have conductivity coefficients about twice that of slab cork.

Experiments on the moisture-absorbing capacities of insulating materials are described where the materials are in equilibrium with air of various humidities, and where they are immersed in water. The determination of specific heats of insulating materials is described, as the constant is important when calculations have to be made of heat transmission through walls, before the steady state has been attained. The mechanical properties of slab cork are dealt with in detail.

D. G. H.

References to Scientific Articles not Abstracted.

PHOTOMICROGRAPHS OF PHILIPPINE STARCHES. By R. N. ALLEN.

THESE appeared in the February issue of the *Philippine Journal of Science*, **38**, 241. (*Cf.* ANALYST, 1929, 686.)

Report of the Chief Inspector of Factories and Workshops, 1928.

INDUSTRIAL DISEASES.*

In addition to industrial diseases of a well-recognised type, attention is directed to others arising from the use of chemical substances hitherto little known outside the laboratory.

Lead Poisoning.—This showed a decrease (326 cases notified and 43 fatal). Two cases were attributed to the use of "flake white," which is practically entirely composed of lead carbonate, and hitherto has not been labelled "lead."

Arsenical Poisoning.—Two fatal cases of arsenical poisoning were due to (1) accidental ingestion of arsenical sheep dip, and (2) ulceration caused by arsenic in emerald green, etc., extending over some years. An examination of 14 men in contact with a powder containing arsenic and an alkali, disclosed circumscribed ulceration in 4, effects on the nasal septum in 7 and well marked dermatitis in 12.

Mercurial Poisoning.—Of 4 cases of mercurial poisoning, 3 occurred in the manufacture of thermometers and 1 of electric meters.

Aniline.—Since 15 of the 41 aniline poisoning cases occurred in June, July and August, the influence of hot weather is to some extent indicated. One of the most severe cases was due to accidental splashing of clothing with aniline oil, and another case to use of an ink remover containing aniline oil.

Hydrogen Arsenide.—Inhalation of arseniuretted hydrogen accounted for 6 toxic poisoning cases, and other cases were due to escapes of the gas which were not anticipated. In one, saw-dust was mechanically stirred in an open tank containing molten tin, and 10 of 15 men present were affected; an analysis of the skimmings from the tank showed 0·29 per cent. of arsenic.

Hydrogen Sulphide.—Nine cases of hydrogen sulphide poisoning (3 fatal) were reported, two being due to the charge of sulphuric acid being run too quickly into a vat containing sodium sulphide solution.

Anthrax.—Three of 24 anthrax cases proved fatal, the increase of cases being due to increased importation of infected hides from China. Drs. Jordan Lloyd and Robertson are studying methods for disinfecting the hides, and a laboratory method making, use of a sulphonated oil in conjunction with a disinfectant, is being worked out.

Dermatitis.—This is not notifiable, but 662 cases were referred, showing a steady increase, which indicates that increased importance is being attributed to the condition. Paraffin, turpentine and methylated spirits, as well as alkalis, are used to cleanse hands and arms after work, and unless these agents are themselves removed very thoroughly, they are liable to cause dermatitis.

D. G. H.

* Obtainable from H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 2s. 6d. net.

Ministry of Agriculture and Fisheries.

EGG PRESERVATION AND THE REGISTRATION OF PREMISES.

THE following Press notice has been issued by the Ministry:

It is clear, from information which continues to reach the Ministry from time to time, that in some quarters the provisions of the Agricultural Produce (Grading and Marking) Act, 1928, regarding the registration of premises used for the preservation of eggs are not yet fully understood. The position may be briefly summarised as follows:—

For the purposes of the above Act, the various processes for preserving eggs have been divided into two classes:—

(*a*) Those the use of which can subsequently be detected by chemical analysis, because the composition of the shell has been altered by the pores of the shell having become filled with the preserving material; and

(*b*) those that cannot be so detected because the shell is not affected in any way.

Processes such as immersion in lime-water, water-glass or oil come into the first category, and therefore under the operation of Section 3 of the Act. Premises used for the preservation of eggs by such processes are *not required to be registered.*

The only processes in the second category at present employed in this country on a commercial scale are cold storage and chemical storage, *i.e.*, storage in a gas. British eggs so preserved come within the scope of Section 4, and must not be moved from the place of storage unless each egg is marked in the prescribed manner. Premises used for the cold storage or chemical storage of eggs *are required to be registered* under Section 4 of the Act by, as regards England and Wales, the council of the county or county borough (or in the case of the administrative county of London by the Common Council of the City of London or the Council of the Metropolitan Borough) in which the premises are situated.

Queensland.

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDING JUNE 30TH, 1929.

DR. J. B. HENDERSON, in his annual report, states that the total number of samples examined during the year was 6858, of which 1986 were for the Health Department, and 1568 for the Customs. Of the samples for the Health Department, 766 were formal samples taken in accordance with the Health Acts, and 237 of these were condemned as adulterated or below the standards.

MILK.—Of the 715 legal samples, 506 passed the standard and 57 were genuine, but below the standard.

The improvement in the milk supply during 1927–28, as compared with other years, has unfortunately not been maintained; in fact, the proportion of adulteration this year is much higher than it has been for many years. The only redeeming feature of the position is the continued improvement in the cleanliness of the supply, as adjudged from its comparative freedom from visible dirt and from bacteria.

Nearly 8 per cent. of the samples received were genuine milks which failed to conform with the legal standard for milk. Probably nowhere else in the British Empire is the milk vendor so thoroughly safeguarded from unfair prosecution as in Queensland. Only results from fresh samples are accepted for the purposes of legal prosecution, and the umpire sample is kept in cold storage, so that it will be in a fresh condition for analysis when required.

THE FREEZING-POINT TEST.—For more than twenty years the freezing-point test has been used in the routine examination of milk in this laboratory. Following a paper on this subject which Dr. Henderson read before the Queensland Royal Society in 1909, the Dominion Laboratory of Wellington, New Zealand, investigated and adopted the freezing-point method for determining added water in milk, and has now employed it for fifteen years with eminently satisfactory results. According to a recent report from that laboratory, the maximum variation in the freezing point of milk is from —0·545° C. to —0·565° C. Only one out of 270 samples recorded above —0·55° C. These results confirm those obtained in the Queensland Government Laboratory, and those of many other observers in other parts of the world. Dr. Monier Williams reported in 1912 to the Local Government Board of Great Britain that the freezing point is "the most constant of any of the properties exhibited by milk." This capable observer, however, retarded general adoption of the method in Great Britain by stating that "owing to the experimental difficulties involved in obtaining reliable results, it is somewhat doubtful whether the method is capable of general application for purposes of milk control." In Queensland, however, the mechanism of the test has been reduced to such simplicity that any ordinarily trained observer can determine the proportion of adulteration to within one per cent. of the truth.

LEAD ARSENATE IN CABBAGES.—In last year's annual report it was noted that arsenate of lead had been found in cabbages in dangerous proportion. The Food and Drugs Regulations provide for no arsenic or lead in vegetables. A number of growers, particularly in one district, took no notice of the warnings given, and a number of consignments of cabbage contaminated with arsenate of lead have been seized in the markets and destroyed. Many of these cabbages contained comparatively high amounts of arsenate of lead, four containing between fifteen grains and seventeen grains. One, on which the white stains of arsenate of lead were freely visible, was boiled with salt and a little soda exactly as in an ordinary household. After straining, it was found, on analysis, that the arsenate of lead, as a result of the boiling, had become evenly distributed throughout the cabbage and the water. The total arsenate of lead present was fifteen grains. An ordinary helping of about three ounces of this cabbage would contain 0·25 grain of lead (calculated as metal) and 0·375 grain of arsenic (calculated as As_2O_5). Children are being advised at school to drink a cupful of cabbage water when they get the chance—probably for the vitamin content. A cupful (say nine ounces) of water from this cabbage would contain 1·1 grain of lead (calculated as metal) and 0·6 grain of arsenic (calculated as As_2O_5), and the maximum medicinal dose of arsenic for an adult is only 0·06 grain. It is quite evident that there must have been cases of fairly acute poisoning from some of these cabbages. The symptoms of gastric and intestinal irritation in such cases occurring after a meal would not unlikely and not unnaturally be classed as "ptomaine poisoning." There would also be a certainty of chronic lead poisoning if such contaminated cabbages were regularly used as a food. The drastic but necessary destruction of contaminated consignments will probably put an end to this highly dangerous practice.

LEAD IN SODA WATER.—Of 119 samples of soda water examined, 69 samples contained lead in the proportion of 1/100th grain or more per gallon. While the proportion of lead has been markedly reduced since 1926–27, it is important, from a health standpoint, that soda water should be entirely free from such a toxic substance as lead. It would be interesting to know if the country that is supplying carbonators containing lead solder to Australia is also providing its own inhabitants with soda fountain drinks containing lead in solution. Queensland and Palestine

are the only countries, so far, where we have seen the presence of lead in soda water reported.

ORANGE CORDIALS.—Of twelve samples of orange cordials examined, seven passed the fruit cordial standard, which requires the presence of not less than 20 per cent. of fruit juice. The aerated orange beverages on the market contained from nil to 10 per cent. of orange juice. The orange drink stalls were found to be dispensing a beverage containing about 10 per cent. of orange juice. It is important, from the aspect of national health and the interests of our orchardists, that the use of pure fruit drinks should be fostered in every possible way. A regulation appears to be necessary, stipulating for a minimum proportion of, say, 5 per cent. of orange juice in orange beverages, and the elimination of preservative and artificial colouring from all drinks sold over the counter for immediate consumption and purporting to be made on the premises from fresh fruit juice.

MINCED MEAT.—Of twenty-two samples of minced meat and sausages examined, thirteen failed to meet the standard in regard to preservative, the excess of sulphur dioxide in the sausages ranging from 2 to 243 per cent. Preservative is now forbidden in minced meat.

CHEWING GUM.—Three samples of chewing gum contained drugs in the form of acetylsalicylic acid and phenolphthalein. This method of administering drugs is undoubtedly dangerous.

FLESH-REDUCING SOAP.—A sample of soap, sold at a fabulous price, and described as flesh-reducing, was found to be ordinary toilet soap adulterated with talc. A liquid preparation for reducing adipose tissue consisted of alcohol, soap and camphor. The selling price of this simple mixture worked out at nearly £5 per pint.

ANILINE DYES IN PAINTS.—The samples of paints examined were mainly those tendered to the State Stores Board, and advice was given as to the relative qualities and values. A most objectionable practice has recently been adopted by certain manufacturers, of adding aniline dyes in different proportions to some of the paints. These dyes are being fairly freely used in the reds, browns, and stone colours, and have been met with in the green. They are not lasting in daylight, and paints tinted with them must alter in colour comparatively soon after being applied. All such paints have been rejected for Government use. A case, not that of a Government building, was recently brought to the notice of the Government Analyst, where a house which had been painted a light stone colour had bleached to white in three months wherever strong light fell on the paint.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Examination of Honey. J. Fiehe and W. Kordatzki. (*Z. Unters. Lebensm.*, 1929, **58**, 69–76.)—Further comparative experiments (*cf.* ANALYST, 1929, 108, 241) have been made on methods for the determination of oxymethylfurfural in honey, and the following modification of Troje's method (*loc. cit.*) has been thoroughly tested and found to give the most reliable results. A solution

of 100 grms. of honey in 400 c.c. of water is shaken with 5 c.c. each of 30 per cent. zinc acetate and 15 per cent. potassium ferrocyanide solutions, filtered, and extracted with 50 c.c. of ether. The extract is shaken with 50 c.c. of petroleum spirit and 10 grms. of anhydrous sodium sulphate, evaporated at a low temperature after 24 hours, and the residue extracted with 20 c.c. of water. For the iodine method an aliquot part of the honey solution (sufficient to leave at least two-thirds of the iodine unconsumed) is mixed with 10 c.c. of 0·1 *N* iodine solution, and diluted to 100 c.c., the alkalinity being adjusted to 0·5 *N*. After 2 hours 25 c.c. of *N* sulphuric acid are added, and the solution titrated with 0·1 *N* thiosulphate solution (1 c.c. 0·1 *N* iodine solution=677 mgrms. of oxymethylfurfural). For the phloroglucide precipitation the authors add 30 c.c. of a 0·625 per cent. solution of diresorcinol-free phloroglucinol in 16 per cent. hydrochloric acid to 10 c.c. each of honey extract and 32 per cent. hydrochloric acid. After 24 hours the precipitate is filtered off, washed with 20 c.c. of water in 5 c.c. portions, dried at 100° C. for 3 hours and weighed. Then 2, 5, 10, 15, 20, 25, 30 and 36 mgrms. of phloroglucide correspond with 2·3, 4·2, 5·9, 7·9, 9·9, 12·0, 14·0, and 16·3 mgrms. of oxymethylfurfural, respectively. Lenk's method (*loc. cit.*) depends on the reduction of an alkaline solution of a copper salt by oxymethylfurfural. Experiments with 21 samples showed that no genuine honey contained oxymethylfurfural, and that every artificial or mixed honey contained this compound in quantities which, in the latter case, were proportional to the amount of artificial honey present. The iodine and phloroglucide methods together may, therefore, give a reliable indication of the nature of the honey, though the iodine method alone is unreliable (*loc. cit.*), as it is influenced by aromatic substances in the sample. J. G.

Reducing Powers of Different Sugars for the Ferricyanide Reagent used in the Gasometric Sugar Method. J. A. Hawkins. (*J. Biol. Chem.*, 1929, **84**, 79–82.)—The glucose-reducing equivalents of mannose, galactose, fructose, arabinose, xylose, maltose and lactose for potassium ferricyanide have been determined under conditions of the macro blood gasometric method of Van Slyke and Hawkins (*J. Biol. Chem.*, 1928, **79**, 739). This method depends upon the quantitative reduction of potassium ferricyanide in an alkaline solution well buffered by a mixture of potassium carbonate and potassium bicarbonate, the excess ferric salt being afterwards measured by the amount of nitrogen gas which it frees from an excess of hydrazine in the Van Slyke–Neill (*J. Biol. Chem.*, 1924, **61**, 523) manometric apparatus. The relative reducing values of different sugars vary greatly with the conditions of analysis; consequently, when a new method of sugar determination is introduced, the reduction factors must be ascertained for each individual sugar before it can be determined by the method. A table shows the results. The amount of ferricyanide reduced is directly proportional to the amount of glucose, mannose, maltose, or lactose present; the amount of ferricyanide reduced is directly proportional to the amount of fructose, arabinose, or xylose present when the concentration of these sugars does not exceed 0·1 mgrm. per c.c. in the standard solution. The difference in amount of ferricyanide reduced

per mgrm. of sugar when the concentration of fructose, arabinose, or xylose is 0·2 mgrm. per c.c. is only 5 per cent. less than when the concentration is 0·1 mgrm. or less in the standard solution. It is possible to determine the concentrations of these sugars, when one sugar alone is present in solution, by use of the factors and conditions described for the macro blood gasometric method. P. H. P.

Micro Time Method for the Determination of Reducing Sugars, and its Application to Analysis of Blood and Urine. J. A. Hawkins. (*J. Biol. Chem.*, 1929, **84**, 69–77.)—The method of Hawkins and Van Slyke (*J. Biol. Chem.*, 1929, **81**, 459), in which sugars are determinedly the time they require to reduce a known amount of yellow ferricyanide solution completely to colourless ferrocyanide, has been refined so that 0·2 c.c. of blood suffices for duplicate analyses. In the micro method the reaction is carried out in small test-tubes heated in a porcelain dish, which provides a brilliant white background. The accuracy ($\pm$ 5 per cent. of the amount determined) and the time required (75 to 300 seconds) are the same as with larger samples and with the previous technique. The number of mgrms. of sugar per 100 c.c. of blood is read from a time curve drawn from the average results obtained from the reduction of ferricyanide by standard glucose solutions under conditions of blood determinations. A diagram shows the comparison of results obtained by the Van Slyke and Hawkins gasometric method with those yielded by the micro blood sugar method, in analyses of 20 bloods, normal and pathological. A procedure is outlined for the application to urine analyses of the same reagents and apparatus used for blood sugar determinations, although such a micro method is not required for urine. The analysis is planned for use with urines, such as those encountered in diabetes, in which the glycosuria is so gross that its significant variations can be satisfactorily shown by measurement of the total reducing substances. The method is accurate to within 0·1 grm. of glucose per 100 c.c. of urine. A curve is given from which the amount of sugar in the urine may be found, and a table shows the comparison of the Van Slyke and Hawkins gasometric and the micro time methods for sugar in diabetic urines. P. H. P.

Pecan Oil. G. S. Jamieson and S. I. Gertler. (*Oil and Fat Ind.*, 1929, **6**, 23–24.)—Oil expressed from pecan nut waste (*Hicoria pecan*) had a mild pleasant flavour and was suitable for salad oil. The nuts contain 60–70 per cent. of oil, but, owing to the value of the nuts for edible purposes, only the waste is available for oil production. The sample examined had the following characteristics:—Sp. gr. at 25°/25°, 0·9141; $n_D^{25°}$, 1·4692; saponification value, 190·0, iodine value (Hanus) 100·0; Reichert–Meissl value, 0·05; Polenske value, 0·30; acid value, 7·0; acetyl value, 7·4; unsaponifiable matter, 0·35 per cent.; saturated acids (corrected), 5·09; unsaturated acids (corrected), 89·54 per cent., of iodine value, 105·5. The composition was as follows:—Oleic acid, 77·8; linolic, 15·8; myristic, trace; palmitic, 3·3; stearic, 1·9; and arachidic acid, 0·1 per cent. D. G. H.

Mlenda Seed and Kullan Nut Oils. (*Bull. Imp. Inst.*, 1929, **27**, 281–286.).—The Mlenda plant (*Sesamum angustifolium*, Engl.) from Tanganyika is grown for

its leaves, and yields small oval and mostly dark coloured seeds with pitted seed coats (distinguishing it from commercial sesame seed). The seeds contained 28·9 per cent. (31·2 per cent. on dry seeds) of a pale green limpid oil of sp. gr. at 15°/15° 0·9365; $n_D^{40°}$, 1·4708; saponification value, 181·6; iodine value (Hübl, 17 hours), 117·7; acid value, 16·8; Baudouin's test, positive. The composition of the meal was: Moisture, 7·5; fat, 7·0; crude protein, 22·2; carbohydrates, 17·2; crude fibre, 39·9; and ash, 6·2 per cent. The seed could not compete with ordinary sesame seed chiefly owing to low oil and high fibre content.

Kullan nuts (*Balanites orbicularis*) from British Somaliland, were ¾ to 1¼ inches long and ½ to ¾ inch in diameter, with pale, rough, thin, brittle woody shells, and crinkled yellowish kernels, ½ to ⅝ inch long and ⅜ to ½ inch in diameter, containing 37·2 per cent. (39·2 per cent. on dry kernels) of a golden-yellow limpid oil, which had the following constants:—Sp. gr. at 15°/15°, 0·9184; $n_D^{40°}$, 1·4623; saponification value, 192·7; iodine value (Hübl 17 hours), 75·9; acid value, 0·3; unsaponifiable matter 0·5 per cent., and solidifying point of fatty acids, 38·6° C. Saponin was present in the residual meal, which was free from cyanogenetic glucosides, but showed the presence of one or more alkaloidal constituents. The meal contained: Moisture, 9·1; crude proteins, 28·8; oil, 7·0; carbohydrates, 47·4; crude fibre, 3·5; and ash, 4·2 per cent. D. G. H.

Japanese Ginger. L. Rosenthaler. (*Amer. J. Pharm.*, 1929, **101**, 653–654.)—There are 3 grades of ginger in Japan, Kinki, Tuegoku and Shilaku. One-year-old rhizome is used at table with salt, and two-years-old as a remedy and an appetiser. Examination of a sample of Japanese ginger showed that single and grouped starch granules were present, the latter being mostly of equal size. The sizes found were (in *mm.*, with length as numerator and width as denominator) 42/28, 28/24·5, 35/24·5, 45·5/30, 35/26, 44/28, 21/21, 21/14, 26/17·5, 17·5/14, 17·5/15, 16/14, 14/10·5, 17·5/10·5, 21/17·5, 13/10·5. The anatomical structure is similar to that of other sorts of ginger. Large oil cells with yellow content are numerous; no red colour is produced by the vessels or fibres with phloroglucinol hydrochloric acid, and the vessels are frequently associated with tubes of tannin. D. G. H.

Monosodium Glutamate as a Chemical Condiment. J. E. S. Han. (*Ind. Eng. Chem.*, 1929, **21**, 984–987.)—Monosodium glutamate is now used to a large extent, particularly in China, as a condiment. It has a meat-like taste in solution, and the highest flavouring efficiency is obtained when it is used in soup and other dishes containing but little common salt. It is prepared chiefly by the hydrolysis of gluten with hydrochloric acid, crystallisation of the glutamic acid hydrochloride, neutralisation of the latter with sodium carbonate, and removal of the sodium chloride by fractional crystallisation. W. P. S.

Determination of Aluminium in Plant Materials. O. B. Winter and O. D. Bird. (*J. Amer. Chem. Soc.*, 1929, **51**, 2964–2968.)—In determining aluminium in vegetable and animal foods, the samples were prepared as for table use, any impurities not removable in this way being scraped off and the parts

washed. Fresh material was dried at about 35° C., and the dry residue ground to pass a 20-mesh sieve. From 1 to 30 grms. of this material is heated in a platinum dish in an electric muffle to just below redness and left overnight, any unburnt carbon being ignored. The ash is digested with hydrochloric acid and centrifuged, the supernatant liquid being decanted and the residue washed once with about 5 c.c. of water by centrifuging and decanting. The undissolved residue is washed into a platinum crucible with a fine jet of water, the water being evaporated and the dry matter ignited, if necessary, fused with 0·5 grm. each of sodium and potassium carbonates, taken up with hydrochloric acid and added to the original solution. After addition of a few drops of nitric acid, boiling to oxidise the iron, and removal of the silica by dehydration, the solution is transferred to a centrifuge tube of about 25 c.c. capacity with marks at 15, 20, and 25 c.c.. The iron and aluminium are precipitated, and the iron is separated by Myers, Mull, and Morrison's method (ANALYST, 1928, **53**, 547); as practically all the materials analysed contain sufficient iron to carry down the aluminium, but not enough phosphoric acid to ensure complete precipitation of the iron and aluminium as phosphates, no iron but about 0·1 grm. of ammonium hydrogen phosphate is added to each sample. The solution is made up to 25 c.c., an aliquot part of this being transferred to a 50 c.c. flask, together with water to 20 c.c., and hydrochloric acid sufficient just to redden added litmus paper. The aluminium is then determined by the colorimetric method described (*J. Amer. Chem. Soc.*, 1929, **51**, 2721). The sodium hydroxide used should be prepared from the metal, and a blank test of all the reagents made, the results being corrected accordingly.

All the materials examined contained aluminium, the parts per million of dry substance varying from 2 in wheat flour to 325 in peanut shells. In all cases of unusually high aluminium content (lettuce, carrot tops, beet tops, etc.) the material is such that the adhering impurities could not be removed completely. Specially cleaned apples, red beets, potatoes, and carrots contained respectively 5·2, 5·9, 4·2, and 22·8 parts per million of dry substance. T. H. P.

Comparative Study of Methyl and Ethyl Protocatechuic Aldehyde. L. Klotz. (*Amer. J. Pharm.*, 1929, **101**, 442–447.)—Vanillin and ethyl vanillin were found to exhibit a great similarity in colour reactions, and the following tests for vanillin can also be used for the detection of ethyl vanillin in flavouring extracts: —(1) *Buard's indole reaction* (*Compt. Rend. Biol.*, 1908). To one drop of alcoholic solution of indole in 16 drops of hydrochloric acid is added a 0·02 per cent. alcoholic solution of vanillin or ethyl vanillin, when a rose-red colour is developed. (2) *Lind's test* (*Z. Wiss. Mikroskop.*, 1885, 495): When one drop of a solution containing 1 per cent. of phloroglucinol is added to 2 c.c. of 1 per cent. solutions of vanillin and ethyl vanillin no colour is formed. With 30 drops vanillin gives a reddish-pink, and ethyl vanillin a light pink colour; both become rose-red on heating. (3) *Ferric chloride*: Ferric chloride test solution (U.S.P.,X., test for phenolic groups) is added to 2 c.c. of 1 per cent. solutions, when a dark blue colour is formed with vanillin, whilst with ethyl vanillin the colour assumes a greenish tint. (4) *Lead*

acetate: Two c.c. of a 1 per cent. vanillin solution produce a heavy white precipitate with lead acetate solution (U.S.P., X.), whilst ethyl vanillin produces only a white turbidity. (5) *Bohrisch's camphor test*: When 0·5 grm. of camphor is dissolved in hydrochloric acid, and 10 drops of the solution are added to 2 c.c. of a 1 per cent. vanillin solution, a dark-green colour results, whilst with ethyl vanillin the colour is similar, but darker in shade. (6) *Friese's formaldehyde test* (*Sudd. Apoth. Ztg.*, 1907, 752): When 5 c.c. of milk, containing traces of formaldehyde, are shaken with 10 c.c. of hydrochloric acid, and a particle of phloroglucinol and vanillin or ethyl vanillin, there is produced a dark blue coloration which does not differ with either compound. (7) *Allen's test for acetone*: On the addition of vanillin or ethyl vanillin to a mixture of equal parts of hydrochloric acid and sulphuric acid and a liquid containing a trace of acetone, a similar dark blue colour results with either compound. (8) *The thalleioquin test* (Hargreaves, *Amer. Pharm. Assoc., J.*, 1926, **15**, 2): Vanillin shows a green coloration, and ethyl vanillin a yellow-green colour when to 2 c.c. of a 1 per cent. solution are added 10 drops of chlorine water and an excess of 10 per cent. ammonium hydroxide; with bromine water instead of chlorine water, vanillin gives a deep yellow-brown colour, and ethyl vanillin an orange colour. (9) *Jolles' test for pentosans*: Both vanillin and ethyl vanillin give a red coloration in the cold with the osazone of laevulose, in presence of hydrochloric acid. (10) *Grofe's test for wood fibre* (*Osterreich. Botan. Z.*, 1905): Wood fibre moistened with vanillin or ethyl vanillin in solution in iso-butyl alcohol and with sulphuric acid gives a blue to blue-green coloration with vanillin, and a similar, though a yellower green coloration with ethyl vanillin. (11) *Raikow's test for chlorine* (*Chem. Ztg.*, **22**, 20): If a solution containing 1 grm. of vanillin or ethyl vanillin is evaporated to dryness, and the residue placed upon benzoic acid which is being heated, a red colour develops in the residue if chlorine is present; the colour obtained with vanillin is rather more pronounced than that given by ethyl vanillin. The reactions are due either to the hydroxy or aldehyde groups, and substituted groups have little or no effect on the colours. Other compounds containing hydroxy or aldehyde groups in the proper position (*e.g.* *p*-hydroxy-benzaldehyde) give similar results. D. G. H.

Two South American Cinchona Barks. L. Rosenthaler. (*Amer. J. Pharm.*, 1929, **101**, 651–652.)—*Castrona bark* consists of flat forms and half tubes, approximately 50 cm. long, 5 cm. broad, and 0·65 cm. thick, with outer and inner surfaces (where not covered with cork or outer bark cells), reddish-brown and, in spots, bright red. In flat forms the outer surface shows irregular longitudinal furrows, and the inner numerous parallel furrows, and in half-tube forms coarse cross-hatchings are present. On heating, white, followed by reddish-brown vapours may appear, and finally some brown-purple tar forms. Latex vessels are absent in cross section, but much sclerotic tissue is present; bast fibres in radiate groups are mostly 790–900 μ long. The total alkaloid content was 3 per cent.

Naradjada bark: The flat forms and half tubes, up to 45 cm. long, 4·5 cm. wide, and 0·8 cm. thick, have mostly smooth outer surfaces, broken in places by shallow

or deep depressions. Fracture in the outer layers is smooth and in the inner fibrous. On heating, white, then slightly red vapours are produced, followed by the formation of a brownish tar. No latex vessels are present. The outer portion is sclerotised, and some stony structure is also present in the inner portion. In addition to normal bast fibres, there are other unusually long ones, and in the radial direction the bast fibres are discontinuous, but in tangential section are in well-marked rows. The longest bast fibre noted was 1275 μ, but they were often from 900 to 1200 μ. Oxalates are present, particularly in the medullary rays, starch granules are few, either single or grouped up to 5. The total alkaloid content was 2·0 per cent.; the general structure is of the *Pubescens* type.

D. G. H.

Determination of "Free Nicotine" in Tobacco. Apparent Dissociation Constants of Nicotine. H. B. Vickery and G. W. Pucher. (*J. Biol. Chem.*, 1929, **84**, 233–241.)—When samples of tobacco are subjected to steam distillation without the addition of alkali, a part of the nicotine usually passes over into the distillate; it has been noted that the relative magnitude of this part varies with the hydrogen ion concentration of the extract. The determination of the "free nicotine," as this volatile part of the nicotine has been called, is of some importance in the chemical examination of tobacco, since the harsh flavour of certain tobaccos has been attributed to a high proportion of this component. Free nicotine is present in tobacco because of the hydrolysis of the nicotine salts in the tissue. The proportion present at ordinary temperatures may, therefore, be read directly from the dissociation curve of nicotine at the point corresponding to the reaction of the sample. Nicotine is a di-acid base, and its apparent dissociation constants were determined by Kolthoff (*Biochem. Z.*, 1925, **162**, 389). Since he used a somewhat impure preparation of the substance and determined only three or four points on each limb of the curve by a colorimetric method, it was thought desirable to repeat the determination. A highly purified nicotine has been prepared, and its dissociation constants have been determined by the electrometric method, and a dissociation curve is given from which the proportion of the total nicotine occurring in the free form in a tobacco extract of known hydrogen ion concentration may be read. A table shows the proportion of free nicotine in various samples of tobacco. The curve from which the amounts of free nicotine are read applies only to the temperature at which the dissociation constants were determined, and the nicotine values represent the proportions free at this temperature. Therefore there is no reason to suppose that the magnitude of the results should duplicate those secured from the same samples by distillation with steam, which are also given. It is suggested that this method for the determination of the free nicotine of tobacco is simpler and more precise than that hitherto employed, and should prove equally useful in forming a judgment of the quality of tobacco.

P. H. P.

Pyrethrum Flowers. I. Determination of the Active Principles. C. B. Gnadinger and C. S. Corl. (*J. Amer. Chem. Soc.*, 1929, **51**, 3054–3064.)—Both pyrethrin I and pyrethrin II reduce alkaline copper solutions and may be determined by Folin's method for sugar in blood (ANALYST, 1920, **45**, 227; 1922,

47, 268). Among the reagents used are: Petroleum spirit, 90–99 per cent. distilling between 20° and 40° C., max. b. pt. 60° C.; a solution of 20 grms. of Horne's basic lead acetate in recently boiled water to 1 litre; alkaline copper solution, prepared by dissolving (1) 2·5 grms. of pure copper sulphate in about 100 c.c. of warm water, and (2) 5 grms. of sodium potassium tartrate and 7·5 grms. of sodium hydroxide in 100 c.c. of cold water, transferring the cold solutions to a 500 c.c. flask and making up to volume—this solution should not be used when more than 3 days old; a solution containing 1 grm. of anhydrous dextrose and 40 c.c. of aldehyde-free alcohol per 200 c.c., which keeps for months; a solution obtained by diluting 10 c.c. of the previous solution and 210 c.c. of aldehyde-free ammonia to 250 c.c.—this solution should be made fresh each week. Use is made of Folin sugar tubes, blown to contain 15·5 c.c. to the base of the constriction, the bore of which should be the same for all tubes in a set; when heated to 78° C., the surface of the liquid must lie within the constricted length.

To determine pyrethrin in pyrethrum flowers, 20 grms. of the ground (about 30-mesh) flowers are extracted for 5 hours with the petroleum spirit in a Soxhlet extractor, the solution being then cooled to about 20° C., left for at least 30 mins., and filtered into a 400 c.c. beaker. After addition of a few grains of ignited sand, the solvent is expelled at a temperature not exceeding 75° C., the residue being at once transferred to a 100 c.c. flask by means of five or six portions of boiling 95 per cent. aldehyde-free alcohol, sufficient of which is used to make the volume 80–85 c.c. The hot solution is treated with 15 c.c. of the basic lead acetate solution, made up to the mark with hot alcohol, well shaken, cooled at once to 20° C., and again made up to the mark with alcohol. After filtration the liquid is treated with about 1 grm. of anhydrous sodium carbonate, shaken frequently during 10 or 15 minutes, and filtered, 10 c.c. of the clear filtrate being immediately pipetted into a Folin tube and there mixed, within the bulb, with 6 c.c. of the alkaline copper solution. Into a second tube, 10 c.c. of standard dextrose solution and 6 c.c. of alkaline copper solution are pipetted. The two tubes are left upright in a bath at 78±0·2° C. for 45 minutes, and then in water at 20° C. for 3 minutes. Each is then treated with 10 c.c. of Folin's reagent, left for 3 minutes, stoppered and mixed, the contents being transferred to a 100 c.c. flask, made up to volume, and, with the first tube only, filtered through a thick asbestos pad in a Gooch crucible, using gentle suction. The solutions are then compared in a Duboscq or Klett colorimeter and the dextrose equivalent to the unknown solution is calculated in the usual way. The corresponding amount of pyrethrin I or of a 50:50 mixture of pyrethrins I and II is read off from the following table, the figures in which represent milligrams.

D.	PI.	PI+II.	D.	PI.	PI+II.	D.	PI.	PI+II.
0·8	5·14	5·48	1·5	9·23	9·85	2·2	14·31	15·26
0·9	5·69	6·07	1·6	9·88	10·54	2·3	15·17	16·18
1·0	6·24	6·66	1·7	10·55	11·25	2·4	16·09	17·16
1·1	6·81	7·26	1·8	11·24	11·99	2·5	17·05	18·19
1·2	7·39	7·88	1·9	11·96	12·76	2·6	18·11	19·32
1·3	7·99	8·52	2·0	12·71	13·56	2·7	19·25	20·53
1·4	8·60	9·17	2·1	13·49	14·39	2·8	20·55	21·92

Blank determinations are advisable. If the blank result lies between 0·05 and 0·1 mgrm. of dextrose, it may be neglected, but reagents giving a higher blank should be discarded. In a number of samples of pyrethrum flowers, the pyrethrin content varied from 0·4 to 1·2 per cent., the stems containing only about 0·04 per cent. The active principles are the same in Japanese as in Dalmatian flowers. With pyrethrin I, a 1:80,000 aqueous solution containing less than 0·5 per cent. of alcohol is fatal to 100 per cent. of cockroaches within 24 hours, the corresponding dilution for pyrethrin II being 1:75,000. T. H. P.

Monobromoguaiacol Carbonate. Determination of Guaiacol Carbonate. L. H. Chernoff. (*J. Amer. Chem. Soc.*, 1929, **51**, 3072–3074.)—Addition of bromine to a methyl alcoholic solution of guaiacol carbonate results in the separation of bromoguaiacol carbonate in acicular crystals, m.pt. 178° C. The formation of this compound serves for the determination of guaiacol carbonate: 0·1–0·5 grm. of the carbonate is heated in a steam-bath in a 100 c.c. Erlenmeyer flask with 10–20 c.c. of methyl alcohol until dissolved. The hot liquid, removed from the bath, is treated with about 1 c.c. of bromine, and left, with occasional shaking to promote crystallisation, for 10 minutes; an equal volume of water is then added and the whole left for a further period of 10 minutes, after which it is filtered through asbestos in a weighed Gooch crucible. The precipitate is washed with 50 per cent. methyl alcohol solution, dried for about an hour at boiling water temperature, and weighed. Multiplication of the weight of the bromine derivative by 0·6343 gives the weight of guaiacol carbonate.

In mixtures with the usual excipients, such as starch, sugar, gum acacia and gum tragacanth, a preliminary separation by means of a solvent like chloroform, in which the carbonate dissolves readily, is advisable. From 0·5 to 0·1 grm. of the powdered material is heated to boiling with 10 c.c. of chloroform and filtered into an evaporating dish, the undissolved residue being well washed with chloroform. After elimination of the solvent on a steam-bath, the residue is dissolved in hot methyl alcohol and brominated as above. T. H. P.

Purification and Preservation of Ether for Anaesthetic Use. S. Palkin and H. R. Watkins. (*Ind. Eng. Chem.*, 1929, **21**, 863–867.)—Ether containing peroxide and aldehydes may be purified by distillation over pyrogallol or permanganate and then passing the distillate through a strongly alkaline solution of either of these reagents. The purified ether may be preserved for more than one year by placing in the container a small quantity of asbestos impregnated with strongly alkaline pyrogallol or permanganate solution. When required for use, the ether may be poured off without resorting to filtration. W. P. S.

Determination of Nitrates in Bismuth Carbonate. G. J. W. Ferrey. (*Quarterly J. Pharm.*, 1929, **2**, 205–216.)—The official method of the Fertiliser and Feeding Stuffs Act, 1926, modified by the use of methyl red as indicator, gave a maximum error of 1·1 per cent. when 5 grms. of sample were taken, and is preferable to the use of Devarda's alloy (McLachlan, ANALYST, 1921, **46**, 383). Seven

possible sources of error in the phenoldisulphonic acid (B.P.) method were also examined, and the conclusion reached that the maximum error need not exceed 5 to 7 per cent., the principal disturbing factor being the quality of the light when the ammoniacal solutions are being matched. The method may fail, however, when the samples under examination differ greatly from the B.P. standard. In the indigo-carmine method (Simmons, ANALYST, 1908, **33**, 440) the 25 c.c. of sulphuric acid should be added in two equal portions, and the titration time should not exceed 40 seconds. The standard indigo-carmine and potassium nitrate solutions are stable for at least 2 months. If 0·5 grm. of carbonate is taken, the method is reliable for the determinations of 4 per cent. or less of subnitrate.

J. G.

Luminescence of Creatinine. G. Reif. (*Z. Unters. Lebensm.*, 1929, **58**, 28–32.)—Solutions of creatinine in a fatty acid (*e.g.* butyric acid) prepared at 100° C., show the same blue luminescence as solid creatinine in the light of the quartz lamp, which changes, however, to yellow-green if the solution is heated at 165° to 170° C. for 10 minutes. The crystals which separate from the cool solution may be recrystallised from alcohol, and are soluble in water and glacial acetic acid, but not in organic solvents. Analysis by combustion showed that they have the same composition as creatinine, and the change is probably tautomeric and involves the production of an enolic form (with a double-bond) from a ketonic form. The colour returns to blue in the presence of 0·1 *N* acid, but is regenerated by alkali. It is not produced with inorganic acids or non-fatty organic acids, while the numerous other amines tested in the same way gave either no colour, or else a blue colour only. The influence on the examination of foodstuffs containing both creatinine and fatty acids is indicated. J. G.

Biochemical.

Silicosis in Industry in Britain. E. L. Middleton. Biophysics of Silica and the Etiology of Silicosis. P. Heffernan. (*Brit. Med. J.*, 1929, Sept. 14, 485–492.)—Silicosis is treated from the point of view of the etiology, pathology, symptomatology, diagnosis, prognosis, nomenclature, and industries concerned. Since only particles in a very fine state of division reach the ultimate pulmonary tissue, the visual appearance of an atmosphere is no criterion of its freedom from danger. In sections of silicotic lung, the average size of the particle is about 1μ. Silica is a normal constituent of both plant and animal cells. Silicosis is regarded as the result of local action of hydrated silica on the pulmonary tissue, the action being of a physico-chemical nature, and the speed of development depending (other things being equal) on the rate of formation of fresh silica hydrosol, and its contact with pulmonary tissue, so that the addition of alkalis (which favour the formation of silica hydrosol from silica) to silica dust, accelerates the development of silicosis. A combination of alkali and silica, such as that found in siliceous scouring powders, only requires wetting for the immediate production of active silica hydrosol, and a variable system of sodium oxide, silica and water,

with the silica in the hydrosol state, is set up. When quartz particles alone enter the lung, hydration is only brought about slowly by the very faintly alkaline tissue juices. These facts explain the very varying times shown in different industries of the appearance of symptoms of silicosis. This slow hydration has been paralleled with Ringer's fluid; asbestiosis is regarded as a true silicosis, and the characteristic "club moss" growths in lungs affected by asbestiosis are regarded as osmotic silica products. D. G. H.

Some Physiological Aspects of Copper in the Organism. F. B. Flinn and J. M. Inouye. (*J. Biol. Chem.*, 1929, **84**, 101–114.)—There is increasing evidence that, up to a certain point, copper may be beneficial to both animals and plants, but that, in excess of this quantity, ill effects sometimes, but not always, ensue. A discussion is given of previous work by various investigators. Protein affects the toxicity of copper; 0·2 grm. of a mucin-like material excreted by cryptobranchs will remove 10·8 mgrms. of copper from a solution containing 75 mgrms. of copper per litre. Copper is shown to have a close affinity for all proteins, and the protective action of food in this connection is mentioned. Some of the physiological effects of copper have now been studied because of the suggestion of Mallory (*Amer. J. Path.*, 1925, **1**, 117) that haemochromatosis may result from the continuous ingestion of small amounts of this metal. The excretion rate and the distribution of the metal in the bodies of animals subjected to known amounts of copper have been determined. The largest amount was recovered from the faeces, a good proportion from the oesophageal tubes, and small proportions from the urines and tissues. A table shows the distribution of copper in the bodies of rats which were given 2 mgrms. of copper per day in their drinking water for 12 months; the liver is the chief depository for the metal. Another table gives the copper content of the livers of various animals with no known copper exposure. Copper is found in the hair, and a very small amount in the bones. The action of bone on metals in solution as chlorides is shown, and the distribution of copper in blood. Copper is found in normal blood. Its average distribution in the blood of 4 dogs which were being given each day 300 mgrms. of very fine copper in capsules, was 2·97 mgrms. per 100 grms. of plasma, and 1·27 mgrms. per 100 grms. of corpuscles. An examination of thirty-three normal human livers showed a copper content of from 2·4 to 15 mgrms. per 100 grms. of tissue. The livers of 1 day old animals often contain as much copper as those of their parents. The evidence from a study of the blood changes occurring in the living animal receiving copper, with reference to the possible formation of methaemoglobin, tends to show that the copper in the blood is in some combination which is acted upon by the hydrosulphite used in the Van-Slyke and Neil method for reducing methaemoglobin to haemoglobin, and that this combination reacts differently from the compounds which aluminium and lead form in the blood, or from the haemocyanin of lobster blood. There is no evidence that copper ingested by the body in the normal way acts as a haemolytic agent. No increase in the storage of copper in the liver was found, except in cases where the animals were given far larger amounts of copper per

kilo. of body weight than man would normally be exposed to in his daily or industrial life. The work indicates that copper may play some important rôle in stimulating blood formation, and that its constant presence in the liver, even in the liver of the foetus, may not be due merely to the fact that this organ has among its functions that of being a filter. The combination in which it is held cannot be judged at this stage, but it must exert an important influence on the haematopoietic system and on the metabolism of the body as a whole. An examination of the blood of guinea pigs and dogs showed that the oxygen-carrying capacity of the blood was increased when copper was being given to the animals.

P. H. P.

Electrolytic Method for the Determination of Small Amounts of Mercury in Body Fluids and Tissues. A. G. Young and F. H. L. Taylor. (*J. Biol. Chem.*, 1929, **84**, 377–391.)—Mercury determinations in physiological fluids require: (1) An adequate method of digestion, (2) an efficient method of concentration, and (3) an accurate method of determination free from complications by interfering agents. Data are presented which indicate: (1) Hydrolytic oxy compounds of mercury are not formed in the presence of sulphuric acid. (2) Reduction of the mercury to the low valence form increases its loss in open digestion. (3) Mercury is not precipitated completely on copper, even after digestion and prolonged standing (but *cf.* Evans and Clarke, ANALYST, 1926, **51**, 224). A method for the determination of mercury is therefore described, which is fairly rapid and accurate for determinations of mercury in physiological fluids, and data showing its accuracy are presented. The upper limit of accuracy is within 1 per cent. of the true value, which compares favourably with other biological methods. An electrolytic method for concentration is combined with a titration method for determination, and obviates difficulties from the presence of interfering agents, or the necessity for expensive apparatus. The msthod has neen used for 400 determinations on physiological fluids without complications, and from these it has been possible to make complete studies of the excretion and distribution of mercury on patients and animals. The wiring diagram for the electrolysis is given, and also a diagram of the electrodes devised. Since the mercury in the electrodes is enclosed it cannot spill into the solutions. The platinum foil for the deposition of mercury is about 1 sq. cm. in size. The electrode vessels are placed under a wooden rack from which the lower shelf has been removed, and the electrodes are then inserted from above, the rubber stoppers fitting the holes and keeping the set rigid. With a potential difference of 6 volts, and a current of 0·5 ampere the deposition is complete overnight. Halogens present during electrolysis do not affect the yield. The procedure for urine is as follows:—In an 800 c.c. Kjeldahl flask 250 c.c. of urine are placed, and diluted with 100 c.c. of water; 2 c.c. of concentrated sulphuric acid and 25 c.c. of nitric acid are added, and the contents mixed, the internal condenser as used by Booth Schreiber and Zwick (*J. Amer. Chem. Soc.*, 1926, **48**, 1815) being kept in place. Then 2 grms. of potassium permanganate are added, together with 10 c.c. of chloroform (this latter to prevent foaming), and digestion is continued with the condenser in place until odour and colour disappear. More

permanganate may be added from time to time as required. When digestion is complete the liquid is transferred to the electrolysing vessel, and the current is allowed to run overnight. If the ammeter shows a lower current than 0·5 amp., it is adjusted by addition of nitric acid, drop by drop, to the electrode vessel. After the deposition of the mercury the electrode is washed with distilled water, and then the deposit is dissolved in hot fuming nitric acid (5 c.c.) contained in the titrating vessel, the electrode is again washed, and the washings added to the mercury solution. The volume is made up to 100 c.c. with distilled water, one drop of potassium permanganate is added to oxidise any possible mercurous compounds formed, the contents are cooled, and 3 per cent. hydrogen peroxide is added, drop by drop, to remove the permanganate colour. Five c.c. of 10 per cent. ferric ammonium alum (chloride-free) are added, and the solution is titrated with 0·05 or 0·01 *N* potassium thiocyanate solution with a Folin-Wu micro sugar burette. Titration is continued until the first rose tint appears. After removal of the deposited mercury all reagents must be chloride-free. Blank determinations should be made, and the results subtracted from the total titration value. No digestion is required in the case of spinal fluids. The method can also be applied to mercury determinations in tissues and faeces. P. H. P.

The Potato as an Index of Iodine Distribution. R. E. Remington, F. B. Culp and H. von Kolnitz. (*J. Amer. Chem. Soc.*, 1929, **51**, 2942–2947.)—The average iodine contents (in parts per billion (1000 millions) of dry matter) of Irish potatoes grown in various districts are: South Carolina, 211; Maine, 195; Idaho, 110; Michigan, 94; Minnesota, 86. Large variations occur in different samples from the same area and from soils of identical type. The iodine content of the potatoes increases progressively from the sea to the Appalachian, the relative amount of clay in the soil increasing similarly. It is suggested that the principal source of the iodine is disintegrated granite rocks, supplemented by mixed commercial fertilisers. The immediate influence of the sea on the iodine content is not seen beyond a very narrow belt along the coast. In determining the iodine, the organic matter was destroyed by simple ignition of the material in a porcelain dish at a temperature not exceeding 450°, organic as well as inorganic iodine being retained by the ash under such conditions. T. H. P.

Gasometric Determination of Methaemoglobin. D. D. Van Slyke and A. Hiller. (*J. Biol. Chem.*, 1929, **84**, 205–210.)—The method of Van Slyke (*J. Biol. Chem.*, 1925, **66**, 409) for methaemoglobin determination has been simplified by the adaptation to it of the carbon monoxide-binding capacity technique of the authors (*J. Biol. Chem.*, 1928, **78**, 807). The principle, as before, is that introduced by Nicloux and Fontes (*Bull. Soc. chim. biol.*, 1924, 728; ANALYST, 1924, **49**, 392). Two determinations are required. In one (A) the normal or active form of haemoglobin, capable of binding oxygen and carbon monoxide, is determined by measuring the carbon monoxide-binding capacity of the haemoglobin-methaemoglobin mixture. In the other (B) sodium hydrosulphite is added,

changing methaemoglobin into active reduced haemoglobin, and the total haemoglobin is determined by the carbon monoxide-binding capacity. The difference, B–A, indicates the methaemoglobin. The technique introduced has the advantage that all the operations, reduction with hydrosulphite, saturation with carbon monoxide, and determination of carbon monoxide bound by haemoglobin, are carried out in the chamber of the Van Slyke-Neill apparatus. Consequently, the procedure is simpler, more rapid, and requires much less blood, as little as 0·2 c.c., or even 0·1 c.c., sufficing for an analysis. In a determination of the carbon monoxide capacity in blood reduced by hydrosulphite, the presence of hydrosulphite and ammonia appears to lower somewhat the affinity of reduced haemoglobin for carbon monoxide, so that 100 mm. tension of the latter, instead of only 30, are required to insure complete conversion of the haemoglobin to carboxyhaemoglobin. A table shows the results obtained with amounts of blood varying from 2 c.c. to 0·1 c.c. The procedure is described in detail. P. H. P.

Reaction of Azine Compounds with Proteolytic Enzymes. G. M. Richardson and R. K. Cannan. (*Biochem. J.*, 1929, **23**, 624–632.)—A number of workers have reported that precipitates are formed when various azine dyes are added to solutions of proteolytic enzymes, and that, in some cases, the mother liquors have lost their protease activity, which has, in part, been transferred to the precipitates. Marston (*Biochem. J.*, 1923, **17**, 851) found that safranine was a specific precipitant for all the protease activities he tested, *viz.* pepsin, trypsin, erepsin, yeast protease and papain, but that it did not remove other non-proteolytic enzymes from solution. Other azonium salts, azines and eurhodines behaved similarly towards trypsin, and Marston concluded that he was observing a specific interaction between the azine nucleus and the structure peculiar to a protease, and drew an analogy between the azine ring as represented by the various dyes used and the piperazine ring which he believes to be a dominant feature of the protein molecule. This argument has recently been used to support the diketopiperazine structure of protein. The authors have now examined the kinetics of protease activity by a quantitative study of the anticatalytic effect of azine compounds on the activity of the protease; they hoped at the same time to assemble data which would permit the precise use of this reaction as an economical means of purifying protease preparations. The results confirm the observation of Marston and others that the addition of safranine or neutral red to a solution of pepsin or trypsin leads to the separation of a flocculent precipitate. In the case of pepsin solutions, including gastric juice itself, the precipitate removed the peptic activity from solution; on the other hand, the supernatant liquors from the trypsin precipitates, lost no significant proportion of their activity. The optimum conditions of concentration and P_H for the complete removal of pepsin from solution by this means have been determined, and a method is described for the recovery of the precipitated pepsin. The minimum efficient concentration of dye was found to be 0·1 per cent., and the optimum P_H for purification just above 3. Azine dyes do not "poison" the catalytic activity of either pepsin or trypsin; thus there

exists in solution under the experimental conditions no significant concentration of a specific protease-azine complex antagonistic to protein hydrolysis. Therefore no support is given by these results to the view of Marston that the azine nucleus reacts specifically with a protease with the formation of a protease-azine complex, and the formation of precipitates when azine dyes are added to protease preparations may not be used as an argument either for the piperazine structure of proteins or for any structural scheme of the mechanism of protease digestion. P. H. P.

Nephelometric Determination of Pepsin. C. G. Van Arkel. (*Pharm. Weekblad*, 1929, **66**, 857–864.)—Pepsin may be determined by physical methods (*e.g.* from the changes in viscosity, electrical conductivity and refractive index of the mixture of enzyme and substrate); or chemically, from the decrease in the amount of substrate, or the increase in the amount of reaction products. The method proposed is based on that of Kleinmann (*Klin. Woch.*, 1924, **14**, 572), and depends on the comparison of the turbidity produced from a 20 per cent. solution of sulpho-salicylic acid and the undigested substrate with that from a standard solution of albumin. The P_H value of 40 c.c. of a dilute serum solution (1:30) is adjusted (*vide infra*), by addition of 2 to 20 c.c. of *N* hydrochloric acid, and the volume diluted to 150 c.c. with physiological salt solution and maintained at 40° C. The pepsin solution (50 c.c. containing 100 mgrms.) is then added at 40° C., and the reaction is stopped at 5 minute intervals by pipetting 5 c.c. into 10 c.c. of 4 *N* sodium hydroxide solution. The nephelometric measurement is made 3 minutes after the addition of 5 c.c. of 25 per cent. hydrochloric acid and 8 c.c. of reagent, and a blank experiment, in which the pepsin is omitted, must be carried out. It was shown that each pepsin solution has its own optimum P_H value between 1·3 and 2·7 (1·5 to 2·7, 1·5 and 2·0 in the cases tested), and that the P_H value depends to a slight extent on the strength of the solution. The P_H value of the mixture of enzyme and substrate, however, may fall outside the optimum range. In all cases the rate of reaction is almost zero after 35 minutes, when 80 per cent. of the protein is decomposed. J. G.

Action of Papain on the Polarisation of Gelatin. Measurement of Proteolytic Activity. H. C. Gore. (*Ind. Eng. Chem. Anal. Edit.*, 1929, **1**, 203–205.)—The destruction of the first 40 per cent. of the mutarotation of gelatin by papain, as measured by the fall in polarisation at 20° C., is a linear function of the amount of enzyme. A method of measurement of the activity of papain is, therefore, proposed, in which 50 c.c. of a clear 2 per cent. solution of commercial food gelatin, adjusted to P_H 4·8 by addition of 10 c.c. of a Walpole buffer solution, are mixed with 40 c.c. of an aqueous solution or suspension of papain at 45° C. After 1 hour, or longer (in which case a drop of toluene should be added), the mixture is cooled rapidly, and maintained at 5° C. for 16 hours, then warmed at 20° C. for 1 hour, and the rotation measured. Similar readings are obtained for the papain solution alone and for the gelatin solution in the absence of papain, and the proteolytic activity (*P*) calculated from the expression W/wt where t is the time in

hours required by w grms. of papain to digest W grms. of air-dry gelatin. W should not exceed 40 per cent., and w is chosen accordingly. For 5 samples of papain P varied from 32 to 65. J. G.

Observations on the Assay of Vitamin *A*. J. C. Drummond and R. A. Morton. (*Biochem. J.*, 1929, **23**, 785–802.)—The biological method of assay of vitamin A is subject to error on the ground of the wide variations that may be encountered, and the necessity of using large groups of animals for each test makes it a costly and laborious matter when many samples have to be examined. It is still uncertain, however, whether the colour reaction of Rosenheim and Drummond, on which an alternative method of determination is based, is due specifically to the vitamin. The authors decided to make a severe comparative examination of the two methods before finally accepting or rejecting the colorimetric method as a routine test, and to extend the comparison to cover a method based on the quantitative examination of the absorption band in the ultra-violet spectrum extending from 280 to 360$\mu\mu$ (maximum near 328$\mu\mu$), believed by Morton and Heilbron (*Biochem. J.*, 1928, **22**, 987; ANALYST, 1928, **53**, 503, 664) to be characteristic of vitamin A. Six samples of cod-liver oil were selected at random from recently collected materials and examined by the three methods. For the biological tests the "curative" or "recovery" method was used. (The investigation was well advanced before Hume and Smith (*Biochem. J.*, 1928, **22**, 504) pointed out the disadvantages of this method, and advised dispensing with the depletion period.) Colorimetric determinations were made by means of a Lovibond tintometer, and also by a spectrophotometer. These two modifications of the test gave very satisfactory agreement. The relative intensities at 328$\mu\mu$ of the absorption band of the cod-liver oils were measured by the photographic technique. By the biological method, in spite of the use of much larger groups of rats (7–12) for each dose than are usually employed, the individual responses of the animals showed such wide variations as to make it a very difficult matter to detect quantitative differences of less than 100 per cent. in the vitamin A potency of cod-liver oils. As far as the relative values of the six oils could be determined by the biological test, they were in agreement with the response to the colour reaction, and with the relative intensities of the absorption band (328$\mu\mu$). There was very close agreement between the results of the colorimetric and spectrographic methods. A comparison of the biological assay with the two physical methods was also made in the case of a number of other oils, and general agreement between the results found; for these the biological tests were not made quite so thoroughly. Tests were carried out on the six cod-liver oils after they had been stored for a year both in the light and in the dark. In view of the statement of other investigators that certain oils (fish-body oils) may be rich in vitamin A without showing the colour reaction, it still seems undesirable to claim that the colorimetric method can generally replace the tedious and inaccurate biological tests. Actually, in a wide experience, no single instance has been found in which there was disagreement between the animal tests and the intensity of the blue colour showing

maximum absorption near 608$\mu\mu$. So far as cod-liver oils are concerned, the authors have no hesitation in recommending the colorimetric and spectrographic methods (taken together) as giving rapid and reliable quantitative results. P. H. P.

Relation of Vitamin *A* Content to Size of Leaves. L. McLaughlin. (*J. Biol. Chem.*, 1929, **84**, 249–256.)—Vitamin *A* is very unequally distributed in the parts of a plant but the leaves contain a large fraction of it; probably it is formed in the leaves and then carried to other tissues. The relative vitamin *A* content of New Zealand spinach leaves of three different sizes has been determined by a rat-growth method. New Zealand spinach plants were chosen for examination because on the same plant may often be found leaves of any size, from those just forming up to others having an upper surface area of 10 to 12 square inches. An attempt was made with each size of leaf to find the quantity of New Zealand spinach which, when supplementing a diet adequate in all respects except vitamin *A*, would promote an increase in weight of 25 grms. in rats whose body stores of vitamin *A* had been depleted. The results show that the potency of small leaves is greater than that of large leaves. With small leaves somewhat less than 90 mgrms. and more than 70 mgrms. per week was required; with medium leaves about 90 mgrms. were necessary; and with large leaves more than 110 mgrms. and less than 120 mgrms. was effective in promoting the desired increase in weight. The experimental period was eight weeks. Charts and tables show the results. The weights and the corresponding surface areas of leaves of three sizes were compared, and the ratio of the thicknesses of the three was calculated. The ratio of the thicknesses is approximately the reverse of the ratio of the leaf potencies, indicating, therefore, that the vitamin *A* content of leaves depends upon the surface area. P. H. P.

Absorption Spectrum of Vitamin *A*. O. Rosenheim and T. A. Webster. (*Biochem. J.*, 1929, **23**, 633.)—It has been claimed repeatedly that vitamin *A* is characterised by a selective absorption in the ultra-violet region at about 320–328$\mu\mu$. The authors have subjected this claim to the experimental test. Dehydroergosterol, a sterol with four double bonds, has been prepared from ergosterol as described by Windaus and Linsert (*Liebig's Ann.*, 1928, **465**, 148), and shown by a photographic method to possess an intense absorption exactly in the same region as that claimed for vitamin *A*. The absorption curve agrees with that obtained by a photo-electric method by Windaus and Linsert. The free sterol, its acetate and the peroxide were each proved, by means of biological tests on rats, to be devoid of growth-promoting properties. The fact that these substances also fail to give a blue colour with arsenic trichloride (or antimony trichloride) is significant, in view of the assumed association of this colour reaction with vitamin *A*. It would seem, therefore, that selective ultra-violet absorption at 320–328$\mu\mu$, at any rate by itself, cannot be taken as a criterion of vitamin *A*. P. H. P.

Alleged Relation of Carotin to Vitamin *A*. W. Duliere, R. A. Morton and J. C. Drummond. (*J. Soc. Chem. Ind.*, 1929, **48**, 316–321T.)—Pure carotin was prepared from the crude material by recrystallisation from hexane in an

atmosphere of nitrogen. After about four recrystallisations the properties of the carotin changed, and it became relatively insoluble and of a more intense colour. The m.pt. rose on recrystallisation from about 170° to 185° C., at which it remained constant. Feeding tests of the "curative" type required very large doses (0·5 mgrm.) to bring about any stimulation of growth, for the activity of the carotin diminishes with purification, and the pure product is regarded as of negligible vitamin *A* potency. The growth-promoting action of liver oils is not due to carotin. No reason is found for associating the vitamin *A* of liver fats with dihydro-α-crocetin, nor can it be affirmed or denied that the potency of certain carotinoids is due to a substance or substances differing from the classical vitamin *A*. Results indicate that the classical vitamin *A* must be a colourless substance, and its intrinsic potency very much higher than that of any sample of carotin or dihydro-α-crocetin for which data have been published. The carotin and antimony trichloride blue and the vitamin *A* and antimony trichloride blue resemble each other, but measurement of the absorption bands shows clearly that they are not identical. D. G. H.

Vitamin *A* and Carotene. I. Association of Vitamin *A* Activity with Carotene in the Carrot Root. T. Moore. (*Biochem. J.*, 1929, **23**, 803–811.)—Previous work on the possibility of a relationship between vitamin *A* activity and carotenoid pigmentation is discussed. The question was re-opened by the work of Euler, Euler and Hellstrom (*Biochem. Z.*, 1928, **203**, 370). These workers pointed out that in previous biological tests of carotene no provision was made for the presence of vitamin *D* in the diet, and that the results obtained cannot, therefore, have been reliable. Preliminary experiments in confirmation of the activity of carotene have been described by Moore (*Lancet*, 1929, i, 499). Tests are now described on young albino rats receiving a basal diet adequate in vitamins *B* and *D*. Under the experimental conditions specified, fresh carrot root was found to be a much richer source of vitamin *A* activity than hitherto supposed. Daily doses of 100 mgrms. of the fresh root sufficed to cure xerophthalmia and restore good growth in the rats deprived of vitamin *A*. Under similar conditions a sample of carrot fat, from which much of the carotene had been removed, was found to be active in a dose of 0·4 mgrm. daily. Carotene (m.pt. 174° C. in air) was found, even after many recrystallisations, to be active in doses of 0·01 mgrm. This agrees with the conclusion of Collison, Hume, Smedley-MacLean and Smith (*Chem. Ind.*, 1929, **48**, 631) that carotene isolated from cabbage fat also possesses intense vitamin *A* activity. A possible explanation is given of the divergent results of other workers. The suggestion of Dulière, Morton and Drummond (*Chem. Ind.*, 1929, **48**, 518), that pure carotene is inactive, and that the activity reported by Euler, Euler and Hellstrom may have been due merely to contaminating traces of vitamin *A*, is improbable for the following reasons:—(1) Carotene samples of a high degree of purity were found invariably to be active. (2) The activity of the carrot fat from which the carotene was crystallised was inferior to that of the isolated pigment. The activity of the pigment, therefore, could not have been

due to the presence of fat carried down as an impurity. (3) Both carotene and carrot fat produce with antimony trichloride a blue coloration which is characterised by an absorption band at 590$\mu\mu$. If the physiological activity of these sources is attributable to the same vitamin *A* as contained in cod-liver oil, intense absorption would be anticipated at 610$\mu\mu$, but no band was visible in this position. There can be no doubt as to the activity of carotene under the experimental conditions used, but it remains to be explained how molecules, differing so obviously as do carotene and the vitamin *A* of cod-liver oil, can be interchangeable in function. Preliminary experiments by the author have indicated that a chemical relationship between carotene and vitamin *A* may exist. P. H. P.

Vitamin *D* in Ergot of Rye. E. Mellanby, E. Surie and D. C. Harrison. (*Biochem. J.*, 1929, **23**, 710–717.)—In the course of some experiments it was observed that ergot of rye had a powerful action in promoting calcification of the bones when added to diets which, in themselves, resulted in the development of rickets. This problem has now been investigated in more detail, in order to study the properties of the calcifying substance in ergot, and to consider its relation to, or identity with, vitamin *D*. Puppies were used for the tests; comparisons were made between the animals in each litter and not between animals in different litters. Owing to its unpleasant taste, ergot can only be given to dogs in relatively small quantities. Even then, they sometimes refuse their food; consequently, in the majority of cases, the puppies given ergot did not grow as well as the other members of the family. When alcoholic and ethereal extracts of ergot replace the ergot itself the difficulties regarding the food intake are avoided. The bone conditions were diagnosed clinically and radiographically. The results of the experiments confirm the fact that ergot of rye is a powerful stimulus to calcification of bone. The substance responsible for the calcifying action is soluble in alcohol and ether, resists saponification, and has the properties, so far as these are known, of vitamin *D*. The irradiation of unground ergot grains by strong sunlight for 12 hours produces no increase, and the irradiation by the mercury-vapour lamp for half-an-hour only a slight increase in the calcifying activity of ergot, although there is abundant ergosterol present. Therefore, the covering of the ergot grains is relatively impermeable even to very abundant ultra-violet radiations. This raised a doubt as to whether the vitamin *D* was due to the direct action of sunlight on the ergosterol present in the ergot. In mushrooms, the one form of fungus tested, there was no evidence of vitamin *D*. Rye germ itself, unaffected by the ergot fungus *Claviceps purpurea*, was found to contain a small quantity of calcifying substance which can be extracted by petroleum spirit. How the ergosterol in ergot becomes activated to vitamin *D* is an unsolved problem. Although at the present time the ultra-violet irradiation of ergosterol is the only known mode of origin of vitamin *D*, it is possible that vitamin *D* can be made from ergosterol by the growing plant independently of ultra-violet radiations. Some samples of ergot contain, roughly, about one-eighth to one-quarter the calcifying activity of cod-liver oil. P. H. P.

Organic Analysis.

Determination of Sugar in Soap and Soap Preparations. K. Braun and E. Walter. (*Chem. Ztg.*, 1929, **53**, 778.)—A solution of 25 grms. of soap in 25 c.c. of water is heated on the water-bath with dilute sulphuric acid (strength not given) for 30 minutes, the fatty acids being separated and the sugar inverted simultaneously. After 12 hours the fatty acids are filtered off, washed with warm water, and the filtrate neutralised to litmus with sodium hydroxide and made up to 200 c.c. or a suitable volume. The precipitate produced from 25 c.c. of this solution and 50 c.c. of Fehling's solution in the usual way is washed free from alkali and dissolved in 50 c.c. of a solution of 50 grms. of ferric sulphate in 200 grms. of concentrated sulphuric acid, diluted to a litre, and the ferrous sulphate produced is titrated with 0·1 *N* potassium permanganate solution, 1 c.c. of which is equivalent to 0·00636 grm. of copper or (from Bertrand's tables) 0·0029 grm. of sugar. J. G.

Determination of the Total Geraniol Content of Citronella Oil. M. Van der Slik and J. Vermeulen. (*Chem. Weekblad*, 1929, **26**, 482–483.)—Ten c.c. of oil are acetylated with 11·3 c.c. of 95 per cent. acetic anhydride in the presence of 1·3 grms. of dry sodium carbonate. The use of sodium carbonate avoids the difficulty and expense of procuring completely anhydrous sodium acetate where large numbers of determinations are involved, and has been shown by comparative determinations on 100 samples not to affect the results.

J. G.

Determination of Mercaptans in Naphtha. P. Borgstrom and E. E. Reid. (*Ind. Eng. Chem. Anal. Edit.*, 1929, **1**, 186–187.)—Ethyl, *n*- and *iso*-propyl, amyl and butyl, *sec*-butyl, pentathiol-2 and benzyl mercaptans were determined in naphtha (I.B.P. 146° C., sulphur 0·028 per cent.) by shaking a known volume with excess of silver nitrate. Two c.c. of iron alum solution and sufficient 0·05 *N* ammonium thiocyanate solution to give a deep red colour are then added, the mixture well shaken, the excess of ammonium thiocyanate removed by 0·05 *N* silver nitrate solution, and the solution finally titrated to a permanent pink colour (*cf.* Birch and Norris, *J. Chem. Soc.*, 1923, **129**, 2545). The silver nitrate titration figure $\times 0{\cdot}001603$ = weight of mercaptan sulphur. Alternatively, the mercaptans may be removed as silver mercaptides with silver nitrate, and the lamp method used for the determination of the residual sulphur in the liquid. This quantity is subtracted from the total sulphur found by the lamp method. The average absolute error is 0·002 per cent. for quantities of 0·05 to 0·1 per cent. of sulphur added, and is due principally to adsorption of silver nitrate by the precipitated mercaptides. Consequently, the mixture must be well shaken, 5 c.c. of alcohol being added, if necessary, before the final titration, to break any emulsion. Reduction of disulphides by zinc and glacial acetic acid decomposes the mercaptans and invalidates the titration method, but the acidified calcium chloride solution and mercury used for the removal of hydrogen sulphide and elemental sulphur, respectively, do not remove the mercaptans studied.

J. G.

Reactions of Tetra-ethyl Lead. G. Edgar and G. Calingaert. (*Ind. Eng. Chem. Anal. Edit.*, 1929, **1**, 221–222.)—The total lead in concentrated anti-knock preparations (which are highly poisonous) is determined by bromination of 1 c.c. at 0° C. in the presence of 25 c.c. of carbon tetrachloride. After evaporation the lead bromide is dissolved in hot ammonium acetate solution, and the lead in the filtered solution precipitated as lead chromate, or titrated while hot with a molybdate solution standardised against a solution of pure lead chloride. A fresh 0·5 per cent. solution of tannic acid is used as outside indicator, 2 drops always being added to 4 drops of solution, and a yellow colour is obtained at the end-point. For dilute solutions, 100 c.c. of petroleum are brominated with excess of a 30 per cent. solution of bromine in carbon tetrachloride, and filtered at once on a Gooch crucible, and the residue washed with petroleum spirit and dissolved in warm nitric acid. The filtered liquid is neutralised with ammonia and either of the above procedures used. The accuracy is 1 per cent. for 0·02 to 0·08 per cent. by volume of lead. Tetraethyl lead itself should be dissolved in 50 c.c. of benzene, and a known volume (15 times the weight of lead) of 0·1 *N* iodine solution added, the excess being titrated after vigorous shaking for 3 minutes. The reaction is $Pb(C_2H_5)_4+I_2=Pb(C_2H_5)_3I+C_2H_5I$, and an accuracy of 0·3 per cent. is obtainable. If di-lead hexaethyl is also present, the sp. gr. of the sample will be raised in proportion, from 1·65 to 1·95 (the value for the latter). If, however, the iodine titrations and the total lead are determined, the proportions may be calculated more accurately from the equation $Pb_2(C_2H_5)_6+I_2=2Pb(C_2H_5)_3I$. Triethyl lead salts are determined in 5 c.c. of sample diluted with 20 c.c. of petroleum spirit, with an accuracy of 2 per cent., by extraction with two 20 c.c. portions of concentrated ammonia, which are then evaporated, and a solution of the residue in nitric acid is analysed for lead. J. G.

Inorganic Analysis.

Detection and Determination of Carbon Disulphide in Fluids. J. A. Pierce. (*Ind. Eng. Chem. Anal. Edit.*, 1929, **1**, 227–228.)—The reagent, which is stable in the dark for a week and should remain colourless, is prepared by addition of 4 c.c. of concentrated ammonia and 3 grms. of hydroxylamine hydrochloride to 50 c.c. of 2 per cent. copper sulphate solution (Ilosvay). If the sample is an oil, it is diluted to one-half with pure chloroform, and 5 c.c. shaken gently with 2 c.c. of reagent so as to avoid an emulsion. One part of carbon disulphide in 30,000 parts of oil gives an opaque chocolate-coloured aqueous layer, which soon clears and leaves a dark, heavy slimy precipitate at the interface. The precipitate contains cuprous sulphide and an unknown substance, whilst dissolved sulphur yields a black lustrous precipitate of cuprous sulphide only, which is easily identified under the microscope. The determination is made by comparison of the colour produced with that from a standard solution of carbon disulphide in an inert oil. J. G.

Rapid Microchemical Determination of Copper and Mercury. (*a*) **G. Spacu and J. Dick.** (*Z. anal. Chem.*, 1929, **78**, 241–244.) (*b*) **G. Spacu and G. Suciu.** (*id.*, 244–247.)—The methods previously described for the

quantitative precipitation of the two metals (ANALYST, 1927, 494; 1929, 618) have been adapted to their microchemical determination. For practical details reference to the original papers is invited. W. R. S.

Rapid Determination of Tin in Tin Plate. K. Heuberger. (*Chem. Zeit.*, 1929, **53**, 788.)—A rapid process consists in dissolving 5 grms. of cuttings in 50 c.c. of water and 75 c.c. of strong hydrochloric acid, the attack taking place in a flask closed with a valve containing bicarbonate solution. When solution, assisted by warming, is complete, the liquid is boiled for a short time and the flask cooled in running water. Twenty c.c. of hydrochloric acid and starch solution are added, and the liquid titrated at once with iodine. Three determinations require half an hour. The results obtained are always a trifle higher than those by the more tedious volatilisation method in a chlorine current, which must be due to a trace of stannic chloride escaping absorption in the receivers. For de-tinned scrap (0·1 to 0·2 per cent. tin), 10 grm. portions are taken. W. R. S.

Adsorption of Phosphoric Acid by Stannic Sulphide. R. Chandelle. (*Bull. Soc. Chim. belge*, 1929, **38**, 255–258.)—Comparative determinations of phosphorus in 0·25 grm. of potassium dihydrogen phosphate in the presence and absence of 0·3 grm. of tin have shown that the error due to adsorption of phosphorus by stannic sulphide is 0·2 per cent. Care must be taken that basic tin salts, which have a greater adsorptive capacity for phosphorus, are not produced, *e.g.* by hydrolysis, $SnS_2+4H_2O \rightleftharpoons H_2SnO_3+H_2O+2H_2S$. To this end a solution of the tin in *aqua regia* is evaporated to dryness, the residue dissolved in fuming hydrochloric acid and a few c.c. of water, and a saturated solution of hydrogen sulphide added. This also serves to precipitate the stannic sulphide which may be subsequently filtered off, the hydrogen sulphide boiled out, and the phosphate precipitated. The precipitate of magnesium pyrophosphate was found to contain 0·146 per cent. of silica. J. G.

Volumetric Determination of Manganese as Dioxide. I. M. Kolthoff and E. B. Sandell. (*Ind. Eng. Chem. Anal. Edit.*, 1929, **1**, 181–185.)—The use of potassium bromate in place of the persulphate for the oxidation of manganese to manganese dioxide is recommended for the determination of this element in ores and manganese steels. A solution (50 c.c.) of sample equivalent to 20 to 150 mgrms. of manganese is made 1·0 *N* with respect to sulphuric or nitric acid, 2 grms. of potassium bromate added, and the solution boiled for 5 to 10 minutes according to the amount of iron present. The solution is filtered (twice if necessary), the precipitate of manganese dioxide washed with six 10 c.c. portions of hot water, and the iodine liberated from 2 grms. of potassium iodide, in the presence of 5 c.c. of 20 per cent. potassium fluoride solution, 75 c.c. of water and 5 c.c. of 4 *N* sulphuric acid, and titrated with 0·1 *N* sodium thiosulphate solution. If iron is absent, 4 grms. of zinc sulphate should be added to the original solution, when 1 c.c. of 0·1 *N* thiosulphate solution=0·002801 grm. Mn. If small amounts of

iron are present, a pure ferric salt is added, so that the amounts of iron and manganese present are approximately equal, and the corresponding factor is 0·002774 grm. Mn. For small amounts of manganese in the presence of large amounts of iron, the latter must be removed by addition of a suspension of zinc oxide to a solution of the sample, but, as some manganese is also removed, the factor is 0·002834. Chromium, lead, nickel, bismuth, and chlorides do not interfere, but large amounts of phosphates, vanadium, tungstates and molybdates, introduce errors, and in the two last cases low results are obtained. J. G.

Separation of Aluminium by 8-Hydroxyquinoline. G. E. F. Lundell and H. B. Knowles. (*Research Paper No.* 86, *U.S. Bureau of Standards, July,* 1929.)—The precipitation of aluminium has been described by Hahn and Vieweg and by Berg (ANALYST, 1927, 431, 611). The authors have tested and established the reliability of the reagent for the separation of aluminium from the elements specified below. (1) *From phosphorus, arsenic, fluorine, boron*:—The slightly acid sulphate or chloride solution (Al_2O_3<0·1 grm. per 100 c.c.) is treated with an excess of reagent, followed by dilute ammonia till alkaline, and then with 5 c.c. of strong ammonia. The liquid is digested at 60° to 70° C. till the precipitate becomes dense and crystalline. After cooling (preferably in ice-water), the precipitate is collected on paper of close texture and washed with dilute ammonia (1:40) containing 25 c.c. of reagent, neutralised with ammonia, per litre. (The reagent is made by the trituration of 2·5 grms. of the base with 5 c.c. of glacial acetic acid, pouring into 100 c.c. of water at 60° C., and filtering after cooling; 1 c.c. precipitates 2·9 mgrms. of alumina.) The precipitate and paper are heated with nitric and sulphuric acids; after destruction of the paper the alumina is precipitated with ammonia, as usual; a correction for silica is applied, if necessary. (2) *From vanadium, tantalum, niobium, titanium, molybdenum*:—In the method described under (1), 10 to 15 c.c. of 3 per cent. hydrogen peroxide are added before the reagent; otherwise the technique is the same. (3) *From uranium*:—The method outlined under (1) is applied, except that ammonium carbonate is used; the faintly acid solution is neutralised with a saturated ammonium carbonate solution, of which an excess of 25 c.c. per 100 c.c. of assay solution is afterwards added. In heating to 50° C. excessive effervescence should be avoided. (4) *From beryllium* (see ANALYST, 1928, 508; 1929, 434):—Double precipitations are hardly required. Rapid, if slightly low, results were obtained with ingot iron and ferrovanadium by dissolving in acid, neutralising with alkali, and pouring slowly into caustic soda solution. An aliquot part of the filtrate was treated as under (1) in the case of the iron, and (2) the ferrovanadium. The reagent will also detect aluminium in phosphoric acid and alkali phosphate (when ammonia gives no precipitate) when added to the ammoniacal solution. W. R. S.

Detection and Determination of Sulphur Dioxide. S. Rothenfusser. (*Z. Unters. Lebensm.*, 1929, **58**, 98–109.)—The sample is heated in a 500 c.c. flask with 300 c.c. of water, 10 c.c. in excess of 25 per cent. phosphoric acid and about

0·5 grm. of pumice powder (and 5 c.c. of paraffin in the case of meats) attached to a vertical condenser, and the distillate is collected in a mixture of 5 c.c. of a filtered 5 per cent. solution of benzidine in 96 per cent. alcohol 5 c.c. of 30 per cent. acetic acid, and 5 c.c. of 3 per cent. hydrogen peroxide are added. The sulphur dioxide is oxidised to sulphuric acid and forms benzidine sulphate which is insoluble in acetic acid. The precipitate is filtered in the cold, washed three times with 5 c.c. of water, dried for 30 minutes at 105° C. and weighed. The factor 0·234 gives the weight of sulphur dioxide, or the precipitate may be titrated with 0·1 *N* sodium hydroxide solution, or decomposed with hot hydrochloric acid, and precipitated with barium chloride. The advantages claimed are quick removal of sulphur dioxide in the presence of the pumice, the high molecular weight of the benzidine compound, and the fact that it is non-volatile and forms characteristic crystals which may be used for identification in qualitative tests. Carbon dioxide is not required, and the solubility of the precipitate is unaffected by the presence of other volatile substances, including alcohol, in the amounts likely to occur. J. G.

Platinised Silica Gels as Catalysts for the Oxidation of Sulphur Dioxide. H. N. Holmes, J. Ramsay and A. L. Elder. (*Ind. Eng. Chem.*, 1929, **21**, 850–853.)—At temperatures about 395° C., that is, slightly below those required for the maximum conversion of sulphur dioxide into sulphur trioxide, platinum deposited on chalky (porous) silica gel is more efficient as a catalyst than platinum on glassy silica gel. At 440° to 450° C., the temperature for maximum conversion, there is but little difference in the efficiency of the two gels as supporters for the platinum catalyst. Under similar conditions, platinum deposited on either of the gels is more efficient than is platinum deposited on asbestos.

W. P. S.

Determination of Silica in the Presence of Fluorspar. W. T. Schrenk and W. H. Ode. (*Ind. Eng. Chem. Anal. Edit.*, 1929, **1**, 201–202.)—The method of Berzelius is accurate but tedious, and the only satisfactory alternative is that suggested in which 0·5 grm. of powdered sample is digested with 15 c.c. of 20 per cent. perchloric acid saturated at 50° C. with boric acid. After the acid fumes have been evolved for 5 minutes the mixture is diluted, the evaporation repeated, and 60 c.c. of water added. The filtered off precipitate is washed free from calcium salts with hot water, ashed in the presence of a little sulphuric acid, and ignited till constant in weight. Silica is finally removed from the residue in the usual way, and the loss in weight determined. The error is $\pm 0{\cdot}05$ per cent. for 0·06 grm. of silica in 0·5 grm. of sample. Omission of the boric acid leads to low results.

J. G.

Physical Methods, Apparatus, etc.

Application of X-rays in the Classification of Fibrous Silicate Minerals commonly termed Asbestos. H. V. Anderson and G. L. Clark. (*Ind. Eng. Chem.*, 1929, **21**, 924–933.)—Thirty different specimens of fibrous minerals from different parts of the world were examined, and illustrations of the diffraction

patterns for the natural fibres, and the same after digestion with hydrochloric acid and after ignition are given. A table of the properties of the minerals includes a description of the appearance of the natural fibre; the calculated identity period in Ångström units, along the fibre axis, from *X*-ray diffraction data; the percentage loss in weight after acid treatment; the percentage loss in weight after heating; the physical properties after heating, etc. W. P. S.

Reviews.

REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY. Vol. XIII for 1928. Issued by the Society of Chemical Industry. Pp. 741. Price to members, 7s. 6d.; to non-members, 12s. 6d.

These annual reports have firmly established themselves in the favour of chemists in all branches of the scientific industries, and the present volume, equal in size to its immediate predecessors, will enhance their reputation.

There are 25 separate sections, that on "Explosives" dealing with the two years 1927–28. Each one of these sections is a mine of information, and an adequate bibliography of the important discoveries, observations and points of progress in the particular subject with which it deals.

Under "General, Plant and Machinery" (A. J. V. Underwood), attention is directed to the larger amounts of capital now being employed in Germany in the manufacture of nitrogenous fertilisers and the liquefaction of coal, and it is stated that the chemical industry is in most countries—including this country—increasing production and showing larger profits. In Great Britain, however, there is no improvement in the staple industries of coal, steel and cotton. The rapid progress in nitrogen fixation (interestingly reviewed also in the section on "Acids, Alkalis, etc.") will mean more severe competition for the Chilian nitrate industry.

A new adsorbent described consists of an inert siliceous material impregnated with calcium chloride, the mixture having a large capacity for taking up water, which is removable on heating. Various new types of viscosimeters are noted, as also a sampling device for solid materials, by which they can be automatically quartered. Another automatic apparatus determines the small amounts of sulphur dioxide in the air, and this should be of use in connection with work on atmospheric pollution.

The section on "Fuels" (H. J. Hodsman) deals with numerous topics, including domestic heating, pulverised coal, smokeless semi-coke and coke, and with the origin and chemistry of coal. Some of these subjects are also referred to in the next section ("Gas, Carbonisation, Tar and Tar Products," by H. Hollings).

A full review of the present position of artificial silk is given in the section on "Fibres, Textiles, etc.," (J. C. Withers), while the dyeing of this artificial fibre and of the older natural fibres is considered in "Bleaching, Dyeing, etc.," by L. G. Lawrie. A short sub-section on analytical methods appears in the former section.

Papers on the identification of artificial silk by means of ultra-violet rays are referred to in the same article. The results of enquiries into the alleged poisonous properties of lead tetraethyl, when used as "dope" in petrol, are discussed in the section on "Acids, Alkalis, etc.," while there are in the volume also articles on stainless steels, corrosion and protection of metals and alloys, chromium plating and the electro-chemical industry generally.

In Dr. Hilditch's section on "Oils, Fats and Waxes," some German figures are given showing that the consumption of margarine in Great Britain exceeds that of butter, but the reviewer thinks the statistics on this point require verification. Vitamin-containing margarines being now on the market, it would seem desirable to call attention to the warning given in another section ("Foods") of the possible danger from foods artificially vitaminised, owing to over-dosage. Important work is described in connection with the constitution of fats, rancidity, the detection of hardened fats, and the differentiation of liver oils from other fish oils. The chemistry of the vitamins is also dealt with in the sections on "Fine Chemicals, Medicinal Substances, etc." (W. H. Linnell) and on "Foods," and these articles reveal the ever-increasing complexity of the subject. Reference is also made in the section on "Foods" (Aumonier and King) to papers on the "fishiness" of certain dairy products, which property has been shown to be due to the presence of appreciable traces of copper in these foods. No reference, however, is made, in this connection, to the possibility of a "fishy" taste being communicated to foods by reason of the presence of fish meal in the diet of dairy animals.

A suggestion for a method of differentiating between artificial cream and the real article is based on the different colloidal condition of the proteins. The writers on "Foods" (p. 583) say, on the subject of preservatives in foods: "There is some evidence that the public are not altogether satisfied with the results of two years' experience of the Preservatives Regulations. . . . An epidemic of paratyphoid has been commented on in this connection." If the cogency of the evidence against the Regulations is to be assessed on the last sentence quoted, it may be said that the critics, spoken of by the writers of this section, are ill-informed. No preservative known, used in the amounts possible in foods, would have any effect on such infected food; and, had there been no regulations restricting the use of preservatives, the infected food would still have been toxic.

The methods in use for the rapid determination of sulphur dioxide in foodstuffs, recommended by a Committee of chemists engaged in the food manufacturing industries, and published in THE ANALYST, receive favourable mention, and those who have experience of them will agree that these methods are reliable and accurate.

The interesting article on "Soils and Fertilisers," by E. M. Crowther, should be read by all agricultural chemists.

The typographical errors in the volume are remarkably few, and those noticed are fairly obvious. There are adequate indexes of authors and subjects, and the book is throughout a worthy production.

ARNOLD R. TANKARD.

THE ANALYSIS OF DRUGS AND CHEMICALS. By NORMAN EVERS, B.Sc., F.I.C., and G. D. ELSDON, B.Sc., F.I.C. Pp. x+372. 8vo. London: Charles Griffin & Co., Ltd. 1929. Price 25s. net.

In their introduction the authors rightly call attention to the fact that one of them is a pharmaceutical works chemist, and the other a public analyst. From such a combination of experienced workers, it is reasonable to expect something exceptional in the way of a book on the analysis of drugs and chemicals, and so far as one can tell from perusal of its contents, such an expectation is not likely to be disappointed. There is an admirable introduction on laboratory methods and a useful appendix of 25 pages of tables.

The subject-matter proper is divided into six parts—inorganic drugs and chemicals; organic chemicals; crude drugs; galenicals; fixed oils, fats and waxes; and essential oils. Where general methods of examination are feasible, they are described in the introduction to each part, and under each material dealt with, practically everything the analyst requires to know for its examination is given with a brevity and clarity that are refreshing. The few slips noticed are not such as to detract from the value of the book as a trustworthy analytical guide; for example, it seems a pity in a chemical text book to apply the term "arsenobenzene" to what is a derivative of this substance, when the name "arsphenamine" is available, and is in common use. The fact that "arsenobenzene" is so used in the Therapeutic Substances Act does not justify chemists in perpetuating this official misuse of the term. Similarly, there are advantages in adhering to the usual British plan of writing *iso*Butyl- and *iso*Amyl- instead of *Iso*butyl- and *Iso*amyl (p. 128). Apart from trifling points of this kind, the book has been carefully prepared, and is in every way a creditable production on which the authors are to be congratulated. T. A. HENRY.

PRACTICAL PLANT BIOCHEMISTRY. By MURIEL WHELDALE ONSLOW, M.A., Lecturer in Plant Biochemistry, University of Cambridge. Third edition. Pp. iv+206. Cambridge: University Press. 1929. Price 12s. 6d. net.

The first edition of Mrs. Onslow's *Practical Plant Biochemistry* appeared in 1920, the second one in 1923, and there is no doubt that there was a demand for the third edition. The book has become indispensable to every student and teacher of plant chemistry. In many ways the present edition differs very little from the preceding one, and, in glancing through, one gets the impression of a reprint. Even as regards points about which our views have undergone fundamental changes, subject-matter, and formulae, such as that for phytol (p. 39), have not been revised. On the other hand, all sugar formulae have been changed from the fiver ring to the sixer ring structure, which is perhaps too confidently accepted, since these formulae, although fashionable at present, are still open to satisfactory confirmation.

In spite of these minor points, perhaps of exaggerated importance in the eyes of the reviewer, Mrs. Onslow's book remains an invaluable chart to all those who explore the field of Plant Chemistry. M. NIERENSTEIN.

AN INTRODUCTION TO THE CHEMISTRY OF PLANT PRODUCTS. Vol. II: METABOLIC PROCESSES. By P. HAAS, D.Sc., Ph.D., and T. G. HILL, D.Sc., A.R.C.S. Second edition. Pp. viii+220. London: Longmans, Green & Co. Price 10s. 6d. net.

It must require a certain amount of courage on the part of an author to write a book on the metabolic processes of plants, if only for the reason that so little is known with certainty about these processes. A subject in this condition is apt to accumulate about itself a large number of contradictory and inconclusive observations, and the first duty of the writer of a text book is that of the selective critic, the second that of presenting the selected data as briefly and clearly as possible, so that his readers may get a trustworthy idea of the present state of the particular problem.

Messrs. Haas and Hill have divided their material into six chapters, the first dealing with the living plant from germination to reproduction, and the remaining five with growth, respiration and the synthesis of carbohydrates, fats and proteins, the five great problems with which plant physiologists are concerned. The treatment of each is admirably adapted to distinguish established fact from plausible speculation, and to stimulate interest in, and further work on, these problems.

The reviewer, as a chemist, has no right to complain of biological terminology, but he does venture to suggest that it must be discouraging to a young chemist beginning to take an interest in phytochemical problems to meet with such a paragraph as the following on the third page of this book:

"Circumnutative and other autonomous movements may be explained by such conceptions as rectipetality and associated engrams; whilst in explanation of tropisms various mechanistic hypotheses have been formulated, some chemical, the hormone theory of gravitational stimulus of roots, for instance; others physical, the statolith theory, for example."

It is only fair to add that this is practically the sole lapse into technical obscurity, but it is noticeable because it comes so early in the book. The first volume, which has already been noticed in THE ANALYST (1928, **53**, 681), forms with this companion volume an admirable introduction to the study of plant products, which will be no less popular with students and teachers than the previous editions.

T. A. HENRY.

A HANDBOOK OF CLINICAL CHEMICAL PATHOLOGY. By FRANK SCOTT FOWWEATHER, M.D., M.Sc., D.P.H., F.I.C. Pp. x+216. London: J. A. Churchill. 1929. Price 8s. 6d. net.

The rapid growth of Chemical Pathology has raised it to a position of great importance as an aid to clinical diagnosis, treatment and prognosis in all branches of medicine. In view of the ever-increasing additions to the literature, a book dealing with the interpretation of analyses, rather than technical details, should be welcomed by both medical practitioner and analyst. Dr. Fowweather may be congratulated on producing a work of this character.

In the foreword by Lord Moynihan, and in the preface, it is clearly indicated that the book is in no way intended to be a practical manual for chemists, and no attempt is made to describe in detail the actual methods of chemical analysis. The author has, in the main, confined himself to the consideration of the theory of chemical processes in disease; the indications for, and clinical procedure involved in carrying out the required tests (including the taking and preservation of specimens); and the interpretation of the results of chemical analysis.

The subject-matter is well arranged and covers the field of chemical pathology with remarkable completeness. The chemical investigation of the functions of the alimentary tract and of the organs concerned in the processes of digestion and excretion receives full treatment. The author's statement on page 76 to the effect that, "Personally, I have rarely got a convincing biphasic reaction (*re* Van den Bergh Test) even where it is most to be expected," will occasion some surprise. In the hands of others the frequent occurrence of this type of reaction constitutes one of the serious limitations of the test as a clinical aid.

The author raises an interesting point with regard to the estimation of fat in faeces. It is his opinion that, since the reaction of the faeces is often alkaline, a certain amount of hydrolysis of fat must result from the usual practice of drying the faeces at a high temperature in the preparatory stages of analysis. To obviate this difficulty he suggests that the differential fatty content of the fresh stool should first be estimated, and that the values so determined should subsequently be expressed as percentages of the total dry matter as estimated from the desiccation of an equal portion of the fresh material. The use of a vacuum-desiccator at room temperature in the preliminary steps of the preparation of a dried specimen of faeces would exclude the possibility of hydrolysis, and is certain to commend itself to chemists as a cleaner and better way out of the difficulty than the method advocated.

The chapter on "Tests on the Cerebro-Spinal Fluid" would benefit from the addition of a table embodying a summary of the comparative findings in the various diseases of the Central Nervous System. The concise theoretical treatment of such subjects as "The Acid-Base Equilibrium of the Blood," "Ossification; Calcification; and Calculus Formation," "The Changes in the Cholesterol, Phosphorus, and Calcium of the Blood," and "Vitamins and Deficiency Diseases," considerably enhance the value of the volume as a handbook of reference.

The author is clearly an enthusiast, for, having led the reader skilfully through the range of chemical pathology from P_H values to vitamins, he finishes on a lofty note by quoting comic verse—a method of expression which is, perhaps regrettably, unusual in works of this character.

The book is well indexed, but it seems a pity that the principal references to the various topics are not indicated in heavy print.

In my opinion the work admirably fulfils its mission, and I am glad to add it to my bookshelves.

W. HURST BROWN.