

# THE ANALYST

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

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AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 3rd, the President, Mr. John Evans, M.Sc., F.I.C., being in the chair.

Certificates were read in favour of:—Victor Cecil Branson, A.R.C.Sc., D.I.C., B.Sc., A.I.C., Roydon George Cowdell, Joseph Davies, F.I.C., Frank Akerman Hatch, A.I.C., Herbert Lloyd Hind, B.Sc., F.I.C., Alexander Marr, A.M.C.T., Daniel Donald Moir, M.Sc., F.I.C., Teunis Potjewijd, D.Sc., Magnus A. Pike, B.Sc., Walter James Rees, M.Sc., F.I.C., James Sandilands, F.I.C., William Wilders Taylor, B.Sc., F.I.C., William Pearson Thistlethwaite, B.Sc., Frederick Thomas, M.Sc., Dennis Gordon Tompkins, B.Sc., A.I.C.

The following were elected Members of the Society:—John Ferguson Brown, B.Sc., A.I.C., Carl Emil Resch, B.Sc., Wilfred Smith, B.Sc., A.I.C., Sidney George Edward Stevens, B.Sc., A.I.C.

The following papers were read and discussed:—"The Determination of Lead in Biological Material, with Special Reference to Bone," by G. Roche Lynch, O.B.E., M.B., B.Sc., D.P.H., F.I.C., R. H. Slater, D.Sc., Ph.D., F.R.S.E., A.I.C., and T. G. Osler, M.B., Ch.B., M.R.C.S., L.R.C.P.; "The Determination of 'Ethyl' Vanillin," by H. C. Lockwood, B.Sc., A.I.C.; and "The Detection and Identification of Metallic Particles in Manufactured Products," by H. C. Lockwood, B.Sc., A.I.C.

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### NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Manchester on October 13th. The Chairman (Professor W. H. Roberts) presided over an attendance of thirty-five.

The following papers were read and discussed:—"The Composition of the Amniotic Fluid," by Arnold R. Tankard, F.I.C., D. J. T. Bagnall, F.I.C., and F. Morris, F.I.C.; "A Note on the Dictionary of Colour Standards of the British Colour Council," by Arnold R. Tankard, F.I.C.; and "Mrs. Beeton, the Housewife and the Factory," by E. Hinks, B.Sc., F.I.C.

## Standards for Purity and the Determination of "Ethyl" Vanillin

By H. C. LOCKWOOD, B.Sc., A.I.C.

(Read at the Meeting, October 3, 1934)

VANILLIN and its homologue, *m*-ethoxy-*p*-hydroxybenzaldehyde, are very similar in chemical reactions. The flavour of "ethyl" vanillin is four or five times as strong as that of ordinary vanillin, and it is claimed that it resembles more closely that of vanilla, the natural product. Since the price of "ethyl" vanillin is about two and a quarter times that of vanillin, it was considered possible that adulteration might occur. To detect this, the reactions of the two substances were studied to see if it were possible to obtain a characteristic divergence. Most of the tests give identical qualitative reactions, but the following method was devised and found to be satisfactory.

**BROMINE TEST.**—Two grms. of "ethyl" vanillin are mixed with 5 ml. of cold water in a small beaker and allowed to soak for 15 minutes. The mixture is then filtered through a 5.5 cm. filter paper, and 1.7 ml. of the filtrate is collected in a dry 10-ml. graduated measure. The filtration is aided by pressing the mixture into the filter paper with a glass rod. The solution should give a slightly acid reaction with litmus paper. The measured volume of the filtrate is then diluted to 5 ml., giving a one-third saturated solution. To this is added 0.5 ml. of saturated bromine water.

If the "ethyl" vanillin is free from vanillin, the solution is at first yellow or orange changing to yellow, with no precipitation or cloudiness, whilst in the presence of vanillin a red colour is first formed, and finally a red-brown precipitate. The test is capable of detecting the addition of 0.5 per cent. of vanillin to "ethyl" vanillin.

The test depends for its success on the difference in solubilities of vanillin and "ethyl" vanillin, the cold saturated solutions containing 0.8 and 0.4 per cent., respectively.

Some other chemical impurities which may possibly be present, such as piperonal, are capable of producing a cloudiness, but not the red colour caused by the presence of vanillin.

**MELTING-POINT.**—Vanillin and "ethyl" vanillin melt at 82° and 77° C., respectively. On mixing, a eutectic point is reached at about 50° C., when the mixture contains 40 per cent. of vanillin and 60 per cent. of "ethyl" vanillin. A mixture of 90 per cent. of vanillin and 10 per cent. of "ethyl" vanillin, after fusing together and solidifying, melts at 77° C., so that only this proportion could hope to pass as pure "ethyl" vanillin, and the bromine test would then detect the adulteration.

**DETERMINATION OF "ETHYL" VANILLIN.**—It was found that, although vanillin and "ethyl" vanillin reacted in a similar way, there were differences of

sufficient magnitude to render the usual methods for the former unreliable for the latter. The following processes were tried:

- (a) The semicarbazide precipitation method of Phillips (ANALYST, 1923, 48, 367), which gives satisfactory results with vanillin, was tried, but low results were obtained. This was due to the higher solubility of the "ethyl" vanillin semicarbazones which is, according to the figures below, about six times as soluble as the vanillin compound. Saturated aqueous solutions of the semicarbazones were prepared at 15.5° C. and found to contain the following amounts:

Vanillin semicarbazone	6 mgrms. per 100 ml.
"Ethyl" vanillin semicarbazone	35 " " 100 "

The solubility of "ethyl" vanillin semicarbazone in the reaction mixture was also studied and found to be 27 mgrms.

- (b) The *p*-toluidine method gave fairly good results if the precipitate was not dried above 50° C. The objection was that a constant weight was not reached, owing to the volatile nature of the precipitate.
- (c) The 1929 Annual Report of Schimmel & Co. (p. 123) contains a titrimetric method in which thymol-phthalein is used as an indicator. The end-point is very indefinite, which reduces the accuracy of the process.
- (d) Palfray, Sabetay, and Soutag (*Compt. rend.*, 1932, 194, 1502; Abs. ANALYST, 1932, 57, 472) give a method for aromatic aldehydes based on Cannizzaro's and Claisen's reactions, using potassium hydroxide in benzyl alcohol. After refluxing, the alcohol was very dark brown owing to decomposition, and it was impossible to titrate it.
- (e) A method based on iodine absorption was tried, but without success.
- (f) Zeisel's reaction for methoxy and ethoxy groups gave low results with pure specimens:—Vanillin gave 97.9 and "ethyl" vanillin 95.5 per cent. It is generally accepted that compounds containing ethoxy groups give low results by this method, which is also too tedious for control analysis.
- (g) A process based on bromine absorption was devised, and, after a suitable sealing material for the stoppers had been found, it gave duplicate results which agreed closely. Of the various substances tested to prevent loss of bromine through the stoppers, orthophosphoric acid was found to be the most effective. Bromine was found to be insoluble in the acid and also without action upon it.

BROMINE ABSORPTION METHOD.—The following solutions are required:—

- (a) Bromine solution (2.5 per cent.) is prepared by dissolving 0.82 ml. of bromine in each 100 ml. of glacial acetic acid. The solution keeps well in the dark.
- (b) Sodium thiosulphate (5/32 *N*). Dissolve 38.78 grms. of pure sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in water and make up to 1 litre.

One ml. of 5/32 *N* sodium thiosulphate is equivalent to

0.0125	gram.	of	bromine
or 0.01188	"	"	vanillin
or 0.01297	"	"	"ethyl" vanillin.

- (c) Each determination and blank requires a thin glass phial containing 3 grms. of potassium iodide dissolved in 3 ml. of water, which gives a volume of 4 ml. The glass phials are conveniently blown to  $\frac{1}{2}$ -inch diameter from  $\frac{1}{4}$ -inch tubing, and, after introduction of the potassium iodide solution, they are sealed. The tubes should be washed and prepared just before use, as potassium iodide solution liberates iodine on keeping.

The "ethyl" vanillin (0.5 grm.) is weighed to 0.1 mgrm. in a small tube. The tube is introduced into a stoppered stout glass bottle of 400 to 600 ml. capacity, containing a phial of potassium iodide solution. The tube is conveniently slid down a cylinder of paper inside the neck of the bottle. The contents of the tube are shaken out by bumping and rotating the bottle, since, if left in the narrow tube, the substance dissolves with difficulty.

The bromine is added by means of a 50-ml. pipette fitted with a cork and side-tube, so that it can be filled by pressure. The pipette is filled once with the solution and allowed to empty before use. Fifty ml. are pipetted for the determination and the blank test. The stopper is then smeared with syrupy orthophosphoric acid of sp.gr. 1.73. When the "ethyl" vanillin has dissolved, the bottles are placed in the dark and rotated after the first hour. At the end of six hours each bottle is shaken vertically, so that the glass phial is broken by hitting the top or bottom, since there is a distinct possibility of breaking the absorption bottle if the phial strikes the side. The liberated iodine is titrated with  $5/32 N$  thiosulphate solution. This is conveniently done by adding 50 ml. of  $5/32 N$  thiosulphate solution to each bottle from a pipette, counting the same number of drops, and continuing the titration from a burette, or using a 100-ml. burette having a bulb for the first 50 ml. Towards the end of the titration starch solution is added, and the end-point is given to one drop.

The blank should require 92 to 97 ml., and 0.5 grm. of pure "ethyl" vanillin accounts for 38.55 ml.  $5/32 N$  thiosulphate solution. From the difference between the blank and test solution is calculated the purity of the "ethyl" vanillin. The titrations must be carried out with the greatest accuracy, since 0.1 ml. of  $5/32 N$  thiosulphate solution is equivalent to 0.26 per cent. of "ethyl" vanillin when using 0.5 grm.

Two sets of results in triplicate were as follows:

1.	99.9	99.9	100.0 per cent.
2.	100.0	100.2	100.0 „

By this method vanillin gives results accurate to about 1 per cent.

The monobromo derivatives of vanillin and "ethyl" vanillin have melting points of 162° and 140° C., respectively.

I am indebted to Messrs. Cadbury Brothers, Ltd., for permission to publish these methods, which were investigated in their laboratories at Bournville.

## Rapid Determination of Nitrogen by a Kjeldahl-Nessler Process

By W. H. KITTO, B.Sc.

THE range of work in some of the small-staffed official laboratories in the colonies is very wide, and when engaged upon major forensic problems an officer is frequently called upon to give a quick decision, *e.g.* as to whether a sample of condensed milk is a "whole-milk" product, whether a sample of human milk is of approximately average composition, whether bread advertised as specially prepared for diabetics is suitable, and so on. In connection with such samples there is need of a method for rapidly determining nitrogen with a degree of accuracy which, whilst not necessarily as great as that of the usual Kjeldahl process, would be sufficient for the purposes indicated.

Experiments were therefore made with the object of finding some method of Kjeldahl oxidation which, although much faster than the standard procedure, would yield an extract suitable for the determination of nitrogen by direct nesslerisation.

A catalyst oxidiser recommended had the percentage composition:—anhydrous sodium sulphate, 90; mercuric sulphate, 7; copper sulphate, 1.5; precipitated selenium, 1.5 per cent. It is used in quantities of 10 grms. of the mixture with 1.75 gm. of sample (of cereal meal) and 20 ml. of sulphuric acid.

This mixture (and a similar mixture in which the selenium was replaced by an equivalent amount of sodium selenate) was found to work excellently; extracts from the above quantities were clear after about 25 minutes, but were heated for 50 minutes, and, after the usual distillation, gave results which agreed well with those obtained by standard procedure.

Attempts to nesslerise these extracts, however, failed, owing to heavy precipitation, and it appeared probable that this difficulty would be encountered whenever mercury was employed as catalyst.

It was therefore decided to try the mixture recommended by Chiles (*J. Amer. Chem. Soc.*, 1928, 50, 217) for colorimetric Kjeldahl determinations (concentrated sulphuric acid, 70 ml.; water, 50 ml.; 20 per cent. perchloric acid, 20 ml.; anhydrous sodium sulphate, 15 grms.; copper sulphate, 1 gm.). Thirty-five ml. of this mixture were taken with 1.75 gm. of a bread sample. Oxidation was slow, and the results on distillation were appreciably lower than those given by the standard procedure. It was found, however, that the results obtained by nesslerisation of the extract after appropriate dilution agreed satisfactorily with those obtained by distillation.

It was decided to try the effect of adding selenium to Chiles's mixture. As only sodium selenate was available, this was employed in the proportion of 1.15 gm. to each 100 ml. of Chiles's mixture. The result was a very marked acceleration of the oxidation.

Wheat flour (1.75 gm.) digested with 35 ml. of Chiles's mixture became clear in 45 minutes, and distillation, after 1½ hours' total heating, gave a result which

agreed well with the true value. Moreover, nesslerisation, after appropriate dilution of this digest, gave very satisfactory results.

In order to expedite nesslerisation over a considerable range, without the trouble involved in making up fresh standard solutions on each occasion, use was made of the Hellige comparator, in which the colours of nesslerised solutions in standard troughs may be matched against permanent standard shades mounted in groups of 9 on rotating discs.

It was found very desirable to standardise these discs with ammonia solutions, and from the results of duplicate standardisation with solutions of ammonium chloride and sulphate a curve was obtained from which a table was prepared giving the ammonia-content, in mgrms. per 100 ml. for any observed or estimated Hellige reading up to a maximum of 1.3 mgrm. per 100 ml. For all concentrations of ammonia above 0.4 mgrm. per 100 ml. it was found advisable to add 4 ml. of Nessler's solution per 100 ml. instead of the 2 ml. used at lower concentrations; this was done in the standardisations of the discs and in subsequent comparisons.

TESTS OF THE METHOD WITH VARIOUS SUBSTANCES.—Quantities of 0.2 to 0.5 gm. of the substances given below were oxidised in 100-ml. Kjeldahl flasks, and, after neutralisation (see below) and dilution, were nesslerised at three different strengths, and the ammonia-contents were estimated by Hellige comparator readings.

There was satisfactory agreement between the ammonia-contents deduced from readings at the different strengths, and the average nitrogen-contents deduced therefrom agreed satisfactorily with those obtained by the standard Kjeldahl procedure. The actual figures obtained were:

		Nitrogen	
		Ordinary Kjeldahl method Per Cent.	Proposed method Per Cent.
Wheat flour	.. ..	1.68	1.75
Special bread	.. ..	2.31	2.32
Barley "A"	.. ..	1.37	1.32
Barley "B"	.. ..	1.72	1.65

The method also gave satisfactory results with milk, and it was found that 2 ml. of a well-mixed sample, measured with an Ostwald pipette, was a convenient amount with which to work.

In nearly all cases the nesslerised solutions were perfectly clear, but, with some at the higher concentrations, there was a suggestion of opalescence which did not, however, affect the shades or interfere with the readings through the 4-cm. trough, or appear to prevent the concordance of the results obtained.

Nesslerising at three different concentrations was adopted with a view to eliminating any small errors associated with the colorimetric assessment by means of the discs. Blank determinations with the reagents proved that they did not interfere.

DETAILED DIRECTIONS FOR PROCEDURE.—The conversion reagent consists of Chiles's mixture (*vide supra*), to which powdered sodium selenate is added in the proportion of 1.15 gm. per 100 ml.

As there is a tendency for some of the components to separate out, this mixture should always be well shaken before use.

A quantity of 0.5 grm. of a solid substance (such as wheat flour), of 2 ml. of a liquid such as milk, or diluted condensed milk, is introduced into a 100-ml. Kjeldahl flask, together with two small glass beads, and 12.5 ml. of the conversion reagent. The flask is heated gently, with shaking, for the first five minutes, and the heating then continued in the usual way. If  $t$  is the time taken to clear (which is usually about 20 minutes), heat for a total period of  $1.75t$ . Cool, and wash into a 250-ml. flask, and adjust to the mark. Take 10 ml. of this diluted solution, add phenolphthalein, and titrate with  $N$  sodium hydroxide solution (using a graduated 10-ml. pipette). Let the amount of alkali required be  $s$  ml. Now transfer 40 ml. from the 250-ml. flask, to a 100-ml. flask, add  $(4s-1)$  ml. of  $N$  sodium hydroxide solution, to produce a faintly acid reaction, and adjust to the mark. Take 20 ml. of this mixture and nesslerise, using 4 ml. of Nessler's reagent and diluting to 100 ml. If the depth of colour is moderate, nesslerise two other quantities of 10 ml. and 30 ml., respectively, using 2 ml. and 4 ml. of Nessler's reagent, respectively, and making up to 100 ml. If with 20 ml. the colour obtained is deep, take two smaller quantities; and if it is unduly pale, take two larger ones for nesslerisation, using 2 ml. of Nessler's reagent for the lower and 4 ml. for the higher concentrations. The ammonia-contents of the nesslerised solutions are then determined in the 4-cm. trough of the Hellige comparator by comparison with the standardised discs.

Although the detailed directions may suggest that the procedure is complicated and lengthy, the actual operations are simple and rapid; apart from the pause of 10 minutes for the development of the Nessler colours, the dilution, neutralisation, nesslerisation, and comparator measurements take only a few minutes.

It is not suggested that the above procedure will be universally applicable without modification. The use of a stabiliser, such as gum arabic as recommended by Chiles (*loc. cit.*), may be advisable in some cases, and, in the presence of appreciable amounts of the alkaline earths, the addition of Rochelle salt might be beneficial in the nesslerisation.

I wish to acknowledge the assistance given to me by Mr. A. W. Facer, B.A., F.I.C., in connection with this investigation.

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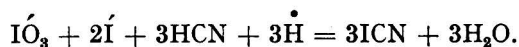
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## The Determination of Vanadium with Potassium Iodate, with Notes on Chloramine-T as an Oxidising Agent

By A. J. BERRY, M.A.

THE analytical chemistry of vanadium is much concerned with the various states of oxidation of that element. Thus it is well known that the more powerful oxidising agents, such as potassium permanganate, can effect quantitative transformation of any of the lower stages into the quinquevalent condition. Reduction from the quinquevalent to the quadrivalent condition can be effected by the milder reducing agents, such as ferrous sulphate and sulphur dioxide. With liquid amalgams, either the bivalent or the quadrivalent stage may be realised, according as zinc amalgam (Nakazono, *J. Jap. Chem. Soc.*, 1921, **42**, 751) or bismuth amalgam (Someya, *Z. anorg. Chem.*, 1924, **138**, 291) is employed as the reducing agent. Someya has also shown that when vanadium salts are reduced to the bivalent condition in the presence of a small quantity of a dyestuff such as phenosafranine in acid solution, the latter is also reduced to the leuco compound. When the resulting solution is titrated with a suitable oxidising agent, the dyestuff is reconverted into the coloured form at the stage when quantitative transformation of the vanadium from the (violet) bivalent form into the (green) trivalent state has been effected (*Z. anorg. Chem.*, 1928, **169**, 293).

Very little, if indeed any, work has hitherto been done on the direct titration of vanadium salts with potassium iodate. As is well known, this reagent, when used in the presence of a high concentration of hydrochloric acid, can effect the quantitative oxidation of a number of substances (Andrews, *J. Amer. Chem. Soc.*, 1903, **25**, 756). Thus thalious salts may be determined by direct titration with potassium iodate (Berry, *ANALYST*, 1926, **51**, 137). Another method of using potassium iodate in volumetric analysis, which may be considered as a modification of Andrews' procedure, has been described in a series of publications by Lang (*Z. anorg. Chem.*, 1922, **122**, 332, and subsequently). In Lang's method the oxidation is effected in the presence of hydrocyanic acid, the iodine being oxidised to a colourless solution of iodine cyanide:



It has been claimed by Lang and others that the "iodine cyanide" method is preferable to Andrews' "iodine monochloride" method, because (a) a very much lower concentration of hydrochloric acid is required, and (b) the end-point of the reaction can be recognised with the aid of starch, instead of using an organic solvent such as chloroform. Against this, however, it must be urged that in some titrations the end-point is less easy to recognise, and also that the evolution of the vapour of hydrocyanic acid is highly objectionable. For many purposes the two methods may be regarded as equally applicable, but such is not the case with



vanadium salts. In the experiments to be described in this paper it will be seen that bivalent vanadium can be oxidised exactly to the tervalent condition by Lang's method, whereas, when Andrews' method is used, there is a slow further oxidation to the quadrivalent condition, the reaction being ill-suited to volumetric analysis. These experiments have also shown that oxidation of vanadium from the bivalent to the tervalent stage is effected with greater accuracy by Lang's method than with ferric sulphate, with phenosafranine as indicator.

Solutions of vanadic acid were readily prepared for this work by dissolving ammonium metavanadate (10 grms.) in aqueous sodium hydroxide solution, adding excess of dilute sulphuric acid, and then diluting the resulting solution with water to the desired volume (one litre). Solutions of vanadyl sulphate were prepared from this by reduction with sulphur dioxide. Those of vanadous sulphate were prepared, sometimes from vanadyl sulphate, and at other times directly from vanadic acid by the reducing action of zinc amalgam. A large number of analyses were made, of which the following may be quoted to illustrate the more interesting results. The following solutions were used:

Potassium iodate, 3.82 grms. per litre; potassium iodide, 17.5 grms. per litre; hydrochloric acid, about 10 per cent.; potassium cyanide, 5 per cent. Fresh starch solutions were prepared for each day's work.

Ten ml. of potassium iodide with 25 ml. of hydrochloric acid and 25 ml. of potassium cyanide required 29.6 ml. of potassium iodate.

Twenty ml. of vanadyl sulphate were reduced to vanadous sulphate, and at once added to this colourless solution of iodine cyanide. The volume of potassium iodate required was 24.4 ml. This effected the oxidation  $V^{II}$  to  $V^{III}$ .

When similar experiments were made by Andrews' method, in which 50 ml. of concentrated hydrochloric acid were used, and, of course, no potassium cyanide was present, 10 ml. of potassium iodide required 29.6 ml. of potassium iodate as before, but, on adding the vanadous sulphate to the solution of iodine monochloride, the volume of potassium iodate required was nearly double that formerly needed. Oxidation, however, took place slowly, and the end-point was difficult to attain. It was evident, however, that oxidation had gone to the quadrivalent stage, since the consumption of the oxidising agent was twice as much as before. Moreover, the green colour of the solution at the conclusion of the reaction was identical with that of a mixture of vanadyl sulphate and hydrochloric acid containing iodine monochloride.

By way of comparison with the iodine cyanide experiments, the consumption of available oxygen over an equal but different range, *viz.* from  $V^{IV}$  to  $V^V$ , was found by titrating 20 ml. of the above solution of vanadyl sulphate with a solution of potassium permanganate (3.13 grms. per litre). The volume required was 17.4 ml. It follows that  $24.4 \times 3.82$  grms. of potassium iodate, when used in a Lang titration, are equivalent in oxidising power to  $17.4 \times 3.13$  grms. of potassium permanganate. When these products are divided by the corresponding equivalent weights, the ratios are 1.74 and 1.72, respectively. The accuracy of the iodine cyanide method for effecting quantitative oxidation from the bivalent to the tervalent condition is therefore justified.

Some experiments were made on the oxidation of vanadous sulphate with ferric alum, the end-point being determined with phenosafranine (*cf.* Someya, *loc. cit.*). In all cases oxidation to the tervalent condition was not quantitative but lower, usually about 5 per cent., even when great care was taken to avoid atmospheric oxidation of the vanadous salt. When vanadous sulphate was oxidised in this way with vanadic acid, the end-point of the reaction was found to correspond with a ratio of five parts of  $V^{II}$  to four parts of  $V^V$ , which does not agree with the formation of any simple compound.

In connection with this work, some experiments were made with chloramine-T as the titrant. This compound, the sodium derivative of parachlorotoluene sulphochloramide, was first introduced for volumetric work as a substitute for iodine by Noll (*Chem.-Ztg.*, 1924, 48, 845). It was found that chloramine-T could be used instead of potassium iodate for the direct titration of potassium iodide to iodine monochloride or to iodine cyanide. As an example, the following results may be quoted:

A solution containing 18.66 grms. of chloramine-T per litre was prepared. Twenty ml. of this solution, treated with excess of acidified potassium iodide, required 25.7 ml. of sodium thiosulphate solution (15.98 grms. per litre). The value for the equivalent weight was 143.6.

Twenty ml. of a solution of potassium iodide (17.5 grms. per litre), acidified with 50 ml. of concentrated hydrochloric acid, required 32.5 ml. of chloramine-T. When dilute hydrochloric acid and 25 ml. of 5 per cent. potassium cyanide were used instead of the concentrated acid, the same volume of chloramine-T was required. The value for the equivalent weight was found to be 287.6. It is clear that the equivalent weight of chloramine-T should, when used in an Andrews or a Lang titration, be double that when used in conjunction with excess of acidified potassium iodide where oxidation does not proceed beyond the quantitative liberation of iodine.

Chloramine-T has much to recommend it as a volumetric oxidising agent. Its high equivalent weight, ready solubility, and moderate stability in solution are worthy of note. When kept in bottles of blue glass, the freshly prepared solution was found to lose about 2 per cent. of its oxidising power in the course of a fortnight at the ordinary temperature. In this respect it is decidedly inferior to potassium iodate.

In conclusion, a few words may be added with regard to the oxidation of thalious salts. Potassium iodate is, in my experience, the best reagent for this purpose, and it must be used according to the Andrews procedure. Iodine cyanide cannot be used for the determination of thalious salts, the end-point with starch being entirely unsatisfactory. On the other hand, thalious salts may be determined with accuracy by oxidation with iodine monochloride, followed by oxidation of the iodine by direct titration with chloramine-T in presence of a high concentration of hydrochloric acid. Identical results were also obtained when the thalious salts were oxidised in the presence of dilute hydrochloric acid and excess of potassium bromide by direct titration with chloramine-T, the end-point of the reaction being obtained with methyl orange as in Györy's well-known potassium bromate method for the determination of antimony.

SUMMARY.—Vanadium can be determined volumetrically by oxidation from the  $V^{II}$  to the  $V^{III}$  condition by the iodine cyanide method. The consumption of available oxygen for this range has been checked by oxidising solutions of the same vanadium-content from the  $V^{IV}$  to the  $V^V$  condition with potassium permanganate.

Chloramine-T can be employed in conjunction with potassium iodide, instead of potassium iodate, for the direct titration of various oxidisable substances. In particular, thalious salts can be determined by the iodine monochloride method; the iodine cyanide method cannot, however, be used. Thalious salts can also be determined by titration with chloramine-T, the reagent being used in presence of dilute hydrochloric acid and potassium bromide.

Examples of these results are appended in the following table:—

Substance Analysed (Concentration as prepared for experiment)	Oxidising Agent and method of use	Concentration as determined by analysis
10.0 grms. of $NH_4VO_3$ per litre.	Iodine cyanide ( $V^{II}$ to $V^{III}$ ).	10.2 grms. per litre.
Ditto.	Potassium permanganate ( $V^{IV}$ to $V^V$ ).	10.1 grms. per litre.
10.0 grms. of $TiOH$ per litre.	Iodine monochloride with chloramine-T.	9.91 grms. per litre.
Ditto.	Chloramine-T used with hydrochloric acid and potassium bromide.	9.98 grms. per litre.

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## The Determination of Carbon in Rocks and Minerals

BY B. E. DIXON, M.Sc., A.I.C.

CARBON occurs in rocks in a great variety of forms and to a considerably varying extent. The occurrence, in rocks, of carbon minerals or carbonaceous matter, except when these happened to be of economic importance, does not appear to have received much attention, and it is in any case difficult to determine the nature of these minerals by inspection. It is, therefore, desirable to employ for their analysis a method as widely applicable as possible. The use of the dry combustion method for this purpose has some drawbacks:—(i) When the amount of carbon is small in comparison with that of carbonate it is difficult to determine the carbon accurately by the difference of results obtained by two dissimilar methods, *viz.* total carbon by dry combustion, carbonate by treatment with dilute acids; (ii) if the combustion is complete no carbon must be retained in the ash. This is usually ensured, in the case of siliceous rocks and minerals, by fusion with lead chromate, or with a mixture of lead chromate and potassium chromate.

Highly refractory carbonates present a difficulty. It is impracticable to expel all the carbon dioxide by heating the sample alone in a glass tube. Admixture with lead and potassium chromates also fails to decompose the carbonates completely, and the use of potassium dichromate alone, which yields a more complete melt, is precluded by the large amount of spattering which occurs. Other objections are mentioned by Florentin (*Chim. et Ind.*, 1924, 11, 875) and Schollenberger (*J. Ind. Eng. Chem.*, 1916, 8, 1126).

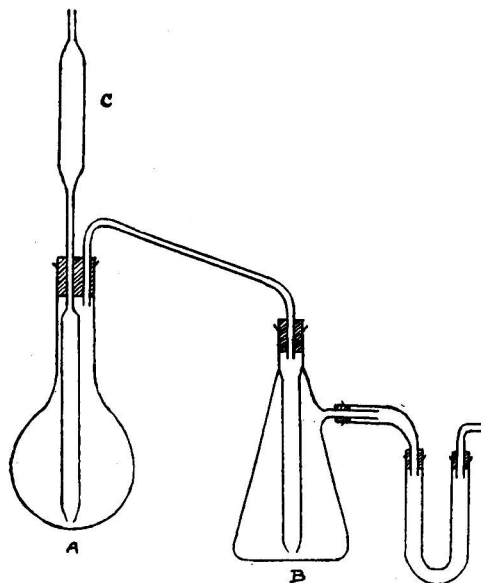
WET COMBUSTION METHODS.—Many wet combustion processes involving the use of sulphuric and chromic acids with various catalysts have been devised for the determination of carbon in soils, graphites, coals, etc. (e.g. Simon, *Compt. rend.*, 1923, 176, 1409; 177, 122; Florentin, *Bull. Soc. Chim.*, 1924, 35, 228). Morgan (*J. Chem. Soc.*, 1904, 85, 1004) obtained accurate results with mixtures of calcite and definite organic substances, and with precipitated carbon from iron, by first decomposing the carbonate with phosphoric acid, then adding chromic acid, and again heating to oxidise the carbon. Morgan's method has the advantages (i) that by using phosphoric acid instead of sulphuric acid, which has itself an oxidising effect, the two forms of carbon are determined by consecutive operations in the same apparatus, and (ii) the risk of absorption of acid fumes is eliminated. Schollenberger (*loc. cit.*) stated that phosphoric and chromic acids would not completely oxidise carbon in soils unless some sulphuric acid were also present.

Since the use of phosphoric acid for the purpose in hand seemed to be more promising than that of sulphuric acid, the carbon in a number of rocks and of carbon minerals often associated with rocks was determined by Morgan's method (Table, Columns 2 and 4). The results showed that, (i) as in the case of the simple sulphuric-chromic process, low results were obtained with some samples, owing to incomplete combustion to carbon dioxide, and (ii) in all cases, provided the temperature of the flask was high enough, no carbon remained in the flask after the operation, the whole being completely expelled as carbon dioxide or other volatile substance. This was evident from inspection of the residue and from later tests (Column 3).

Attempts were made, without success, to render the combustion complete by the addition of catalysts. Apart from the fact that this did not eliminate the source of error (a), p. 742, the fundamental difficulty appeared to be that once the not fully oxidised products of a resistant compound had escaped from the surface of the liquid, they were immune from further oxidising action. There remained, therefore, no alternative to the provision of a further oxidising medium to complete the combustion. A solution was found in the insertion of a second flask provided with a wide inlet-tube and containing phosphoric and chromic acids together with a little mercuric oxide. This flask served the two-fold purpose of acting as a condenser to trap volatile constituents expelled during the determination of carbon dioxide, and, on heating during the second operation, of effectively completing the oxidation of the sample.

METHOD.—The finely-powdered sample (containing 0.05 to 0.1 grm. of carbon) is weighed and introduced into the round-bottomed flask A, fitted with a pipette C, the lower end of which consists of a wide tube drawn out to a point. This flask is connected by a sloping delivery tube with an empty second flask, B,

also having a wide entrance tube narrowing at the lower end; a side-tube fitted with an adapter leads to an empty U-tube, and thence to the usual drying tubes of sulphuric acid and absorption tubes of sodiolite and of sulphuric acid. Forty ml. of phosphoric acid, sp.gr. 1.75, are admitted slowly from the pipette, the flask is heated, and the carbon dioxide determined as usual.



Forty ml. of phosphoric acid, in which are dissolved 4 grms. of chromic acid and 0.1 gm. of mercuric oxide, are then introduced into B, and 4 grms. of chromic acid added to A. A current of air is slowly aspirated through the system, and B is gently heated. Just before gas is freely evolved from B a very small flame is placed under A. It is essential that the contents of B should be gently simmering before there are any signs of decomposition in A, and that they should continue to do so until all the decomposition products have been expelled from A. Towards the end of the operation A is heated fairly strongly for 10 to 15 minutes. At the end of an hour the aspirator tap is closed, the burner under A is extinguished, that under B is turned low for a while and then extinguished. When both flasks are moderately cool, aspiration is continued until the absorption tubes cease to gain in weight.

It is important that the temperature of A should be raised only very gradually when frothing is about to commence. There is then very little tendency for the oxidising liquids to be pushed back, owing to the viscosity of the liquids, the width of the tubes, and the mutual "braking" effect of the two columns.

The effect of the mercury is apparently to enhance the activity of the phosphoric-chromic acid mixture while shortening its active life at high temperature. For this reason, the temperature of the second flask is kept as low as is consistent with efficiency, and, further, no mercury is used in the first flask, since it was desirable, especially with the more refractory minerals, to raise the still active oxidising mixture to a high temperature towards the end of the reaction.

The results obtained are shown in the Table, Columns 2 and 3.

Substance	Dry combustion Total carbon Per Cent.	Phosphoric acid treatment Carbon dioxide Per Cent.	Wet combustion Non-carbonate carbon	
			With 2 flasks Per Cent.	With 1 flask Per Cent.
<i>Graphites</i>				
1. Graphite, Ceylon .. ..	98.05	nil	97.95	96.34
2. Graphite, Borrowdale .. ..	—	omitted	87.10	96.20, 95.35
3. Graphite, Canada .. ..	75.95	omitted	75.75	85.49, 85.57
<i>Bitumens</i>				
4. Kerosene .. ..	85.33	omitted	84.16 <sup>1</sup> , <sup>2</sup>	volatile
5. Ozokerite, Galicia .. ..	84.33	omitted	84.57 <sup>2</sup>	82.41 <sup>2</sup>
6. Bitumen (asphalt), S. Australia .. ..	83.91	omitted	83.68	81.56
7. Native "Pitch" (asphalt), British Guiana .. ..	79.41	nil	79.50	60.98, 71.44
8. Bituminous limestone, Salop	[32.65 + 8.55 <sup>4</sup> = 41.20]	[36.90]	1.19 [4.38]	74.46
9. Oil sand, Greece .. ..	[11.95]	[4.77]	1.93 [7.08]	0.82 [3.00]
<i>Pyrobitumens</i>				
10. Lignite, Devon .. ..	43.83	omitted	43.63	—
11. Cannel, Yorks. .. ..	66.07	omitted	66.12	—
12. Coal, semi-anthracite, South Wales <sup>3</sup> .. ..	79.68	omitted	79.87	79.09
13. Oil shale, Manvers Main ..	[8.08]	[4.05]	1.10 [4.05]	1.10 [4.00]
14. Potassium acetate (24.45 per cent. C) .. ..	—	—	23.40	17.04

REMARKS.—Square brackets indicate percentage of carbon dioxide of sample. All other results are expressed as percentage of carbon.

<sup>1</sup> Eight grms. of chromic acid in each flask.

<sup>2</sup> Heated 90 minutes.

<sup>3</sup> Passed through 250 meshes/inch sieve.

<sup>4</sup> Remaining in ash.

LOSSES FROM THE FIRST FLASK.—An attempt has been made to classify the constituents escaping complete oxidation in the first flask A.

(a) *Volatile, probably undecomposed, constituents expelled during heating with phosphoric acid alone.*—The graphites and the pyrobitumens were apparently free from this source of error. In the cases of Nos. 6, 7, 9, and 8 (a bituminous limestone containing an oil, extractable by carbon bisulphide, of composition C, 84.6 per cent.; H, 11.6 per cent.), oily drops, which sometimes solidified, could be seen distilling over into the second flask.

(b) *"Cracked" or possibly undecomposed products expelled during heating with phosphoric-chromic acid mixture.*—With bitumens containing difficultly volatile, resistant hydrocarbons, the volatilisation process (a) was continued before the acid mixture had time to effect oxidation; e.g. No. 5 formed a few oily drops (containing C, 0.7 per cent. of sample) at this stage and No. 7 evolved heavy fumes which later condensed.

(c) *Carbon monoxide expelled on heating with phosphoric-chromic acid mixture.*—The oxides of carbon formed from the Ceylon graphite, No. 1, by the two methods were determined by passing the resultant gases through the usual absorption tubes and then over iodine pentoxide.

			Carbon dioxide Carbon Per Cent.	Carbon monoxide Carbon Per Cent.
With 1 flask	..	..	96·2	1·1
With 2 flasks	..	..	97·95	trace
Dry combustion	..	..	98·05	

In order to test the efficiency of the hot phosphoric-chromic acid mixture and mercury catalyst in oxidising carbon monoxide, known concentrations of this gas were passed through flask B and the oxides of carbon estimated. It was found that with comparatively rich mixtures of carbon monoxide (*e.g.* those obtained directly by the decomposition of potassium ferrocyanide, oxalic acid, etc., which is difficult to control), only 75 to 80 per cent. oxidation was attained. When dilute mixtures (not more than a few decigrammes of carbon monoxide per litre of air) were bubbled steadily through the simmering oxidant, all but a trace of the gas was oxidised. These may reasonably be assumed to be the conditions under which the gas is liberated from the sample under analysis.

(*d*) *Partly oxidised products other than carbon monoxide expelled on heating with phosphoric-chromic acid mixture.*—This type of loss was not investigated. It was noticed that when too rapid heating of the flask resulted in undue frothing, a non-oily distillate containing organic carbon was sometimes obtained. Those who have studied the sulpho-chromic oxidation agree that it is probably acetic acid or a similar compound that resists further oxidation in some cases (Simon, *Compt. rend.*, 1924, 178, 1816; Hall, Miller and Marmu, *J. Chem. Soc.*, 1906, 89, 596). The results obtained for acetic acid, No. 14, indicate that small amounts of this acid, if formed, would be completely oxidised by the proposed method.

SUMMARY.—A wet combustion method, based on the phosphoric-chromic acid process of G. T. Morgan, is described for the determination of carbonate and non-carbonate carbon in rocks and minerals. It has the following advantages:

(i) The operation is simple and completes in one apparatus and on one sample the determination of both forms of carbon.

(ii) All the typical carbon minerals often occurring associated with rocks such as shales, limestones, sands, etc., tested by this method were found to be completely oxidised.

(iii) The method is specially suited to the determination of carbon in rocks containing a considerable amount of carbonate.

The author wishes to thank Sir Robert Robertson for permission to publish this paper.

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## Notes

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

### THE MICROSCOPICAL EXAMINATION OF HERBS

THE culinary herbs in general use in Great Britain possess many microscopical features by which they may be identified, but when they are mixed together or adulterated with leaves having no aromatic properties, it is essential to have some diagnostic characteristics which afford a means of identifying the various herbs.

During the microscopical examination of a large number of samples it became obvious that among the chief characteristics to which attention had to be directed were the glands and the hairs, and the size of the former and the nature of the latter gave useful proof of the identity of many types of herbs.

The glands vary in size in the different herbs, and the following figures represent many hundreds of measurements made by means of an eye-piece micrometer and a one-quarter inch objective.

#### MEASUREMENTS OF GLANDS IN LEAVES

	Sage	Thyme	Marjoram	Mint	Basil
Minimum diameter	56 $\mu$	62 $\mu$	64 $\mu$	66 $\mu$	66 $\mu$
Maximum „	72 $\mu$	76 $\mu$	78 $\mu$	76 $\mu$	78 $\mu$

For the preparation of the leaves for their microscopical examination the method finally adopted was to treat them with warm 2 per cent. alcoholic potassium hydroxide solution, rinse with water, and finally clear by warming with a solution of chloral hydrate. The leaf fragments were then mounted in 30 per cent. glycerin solution, and after such treatment the glands appeared as clear, regular, spherical discs (unless viewed endwise), and, when measuring their diameters, it was noticed that their size bore some relation to that of the stomata on the same specimens.

In general, the measurements of the diameter of the glands showed this to be approximately three times that of the length of the long axis of the stomata, and, when accurate measurements were made, the following results were obtained:

#### RATIO OF THE MEASUREMENTS OF GLANDS AND STOMATA

	Basil	Mint	Sage	Thyme	Marjoram
Minimum value .. .. .	2.65	2.80	3.12	3.30	3.64
Maximum „ .. .. .	2.78	3.00	3.27	3.40	3.74
Average value for all samples examined . .	2.72	2.87	3.19	3.33	3.68

*Note.*—In this table the length of the stomata is taken as unity.

These results were based on the examination of numerous samples of English and foreign-grown herbs, and to confirm the figures for mint (*Mentha viridis*), the plant was grown in London and the leaves from it afforded the following figures:

	Ratio values	Mean
Brown older leaf ..	2.87	2.86
	2.83	
	2.88	
Green young leaf ..	2.85	2.88
	2.95	
	2.85	



The leaves of both French and Dalmatian sage were examined in this manner, and in every case the ratio was found to be within the above-mentioned limits.

It is essential that as many measurements as possible should be made, both of the diameters of the glands and of the long axis of the stomata, in order to obtain a reasonably accurate average-ratio value.

It should not be inferred that these limits are specific for the respective leaves, but they represent the values obtained with some hundred samples, and recent examinations have confirmed the figures.

I wish to record my thanks to Mr. C. E. Sage, in whose laboratories this investigation was carried out, and to whom I am indebted for permission to publish the results.

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### THE COMPOSITION OF THE SATURATED FATTY ACIDS OF JAPANESE CHRYSALIS OIL

VERY little has been published on the saturated fatty acids of chrysalis oil. Tsujimoto (*C.I.*, 1908, 1910), in one of his papers on this oil referred to an acid (m.pt. 59° C.; formula,  $C_{17}H_{34}O_2$ ), and suggested that it was probably a mixture of acids of the  $C_{16}$  and  $C_{18}$  series. Kawase and his co-workers (*J. Soc. Chem. Ind.*, 1921, 40, 664r), however, isolated an *isopalmitic* acid (m.pt. 57–59°) and palmitic acid from the saturated acids. According to them this *isopalmitic* acid crystallises from alcohol in flat prisms, and both the acid and its magnesium salt are less soluble in alcohol than palmitic acid or magnesium palmitate. Its methyl ester melted at 28° C., and distilled more rapidly than methyl palmitate under reduced pressure.

The sample of chrysalis oil used in our investigation had the following characteristics:—sp.gr. at 15°/4° C., 0.9242;  $n_D^{20}$ , 1.4750; acid value, 4.0; saponification value, 198.8; iodine value (Wijs), 128.6.

The mixed fatty acids (ca. 700 grms.) prepared from the oil were separated into solid and liquid acids by the lead salt and alcohol method. The solid acids (about 25.7 per cent.) melted at 55 to 56° C., and had neutralisation value 212.8, and iodine value, 14.3. They were methylated in the usual manner, and the esters were separated by fractional distillation under reduced pressure into the following fractions:

Fraction No.	B.pt. (°C.)	Yield Grms.	M.pt. (°C.)	$n_D^{40}$	Iodine value (Wijs)	Sapon. value	Sapon. value (calculated)
1	-180	4	28.5–29	1.4339	4.5	208.1	
2	180–185	11	27.6–28	„	5.7	208.0	$C_{16}H_{31}O_2CH_3$
3	185–187	30	27.6–28	1.4343	7.3	208.4	=207.57
4	187–189	30	24.8–25.4	1.4347	10.1	205.4	
5	189–191	36	25.1–25.5	„	12.2	204.3	
6	191–193	20	21.8–22.2	1.4350	16.3	204.0	$C_{17}H_{33}O_2CH_3$
7	193–195	12	21.5–22	„	19.8	203.9	=197.33
8	195–198	11	21.3–21.6	1.4370	29.0	203.4	
9	198–200	10	22.5–23	1.4392	34.5	195.6	
10	200–202	6	28.3–28.7	1.4408	37.7	195.5	$C_{18}H_{35}O_2CH_3$
11	(Residue)	8	29.5–30	„	38.1	170.9	=188.07

Sum 178 grms. Loss approx. 8 grms.

A large amount of palmitic acid was separated from fractions 1, 2 and 3, and a small quantity of stearic acid from fractions 8, 9 and 10, but no indication

was obtained of the so-called *isopalmitic acid* found by Kawase. The crude fatty acids from fraction 6 were recrystallised thrice from 95 per cent. alcohol and twice from petroleum spirit. The resulting acid (m.pt. 58–58.6° C., neutralisation value 207.6) seemed to be a chemical individual, but it will probably be found to be a mixture of C<sub>16</sub> and C<sub>18</sub> acids, as Tsujimoto suggested. Moreover, it is an interesting fact that an acid corresponding with C<sub>20</sub> or C<sub>22</sub> was found in the residue.

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### FUSED BEADS ON PLATINUM WIRE AS SOLVENTS FOR SMALL PARTICLES OF INSOLUBLE MATERIAL

WHEN a small particle of a substance insoluble in acid has to be dealt with, the usual microchemical methods are not very convenient. Fusion on platinum foil or a small platinum spatula or very small platinum vessel causes creeping of the fusion mixture. I find that the most satisfactory medium is a fused bead on a 0.009 inch platinum wire, the bead being about 1 mm. across. When a fusion has to be undertaken with a nitrate the platinum wire should be twisted into a spiral, 1 mm. in diameter; two turns are sufficient to prevent loss of the bead.

These experiments decided me to try the possibilities of the borax bead as a solvent. Borax has the advantages of dissolving a large number of substances, including many silicates, and of giving a clear bead, so that the completion of solution is obvious. It also enables one to control the saturation of the solution by the size of the bead.

In order to decide what group a substance is in, a bead of microcosmic salt is useful, as it is acid. I prefer a spirit lamp with a small flame for making the bead.

If the bead is placed in dilute hydrochloric acid, the presence of silver is at once shown by a copious amorphous precipitate forming round it. If lead is present, the bead dissolves without separation of lead chloride crystals, but the addition of potassium iodide produces a precipitate. If a borax bead containing lead is placed in potassium iodide solution, crystals of lead iodide are formed on the bead.

If the microcosmic salt bead is placed in a weak solution of hydrochloric acid saturated with hydrogen sulphide gas, a precipitate round the bead of the sulphides in Group II is quickly formed. Dilute acetic acid saturated with hydrogen sulphide gives a white precipitate with a microcosmic salt bead containing zinc. Zinc in a borax bead will give a precipitate with ammonium sulphide.

Ammonium carbonate and ammonia give an opaque bead and a white precipitate with metals of the calcium group. Dilute sulphuric acid gives an amorphous precipitate with barium, and a crystalline precipitate with strontium or calcium.

The various specific reactions sometimes take place on the bead direct and sometimes require previous solution or treatment with hydrochloric or nitric acid. A minute drop from a drawn-out narrow glass tube just sufficient to immerse the bead is used.

An acid solution of potassium ferrocyanide gives a red precipitate with copper, and a blue one with iron. Antimony, tin and bismuth beads yield the appropriate precipitate with calcium chloride and potassium iodide, and the characteristic brown crystals are obtained with a bead containing lead and copper acetate and potassium nitrite. Platinic chloride gives a yellow precipitate with a bead containing potassium.

An important universal reagent in microchemical analysis is potassium mercury thiocyanate. A drop of strong hydrochloric acid is placed on the bead

and evaporated to dryness, the undissolved portion of the bead is removed, and the dry salts are dissolved in a drop of water and brought into contact with the thiocyanate reagent on the glass slide.

In order to test for silver with chromate the bead is immersed in a drop of nitric acid and evaporated to dryness; the remainder of the bead is removed, the residue is dissolved in water, and a crystal of potassium chromate is introduced.

In testing for manganese with potassium chromate a sodium carbonate bead is used; it is dissolved in hydrochloric acid, the solution is evaporated to dryness, and the residue is dissolved in water and the solution is tested with a crystal of potassium chromate. This is the only reaction I have found where neither borax nor microcosmic salt is suitable.

A bead containing an aluminium salt forms a red lake if immersed in ammonia containing a little alizarin dissolved in it.

In testing for cobalt with potassium nitrite and for nickel with dimethylglyoxime, the liquid is first evaporated in hydrochloric acid.

Magnesia is best tested for in a microcosmic salt bead: Evaporate with a drop of water, remove the bead, moisten the residue with nitric acid, evaporate again, add ammonia, and scratch the glass with a platinum wire.

The advantages of the bead are: (i) the saturation of the solution is under control; (ii) one drop of solvent, water or acid, is sufficient to dissolve sufficient of the bead to carry out the test, the same bead serving again and again to supply fresh highly concentrated solutions, and where the direct action on the bead of a reagent is possible, the precipitation takes place round the bead, giving the maximum of concentration.

In testing for silica, evaporate with hydrochloric acid, remove the bead, evaporate the residue again with hydrochloric acid, dissolve in water, and add a weak solution of methyl violet; the silica particles are stained and made easily visible.

The metals can easily be electro-deposited from a bead by forming the bead at the end of a straight platinum wire, immersing it, together with another wire, in a conducting solution, and connecting the two wires with a source of electric current. The bead is rapidly dissolved and the metals deposited on the wire, the maximum concentration being thus obtained. The microcosmic salt bead should be used only for special reactions, as it introduces phosphates. The presence of borates and boric acid from the borax bead does not seem to interfere with the reactions given above. Where a neutral bead is required, the borax and microcosmic salt can be mixed in the proper proportions.

Obviously, the method is equally applicable to the many specific tests now available with organic reagents.

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### THE DETECTION OF SMALL QUANTITIES OF GERMANIUM IN THE PRESENCE OF ARSENIC

In a previous communication (ANALYST, 1934, 462) a new electrolytic method for the determination of small quantities of germanium in the presence of arsenic was described.

The present investigation was carried out to determine whether the existing chemical methods of reduction can be improved, and, in particular, be adapted for the determination of germanium when arsenic is present. Müller and Smith (*J. Amer. Chem. Soc.*, 1922, 44, 1909) have detected 0.06 mgrm. of germanium in the Marsh type of apparatus using sodium amalgam as a source of nascent hydrogen; with aluminium and potash they found that 5 mgrms. of germanium dioxide were

needed to give a mirror. The detection in the presence of arsenic was not considered.

**METHOD.**—The apparatus consisted of a round-bottomed flask to which was attached an air condenser, which in turn was connected with a decomposition tube. Into the flask was led a stream of hydrogen gas obtained from a cylinder, the gas passing through a safety trap and a bubbler. The flask was also fitted with a dropping funnel for the introduction of alkali and germanium solution after the apparatus had been filled with hydrogen.

**1. REDUCTION WITH SODIUM AMALGAM.**—Twenty-five grms. of sodium amalgam containing about 3 per cent. of sodium, were placed in the flask, and, when the apparatus had been filled with hydrogen, the solution to be reduced and 10 ml. of 10 per cent. sodium hydroxide solution were added through the dropping funnel. Then the decomposition tube was heated to redness, the flask gently warmed until a brisk evolution of gas resulted, and the rate of hydrogen passing was adjusted to about three bubbles a second. Blank tests showed the materials in use to be free from any mirror-producing substances.

*Detection of Small Quantities of Germanium.*—In this way a definite metallic deposit was obtained in the combustion tube with 0.05 mgrm. of germanium dioxide in 25 minutes. A smaller quantity did not give satisfactory results.

Standard mirrors were prepared from quantities of germanium dioxide ranging from 0.05 mgrm. to 0.1 mgrm., and by matching it was found possible to differentiate between quantities of dioxide varying by 0.01 mgrm.

*Detection in the Presence of Arsenic.*—As with the electrolytic method, arsenic present as an arsenate was found not to be reduced, and the expected germanium stain was obtained. (For oxidation of arsenite to arsenate, see ANALYST, 1934, 462.) A quantity of 120 mgrms. of potassium arsenate was found not to interfere with the deposition of germanium.

**2. REDUCTION WITH ALUMINIUM AND POTASSIUM HYDROXIDE.**—In this reduction the action is so vigorous that the procedure was varied slightly. Three grms. of aluminium turnings were placed in the flask, the germanium solution was added, and potassium hydroxide (23 grms. in 100 ml. of water) was introduced, drop by drop, through the funnel. No mirror was obtained with amounts of germanium dioxide less than 0.16 mgrm.

**3. SOME OTHER REDUCING SOLUTIONS.**—Devarda's alloy was ineffective with as much as 10 mgrms. of germanium dioxide. Hydroxylamine hydrochloride was also tried, but did not reduce 10 mgrms. of germanium dioxide, whilst hydrazine sulphate did not reduce 2.25 mgrms. of the dioxide.

**CONCLUSION.**—The amounts of germanium dioxide which may be estimated by the methods described are as follows:

- (i) Electrolytic method: 0.027 mgrm. in steps of 0.01 mgrm. of  $\text{GeO}_2$  up to 0.1 mgrm. of  $\text{GeO}_2$ .
- (ii) Sodium amalgam: 0.05 mgrm. in steps of 0.01 mgrm. of  $\text{GeO}_2$  up to 0.1 mgrm. of  $\text{GeO}_2$ .
- (iii) Aluminium and potassium hydroxide method: least amount of  $\text{GeO}_2$  detected = 0.16 mgrm.

Only methods 1 and 2 are recommended for purposes of analysis.

When using either of these methods, series of standard mirrors must be prepared by the method and with the apparatus to be employed. In both cases differences of 0.01 mgrm. of  $\text{GeO}_2$  can be recognised. The maximum amount of germanium dioxide which I have used in any one experiment by the electrolytic or sodium amalgam method is 0.1 mgrm., and it is recommended that when larger amounts than 0.1 mgrm. are present in the test, an aliquot part be taken to bring the amount below this figure.

In no case is all the germanium which is placed in the solution recovered in the mirror, but this circumstance does not detract from the usefulness of the method, when care is taken to carry out experiments on the substance of unknown composition in the identical way employed for making the standards. Both the methods may be employed in the presence of arsenic in the quinquevalent condition.

I should like again to express my indebtedness to Dr. H. J. S. Sand for the continued interest which he has taken in the work.

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### THE USE OF ULTRA-VIOLET LIGHT FOR THE DETECTION OF TRACES OF SULPHIDES

THE method described by Grant and Booth (*ANALYST*, 1932, **57**, 514) has been used successfully for the detection of sulphides. The only modification which is applicable is the use of 0.5 ml. of a saturated solution of quinine in water instead of the solid alkaloid; a minimum quantity of quinine should be used in order to ensure the formation of the acid sulphate, which has a more intense fluorescence than the normal salt. The maximum sensitiveness of the test is 0.1 mgrm. of sulphide sulphur, added in the form of a dilute solution of sodium sulphide (1 ml. = 1 mgrm. S.). This was standardised by means of the colour produced, in the presence of ammonia, with a standard solution containing lead. In this connection an attempt was made to find the limiting concentration necessary for the production of the fluorescence of quinine sulphate. It was found that if 0.01 *N* sulphuric acid was added drop by drop to about 15 ml. of a solution of the quinine in a test tube, and this was illuminated horizontally by transmitted filtered ultra-violet light and viewed vertically, a faint blue fluorescence was visible in solutions containing  $1 : 0.5 \times 10^8$  of quinine. If one excepts *X*-ray methods, this would appear to be one of the most sensitive tests known.

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### ULTRA-VIOLET LIGHT AS A MEANS OF DETECTING ARTIFICIAL WATERMARKS

ARTIFICIAL watermarks usually fall into one of two classes, *viz.*:

(i) Those produced by stamping the finished paper with an oily medium which creates the impression of transparency. Such watermarks are usually removed by extraction with ether, and, owing to the presence of oily matter, fluoresce vividly in filtered ultra-violet light, whilst genuine watermarks remain invisible, or at the most appear in dark outline. Frequently the fluorescence is enhanced after the process of extraction with ether, whereas with genuine watermarks there is no alteration.

Artificial watermarks of this type are comparatively easy to recognise, and an application of the method to the detection of a banknote forgery has already been described (*ANALYST*, 1933, **58**, 603).

(ii) In the second type of imitation watermark an impression is produced on the paper before it is completely dried, by means of a circular rubber band carrying the design in relief. It differs from the genuine watermark only in that the latter is applied to the wet pulp on the machine wire before it really becomes

paper, and consequently it is more difficult to identify than the first type mentioned above.

The method now suggested for this purpose depends on the fact that, although both the genuine watermark and the artificial watermark of the second type depend on producing a thin place in the paper, in the former case the wet pulp is squeezed aside from the places where the impression falls, whilst in the latter the almost dry paper is compressed into a denser form. Water will, therefore, penetrate more rapidly through the genuine watermark than through the imitation design, although the thickness may be identical.

The procedure is as follows:—Ordinary icing sugar is dried in the oven, and a mixture of 100 grms. with 0·5 grm. of Rhodamine-6G (concentrated) is ground well in a mortar and transferred to a small bottle provided with a metal screw-cap, the top of which is inset with a piece of 70-mesh bronze gauze so as to form a “pepper-box”; when not in use, the bottle and its contents should be kept in a desiccator containing calcium chloride.

For the actual test the mixture is sprinkled uniformly in a thin layer over the watermark and adjacent portions of the paper, so that the surface just remains visible, and the paper is then placed in a dish of water under a source of filtered ultra-violet light in a dark room. Complete penetration of the water through the paper is indicated by a bright golden fluorescence due to the solution of the dye. With the genuine watermark only, this is found to occur most rapidly through the watermark, the design of which stands out vividly against a dark ground for a few seconds before the remainder of the sheet is penetrated. With imitation watermarks, however, the rate of penetration is uniform throughout the sheet.

This method has also been applied to the determination of the degree of sizing of paper in terms of its resistance to penetration by water, and an end-point is obtained which is considerably sharper and more consistent than those provided by existing methods. Full details will be published shortly.

I am indebted to the Directors of Messrs. John Dickinson & Co., Ltd., for permission to publish these results.

JULIUS GRANT

THE LABORATORIES  
CROXLEY MILLS, HERTS

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## Official Appointments

THE Minister of Health has approved the following appointments:

FREDERICK DIXON as a Public Analyst for the County Borough of Stoke-on-Trent, in addition to Ernest Victor Jones (October 5th).

THOMAS REGINALD HODGSON as a Public Analyst for the County Borough of Stockport, in place of William Marshall (deceased) (October 15th).

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## Notes from the Reports of Public Analysts

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

### CITY OF BIRMINGHAM

#### REPORT OF THE CITY ANALYST FOR THE SECOND QUARTER, 1934

OF the 1426 samples of food and drugs submitted during the quarter, 91 were bought informally. The total number of adulterated or incorrect samples was 96.

**GRAPE FRUIT BUTTER.**—This article, the name of which suggests that a fair amount of butter is present, was found to contain only 2·5 per cent. In appearance and taste it resembled lemon cheese, but in so far, at least, as the fat-content was concerned, it was inferior to the average sample of this commodity, which usually contains about 10 to 15 per cent. of butter. The use of the word "butter" as part of the description of this article would appear to be misleading and unjustifiable.

**TABLE VINEGAR.**—A sample bought as table vinegar was supplied in a bottle labelled "Table Vinegar. Absolutely Pure Wood Vinegar." Table vinegar should consist of malt vinegar, and such a label as the above is a contradiction in terms. The packers were cautioned.

**"DOUBLE-STRENGTH" TEA.**—The label on a sample of tea stated: "One teaspoonful will more than equal two teaspoonfuls of ordinary tea." The amount of extract given by boiling the tea with water was 40 per cent.—a perfectly normal figure, showing that, to make the usual infusion, about the same quantity of the sample would be required as of any other tea. The packers agreed to delete the words in question from the labels. The label on another sample of tea stated that a half-pound would go as far as one pound of ordinary tea and, in addition, the article was described as "double strength." The total boiling-water extract in this case was 42 per cent., which is, again, a normal figure. Representations have been made to the firm concerned.

H. H. BAGNALL

### CITY AND COUNTY OF BRISTOL

#### ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1933

THE number of samples submitted for analysis was 1375, and of these 69 were adulterated.

**BRITISH WINES AND UNFERMENTED CORDIALS.**—Two samples of British wine and six of unfermented cordials were examined, and the following results were obtained:

Description	British Wine		Unfermented Cordial			
	No.	514	517	Lowest	Highest	Average
Sp.gr. at 15·5 °C..	..	1021·9	1076·0	1055·3	1273·1	1116·7
Alcohol by wt., per cent.	..	12·23	9·11	0·16	0·70	0·38
Alcohol by vol., per cent.	..	15·12	11·30	0·19	0·88	0·47
Total solids, per cent.	..	8·90	22·54	14·28	60·42	27·80
Ash, per cent.	..	0·313	0·150	0·005	0·10	0·053

Sulphur dioxide was present in one of the British wines, the amount being 0.036 per cent., but it was not found in the unfermented cordials. Two of the latter, however, contained 0.07 per cent. of benzoic acid and were condemned, while two others contained 0.05 and 0.022 per cent. respectively. Saccharin was detected in three of the unfermented cordials.

LEMONADE TABLETS.—A sample submitted by the Port authority consisted of 96.5 per cent. of citric acid, with colouring matter, but no sugar. It was free from sulphur dioxide and contaminating metals.

E. RUSSELL

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## Palestine

### ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1933

IN his Annual Report, the Government Analyst (Mr. G. W. Baker) states that 9965 samples were examined, and that, in addition to routine work, investigations for the Department of Agriculture and Forests, and for the Research Department, Woolwich, had been continued, and that an investigation on counterfeit coinage had been completed.

EDIBLE FATS AND OILS.—Of the 1332 samples, 1060 were of imported goods. Seventeen of 74 samples of local semni were adulterated, mainly with fat of the coconut type. Twenty-one of 81 olive oils were adulterated, the adulterant being sunflower seed oil (15), arachis oil (5), and sesame oil (1).

POISONING CASES.—Sixty-nine specimens were examined in connection with 18 cases of supposed human poisoning, and in 11 of these poison was found, *viz.* veronal (2), lysol (2), thallium (2), arsenic (3), cyanide (1), alcohol (1).

*Thallium Poisoning.*—The cases of thallium poisoning occurred near Beersheba, where a mother and two children, aged 4 and 7, inadvertently ate some poisoned wheat imported for the destruction of field mice (*cf.* ANALYST, 1933, 58, 547). Twelve hours later vomiting started with slight purging and pronounced abdominal pains, and the elder child, who, it was said, had eaten more of the wheat than his sister, continued to show these symptoms, and died on the fifth day, without medical attention. The younger child was comatose when seen on the eighth day, and died on the ninth day. The mother's symptoms were less severe, and, so far as is known, she eventually recovered. The father did not report the matter until three days after the death of the elder child. Thallium was detected in the portions of viscera submitted, and also in a sample of the "Zelio" grains of which they had eaten.

EXHIBITS IN CASES OF SHOOTING.—All exhibits are now first examined at the central offices of the C.I.D., and are only subsequently examined by the Government Analyst when chemical work is necessary or a confirmatory opinion is required.

Such exhibits totalled 89, as compared with 250 in 1932. They included firearms (4), bullets (24), cartridge cases (25), other related exhibits (36). In one case examination of a fragment of paper and fibre from a wound yielded presumptive evidence that a single ball 16-bore cartridge was concerned. In another instance there was evidence that the composition of the lead in confiscated bullets differed from that in bullets from the scene of the crime. In another case it was shown that four 12-bore cartridge cases were all fired from one shot gun. Eight exhibits were connected with bomb-throwing. In one case traces of potassium chlorate were detected in fragments of the exploded bomb.



**DRUG TRAFFIC.**—In one case of alleged traffic in hashish, two samples of wrapping paper have been submitted for examination. One of these (A) was found in a suspect's house in Palestine and one (B) in a neighbouring country to which it was suspected that hashish had been smuggled. A physical and chemical examination showed that two kinds of paper were present in sample "B". The fluorescence test was of value in this case. Petroleum spirit extracts, from portions which showed green stains in ultra-violet light, gave positive reactions with Beam's test for hashish.

**COUNTERFEIT CURRENCY.**—At the request of the Palestine Currency Board an examination of 763 coins was undertaken with the object of discovering evidence as to origin and other facts which might be of use to the Police. The coins in question had been impounded as counterfeits by the Treasury, and had been tendered, mostly at railway booking offices, over a period of 26 months. A representative selection of 69 coins was sent to the Comptroller at the Royal Mint, whose report included the information that 14 of the coins were struck from 4 pairs of dies and that the remainder were cast coins, mostly from plastic moulds, and a few from metal moulds. The findings in these Laboratories, combined with those at the Mint, classified 262 coins (all 50 mils) as struck counterfeits, five as genuine coins, and the remainder as cast counterfeits, some of which were crude attempts in soft metal.

By low-power microscopical examination, after cleaning with dilute ammonia, and by photography giving a magnification of about 3 diameters in oblique illumination, it was possible to identify by characteristic faults in the coins nine different dies, and it was, moreover, possible to show that at least 5 of these dies, accounting for 67 per cent. of the struck coins, were in the hands of one group of counterfeiters. The weights and diameters of these struck coins were in most cases approximately correct, but the silver-content was considerably higher than that in the genuine currency. Tests carried out showed that, when tendered, they would generally deceive any but experienced cashiers on the look-out for such counterfeits.

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## Siam

### SIXTH REPORT OF THE GOVERNMENT LABORATORY

(FROM APRIL 1ST, 1930, TO MARCH 31ST, 1932)

THE Report of the retiring Director (Mr. A. Marcan, F.I.C.) to the Ministry of Commerce and Communications summarises the official work of the two years since the last report (ANALYST, 1932, 57, 312). The number of samples examined (9193) shows a large increase, owing to additional routine work in connection with opium dross and mint assays for silver.

**DRUGS FOR THE TREATMENT OF LEPROSY.**—Clinical tests showed that the ethyl ester derived from *Taraktogenos ilicifolia* (*Hydnocarpus il.*; cf. ANALYST, 1932, 57, 313) caused much pain on injection, and led to a rise in temperature lasting for 1 or 2 days, whereas the esters from *H. anthelmintica* were painless in use and produced results similar to those given by the esters of *H. Wightiana*, which is the species mainly used in India. Further efforts are being made to produce *ilicifolia* oil suitable for injection, since the esters are not satisfactory.

**PHYSIOLOGICAL ACTION OF KRATOM.**—Mitragynine acetate prepared from kratom leaves (*Mitragyne speciosa*) was sent to Professor Barger and to the late Dr. Dixon at Cambridge for pharmacological tests. It was found to diminish the excitability of plain muscle, to anaesthetise the cornea, and to be toxic to animals in

fairly low doses. In its effect upon the nervous system it resembles cocaine, but there is nothing to suggest that it is effective as an antiseptic against bacteria or pathogenic protozoa. The results afforded no explanation of its action as a drug of addiction.

In the psychological research six human subjects submitted to various laboratory tests after taking doses of 50 to 100 mgrms. of mitragynine acetate and after doses of 0.65 gm. to 1.3 gm. of the powdered leaves. There were indications that both forms of the drug produced the following effects:—Decrease in the time of reaction to stimulus; increased tolerance to heat; increased steadiness and capacity for work; flushing of the skin, apparently due to dilatation of superficial blood vessels. These effects agree with those reported in a survey of the use of the drug in Siam (*cf.* ANALYST, 1929, 54, 475).

SEEDS OF STRYCHNOS SPP.—Two varieties of *Strychnos* seeds containing 1.99 and 1.89 per cent. of strychnine, respectively, have been examined in London and found to be suitable for the manufacture of the alkaloid. Although the exact species to which these two varieties of seeds belong is not yet certain, it is different from *S. nux vomica*. A sample of seeds locally termed "Phya mu lek," was found to be *Strychnos roborans*, and contained no strychnine. Another species recently examined was *S. nux blanda*, and also contained no strychnine. Samples from Burma have been examined elsewhere with similar results, and the seeds are sometimes known as "False nux vomica."

SEEDS OF "SAKAE COMBRETUM QUADRANGULARE."—The seeds of this plant have a local reputation as an anthelmintic, and a sample was sent to England for physiological test several years ago. Dr. T. A. Henry came to the conclusion that the active principle was in the tannin-free water-soluble extract, but this was reported to be without effect on hookworm in dogs by Dr. S. Pessôa of the Instituto de Hygiene, San Paulo, Brazil.

Prof. B. A. McSwiney, of the School of Medicine, Leeds, working with the same extract, found that it was effective only in high concentration (0.5 gm. of seeds per ml.) when tested on round worms *in vitro*. He considered the active principle to be similar to that of *Combretum pilosum*, which also has a reputation as an anthelmintic in India.

In order to provide further material for these tests a quantity of Sakae seeds was extracted with alcohol in the Technical Laboratory, and 0.92 kilo. of dry extract has been sent to Prof. McSwiney.

BARK OF "PICRASMA JAVANICA."—*Picrasma javanica* is a small tree found in the evergreen forest in Northern Siam. The bark has a considerable local reputation as a febrifuge and possesses a bitter taste resembling that of quinine. A small sample had been examined in India and had been reported to contain 0.1 per cent. of an alkaloid resembling quinine.

In Bangkok the bark was extracted with a number of solvents, and it was proved that the active principle was not quinine, although it gave certain reactions for alkaloids and exhibited fluorescence in aqueous solution.

CHINESE EDIBLE BIRD'S NESTS.—A sample of edible bird's nests, a prized luxury food of the Chinese, was submitted by the Rural Economic Survey from Chumporn. The analysis was as follows:—Moisture, 16.3; protein ( $N \times 6.25$ ), 49.8; fat, 0.06; ash, 7.5; water-soluble ash, 5.4 per cent. The ash contained a considerable amount of lime.

EDIBLE SPIDERS.—Some spiders used as food by Lao people were submitted privately by a scientist travelling in the country. The species was described as *Lamphopelma siolaceopides*. The analysis which follows shows that they form a rich nitrogenous food:—Moisture and volatile matter, 12.1; fat, 9.8; nitrogen, 10.1; ash, 5.3 per cent.

## Trinidad and Tobago

### ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1933

In his Annual Report Mr. H. S. Shrewsbury gives an outline of the work undertaken for various Government Departments, including Constabulary, Customs and Excise, the Surgeon-General, Public Work, and the British Admiralty.

**FOOD AND DRUGS ORDINANCE.**—Samples are submitted by officials of the Police or the Preventive Officers of the Customs and Excise Department. Of the 1865 samples submitted, 77 were adulterated; these were mainly milk and watered rum.

**Saccharin in Aerated Waters.**—Two aerated waters contained saccharin and four contained an excessive quantity of lead. It is pleasing to be able to note that there has been almost a cessation of the practice of using saccharin in aerated waters of local manufacture, this being due in a large measure to its use being prohibited under the Ordinance, and the consequent co-operation between the Constabulary and this Department in frequently purchasing and analysing aerated waters and prosecuting vendors whose drinks were found to contain saccharin. Out of 602 sweetened aerated waters taken by officials from all the police stations in the Colony, only two were found to contain saccharin, the vendors in each case being prosecuted, convicted and fined. The percentage of sweet drinks thus found to contain saccharin was only 0.2, as compared with 7.5 for 1932.

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## Department of Scientific and Industrial Research

### REPORT OF THE BUILDING RESEARCH BOARD FOR THE YEAR 1933\*

THE Report of the Board (pp. 1-4), which is signed by the Chairman (Sir Raymond Unwin), deals in outline with the progress of the work by the various Committees, and with the co-operative research initiated in conjunction with other organisations. This is followed by the report of the Director of Building Research (Dr. R. E. Stradling) (pp. 5-104), Intelligence and Minor Investigations (pp. 104-124), an account of the activity of the library (pp. 125-126), appendices giving the staff and a list of reports, etc., published during 1933, and an index (pp. 135-139). There are 43 figures and 20 tables.

Among the items of special interest are the following:

**WEATHERING OF BUILDING STONES.**—In the main, attention has been confined to the limestones, and the fundamental idea underlying their investigation in the laboratory is that their durability depends in the first place on physical structure rather than on chemical composition.

**Portland Stone.**—By means of tests on samples of known quality it has been found possible to classify Portland stone in quality groups by measuring total micro-porosity and saturation coefficient. The method of determining the former property was described in the Report for 1931. "Saturation coefficient" is a term used by Hirschwald (*Handbuch der bautechnischen Gesteinprüfung*, Berlin, Gebrüder Bornträger), and signifies the ratio between the amount of water absorbed by simple soaking for a standard time and the accessible pore space. As a general rule, a material having a coefficient of less than 0.80 is unlikely to be damaged by frost. Recent research, however, has shown that the saturation coefficient is intimately linked with the structural characteristics of the stone, and through them with its general weathering behaviour, apart from the question of frost. A chart

\* H. M. Stationery Office, Adastral House, Kingsway, W.C.2., pp. 139, Price 2/6 net.

is given showing the mean relationship between micro-porosity and saturation coefficient, as calculated from the results given by 165 samples of the normal type of Portland stone, which is characterised by the presence of large inter-connected pore-spaces between the oolitic grains and the lack of a continuous crystalline matrix, such as is found in many oolitic limestones. By measuring micro-porosity or saturation coefficient, or preferably both, a quarry sample can thus be compared with samples of known quality, and it may be inferred that its weathering quality will resemble that of the standard sample with which it most nearly corresponds in these physical characteristics. In applying these tests the practical way is to sample the quarries systematically, and thus to establish the position of the deposits of good and inferior quality.

*Clipsham Stone.*—Clipsham stone is quite different in structure from Portland stone; it is a partly shelly and partly oolitic limestone, in which the relative amounts of shells and oolitic grains vary greatly. So far it has not proved possible to relate micro-porosity, as arbitrarily defined for Portland stone, with the saturation coefficient. But it has been found that quality, as judged by the crystallisation test, tends to decrease with increase in the saturation coefficient.

With Clipsham stone, it is necessary to distinguish two types, and, although there is no sharp dividing line between the one and the other, the two types are more or less readily identifiable by inspection. One type is predominantly shelly, the other is much more oolitic in character. Laboratory tests have led to the conclusion that the more shelly type of stone is of superior weathering quality.

These conclusions have been borne out by the observations of builders and masons. In two buildings marked decay associated with efflorescent salts has been observed. The deleterious salts have affected the oolitic stone much more seriously than the shelly stone, and in one of the buildings where this difference is particularly pronounced the decaying stone has been in position only two years. It is understood that the old masonry was cleaned with an alkaline solution when the repairs were executed. The resulting decay furnishes an illustration of the dangers associated with the use of chemicals for cleaning masonry, and to which attention has been repeatedly directed in previous Reports.

*The Crushing Strength of Building Stones.*—It cannot be too strongly emphasised that the properties of building stones commonly quoted in trade advertisements, and on which architects are presumably invited to form an opinion of quality, often afford no criterion of durability at all; the figures may, in fact, be quite misleading. Crushing strength is a notable example. For instance, it is shown that certain stone of such poor quality that it had suffered excessive decay through exposure for 20 years in London, had nearly twice the crushing strength of stone that had weathered perfectly for 250 years in St. Paul's Cathedral.

*Atmospheric Pollution.*—Tests on the lead peroxide method of estimating sulphur pollution (*The Investigation of Atmospheric Pollution*, 18th Report, 1933, p. 14, cf. ANALYST, 1933, 58, 284) have been continued. The method is now in regular use in 34 stations, and is also being employed in connection with research on the corrosion of non-ferrous metals, the durability of leather in libraries, and the recording of pollution emanating from a localised source.

*Physical Factors influencing Weathering.*—In the tests on pressure deficiency and the water-content of stones it has been found that a centrifugal method gives results closely comparable with those obtained by the hydrostatic method (see Report for 1931). By determining the relative amounts of water held at equilibrium in two different stones in contact it is possible to deduce the direction of transfer between one stone and another and to demonstrate differences between different types of stone.

*Frost Action.*—Laboratory specimens of building materials were subjected to an accelerated test in which the samples were soaked in water and then subjected

to a maximum of 50 cycles of alternate freezing in air to about  $-20^{\circ}\text{C}$ . and thawing in tap water. Each freezing and each thawing lasted for 24 hours. On the roof duplicate specimens were exposed in two different ways; in one the specimens rested half-immersed in water in a tray, and in the other they simply stood on the roof. During the winter of 1932-33 they were exposed to 77 frosts of not less than  $2^{\circ}\text{F}$ .

Several types of bricks were not affected by any of the tests, while others showed marked and rapid disintegration both on the roof and in the laboratory. There were, however, several types which, although they remained sound during the one winter's exposure, failed badly when frozen artificially. It is too early as yet to say whether the latter results are actually anomalous, since some of the exposed bricks may fail in the near future. There are good grounds, nevertheless, for supposing that in certain cases the laboratory test produced effects which are unlikely to result from natural frost.

Nine different varieties of Bath stone were tested by natural exposure tests under varying weather conditions on the roof. Day-to-day measurement of the moisture-content of other similarly-exposed specimens of the same size has shown that, under these conditions, even materials which are known to be very susceptible to frost are seldom sufficiently saturated with water to suffer much damage.

The specimens standing in water, on the other hand, were damaged to varying extents, and it was found that the specimens which suffered the most were those with saturation coefficients greater than 0.80. Those with saturation coefficients below 0.80 did not suffer any significant damage, even under these somewhat severe conditions.

Notwithstanding these results, it is still believed that frost plays a subsidiary part, as compared with the effect of smoke gases, in the weathering of calcareous stones in this country.

*Effect of Soluble Salts.*—Stones impregnated with sodium compounds—hydroxide, carbonate, sulphate, and peroxide—have continued to show serious decay. Appreciable, but less pronounced, decay has occurred in specimens treated with ammonium salts. Potassium salts, sea-water salts and sodium carbonate have caused little, if any, decay.

The effective life of certain of the materials commonly employed as stone preservatives is limited to about 12 to 18 months. Instances are cited in which treatment has even hastened decay.

*Chlorides in Portland Stone.*—Tests, supplemented by observation of the behaviour of blocks in a London building, suggest that Portland stone of poor quality is much more affected by the presence of chlorides than stone of good quality. Recent observations suggest that contaminated stone is seldom, if ever, to be found in the quarries, except in those where the stone may be washed by the sea.

*Relation of Micro-Organisms to the Decay of Stone.*—Experiments have proved that rain water and the sulphur gases of the laboratory can provide sufficient nutriment to support the life of micro-organisms on the surface of stone. It has recently been found that a water extract of sound stone, when added to a crude culture of stone organisms in a solution of sodium thiosulphate, enhances the rate of oxidation of thiosulphate, as compared with the water control. It can be assumed, therefore, that the stone contains a significant supply of food material for such organisms as these—(cf. Paine *et al.*, *Phil. Trans. Roy. Soc.*, 1933, 222 [B], 97).

*MATERIALS.—Asphalts and Bitumens.*—Experiments (described in detail) indicate that it is probable that blisters on asphalt roofs are caused by the thermal expansion of water vapour or air entrapped by moisture in the pores of the concrete beneath the mastic. Their formation appears to be preventable by reducing the moisture-content of the concrete, by eliminating condensation and absorption of water, by using concrete with coarse pores, or by inserting a layer of felt, paper

or the like to prevent the asphalt from adhering to the concrete. The first suggestion is the simplest for application to existing roofs, and the third for new roofs or those being entirely re-laid.

*Cement.*—Direct deductions from data embodied in a diagram of the system—Lime-Alumina-Silica-Ferric Oxide—confirm the view that ferric oxide in Portland cement exists in the form of the compound  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ , and show that in cements made from  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  only, melting begins at  $1338^\circ\text{C}$ .

Considerable attention has been given to the attack of concrete by soil waters and by clays containing sulphates. Tests have indicated that neither removal of the free calcium hydroxide, nor the change of the hydrated silicates and aluminates by autoclaving is alone sufficient to effect more than a partial increase in the resistance to sulphate action. When both occur together the improvement is great.

*Keene's Cement.*—According to his last patent (1838) Keene made his plaster by burning gypsum, adding potash alum as an accelerator, and then reburning and grinding. Other methods are now used, the products differing in properties according to the method of manufacture, but it would appear that no product should be termed "Keene's" unless it possesses the properties of the original product. Unfortunately it has proved impossible to obtain any definite agreement as to what were the essential properties of the original Keene's cement. It is hoped that the proposed specification, by providing a means of differentiating between different types of plaster, will tend to remove some of these difficulties.

*Roofing Slates.*—The effects of cycles of wetting and drying on a representative series of slates have been studied by soaking the specimens in water for 6 hours at laboratory temperatures and drying for 18 hours in an oven at  $110^\circ\text{C}$ . In certain cases the process has been repeated as many as 200 times. The results of the tests are set forth in a table, which also gives the carbon dioxide and sulphur-contents and the results of acid tests. In general, the effects resemble those observed when the specimens are immersed in acid.

Slates that bear the best reputation for durability and contain only negligible quantities of pyrites have been found to withstand more than 100 cycles without being affected, though in some cases lamination may ultimately occur. On the other hand, slates that are attacked within about 20 cycles thereafter decay very rapidly. Specimens of such slates contained from 3 to 3.46 per cent. of ferrous sulphide.

*Florescence in Bricks.*—Research on florescence has been concerned mainly with the question of the permissible limits for the salt content of bricks. The problem is complex because the capacities of the various salts for causing trouble are very different. A brick containing 0.1 per cent. of water-soluble magnesium in the form of sulphate (about 1.0 per cent. of hydrated magnesium sulphate) would almost certainly cause the failure of plaster applied to it, but an equal amount of calcium sulphate might be quite innocuous. A further complication is introduced by the texture of the brick. If a brick is soft and highly porous through underfiring, water will easily gain access to any soluble material it may contain, and recrystallisation of these salts near the surface may cause flaking.

The crystallisation test, described in the last Report, is used as a means of estimating the intrinsic resistance of the material to disruption by the action of soluble salts.

Other points discussed in connection with materials include the durability of bricks underground, the thermal expansion of plate glass, paints, and water proofers. "The Structure and Strength of Materials" forms a section of thirty pages, and "The Efficiency of Buildings from the Standpoint of the User" is discussed under various headings, reference being made to the investigation of the question of infra-red rays and comfort, of which an account has been published (Dufton, *J. Hygiene*, 1933, 33, 476).

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

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**Food and Drugs Analysis**

**Transmission of Light by Egg Albumin.** H. J. Almquist, J. W. Givens, and A. Close. (*Ind. Eng. Chem.*, 1934, 26, 847-848.)—The transmission of light varies in different layers of egg albumin, being lowest in the firm or gelatinous layer; it is correlated with the percentage of mucin in the albumin, and varies with the temperature and  $p_H$  value, which affect the physical condition of the mucin. The changes thus produced cause differences in the candling appearance of eggs, which are not necessarily due to changes in interior quality.

W. P. S.

**Formaldehyde in Canned Marine Products.** G. Lunde and E. Mathiesen. (*Ind. Eng. Chem.*, 1934, 26, 974-976.)—Canned marine products frequently give a positive reaction when tested for formaldehyde by the official tests of the Association of Official Agricultural Chemists. The official tests, in which phenylhydrazine hydrochloride is used as a reagent, cannot be applied directly to liquid foods or aqueous extracts of foods which may contain trimethylamine. The trimethylamine naturally present in fish foods causes a positive reaction in these tests. Of other tests used, only the Hehner test could be satisfactorily applied directly to an aqueous extract of fish, although all the tests could be used on the distillate from an acid distillation. Formaldehyde has been detected in the distillate from fresh and canned herring, crab and other marine products. The amount found in the canned food is somewhat higher than in the fresh fish. The formation of formaldehyde in canned fish appears to be independent of the nature of the container and does not increase during storage. The formaldehyde is not formed during the distillation process, as it can be detected in an aqueous extract of the fish by means of the Hehner test.

S. G. S.

**Iodine-reducing Value of Orange Juice.** M. A. Joslyn and G. L. Marsh. (*Ind. Eng. Chem.*, 1934, 26, 857-860.)—Loss in the iodine-reducing value of orange juice is due to oxidation and is not caused by the action of preservatives of the benzoate type or by heat treatment in the absence of air.

W. P. S.

**Determination of Citric Acid as Pentabromoacetone and its Application to Wine.** O. Reichard. (*Z. Unt. Lebensm.*, 1934, 68, 138-172.)—The conditions for the quantitative conversion of citric acid in aqueous solution into pentabromoacetone have been established. The treatment with potassium bromide, sulphuric acid and potassium permanganate must be carried out at a temperature not higher than 5° C., and bromine must be present in such quantity that the ratio bromine: citric acid is not less than 2, and the ratio potassium bromide : citric acid not below 3. The amount of potassium permanganate present must produce a persistent violet colour or a separation of manganese dioxide. After being washed with water, the collected pentabromoacetone is dried for 2 hours in a desiccator over sulphuric acid. It may be identified by the melting-point (71° to 72° C. for

the crude, and 73° C. for the purified product), the crystalline form, the colour reactions with resorcinol and phloroglucinol, and, after decomposition by alkali, by the isonitrile reaction.

In the amounts occurring in wines, glycerol and such organic acids as malic, lactic, tartaric and acetic acids do not interfere with the determination, provided that the above conditions are fulfilled; preliminary separation of the citric acid is usually unnecessary. The presence of more than 5 grms. of sugar per litre renders direct bromination of the citric acid impracticable. In this case either the sugar is first fermented away or the citric acid is precipitated as barium salt, which is washed with 50 per cent. (by vol.) alcohol and subsequently brominated. With both red and white dry berry and grape wines, with and without added citric acid, the method gives accurate results. With a dry wine containing only little citric acid, precipitation of the barium salt, followed by bromination, is advisable. Details are given of the procedure to be followed in the various cases.

T. H. P.

**Detection of Sorbitol in Fruit Products.** G. Reif. (*Z. Unt. Lebensm.*, 1934, 68, 179-186.)—The removal of fruit constituents which interfere with the reaction of sorbitol with benzaldehyde may be effected by the following procedure: From 5 to 10 grms. of the fruit juice or, when sorbitol-free juices are present, up to 40 grms. are dissolved in 5 to 10 times the quantity of tepid water, the solution being then fermented at 25° to 27° C. With jams, fruit jellies, etc., 15 to 75 grms., mixed with 5 to 10 times as much water, are heated for 1 to 2 hours on a boiling water-bath and the resulting solution cooled and fermented. When fermentation is complete (up to 8 days), the liquid is filtered by suction through asbestos and the filtrate, if coloured, is boiled gently for 2 to 3 minutes with 3 to 7 grms. of pure animal charcoal and again filtered through either asbestos or Seitz filtering material. The clear liquid is evaporated under diminished pressure at 50° to 60° C. to a syrup, which is heated with two or three 30-ml. quantities of ethyl or methyl alcohol, this being absolute if the residue treated contains much sugar or colouring matter from the fruit. The united extracts are left for about an hour, and are then passed through a dry filter, the filtrate being evaporated, under diminished pressure and at a low temperature, to a syrup. If caramel has formed, the syrup is dissolved in water and treated with a little charcoal. The final residue is treated with 1 ml. or, if then too viscous owing to the presence of sugar or lactic acid, with a further 0.2 ml. of dilute sulphuric acid (1 : 1), and then with 0.1 ml. of benzaldehyde. If no benzylidenesorbitol crystals then separate, up to 0.1 ml. of the aldehyde is added dropwise. The mixture is then shaken—for 15 minutes if very small amounts of sorbitol are present. After standing for about 12 hours in a cold chamber, the mass is taken up in about 100 ml. of water and the extract is filtered, after an hour, through a fritted glass crucible or a hardened filter-paper on a Gooch crucible. The benzylidenesorbitol is identified by conversion into hexa-acetyl-sorbitol or by its colour reaction with acetone. Sorbitol is found in apples, pears, quinces, cherries, mirabels, greengages, plums, peaches, apricots, raisins, currants, sultanas, and dried dates, but not in grapes, raspberries, redcurrants, bilberries, cranberries, gooseberries, strawberries, oranges, mandarins, lemons, bananas,



pineapples, figs (fresh or dried), or hips. Fruit products made from one and the same kind of fruit may contain widely varying proportions of sorbitol, the amount depending mainly on the condition as regards ripeness of the fruit used.

T. H. P.

**“Soy” Oil.** T. Takei. (*J. Soc. Chem. Ind. Japan*, 1934, 37, 356–357B.)—Soy oil, a by-product of soy-brewing, which is a dark brownish-red oil, opaque when observed in reflected light, is found floating on the surface of the soy after pressing. It is difficult to bleach and deodorise by the usual processes. Hitherto, considered as a mixture of soya and wheat oils together with some decomposition products, it is now found to consist mostly of a mixture of ethyl esters of various fatty acids, and is susceptible to refining by distillation. The constants of the oil are:—sp.gr. at 15° C., 0.89266;  $n_D^{20}$ , 1.4630; relative viscosity at 16° C., 13.155; flash-point, 76.5° C.; saponification value, 186.38; iodine value, 102 to 132 (3 samples); acid value, 39.15–45.19. The results obtained on distillation were as follows:

	Temp. °C.	Yield per cent.	Saponification value	Iodine value	Acid value
	200	6	214.27	116.10	20.55
Distillation with steam	200–220	8.5	182.30	95.90	23.89
	220–240	31.4	193.50	66.91	28.98
	240–260	26.3	188.89	78.31	61.61
	260–300	21.5	177.35	118.80	120.23
		93.7			
Distillation <i>in vacuo</i>	170–180	27.06	190.45	120.14	19.69
	180–190	27.06	185.04	131.77	22.85
	180–190	21.76	198.99	139.36	41.49
	190–195	7.35	194.25	144.88	85.22
	195	3.53	192.65	141.26	127.94
		86.76			

D. G. H.

**Drying Properties of the Polymerised Products of Sardine Oil and of Methyl Esters Derived from Sardine Oil.** K. Kino. (*J. Soc. Chem. Ind. Japan*, 1934, 37, 439–442B.)—Twelve 700-ml. samples of sardine oil and of the methyl esters of the highly unsaturated fatty acids and of the liquid fatty acids were heated at 290 to 300° C. in an atmosphere of hydrogen, and at suitable intervals 30-ml. samples of the polymerised products were withdrawn. The samples from the methyl esters were distilled under reduced pressure (3 mm.), the iodine values and molecular weights of all the fractions were determined, and drying tests were made. During the first hour the iodine values of the polymerised esters decreased rapidly, but the molecular weights of distillation residues increased to nearly twice those of the original esters, thus confirming a preferential intramolecular reaction between two double bonds in one molecule of methyl esters of highly unsaturated acids. Distillation residues taken after 5 hours' treatment dried after 7 or 8 days at 30° C., but those taken after still further treatment took much longer to dry. The acetone-insoluble products from the polymerised oils did not change in appearance in 2 months, nor did the polymerised oils themselves.

D. G. H.

**Fatty Substances of Shell Fish, Oyster, etc.** M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1934, 37, 436-439B.)—The fatty substance present in the oyster (*Ostrea gigas*), onagai (*Mya arenaria*), ezohibari (*Volsella modiolus*), akanishi (*Rapana thomasiiana*), and ushinotsume (*Cellana nigrolineata*) was found to contain in each case the peculiar sterol previously found by the authors in other shell fish, and giving a characteristic red colour reaction when a drop of sulphuric acid is added to 5 mgrms. of the sample dissolved in 3 ml. of acetic anhydride. This substance, now called conchasterol, was obtained in a pure state from hamaguri by dissolving 1 grm. in 100 ml. of methanol, and repeatedly recrystallising the crystals from about 100 times as much solvent. The m.pt. is 133 to 134° C., and the m.pt. of the acetyl compound after 4 recrystallisations from alcohol, 144.5 to 145.5° C. Conchasterol was also found in tarabagani liver (*Paralithodes Crustacea*), and in calamary (*Cephalopod*) oils, but is absent from fish body and liver oils, and from whale blubber and liver oil. D. G. H.

**Formation of Isomeric Unsaturated Fatty Acids in the Hydrogenation of Oils.** S. Ueno. (*J. Soc. Ind. Japan*, 1934, 37, 457-458B.)—Japanese sardine oil was hydrogenated at high temperatures (250-300° C.) with large proportions of catalyst (up to 10 per cent. of nickel) at ordinary pressure, hydrogenation being stopped when the m.pt. of the oil was approximately 40° C. The oil was then filtered, saponified and decomposed with mineral acid, and the solid fatty acids were separated by the lead salt and alcohol method. The amount of *iso*-oleic acid was then calculated from the iodine value. It was found that under these conditions the yield of *iso*-oleic acid was diminished. The quantity of catalyst used bore no relation to the formation of the *iso* acid, and at temperatures above 275° C. the formation ratios were much more irregular than at 250° C., presumably owing to polymerisation and decomposition. D. G. H.

**Colorimetric Determination of Chlorogenic and Caffeic Acids in Roasted Coffee.** W. Plücker and W. Keilholz. (*Z. Unt. Lebensm.*, 1934, 68, 97-109.)—Roasted coffee is found to contain an ingredient which disturbs the determination of chlorogenic acid by Hoepfner's colorimetric method (*ANALYST*, 1933, 58, 100, 702). Detailed examination of the procedure of this method shows that the intensity of the colour produced is greatly influenced by the quantities of the reagents added. This influence may be markedly diminished by adding an acetate buffer solution in place of the acetic acid. The following modified method is hence suggested: 10 ml. of the chlorogenic acid solution are treated in a test-tube with 0.3 ml. of a solution containing 10 ml. of glacial acetic acid and 30 grms. of sodium hydroxide in 100 ml. of water. The liquid is cooled to 8° C., treated with 0.3 ml. of 40 per cent. sodium nitrite solution, kept at exactly 8° C. for 3 minutes, and afterwards treated with 0.3 ml. of 10 per cent. sodium hydroxide solution. The transparency of a 1-cm. layer of the solution is then determined by means of a step-photometer. A table is given showing the values of the transparency towards different light filters for solutions of chlorogenic acid of different concentrations.

Details are given of the procedure to be followed in applying this method to

the determination of chlorogenic acid in raw coffee. The results obtained with a number of samples agree well with those given by Hoepfner's method. A further method is described, in which the chlorogenic acid is converted, by treatment with potassium hydroxide, into caffeic acid (*ANALYST*, 1933, 58, 701). This is then treated with sodium nitrite, and the colour intensity is measured photometrically.

T. H. P.

**U.S.P. Test for Soluble Alkalis and Alkalinity in Milk of Magnesia and Magnesium Oxide.** H. Wales. (*J.A.O.A.C.*, 1934, 17, 536-539.)—In order to ascertain the end-point for the assay of milk of magnesia and magnesium oxide, solutions of magnesium sulphate and magnesium chloride containing acid in slight excess were titrated potentiometrically with sodium hydroxide solution. The end-points, characterised by sharp breaks in the curves, lie between  $p_H$  4 and 8. As the transition intervals for methyl orange and phenolphthalein are, respectively,  $p_H = 3.1$  to  $4.4$  and  $8.2$  to  $10.0$ , neither of these indicators is applicable. Methyl red, with transition interval at  $p_H = 4.2$  to  $6.3$ , is, however, suitable.

To test for soluble alkalis in milk of magnesia, the Revision Committee for U.S.P. XI suggests the following procedure:—Twenty ml. are diluted to 200 ml. with distilled water and filtered, 50 ml. of the filtrate being titrated with  $0.1 N$  sulphuric acid in presence of methyl red; not more than  $0.4$  ml. should be required. Eight samples of commercial milk of magnesia gave results ranging from  $0.25$  to  $0.80$  ml. and three laboratory preparations  $0.33$  to  $0.35$ . The titrations were followed potentiometrically, all the curves thus obtained showing a change in slope at  $p_H =$  about  $6$ , owing to presence of carbonate. Products more alkaline than magnesium hydroxide were not present in more than negligible amount. There is no connection between the  $p_H$  value of the solution of the milk and the result of the titration for soluble alkalis.

T. H. P.

**Differentiation between Light and Heavy Magnesium Oxide.** H. Wales and G. L. Keenan. (*J.A.O.A.C.*, 1934, 17, 534-536.)—The Revision Committee of U.S.P. XI proposes the following test to distinguish between light and heavy grades of magnesium oxide: "Place 1 gm. of magnesium oxide, previously sifted through a No. 100 sieve, in a 50-ml. graduated cylinder provided with a glass stopper. . . . Add distilled water until a volume of 50 ml. is obtained. Agitate the mixture for exactly one minute and set it aside for sedimentation. Within fifteen minutes the column of magnesium oxide measures not less than 30 ml. in case of the light oxide and not more than 5 ml. in case of the heavy oxide." The results of an examination of eight samples made by three manufacturers show that this proposed test cannot be depended on to distinguish between the two grades.

A better criterion is afforded by a weight-bulk relation, determined by measuring the volume occupied in a graduated cylinder by a definite weight of the oxide (*cf.* Liverseege, Bagnall and Lerrigo, *Pharm. J.*, 1926, 117, 146), but the procedure must be accurately standardised if consistent results are to be obtained. Microscopic examination appears to be a still more promising means of differentiation.

T. H. P.

## Biochemical

**Role of Copper in Carbohydrate Metabolism.** H. L. Keil and V. E. Nelson. (*J. Biol. Chem.*, 1934, **106**, 343-349.)—The oral administration of copper alone to anaemic rats produced a type of glucose tolerance curve different from that obtained with the same animal before the ingestion of the mineral. A significant lowering of the maximum point demonstrates a role of copper in nutrition apart from that of haemoglobin formation. Since the haemoglobin values were unaltered, the effect was not due to ordinary physiological oxidative processes, but must have arisen from some hitherto undescribed property of copper. Sugar tolerance tests showed that pure iron alone does not improve the glucose utilisation. An increase of haemoglobin in anaemic rats produces a proportional increase in sugar tolerance, together with a lowered glucose level in the blood after a 24-hour fast. Animals suffering from nutritional anaemia give higher blood-sugar values after 24 hours of fasting than are obtained with normal controls of the same age, and this is independent of sex. S. G. S.

**Preparation of Sodium Tungstate Free from Molybdate, together with a simplified Process for the Preparation of a Correct Uric Acid Reagent.** O. Folin. (*J. Biol. Chem.*, 1934, **106**, 311-314.)—The molybdates are converted into sulphomolybdates which are soluble in alcohol and water and can be easily separated from the alcohol-insoluble tungstate. The sodium tungstate (1000 grms.) is dissolved in 2000 ml. of water, and dilute hydrochloric acid (1 : 1) is added slowly, with stirring, until the solution is neutral to litmus paper. The liquid is then transferred to a large flask and hydrogen sulphide is passed into it, in a moderately rapid stream, for 15 to 20 minutes, after which the flask is then stoppered and allowed to stand overnight. After standing, the solution is transferred to large beakers, and to it is added, very slowly at first, and with constant stirring, about two-thirds of its volume of alcohol. The paratungstate is precipitated, and the coloured sulphomolybdates remain in solution. The mixture is allowed to stand until the next day, when it is filtered by decantation on a large Buchner funnel, and the residue is washed with 50 per cent. alcohol until the filtrate is colourless. The precipitate is then transferred to a 4-litre beaker, 1.5 litre of water and about 2 ml. of bromine are added, and the whole is stirred for a few minutes, and then heated over a burner, the stirring being continued until all the surplus bromine has been removed. The heating is continued, and clear, saturated sodium hydroxide solution is added until the solution gives a permanent and fairly strong reaction to phenolphthalein paper. The solution is then cooled and filtered, if necessary, the tungstate is precipitated with alcohol as before, and the precipitate is dried. The sodium tungstate thus obtained gives a moderate, permanently alkaline reaction to phenolphthalein, its solutions are clear, and it does not give the slightest trace of pink colour in the potassium xanthate test for molybdate described by Folin and Trimble (*J. Biol. Chem.*, 1924, **60**, 474).

The uric acid reagent may be prepared by placing 100 grms. of the sodium tungstate in a 500-ml. Florence flask. From 32 to 33 ml. of 85 per cent. phosphoric acid are mixed with 150 ml. of water, and this solution is poured on to the tungstate

and mixed. A few pebbles are added, and the solution is boiled very gently over a micro-burner for 1 hour. Loss of liquid is prevented by using, as a condenser, a funnel holding a 200-ml. flask filled with cold water. After boiling, the solution is decolorised with bromine water and the excess of bromine is boiled off. The solution is then cooled and diluted to 500 ml. If the reagent so obtained gives a blank with urea cyanide, with or without tyrosine, 3 to 5 grms. more of sodium tungstate are added, and the solution boiled for 10 to 15 minutes, cooled and decolorised as before. S. G. S.

**Insulin-Content of the Pancreas in Cattle of Various Ages.** A. M. Fisher and D. A. Scott. (*J. Biol. Chem.*, 1934, **106**, 305-310.)—The amount of insulin which can be extracted per grm. of beef pancreas has been found to vary with the age of the animal. Foetal beef pancreas is relatively rich in this hormone. In cows of over 7 years of age pregnancy does not appear to affect the insulin-content of the pancreas. The amounts found varied from 33 international units per grm. for foetal calves under 5 months old, to 2 international units per grm. for cows of over 7 years old, the decrease being progressive with increasing age. S. G. S.

**Further Investigations on the New Vitamin B Growth-promoting Factor for Rats, found in Whole Wheat.** N. Halliday. (*J. Biol. Chem.*, 1934, **106**, 29-40.)—Bran is a fairly good, but wheat germ is the richest source of this new vitamin factor. It may be extracted with dilute acid or dilute alcohol, but not with ether. By the use of a method similar to that described by Peters and his colleagues (*Biochem. J.*, 1933, **27**, 225, and *Nature*, 1933, **131**, 617) it has been possible to prepare a crystalline concentrate. In many respects this is very similar to vitamin B<sub>4</sub>, but the differences are too great to warrant a definite conclusion. S. G. S.

**Effects of Ascorbic Acid (Vitamin C) on Toxins.** E. Harde. (*Compt. rend.*, 1934, **199**, 618-620.)—Mice, which are more resistant to certain infections than guinea-pigs, are capable of synthesising large amounts of ascorbic acid in their bodies. These animals thrive on diets which would be scorbutic to guinea-pigs. It is already known that ascorbic acid has the power of neutralising diphtheria toxin, both *in vitro* and *in vivo*, and this is associated with the disappearance of ascorbic acid now discovered in the cortex of the suprarenal glands, either of guinea-pigs which have died from diphtheria or of mice which have died from *B. typhi murium* infection. The silver nitrate method, described by Szent-Györgyi (*Biochem. J.*, 1933, **22**, 1387), was used for these experiments. It was also found that when guinea-pigs were given an injection of a toxin, followed by injections of ascorbic acid, although induration and sloughing may occur at the site of injection, yet the animals survived. It is suggested that ascorbic acid has marked protective powers, especially in infections and intoxications which give lesions in the cortex of the suprarenal glands and in the gastro-intestinal tract. S. G. S.

**Vitamin C Content of Human Tissues.** M. Yavorsky, P. Almaden and C. G. King. (*J. Biol. Chem.*, 1934, **106**, 525-529.)—Human tissues from hospital autopsies were examined for vitamin C within twenty-four hours of death. The determinations were carried out by titrating a trichloroacetic acid (8 to 10 per cent.)

extract of the tissue with 2, 6-dichlorophenolindophenol. The results corresponded with the figures obtained for guinea-pig tissues, and suggest that latent human scurvy is fairly common. Arranged in descending order of their vitamin C contents, the various tissues are:—adrenal glands, brains, pancreas, liver, spleen, kidney, lung, heart, muscle. Below the age of ten years, the thymus has a value as high as that for the pancreas. The average values ranged from 0.55 mgrm. per gm. for the adrenals to 0.04 mgrm. per gm. for the heart, but individuals varied as much as from three times down to one-tenth of the average value. S. G. S.

## Bacteriological

**Bacillus Tuberculosis in Butter.** J. W. Edington. (*Lancet*, 1934, ii, 81.)—Some of the technical difficulties met with in carrying out the biological test for the presence of *B. tuberculosis* in butter may be avoided by the following process: From 60 to 100 grms. of butter are melted at 40° C. in 150 ml. of distilled water in a beaker. This is then pumped twice through a cream-making machine into a centrifuge tube, and the solution is centrifuged at 3000 r.p.m. for 30 minutes. The cream is removed with the aid of a stout wire, the supernatant liquid is poured off, and the deposit is suspended in 5 ml. of saline solution. This solution is then inoculated subcutaneously in equal amounts in the antero-internal aspects of the right thigh of each of two guinea-pigs, the inguinal glands having been previously squeezed according to the method of Bloch (*Berl. klin. Woch.*, 1907, 44, 511). After one month the animals are killed and examined carefully for the presence of tuberculosis arising from the site of inoculation. The examination of 15 samples of Danish and 25 samples of New Zealand and Australian butters revealed the presence of *B. tuberculosis* in one sample of Danish origin. Since all these butters are usually believed to be made from pasteurised cream, the finding of a sample containing this organism is disconcerting. S. G. S.

**Orthophenylphenol as an Antiseptic.** H. C. Fuller. (*Ind. Eng. Chem.*, 1934, 26, 946.)—Orthophenylphenol and its derivatives have a high antiseptic value and are relatively non-toxic to animals. The compounds also have definite penetrating powers, and can be used, not only for their own effect, but also to bring about the penetration of other chemicals that ordinarily do not exert their effects beyond the surface of the skin. It has been found useful in this respect in salves, ointments and sprays for treating colds, rheumatic conditions and muscular aches, and also in throat tablets and gargles. In addition, it is well tolerated by children. The soluble sodium salt, dissolved in physiological salt solution, was used for intravenous injection in *Streptococcal* and *Staphylococcal* infections, and showed a definite curative effect without any injury to animal or human patients. S. G. S.

**Examination of Soils by Means of *Aspergillus Niger*.** A. M. Smith and A. Dryburgh. (*J. Soc. Chem. Ind.*, 1934, 53, 250–254t.)—Since the *Aspergillus* method for soil examination is cheap and speedy, the more important factors concerned in the laboratory technique have been examined. It was found that considerable latitude in the concentration of inoculum employed is allowable;

that ammonium nitrate or sulphate is better than citrate as a supply of nitrogen, and that the vessels used should not vary in diameter by more than a few mm., since area of growth is a much more important factor than actual amount of suspension. For the determination of "available potash," 2.5 grms. of soil are placed in a bottle of 130 ml. capacity, with diameter 5.5 cm.; and 30 ml. of nutrient solution are added [sucrose, 10; citric acid, 1; peptone, 0.1;  $P_2O_5$  (as ammonium dihydrogen phosphate), 0.075; ammonium nitrate, 0.36; magnesium sulphate, 0.03; copper, 0.00015; iron, 0.0001; and zinc (all as sulphates), 0.0001 per cent.] A few drops of conidia suspension are added, the mixture is incubated for 6 days at 35° C., the mycelium is removed with forceps, washed, dried overnight at 50 to 60° C., then for 2 hours at 60 to 100° C., finally for 2 hours at 100° to 105° C., and cooled and weighed. The same procedure is followed for "available phosphate," except that 5 grms. of soil are taken and the nutrient solution contains 0.02 per cent. of  $K_2O$  as potassium sulphate and no phosphate. In routine work the experiments are carried out in quadruplicate and 4 mycelia are weighed together, and the average weight is taken. The cultures are prepared on slopes of agar containing 1 per cent. of glucose, 0.1 per cent. of asparagine, and 0.05 per cent. of dipotassium hydrogen phosphate in tap water. A small quantity of conidia is taken from the slope with a moist wire-loop and shaken up with a few ml. of distilled water, and 3 drops of the suspension are used. In working with 7 soils and 3 strains of organism, strain was found to have a specific effect in the determination of potassium, and there was a distinct interaction between soil and strain. Since sufficient acid must be present in the soil-culture solution suspension to prevent growth of various soil micro-organisms, the initial reaction of a soil may have little influence on the final  $p_H$  value of suspension. Experiments were made with an infertile sandy loam treated with increasing amounts of calcium hydroxide in 1931, and on a normal clay loam, one sample of which had been treated with calcium hydroxide since 1930 to decrease acidity, and the other with sulphur to increase acidity. Seventy pots of soil were treated, and it is concluded that whatever effect excess of calcium carbonate in the soil may have on the fungus development, normal application of lime to correct soil acidity would not exert any practical influence. In comparing the Mitscherlich and *Aspergillus* methods for 40 soils, the correlation coefficient was 0.77 for the phosphate figures, but only 0.40 for the potassium figures. That the *Aspergillus* method is not so sensitive as the other common methods, such as those of Mitscherlich or Neubauer or extraction methods, may be partly due to the fact that the mycelium weight is not a direct measure of the nutrient uptake, since the composition of the mycelium varies irregularly, and its analysis is impracticable. There seems little doubt that the decisive factor in the growth of the organism is the nutrient content of the soil, and the behaviour of *Aspergillus* certainly seems to be sufficiently constant to enable the soils to be placed into 2 or 3 large groups according to their fertiliser requirements. The occurrence of border-line cases is common to any method of estimating soil fertility, but it will be necessary to examine a greater variety of soil types from suitable field experiments, in order to establish the reliability of the *Aspergillus* method.

D. G. H.

## Water Analysis

**Removal of Iron and Manganese from Water.** S. B. Applebaum and M. E. Bretschger. (*Ind. Eng. Chem.*, 1934, 26, 925-931.)—Iron and manganese in water supplies, in amounts greater than 0.3 to 0.5 p.p.m., may cause an unpleasant taste, unsightly stains and troublesome deposits, affecting both domestic and industrial use. In general, iron and manganese may be removed by two methods. The first is by oxidation to the higher oxides and hydroxides, which are insoluble and can be removed by filtration. The second method is by base exchange through zeolite without oxidation. The oxidation reactions are interfered with by a number of factors, such as the presence of free carbon dioxide, low total solids, low  $p_H$  value and organic matter. The various types of iron and manganese removal methods consist of (i) a simple form of aeration followed by filtration, (ii) more thorough aeration for removal of free carbon dioxide, followed by filtration, (iii) aeration, followed by basin settling and final filtration, (iv) aeration, liming, basin settling and filtration, (v) similar to (iv), but using special coagulants such as aluminium compounds, potassium permanganate, and chlorinated copperas, together with an adjustment of the  $p_H$  value, (vi) oxidation and filtration through manganese zeolite, (vii) filtration through sodium zeolite without oxidation. The authors suggest that, for any given water supply and set of engineering conditions, experimental studies should be made, both in the laboratory and in the field, in order to determine the optimum conditions of working.

S. G. S.

**Removal of Fluorides from Drinking Water.** R. H. McKee and W. S. Johnston. (*Ind. Eng. Chem.*, 1934, 26, 849-851.)—The presence of fluorine in drinking water to the extent of 5 to 17 parts per million is known to be the cause of mottled enamel on teeth. Adsorption by carbon removes fluorides from potable waters, but some carbons are much less efficient than others. The most satisfactory results are obtained with a carbon which is a residue discarded by the soda pulp industry, but, even with this, there is no removal of fluoride until the  $p_H$  value of the water has been reduced to about 3. Attempts to reduce the fluorine to less than 1 part per million have been unsuccessful.

W. P. S.

## Organic Analysis

**Analytical Uses of 2-Propanol.** G. W. Ferner and M. G. Mellon. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 345-348.)—Owing to the close similarity in physical properties, *iso*-propyl may be used instead of ethyl alcohol for many purposes in analytical chemistry, as, for instance, the following:—(i) As solvent for reagents like dimethylglyoxime, hydroxyquinoline; (ii) to reduce the solubility of a precipitate such as calcium sulphate (where this is permissible with ethanol); (iii) to effect separations, *e.g.* the separation of sodium chloride from magnesium chloride according to the method of Hillebrand and Lundell, "Applied Inorganic Analysis," or in the separation of calcium from barium by extraction of the nitrate with alcohol and ether; (iv) to wash precipitates in order to hasten drying, *e.g.* lead sulphate,



nickel glyoxime (a list of 16 precipitates is given). 2-Propanol may not be used in place of ethanol for the flame test for borates or for the acetate tests of the U.S. Pharmacopoeia. The turmeric test for boric acid is less sensitive when 2-propanol is used. For the preparation of concentrated alcoholic potash solution, anhydrous 2-propanol is necessary, as in presence of water the alcohol is "salted-out" to some extent.

S. G. C.

**Haloform Reaction. XIV. Improved Iodoform Test. R. C. Fuson and C. W. Tullock.** (*J. Amer. Chem. Soc.*, 1934, 56, 1638-1640.)—The following procedure, which is applicable to substances which are insoluble in water, is stated to be more reliable than that in present use. The sample (0.1 ml. of liquid or 0.1 grm. of solid) is dissolved in 5 ml. of dioxan in a test-tube (diameter 150 mm.), and 1 ml. of a 10 per cent. solution of sodium hydroxide is added, followed by sufficient of a solution containing 100 grms. of iodine and 200 grms. of potassium iodide in 800 ml. of water, to produce a definite dark colour (indicating an excess) which does not disappear after 5 minutes. The mixture is heated at 60° C. for less than 2 minutes, more reagent being added with shaking, to maintain the dark colour, and the excess of iodine is removed by addition of a few drops of the sodium hydroxide solution. The test-tube is then filled with water, and after 15 minutes the precipitated iodoform is separated by filtration, and, if red in colour (owing to the presence of carbon tetraiodide), it is suspended in 3 ml. of dioxan and 1 ml. of the sodium hydroxide solution is added. When the mixture has become lemon-yellow, it is again diluted and filtered, and the m.pt. of the iodoform (119° to 121° C.) is determined. Application of the test to 96 compounds (including alcohols, acids and their derivatives, aliphatic unsaturated and mixed ketones and diketones) indicated that it is positive for compounds which contain the grouping  $\text{CH}_3\text{CO}-$ ,  $\text{CH}_2\text{ICO}-$  or  $\text{CHI}_2\text{CO}-$ , joined to a hydrogen or carbon atom which is not linked to hydrogen atoms or to a group associated with powerful steric hindrance. It is also positive for compounds which decompose to give the above groupings, and negative in cases where these groupings are hydrolysed by the reagent before iodination. Benzoyl acetone and certain nitro- and amino-compounds show a premature appearance of a brown colour, and the true colour does not appear until the end of the reaction. The mechanism of the reaction is explained by the three-fold effect of the reagent, *viz.* oxidation of alcohols or amines, replacement of active hydrogen atoms, and cleavage of carbon chains (*cf.* Woodward and Fuson, *id.*, 1933, 55, 3472), and this explanation is discussed for individual cases.

J. G.

**Identification of Amines as 2, 4-Dinitrobenzoates. C. A. Buehler and J. D. Calfee.** (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 351-352.)—2, 4-Dinitrobenzoic acid combines with a wide variety of aromatic and aliphatic amines, and the salts formed may be readily purified for identification purposes. The 2, 4-dinitrobenzoates of some 38 common amines have been prepared, and the melting-points are tabulated in the paper together with the melting-points of the corresponding 3, 5-dinitrobenzoates. The method of preparation of 2, 4-dinitrobenzoic acid is also described.

S. G. C.

**Properties of Adipoïne, a Cyclic Sugar.** G. P. G. Moeys and N. Schoorl. (*Pharm. Weekblad*, 1934, 71, 1026-1029).—Adipoïne ( $\alpha$ -hydroxy-cyclohexanone) was prepared (*cf.* Kötze and Grethe, *J. prakt. Chem.*, 1906, 80, 487) by the chlorination of  $\alpha$ -cyclohexanone, and treatment of the resulting compound with potassium carbonate. The recrystallised adipoïne melted at 91° C. (*cf.* Bergmann and Giërth, *Ann.*, 1926, 448, 48), and was very volatile in steam; its solubility in water was 1:1750; in absolute alcohol, 1:400; and in ether, 1:1000. The evidence that it is a typical sugar is based on the analytical criteria of Milius and Schoorl (*Pharm. Weekblad*, 1916, 53, 1249), *viz.* (1) A cupric salt is reduced to cuprous oxide in the cold in the presence of sodium hydroxide solution (Trommer reaction). (2) Osazones were prepared (after Denigès) and the m.pts. after recrystallisation were determined (osazone from phenylhydrazine, 152 to 153° C.; *p*-bromophenyl-osazone, 183 to 185° C.; *p*-nitrophenyl-osazone, 236 to 237° C.). (iii) In Rose's reaction (*Z. anal. Chem.*, 1931, 87, 110), which is said to be specific for "open" sugars, a purple colour is produced on warming a solution of the sample with 2 *N* sodium carbonate solution and a drop of an alcoholic solution of *o*-dinitrobenzene, and this gave a positive result with a 1 : 2000 solution of adipoïne. (iv) The mean ratio of the rates of reduction of Luff's and Fehling's solutions was determined on 10 to 50 mgrms. of adipoïne, with 25 and 20 ml. of reagent, heated for 10 and 2 minutes, respectively; since 1.35 and 0.82 atoms of oxygen per molecule of adipoïne were involved, respectively, the ratio is 1.65 : 1, which is a normal value for sugars. Evidence of the *cyclo*-hydroxy-desmotropic change on reduction suggested by Bergmann and Giërth (*loc. cit.*) was also obtained. J. G.

**Studies on the Merino Fleece. II. Separation of Cholesterol and "Isocholesterol" of Wool Wax.** M. R. Freney. (*J. Soc. Chem. Ind.*, 1934, 53, 289-291t. *Cf.* ANALYST, 1934, 59, 500).—The Twsett method of chromatographic adsorption has been applied to the colourless sterols of wool wax. The adsorbing medium used was alumina in the form of a column, 2.5 cm. in diameter and 16 cm. long, and the 2.5 grms. of crude unsaponifiable matter of wool wax (obtained by ethereal saponification in the cold, and having m.pt. 45° C., and  $[\alpha]_D + 1^\circ$ ) was dissolved in 100 ml. of hot solvent (benzene 40, and petroleum spirit 60 per cent.), and drawn by suction slowly through this column, which was first wetted with solvent. The column was subsequently washed with 200 ml. of hot solvent, and the alumina was pushed out and divided into 5 lengths or fractions. Each of these was extracted with 150 ml. of boiling solvent (methyl alcohol 80, and benzene 20 per cent.), which was then decanted, filtered and evaporated to 10 to 20 ml. Any white crystals which separated overnight were filtered off and washed with methyl alcohol, and the filtrate was evaporated to dryness. The crystals were heated with acetic anhydride, and the acetates were crystallised and washed with methyl alcohol. A recovery of over 85 per cent. of the original material was made. Fractions 1 and 2 (from the top of the column) gave no crystals under the conditions described. Those obtained from fraction (3) differed only slightly from cholesteryl acetate, whilst fraction (5) yielded crystals approximating closely to those of *isocholesteryl* acetate, and these comprised the bulk of the fraction. Cholesterol and *isocholesterol* may therefore be separated with

comparative ease from wool wax. A sample of very crude *isocholesterol*, and also a purer sample were subjected to similar treatment, but a separation of *lanosterol* and *agnosterol* could not be effected. D. G. H.

**Determination of Strong Acid and of Buffer Salts in Vegetable-tanned Leather.** R. F. Innes. (*J. Inter. Soc. Leather Trades Chem.*, 1934, 18, 457-464.)—The basis of the present work is that of Richardson (*Proc. Roy. Soc.*, 1934, 115 [B], 170), who found that if acids are made up in 90 per cent. acetone solution, the ionisation of weak organic acids (of  $p_H$  3 or over) is almost completely suppressed; that of stronger organic acids of  $p_H$  less than 3 (*e.g.* citric, tartaric, oxalic) is almost suppressed, but that of "true strong acids" is not greatly affected. Thus hydrochloric acid in admixture with oxalic acid may be titrated alone by using a suitable indicator. With sulphuric acid it is not quite so simple, owing to its second ionisation in 90 per cent. acetone, giving a  $p_H$  value by titration of about 3.3. These facts may be applied to a determination of strong acids in the leather by placing a convenient weight of leather (say 10 grms.) in an 8-cm. filter funnel to the stem of which is fixed a piece of rubber tubing and clamp. A piece of broken porcelain at the bottom of the funnel prevents entry of fragments of leather into the tube. The leather is covered with water, which is left standing overnight, after which it is withdrawn through the tube and the process repeated several times, 20 minutes' contact being allowed each time. One hundred ml. of extract are collected, and, after mixing, 5 ml. are taken for titration after addition of 45 ml. of acetone. If the  $p_H$  value is less than 3.4, strong acid is present, and 0.02 *N* sodium hydroxide solution will give a measure of the acidity; a second extraction is then desirable. If the  $p_H$  is 3.4, a trace of strong acid is present, and if it is sulphuric acid, cannot exceed 0.004 *N* in the undiluted extract or 0.2 per cent. on the leather. If the  $p_H$  is over 3.4 and under 4.0, the equivalent of sulphuric acid present is less than 0.1 per cent. on the leather. If the initial  $p_H$  value is over 4.0, strong acid is absent, and titration with 0.02 *N* alcoholic hydrochloric acid will give a measure of the amount of buffer salt present. The method was successfully applied to Nigerian-dyed leather, English-dyed leather containing "protective agent," and sumach-tanned crust leather, all of which showed the presence of salts of organic acids, whilst English-dyed and mimosa crust leather had only a trace. It is suggested that a leather should be regarded as free from strong acid only when the  $p_H$  value of its aqueous extract in the proportion of 1 grm. per 10 ml. (when mixed with acetone to a concentration of 90 per cent. acetone) is 4.0 or over, and that no tolerance figure be allowed. D. G. H.

**Determination of Total Sulphur in Keratins.** J. Barritt. (*J. Soc. Chem. Ind.*, 1934, 53, 291-294 $\tau$ .)—*Wet Oxidation.*—The Mackay methods (*id.*, 1930, 49, 233, 401 $\tau$ ) were investigated, but it was found difficult to obtain reproducible results having the required degree of accuracy. Samples (0.8 grm.) were, therefore, hydrolysed for 2 to 4 hours with 20 ml. of 20 per cent. hydrochloric acid, and the Benedict-Denis method, as modified by Rimington (*id.*, 1930, 49, 139 $\tau$ ), was applied, the barium sulphate being dried in a small Gooch crucible at 140° C. Samples were also boiled under a reflux condenser for 1 to 2 hours with 20 ml. of concentrated nitric acid, the solution being then diluted to 50 ml. and

20 ml. taken for the determination. In both cases the variations from the means were of the same order, but the latter method (and also the Carius method) gave slightly higher results (by about 0.13 per cent.), indicating a loss of volatile sulphur (e.g. as hydrogen sulphide) on boiling with hydrochloric acid (*cf. infra*). *Dry Oxidation*.—A bomb designed for the determination of sulphur in coal (*cf. Farrar and King, J. Text. Inst., 1926, 17, 588r*) has been modified for the present purpose, and consists of a mild steel cartridge (8 × 2.3 cm.) 2 to 3 mm. thick, which fits into an outer steel case. Samples (less than 0.5 gm.) are mixed with sodium peroxide with steel forceps, and are filled into the cartridge so that the layers of mixture are between layers of peroxide, the lid being clamped on when the bomb is three-fourths full. The bomb is then heated in an inclined position for 10 minutes, after which it is cooled, and the contents are leached out and made just acid with hydrochloric acid. Iron is removed with ammonia, and the sulphates in the filtrate are precipitated. The results are in close agreement with the nitric acid method (*i.e.* 3.73 per cent. of sulphur on the dry weight). In all cases the wool is first pulled out, degreased with benzene at 60° C., dried, washed in 6 changes of distilled water, air-dried, and finally conditioned for several days. The experiment of Hoffman and Gortner (*J. Amer. Chem. Soc., 1922, 44, 341*) on the hydrolysis of cystine by 20 per cent. hydrochloric acid was repeated, the gases being carried over into a solution of cadmium acetate. The results indicate that a very small amount of volatile sulphur compounds is obtained, although small quantities of hydrogen sulphide were detectable when wool was added, and this could not be fixed by the further addition of salts which form insoluble sulphides. Since similar results are obtained on the hydrolysis of casein, which is rich in methionine, the only sulphur-containing compound other than cystine so far isolated from wool (about 0.5 per cent. present), the low results obtained by the hydrochloric acid method (*supra*) remain unexplained. J. G.

## Inorganic Analysis

### Detection and Determination of small Quantities of Bromine.

**J. Frezouls.** (*Ann. Falsificat., 1934, 27, 351–357.*)—The proposed method is a modification of that of Denigès and Chelle, *i.e.* liberation of the element by means of chromic acid in presence of fuchsin-sulphuric acid reagent (*Ann. Chim. anal., 1913, 11; 1918, 81; J. Soc. Chem. Ind., 1913, 32, 141; 1918, 37, 284A*). The oxidiser recommended by the author is a solution of 1 gm. of ammonium persulphate in 10 ml. of cold strong sulphuric acid. The solution keeps for about a fortnight if stored in the dark. Ten ml. of the solution to be tested (maximum bromine-content, 0.01 gm.) are treated with a drop of hydrochloric acid if free from chloride, 2 ml. of fuchsin reagent, 3 drops of oxidiser, and 1 ml. of chloroform, and the tube is shaken repeatedly; the chloroform layer becomes reddish-violet. The fuchsin reagent should be quite colourless, which is brought about by agitation with infusorial earth (treated with dilute sulphuric acid, washed, and dried) and filtration. The reaction may be used for the colorimetric determination of bromine; with the above quantities the sensitiveness is 0.005 mgrm. W. R. S.

**New Colour Reaction of Ammonia.** L. Lapin and W. Hein. (*Z. anal. Chem.*, 1934, 98, 236-240.)—The reaction is based on the appearance of a blue colour when a solution containing ammonium salt is shaken with hypobromite and thymol. The reagents are: a 25 per cent. solution of thymol in alcohol, and sodium hypobromite freshly prepared from 1 volume of 2 *N* sodium hydroxide solution, and 2 volumes of saturated bromine water. The liquid to be tested (5 ml.) is first mixed in a wide test-tube with 1 ml. of thymol solution, then with 12 to 15 ml. of hypobromite solution, and, after one to two minutes, with 5 ml. of ether or xylene. The liquid is cautiously mixed by inverting the tube several times, when the coloured compound dissolves in the solvent. The sensitiveness is 0.01 mgrm. of ammonia per 100 ml., *i.e.* one-fifth of that of Nessler's reaction. The only interfering metals are lead and platinum, which cause a brownish tint in the ethereal layer; the interference of lead is counteracted by addition of sulphate. Sulphide ion requires an excess of hypobromite. Hydroxylamine and hydrazine salts, as well as hydrogen peroxide, weaken the intensity of the colour. Organic compounds do not interfere, with the exception of aniline, which imparts a yellowish-pink tint to the ether.

W. R. S.

**Colorimetric Standards for Silica.** H. W. Swank and M. G. Mellon. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 348-350.)—In various methods in which the yellow silicomolybdic acid is determined colorimetrically, permanent colour standards of picric acid (King and Lucas, *J. Amer. Chem. Soc.*, 1928, 50, 2395) or potassium chromate (Amer. Public Health Assoc., "Standard Methods of Water Analysis," 1933, p. 66) have been adopted. As a result of a study of the comparison of the coloured silicomolybdic acid solution with these standards with the aid of visual and photo-electric colorimeters, Nessler tubes, and a spectrophotometer, it was concluded that these permanent colour standards do not reproduce the colour of the silica solution sufficiently satisfactorily. It was found, however, that a solution of potassium chromate when suitably buffered, as with borax, gave a very good reproduction of the silica colour. The following table gives the concentration of buffered potassium chromate and silica for equivalent colour:

Potassium chromate <sup>1</sup> ml.	Silica <sup>2</sup> p.p.m.	Potassium chromate ml.	Silica p.p.m.
0.0	0	8.0	16
1.0	2	9.0	18
2.0	4	10.0	20
3.0	6	11.0	22
4.0	8	12.0	24
5.0	10	13.0	26
6.0	12	14.0	28
7.0	14	15.0	30

<sup>1</sup> 0.63 gm. of potassium chromate per litre; the volumes specified are to be diluted with 25 ml. of a 1 per cent. solution of borax and enough water to make a total of 55 ml.

<sup>2</sup> 50 ml. of sample solution, together with 5 ml. of reagent, as recommended in the A.P.H.A. method (see reference above).

S. G. C.

**Testing China Clay.** J. Grant. (*Sands, Clays and Minerals*, 1934, 2, 49–51.)—These tests have special reference to the paper and kindred industries. The moisture is determined by heating at 105° C. until the weight is constant, and should be about 10 per cent.; a figure below 7 per cent. indicates over-drying, and is frequently accompanied by a poor colour, dirt, and a high rate of settlement from suspension. Colour is assessed by comparison with a standard of a paste with water, glycerin or oil, and also after drying the paste with water; this is conveniently carried out on a white tile with wedge-shaped depressions, but the possibilities of photo-electric methods for obtaining numerical values of colour are also discussed. Foreign tinting colouring-matters can usually be detected by one of the following tests:—(i) Particles of the clay are blown on to the surface of distilled water, clear lime water and 10 per cent. hydrochloric acid, a trail of colour then being produced in one or other of the reagents behind each particle as it sinks. (ii) Since ultramarine is decolorised by acids and Prussian blue by alkalis, pastes made with the appropriate reagents will differ in shade from those made with water. (iii) A thick paste (about 25 ml.) of clay and ammonia is dried on the water-bath in a 100-ml. beaker, and any added colour then concentrates in a narrow ring on the wall of the beaker just above the surface of the clay, and may even be removed for examination; the faint brown ring frequently obtained with unadulterated clays is due to traces of organic matter, and should be neglected. (iv) China clay normally appears blue-violet in filtered ultra-violet light, but the presence of minute quantities of many tinting colours is sufficient to modify this considerably (*cf. id.*, 1933, 1, 7); examples are cited. Other loadings may also be distinguished from clay in this way. Grit is determined by washing the clay through an appropriate sieve (*e.g.* 200-mesh), and weighing the dried residue. Iron is determined by the thiocyanate reaction on an extract of the clay in boiling 10 per cent. hydrochloric acid. A test with a drop of acid under the microscope is used for calcium carbonate, and the barium chloride test for calcium sulphate should also be applied. Since plasticity and the rate of settlement are affected by the presence of traces of vegetable colloidal matter adsorbed on the clay during the washing operations, and by  $p_H$  value, weighed samples should first be boiled with water to expel air, and the cooled suspension dispersed in 0.001 *N* sodium hydroxide solution. A quantity of the suspension, equivalent to 10 grms. of clay, is then diluted to 100 ml. and shaken well in a cylinder, the volume of clear liquid formed during settlement being noted after various intervals of time; if desired, a curve may be plotted. Observations of the rate of disintegration of a lump of clay in water without external aid are also useful. J. G.

## Microchemical

**Microchemical Tests. XI. L. Rosenthaler.** (*Mikrochem.*, 1933–34, 14, 363–369.)—1. *Silico-fluorides of Alkaloids.*—When solutions of the following alkaloid salts are treated with solid ammonium silico-fluoride, crystals are formed. *Quinine*: Needles. *Diocaine*: Small needles, often grouped into stars. *Codeine*: Branched groups of needles and three-cornered plates (photo-micrograph). *Pantocaine*: At first feathery crystals and rods, then tablets, mainly with irregular

outlines (photo-micrograph). *Psicaine*: Flat tablets, six-sided or star-shaped. *Stovaine*: Characteristic narrow crystals, six-sided above and joined to tablets or prisms (photo-micrograph). *Strychnine*: Rods, mainly grouped together. The reaction with pantocaine may be used as a test for silicofluorides. When solid pantocaine is used the reaction proceeds in dilutions up to 1 : 1000, and is as sensitive as the reaction with sodium chloride, although less sensitive than that with barium acetate. As tests for alkaloids, the reaction with silicofluorides is useful with the local anesthetic compounds, most of which give no precipitation.

2. *Crystal Precipitation of Veramon*.—Veramon is a mixture of 1 molecule of pyrimidon and 1 molecule of the compound (pyrimidon + diethyl barbituric acid). Therefore reagents were tested that gave reactions with barbituric acid; of these, the Zwikker copper-pyridine reaction, and the reaction with ammonium phosphate, are positive. The reactions with lead acetate, thallium acetate, iodine and bromine are negative. With bromine only the long fine needles are formed that are obtained from pyrimidon alone.

3. *Crystal Precipitation of p-Chlorobenzoic Acid*.—This compound is often used as a preservative. Suitable reagents are silver nitrate, mercuric acetate, uranium nitrate and aluminium nitrate, used in the solid form. The *p*-chlorobenzoic acid is best used as a solution of its calcium salt, when the use of sulphate or sulphuric acid (which would form calcium sulphate crystals) is to be avoided. *Silver nitrate*: Rods, and many-sided crystals and some small plate with irregular edges (photo-micrograph). Limit concentration:\* 1 : 2500. *Mercuric acetate*: Bushes and star-like groups of needle-shaped crystals. Limit concentration: 1 : 2500. *Uranium nitrate*: From a 1 : 100 solution small spherical crystals are formed, and from dilute solutions (1 : 500) rods and needles, mainly in groups. Limit concentration: 1 : 2500. *Aluminium nitrate*: Groups of small needles. Limit concentration: 1 : 50,000. The 1 : 100 solutions, with the nitrates of cerium and lanthanum, give precipitates rapidly becoming crystalline. The free acid is precipitated from the sodium and calcium salts, with hydrochloric acid; for the *p*-acid the limit concentration is 1 : 2500. The appearance of the free acid is indistinguishable from that of the crystals formed with mercuric acetate, uranium nitrate and aluminium nitrate, therefore, in these cases it is probable that the free acid is also formed by hydrolysis. Free *p*-chlorobenzoic acid may also be obtained from the test substance by micro-sublimation. The small crystals obtained may be recrystallised from hot water.

4. *Reactions of Phenols in Sodium Carbonate Solution*.—Phenols alone give no precipitate with iodine in potassium iodide, but give crystalline precipitates in the presence of sodium carbonate. For the following reactions a mixture of one part of concentrated iodine solution (iodine 0.5, potassium iodide 2, water 2) and two parts of saturated sodium carbonate solution is used. With this solution most phenols give brown amorphous precipitates and a few of them crystalline precipitates. *Phenol*: Groups of needles at once, with long divided needles at the edges. *p-Chlorophenol*: Needles, mainly in groups, formed at once, some amorphous

\* As *Limit concentration* and *Limit of Identification* have been used in the translation of Emich's "*Laboratory Manual*," these terms will be used in future in place of *Limit of dilution* and *Smallest amount recognisable*.—ABSTRACTOR.

particles. *β-Naphthol*: Interspersed among brown amorphous particles, some long colourless needles. *Hydroquinone*: Quinhydrone crystals, and, later, darker amorphous particles. The phenolic acids behave similarly to the phenols; thus salicylic acid also slowly gives groups of needles interspersed among brown amorphous grains.

5. *Crystal Precipitation of Phenolic Acids with p-nitroso-dimethylaniline*.—Salicylic acid, *p*-hydroxybenzoic acid, gallic acid, the three salicylic acids (*o*-, *m*-, and *p*-cresolinic acid) and  $\alpha$ -hydroxynaphthoic acid, give crystalline precipitates with *p*-nitroso-dimethylaniline solution (0.1 grm. reagent in 5 ml. of water, 0.1 grm. sodium acetate, and filtered). The crystals formed are similar in each case, usually rods or prisms, and can be distinguished only by cryoscopic measurement. Only hydroxybenzoic acid is different, as it gives four-cornered plates.

6. *Crystal Precipitation of Iso-propyl-antipyrine*.—*Iso-propyl-antipyrine* is a crystalline powder, melting at 99° C., and is a constituent of the tablets "Saridol." The following are the reactions of the solution in dilute hydrochloric acid with the following reagents:—*Potassium dichromate*: Needles, rods, some forming rosettes (photo-micrograph). *Sodium perchlorate*: Similar crystals, some platelets. *Reinecke's salt* (solution): At first amorphous, then groups of five two-branched needles. [*Tetra-nitro-diamine-cobalti*] *potassium*: Branched bushes of bent thread-like crystals (photo-micrograph). *Potassium iodide*: Rods and many-sided irregular plates. The reaction with stannous chloride and potassium iodide is described below (7). The reaction with Reinecke's salt is the most sensitive; the limit concentration is 1 : 4000.

7. *Crystal Precipitation of Tin with Iso-propyl-antipyrine*.—A solution of the reagent in dilute hydrochloric acid on adding to a drop of stannous chloride solution rapidly gives, on stirring, colourless crystals, double pyramids, seed-shaped, and star-shaped. Bismuth and antimony do not react. The reaction is not very sensitive, as at dilutions of tin less than 1 per cent. it does not occur. The reaction can be made more sensitive (to 1 : 500) if potassium iodide is added. Dark orange rosettes of crystals are formed in an orange-violet solution. Bismuth and antimony interfere, although alone they give only amorphous precipitates with the reagent.

8. *Differentiation of Barium from Calcium and Strontium*.—When a solution of a barium salt is treated with a 5 per cent. solution of sodium 6-chloro-5-nitro-toluene sulphonate little grains are first formed, and finally long radiating needles (photo-micrograph). Calcium and strontium do not react, even in 10 per cent. solutions, but interfere when present in large amounts; a solution containing 1 per cent. of the three metals gives the barium reaction. Limit concentration (for barium alone) 1 : 2000.

9. *Crystal Precipitation of Cobalt*.—When a 1 per cent. solution of cobalt chloride is treated with a grain of potassium chromate, a brown amorphous precipitate is formed. If, however, salts of aluminium, manganese or tin are present, brown crystals are formed; the reaction is not very sensitive.

10. *A Sensitive Colour Reaction for the Alkaline Earths*.—When 1 ml. of a 1 : 10,000 solution of a salt of calcium, barium or strontium is treated with 1 ml.



of a tannin solution (1 : 1000) and two drops of *N*/10 alkali, a greenish colour is formed, and a blue-green colour or precipitate in concentrated solutions. A blank test should be made.

J. W. M.

**Micro-determination of Fluorine in Organic Substances.** D. M. Hubbard and A. L. Henne. (*J. Amer. Chem. Soc.*, 1934, **56**, 1078–1080.)—The method consists in decomposing the organic molecule over silica heated to 900° C. in a combustion tube. The silicon tetrafluoride formed is collected in water or in a weak alkaline solution, and the fluorine ion is titrated by means of cerous nitrate. It is essential to sweep out the combustion tube with hydrogen to remove adsorbed silicon fluoride and to reduce silicon oxyfluoride. Gases containing both fluorine and chlorine were analysed, as the chlorine can be determined in the same sample. *Detail.*—About 10 ml. of the sample are measured accurately in a mercury gas-burette, and the volume is increased to 100 ml. by admitting 90 ml. of air or oxygen. The mixture is then forced slowly through the combustion tube, which consists of a 30-cm. silica tube packed with crushed silica graded to 20–40 mesh, and held in place with glass wool. Moist strips of cloth dipping into water are used to keep the ends cool. The middle portion of the combustion tube is heated by means of an electric furnace consisting of a silica-tube, 17.5 cm. long and 15.5 mm. internal, and 22 mm. external diameter, wound round with 7.2 m. of No. 30 nichrome wire over 15 cm. of its length. The whole is wrapped in insulated packing and a rheostat is used to allow of adjustment of temperature. A second 100 ml. of air or oxygen is forced slowly through the burette, followed by 100 ml. of nitrogen, 200 ml. of hydrogen and finally 100 ml. of nitrogen. By this time the fluorine is all carried into the absorption tube as silicon tetrafluoride, and the chlorine as chlorine. The absorption tube consists of a U-tube, 12 mm. in diameter, constricted several times to make 9 successive bulbs, with a horizontal tube connected with the combustion tube by means of a small piece of rubber tubing. The absorption tube contains 10 ml. of 0.1 per cent. sodium hydroxide solution and 1 ml. of superoxol, to hydrolyse the silicon tetrafluoride and to reduce the chlorine to hydrogen chloride. The chlorine is titrated by the usual Volhard method, and the fluorine is titrated by a modification of Batchelder's method (Batchelder and Meloche, *J. Amer. Chem. Soc.*, 1931, **53**, 2131). The contents of the tube are washed with 150 ml. of water into a 250-ml. beaker, 1 ml. of superoxol is added, and the mixture is boiled to remove excess of hydrogen peroxide. The silica is filtered off, and the filtrate is diluted to 250 ml. A 25-ml. portion is neutralised with *N* nitric acid, and finally with 0.02 *N* nitric acid, with phenol red as indicator. After each addition of acid the solution is heated to remove carbon dioxide, and, when neutral, it is evaporated to 5 ml. (not more), and 2 drops of methyl red and 10 drops of bromocresol green indicator solution are added. A green colour develops. The mixture is titrated at 80° C., with frequent shaking, against a solution of cerium nitrate hexahydrate (7.6206 grms. in 2 litres; 1 ml. ≡ 5 mgrms. of fluorine), using a micro-burette. The end-point is taken at the maximum strength of purplish-red colour, viewed preferably by transmitted light. Very accurate results were obtained, the differences from the calculated being less than 1 per cent. The accuracy with which the sample can be measured is shown to be the limiting factor in the accuracy of the results.

J. W. M.

**Micro-method for the Determination of Free and Combined Cholesterol.** R. Schoenheimer and W. P. Sperry. (*J. Biol. Chem.*, 1934, **106**, 745-760.)—The method consists in the precipitation of cholesterol with digitonin, followed by the application of a colour reaction to the precipitate, and it is claimed that 0.02 to 0.15 mgrm. of cholesterol may be determined in 0.2 ml. of blood or serum at the rate of sixteen to eighteen analyses per day. Approximately 3 ml. of a mixture of acetone and absolute alcohol (1 : 1) are placed in a 5-ml. volumetric flask and heated to boiling on a steam-bath; 0.2 ml. of serum or blood is added slowly to the hot solution from a capillary pipette with shaking. The stopper is inserted, and the flask is then shaken vigorously to break up any clumps of protein which may have formed. The stopper is removed and washed, and the contents of the flask are again heated to boiling. The flask is cooled to room temperature, and the contents are made up to volume with acetone and alcohol, mixed thoroughly, and filtered through a small dry filter; the filtrate should be clear. For the precipitation of free cholesterol, 2 ml. of the filtrate are pipetted into an ordinary 15-ml. conical centrifuge tube, 1 ml. of digitonin solution is added, and the solution is stirred thoroughly with a stirring rod, which is left in the tube. The tube is placed in a preserving jar (pint or quart size), the cover is placed on tightly, and the jar is left overnight at room temperature. After standing, the tube is removed to a test-tube rack, and the solution is stirred gently to free particles of precipitate which may adhere to the walls of the tube; the stirring rod is removed carefully without touching the upper part of the tube, and laid on a rack so that no adherent precipitate is rubbed off; the tube is then centrifuged at about 2500 r.p.m. for 15 minutes. The supernatant solution is drawn off slowly with a fine capillary pipette to which suction is cautiously applied with a pump. Care is taken not to touch the wall of the centrifuge tube with the pipette or to stir up the precipitate. A few particles, which are probably cholesterol ester, usually float at or near the surface and are drawn off with the solution. The stirring rod is placed in the tube, and the tube and rod are washed with 1.5 to 2.0 ml. of acetone-ether (1 : 2) from a dropping pipette. After stirring, the rod is removed as before, the tube is centrifuged for five minutes, and the supernatant solution is again removed. The precipitate is then washed twice more in this manner with ether alone. After the last washing the rod is placed in the tube, which is dried by immersion in a water-bath at 40° C. The dried precipitate of cholesterol digitonide is now dissolved in 1 ml. of glacial acetic acid, care being taken that all particles adhering to the sides of the tube are dissolved. Warming to 60° C. may hasten this solution. The tube is then placed in a water-bath at 25° C. in the dark and left for a few moments. It is then removed, and 2 ml. of acetic anhydride are added, followed by 0.1 ml. of concentrated sulphuric acid, preferably from an automatic micro-burette. The solution is now stirred vigorously (the rod still in the tube), and the tube is replaced in the water-bath in the dark. At any time between 27 and 37 minutes after addition of the sulphuric acid the colour can be determined, and other tubes may be similarly treated in the meantime. The colour may be determined in a Pulfrich photometer or a colorimeter, using a solution of anhydrous cholesterol in acetic acid as a standard. The total amount of cholesterol may be determined by pipetting 1 ml. of the acetone-alcohol

extract, into a centrifuge tube, adding to it one drop of potassium hydroxide solution (10 grm. of pure KOH in 20 ml. of water), and stirring with a stirring rod, which is left in the tube. The tube is then placed in a preserving jar containing a layer of sand about 3 cm. deep, which has been heated to about 40° C. The cover is clamped on tightly, and the jar is kept at 37–40° C. for half an hour. After hydrolysis the tube is cooled, 1 ml. of acetone-alcohol solution is added, and the solution is titrated with 5 per cent. hydrochloric acid, phenolphthalein being used as an indicator. The solution is stirred after the addition of each drop, and care is taken to insure that a definite excess of acid is present; 1 ml. of digitonin solution is added, the solution is stirred thoroughly, the tube centrifuged for 5 minutes, and washed as in the determination of free cholesterol, except that only one washing with ether is necessary. The colour reaction is then carried out as previously described. The ether used in this work was purified by washing with sodium sulphite, then several times with water, and finally distilling over calcium chloride. The digitonin solution was prepared by dissolving 1 grm. of digitonin in 1000 ml. of water, and the solution was kept in ice for at least twenty-four hours. The supernatant solution was filtered and concentrated to 500 ml. by immersing the containing flask (preferably having inlet and outlet tubes) in boiling water, and drawing air through the space above the liquid. The original paper is supplemented by numerous footnotes commenting on the process. S. G. S.

**Microchemistry of Atophan.** M. Wagenaar. (*Pharm. Weekblad*, 1934, 71, 1100–1103.)—Atophan (phenyl cinchoninic acid) is insoluble in water, but soluble in alcohol, ether or solutions of alkalis. It is best prepared for the under-mentioned tests by sublimation (at approximately 200° C.), but this requires care, as some carbon dioxide may be liberated, and it is not quantitative for amounts of less than 1 mgrm. According to van Zijp (*id.*, 1930, 67, 192) hydriodic acid containing a little iodine produces brown droplets which deposit brown needles; if a solution of iodine in potassium iodide solution is present, these appear as dark blue or black star-shaped aggregates. Denigès (*Mikrochemie*, 1931–1932, 10, 430) evaporated a solution of atophan in ammonia, and noted the formation of star-shaped aggregates of negative double-refracting crystals at the edges of the drop; addition of sulphuric acid to this solution gave a heavier precipitate containing numerous globular aggregates. The present author, however, obtained better results with hydrochloric acid or ammonium chloride (sensitiveness 0.05 mgrm., 1 : 200), or with nitric acid or ammonium nitrate (0.1 mgrm.); other ammonium salts also gave good results, but precipitation of solutions of atophan in sodium hydroxide solution with sodium chloride or sodium sulphate was less successful. If a crystal of atophan is suspended in a solution of iodine in potassium iodide solution and a drop of dilute sulphuric, selenic or phosphoric acid is added, a precipitate results which is soluble on addition of acetone; on evaporation the resulting solution deposits red-brown or grey dichroic plates (sensitiveness 0.05 mgrm., 1 : 200). Similar, but less sensitive, results are obtained with organic acids, or by adding an excess of glacial acetic acid and a drop of acetone to a solution of the crystal in ammonia. A mixture of a crystal of atophan, chloral hydrate, the iodine-iodide reagent and a drop of dilute hydrochloric acid deposits

matted masses of blue crystals, the colour of which is removed by sodium thiosulphate solution (*cf.* narceine and coumarin) and varies in shade according to the concentration of the acid. A crystalline bromine-addition product is formed, usually as yellow crystals, by suspending a crystal of the sample in bromine water (sensitiveness 0.1 mgrm.). Photo-micrographs of some of the crystals are given.

J. G.

## Physical Methods, Apparatus, etc.

**The "Brittle-Point" of Bituminous Road Materials.** W. E. Golding and F. M. Potter. (*Chem. and Ind.*, 1934, 53, 628-629.)—An examination has been made of the Fraass Test (*Asphalt und Teer*, 1930, 13, 367, *World Petroleum Congress*, 1933), which is a method for the determination of the temperature at which plastic binders, *e.g.* asphalt, employed in road construction, pass from the plastic to the brittle state. An apparatus is employed in which a thin steel strip, previously coated on one side with a layer of binder of standard thickness, may be bent while it is kept inside a glass tube supported in a transparent vacuum flask which contains the cooling medium. The authors prefer to use a mixture of carbon dioxide snow and ether as giving the best control of the rate of cooling. The rate of fall of temperature is adjusted to not more than one degree per minute, and the test-strip is bent at each degree fall in temperature, commencing at about 10° above the expected brittle-point. The break is observed by illuminating the strip. The standard quantity of binder for each test is 0.4 ml., and may be weighed on to a steel strip or delivered from a small press. The mould of the press is cylindrical (20 mm. in diameter by 20 mm. high), and in the bottom is a slit 20 mm. long by 0.5 mm. wide, through which is extruded a strip of standard dimensions. The binder is applied to the steel strip (40 mm. by 20 mm. by 0.15 mm.), and the projecting ends removed. The steel strip with the layer of binder is carefully heated on a horizontal steel plate until air and moisture have been removed. The final removal of minute air bubbles from the surface is accomplished by the careful passage of a pinhead gas flame over the surface of the binder. When cool, the test-piece is placed in the clip of the bending apparatus. Results obtained by this process, while probably sufficiently good for ordinary work, were somewhat variable, owing to factors which could not be sufficiently well controlled, *viz.* variations in the thickness of the asphalt layer and slight differences in the individual heating of each strip, which affected the degree of adhesion of the material to the steel. It was found better to weigh out 0.4 ml. of the material on to each steel strip, and to allow the binder to spread itself over the strip by standardised heat treatment. Heating in a hot-air oven at 105° to 110° C. for 20 minutes was satisfactory for a binder of the consistency of standard paving asphalt, but, for a softer material, a lower temperature and a shorter period of heating would probably suffice. With samples of residual bitumen, the break at the brittle-point consisted of a single fracture across the strip, with the broken ends standing away from the bent steel support. Coal-tar products adhered more strongly to the steel, and at the brittle-point the material remained adherent and merely showed cracks.

S. G. C.

**Spectroscopic Determination of Fluorine in Water.** A. W. Petrey. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 343-345.)—The method is based on the appearance of the calcium fluoride band spectrum (in which the band with head at  $\lambda 5291$  is the most sensitive part) in the spark or arc spectrum of the mineral residue of the water, and it is suitable for waters containing about 0.025 to 1.5 per cent. of fluorine in the residue. About 12.5 mgrms. of residue, obtained by evaporation of the water, observing the usual precautions, and ignited at about  $500^{\circ}\text{C}$ ., are tightly pressed into the cavity of a graphite anode which has been impregnated with calcium chloride; a copper cathode is used. The residue is completely volatilised by arcing, the spectrum being photographed meanwhile. The spectrum is compared with standard spectra after optical projection on an aluminium screen. The standards are prepared by adding sodium fluoride solution to a suspension of calcium carbonate, evaporating off the water, and thoroughly pulverising the residue; a range of 7 standards containing 0.025 to 1.5 per cent. of fluorine should be prepared, and the spectra photographed. In testing waters containing a considerable amount of salts, a similar quantity of these should be introduced into the carbonate-fluoride standards. Alternative to the photographic method, a visual method may be used in which the time required for the disappearance of the calcium fluoride spectrum is noted; the amount of fluoride present may be read from a curve obtained by plotting the concentration of fluoride with the time for disappearance of the spectrum in a series of standards prepared as for the photographic method. The visual method is limited to residues consisting essentially of calcium and magnesium salts. S. G. C.

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## Reviews

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. Supplement Vol. I, A-M. By J. F. THORPE, D.Sc., F.R.S., and M. A. WHITELEY, D.Sc., and eminent contributors. Pp. 680. London: Longmans, Green & Co. 1934. Price 60s.

Seven years have passed since the last volume of "Thorpe" was published—13 years since the first volume of the edition—during which time very great advances have been made in technical chemistry. We are told, and verily believe, that the best method of bringing the Dictionary up to date was the subject of earnest discussion between Editors and Publishers. This volume is part of the result. Two supplementary volumes are being issued dealing with sections in which the greatest advances have been made, and the contributors give concise accounts of the present state of knowledge in their sections. Much new knowledge and many new subjects are also included.

It is impossible adequately to comment on all the matter in the volume before us; suffice to say that it follows the style and maintains the excellent standard to which we have become accustomed in Thorpe's Dictionary. Whatever a chemist's special branch, his bookshelf is not complete without "Thorpe," and now will not be complete without the supplement. One method open to a reviewer of such a volume is to dip into it somewhat as one does into a bran tub; another, perhaps

better is to take the volume into use and refer to it on all the problems that arise in the analyst's laboratory in the course of a month or so. The reviewer has applied both methods and is well satisfied with the results. All the articles tested are good; some are excellent.

Perhaps the first section to mention is "Analysis"—30 pages—from the able and versatile pen of Professor Morgan; all the new organic substances recently introduced for the determination of various metals are described in sufficient detail, also new volumetric and gravimetric processes for rare, as well as common, elements and radicles. Carbohydrates occupy about 20 pages, largely indicating the new views on structure, but new sugars and uronic acids are all included. Carbon tetrachloride, decolorising carbons and other subjects receive the detailed treatment concordant with their increased industrial importance. There is a long section on the new dyes, including those for artificial silks and union fabrics. Co-ordination compounds, chemical warfare, corrosion, enzymes, explosion, explosives . . . the list is almost endless, glue, glycerine, iron and steel, hafnium, ketenes, milk. One lingers on milk with some disappointment, as the opportunity has been missed of an authoritative survey of such matters as spray- and roller-dried milk, condensed milk, tinned cream, and of the controversy between the advocates of pasteurisation and non-pasteurisation. A critical outline of recent work on the freezing-point would have been welcomed. It appears that our knowledge of the real constitution of milk has hardly advanced at all.

Perhaps the aspect which most deserves commendation is the skill with which editors and authors have selected their subjects and balanced theoretical matter with industrial practice. The distinction between "pure" and "applied" chemistry is rapidly vanishing, as no new chemical industry can flourish without sure theoretical foundation; the theoretical knowledge of to-day is the industrial practice to-morrow. So our Editors have seen to it that the theory underlying almost every technical product with which they deal is adequately described. The publication of this supplement will further secure for "Thorpe" the unique place it has long held in English chemical literature. It is the first place to turn to on an unknown problem; the details required may not be found, but usually there will be general information and references showing where further knowledge is to be obtained. It is one of the most nearly "indispensable" books we have.

H. E. COX

GERMAN-ENGLISH CHEMICAL TERMINOLOGY. By A. KING and H. FROMHERZ.  
Pp. xvii + 324. London: T. Murby. 1934. Price 12s. 6d. bound.

As stated on the folder, "the object of this book is primarily to aid English-speaking and German students, scientists and other people interested in chemistry and its allied subjects, to acquire a knowledge of the chief terms used in the chemical literature of the language foreign to them," and, it might be added, to acquire a knowledge of the language in general and the structure of sentences. The chemical terms are introduced by writing a text-book of chemistry in English and German printed on opposite pages so that each paragraph is directly opposite to its literal translation. When a term is introduced for the first time it is printed in italics, and the book contains over 4000 expressions.

The subject-matter is divided into elementary, inorganic, organic and physical chemistry, with a chapter on modern theories of the structure of matter, and appendices consisting of a table of atomic weights, mathematical expressions, and a useful list of both English and German abbreviations. There is a competent index in both languages.

The range of terms included is extremely large; for example, the section on laboratory equipment and apparatus covers terms used in glass-blowing and soldering as well as names of general apparatus, including equivalents such as "carboy of acid," "Säure ballons," among the less-known terms which can be very useful to a student working in a foreign laboratory.

This method of learning German is vastly superior to ordinary translation with a dictionary, since not only is the correct translation given, but the term is also described in its context. The text has obviously been very carefully written by both authors, so that a literal translation is possible, and the subject-matter is well graduated, so that the later chapters are more difficult both in language and in chemistry.

As a means of studying German the book is to be recommended both to preliminary and advanced students. Those who consider themselves familiar with the German language will be surprised to find the large number of useful expressions that are new to them. The book is also valuable to those who have to compose letters in German to scientific colleagues.

A secondary use of the book is that it is also a very clear concise textbook of chemistry, both for students and for specialists who wish to refer to elementary facts or theories of other branches of chemistry. In this connection such a section as that on crystallography and the description of crystallographic series, which is not available in most textbooks of elementary chemistry, is very useful.

The section on inorganic chemistry (50 pp.) contains a brief description of the non-metallic elements, a sub-section on qualitative analysis consisting of a description of dry tests and group separations, and tests for anions. Since the book is not intended primarily as a textbook, only the conventional methods are described, and these include neither micro methods nor "spot" tests. There is also a well-written chapter on the technical preparation and uses of metals. The organic section (50 pp.) contains a brief description of the main groups of aliphatic and aromatic compounds, and a note on the enzymes. The section on physical chemistry (70 pp.) is the most complete and is the most useful when the book is to be used for reference.

The authors are to be congratulated on having successfully achieved a dual purpose.

JANET W. MATTHEWS

REPORT OF THE SOCIETY OF DYERS AND COLOURISTS ON THE WORK OF THE FASTNESS COMMITTEE IN FIXING STANDARDS FOR LIGHT, PERSPIRATION AND WASHING. ANON. Pp. 52. Bradford: The Society of Dyers and Colourists. 1934.

This little book will be read with considerable interest by all concerned with textiles or dyes, whether from the technical or analytical point of view. This

statement applies, perhaps, most forcibly to the section dealing with fastness to light, as will be appreciated by those who have become accustomed to seeing their laboratory windows decked out with coloured strips undergoing fading-tests, or who have many times waited in vain for the sun to shine.

It is now recognised that the carbon arc is the most suitable source of light for accelerated laboratory fading tests, and two types of these lamps are described, in which provision is made for exposure under controlled conditions of temperature and humidity. In the case of daylight tests, samples are graded into 8 categories by exposing them simultaneously and under specified conditions with 7 red and 7 blue standardised dyeings on a specified worsted serge; the dyes were selected so as to form a series showing a regular gradation in the degree of fastness, independent of temperature, humidity, atmospheric impurities and the quality of the light source. If one may venture on criticisms of such a method, they are first, that a set of standards must be sacrificed for each test, with the consequent possibility of "wandering" from the original shade when successive batches are made up over a long period of time; and, secondly, that the degree of fastness of the sample, unlike that of the standard, may not be independent of the quality of the light. There is something, therefore, to be said for a method in which the time of exposure is determined by the total amount of active light falling alike on the standard and sample (*cf.* ANALYST, 1934, 59, 439), even if such a method is open to other objections.

The work on perspiration tests involved determinations of the compositions and properties of perspiration itself, and is of great interest and importance on this account alone. On the basis of this work, formulae for synthetic acid and alkaline perspiration liquors have been evolved, corresponding with freshly-shed and old excretions, respectively. The reviewer has found (from experiments in connection with the handling of acid- and alkali-sensitive security-papers) that the sweat of Asiatics has a lower  $p_H$  value than that of the average Englishman in the marketing of textiles for export; this difference may well give rise to a problem for which the present Report provides little assistance. However, the test described (which involves incubation at 37° C. for 4 hours) should always give an indication when a particular dye is totally unsuitable for human wear.

Four washing-tests are suggested, which vary in severity from the equivalent of a mild home-wash to the effect of four of the more devastating laundry-washes. A wheel-type washing machine of standardised design is described, and a series of ten red and blue standard dyeings enables the results to be classified by comparison.

The bridging of the gap between empirical and exact science is never an easy one. The Society is, therefore, to be warmly congratulated on the success with which it has achieved its particularly difficult task, since there is not the least doubt that the methods described will bear favourable comparison with those suggested by similar bodies in other countries.

JULIUS GRANT