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## Obituary

### ARTHUR ROBERT LING

WITH the passing of Arthur Robert Ling on May 14th at the age of 75 the chemical profession has lost an enthusiast whose work ever bore evidence of intensive and careful thought and painstaking investigation.

The foundation for his chemical career was well and truly laid under the late Professor H. E. Armstrong at Finsbury Technical College in the early eighties, and his first contact with commercial life was made as junior chemist in the laboratories of the Beetroot Sugar Association of London, where he subsequently became chief chemist. In 1898 he joined forces with the late B. E. R. Newlands, and for five years they practised jointly as sugar specialists and general consultants. Ling then started an independent practice in Great Tower Street, widening his specialist sphere to include brewing and malting.

His natural bent towards research, which was first developed at Finsbury in work on derivatives of quinones, continued throughout his career. His association with sugar, starch and other carbohydrates roused his interest in the then obscure chemistry of these substances, and in the first decade of the present century he published many papers on the action of diastase on starch and the resulting products. His interest in this branch of research never flagged, and, indeed, his last publications were on kindred matters.

Ling became a member of our Society in 1894, served on the Council in 1899–1900, and again in 1908–9, and was a Vice-President in 1911–12. He was Honorary Secretary and subsequently Chairman of the London Section of the Society of Chemical Industry, and served on the Council of the Chemical Society. He was elected a Fellow of the Institute of Chemistry in 1888.

When it was decided to start courses of instruction on the fermentation industries at the Sir John Cass Institute, Ling was appointed lecturer. This was a prelude to his appointment, in 1920, to the Chair of Biochemistry of Fermentation at Birmingham University as the successor of Adrian Brown. Ling was never really at home in commercial circles and he now found his true niche—one that he

filled with distinction. His services to the University were officially recognised when the Honorary Degree of M.Sc. was conferred upon him, and again on his retirement in 1931, when he was awarded the title of Emeritus Professor.

For many years he was Technical Editor of the *Brewers' Journal* and he was Editor of the *Journal of the Institute of Brewing* for a quarter of a century.

He had a very wide knowledge of contemporary scientific literature and himself contributed a full quota to it. A great many of his original studies were published jointly with those assisting him in the work, and this was typical of the encouragement that he gave to younger men.

He was generous and cheery in disposition, although he had met with his full share of personal sorrow. Early in the present century he lost both his sons while they were still lads, and in 1935 his wife died.

Ling served his day and generation well and conferred much of lasting use on the chemical and biological world. THEODORE RENDLE

# Some Applications of the Nitro-Ferrocyanide Reaction: A New Formula for Urea

BY W. R. FEARON, M.B., Sc.D., F.I.C.

IT has long been known that the sodium nitro-ferrocyanide (nitroprusside) reagent used for the detection of ketones and thiols undergoes a spontaneous oxidation in aqueous solutions exposed to air and light. This change both extends the reactivity and increases the oxidising power of the reagent. For example, the recently prepared reagent gives no immediate colour when added to a guaiacum suspension, whereas the oxidised reagent at once yields a guaiacum-blue pigment.

Similarly, the oxidised reagent in alkaline solution develops an orange-red colour with primary and secondary alcohols, including glycerol, with *p*-cresol, and with urea, guanidine, and their derivatives, none of which compounds gives a colour with the fresh reagent.

The rate and intensity of pigment-formation depend on both the temperature and the state of oxidation of the reagent, and can be increased by addition of an oxidising agent. The reaction was first systematically applied by Tiegs and by Marston, in 1924, and improved by Weber,[9] who introduced the use of a "guanidine reagent," consisting of a mixture of 1 part of 10 per cent. sodium hydroxide solution, 1 part of 10 per cent. sodium nitro-ferrocyanide solution, 1 part of 10 per cent. potassium ferricyanide solution and 9 parts of distilled water. This reagent is very sensitive but of low selectivity, a disadvantage overcome by using Norit to extract the guanidines from solution previous to application of the test (Andes and Myers).[1]

THE SCOPE OF THE NITRO-FERROCYANIDE REACTION.—The following general conclusions have been reached or confirmed during a study of the interaction of both forms of the reagent with some forty different types of compound.

(A) In alkaline solution, a 2 per cent. recently prepared nitro-ferrocyanide reagent yields red or purple pigments with compounds containing (i) an un-ionised thiol group, –SH, or (ii) an enolisable ketone of the system RH—CO—R′ ⇌ R=C(OH)—R′, where R and R′ are hydrocarbon radicles, one of which, at least, is aliphatic.

Thus: (i) cysteine and glutathione both give a colour, whilst cystine, which occurs in solution as the disulphide –S–S–, does not react; and (ii) both acetone and phenyl-methyl ketone yield typical pigments, whilst diphenyl ketone does not. All these pigments may be formed in presence of either strong alkalis (NaOH) or weak alkalis ($NH_4OH$), and have the common character of being acid-stable, the tint becoming violet on addition of weak acetic acid.

(B) A related form of the colour reaction is given, under restricted conditions, by ketonoid compounds in which R is an imino group linked on both sides to carbon. These reactions are evoked only in presence of strong alkalis, and the pigments are acid-labile, being bleached at once on addition of acetic acid. Cyanuric acid and creatinine provide examples of this form of the reaction.

Aliphatic aldehydes higher than formaldehyde yield a type A reaction with the reagent, but the colour eventually fades owing to aldol formation. Amides do not react. Monosubstituted hydrazines yield ketones with which they unite to form hydrazones, some of which give a type A reaction (Denigès' test for phenylhydrazine).

*The Nitro-ferrocyanide Reaction with Urea.—Test.*—About 5 ml. of a 2 to 3 per cent. aqueous solution of urea is made alkaline by addition of 3 or 4 drops of 10 per cent. sodium hydroxide solution. Ten drops of a 1 per cent. solution of iodine in potassium iodide are added, and the mixture is shaken until the iodine has been bleached to a pale yellow. Then, 3 or 4 drops of a recently prepared 2 per cent. sodium nitro-ferrocyanide solution are added. On standing for a few minutes, the golden-yellow colour of the mixture gradually changes to a ruby-red, which is permanent if sufficient urea is present.

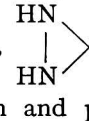
An alternative and more rapid form of the test consists in adding 2 or 3 drops of 2 per cent. potassium persulphate solution to the urea solution, which must not be alkaline, heating the mixture for about half-a-minute, or just to the point of boiling, and then adding the nitro-ferrocyanide reagent, followed by a minimal amount of the alkali. Here, the red colour appears at once, but care must be taken to avoid destruction of the pigment by the alkali. Under controlled conditions this form of the test will reveal urea in concentrations down to about 0·2 per cent. It is inhibited by ammonium salts, which compete with the oxidiser.

Although the test described above is neither very sensitive nor specific, since it is given by all mono-substituted ureas and guanidines, its importance is due to the light it throws on the structure of urea in solution. Accepting the amidine structure as a possible form in which urea can exist in solution, and the only one likely to react, the obvious point of attack in the molecule is the imino group, and the product is a carbamate.

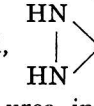
$$\underset{\text{(amidine form)}}{\underset{\text{Urea}}{HO–C(NH)–NH_2}} \rightarrow \underset{\text{Sodium carbamate}}{NaO–CO–NH_2} + NH_3$$

This explanation cannot be correct, since none of the alkaline or other soluble carbamates gives a colour reaction with either the unoxidised or the oxidised

reagent. Ethyl carbamate, it is true, develops a pink colour after some hours in contact with the oxidised reagent, but this is due to hydrolytic release of the ethyl alcohol and its conversion into acetaldehyde. This is a type A pigment, and differs from the urea pigment in being acid-stable.

To investigate the problem, a study was made of the products of partial oxidation of urea in weak alkaline solution by bromine and other halogens, ferricyanide, persulphate and peroxide. It is well known that urea in moderately or strongly alkaline solutions is violently attacked by hypobromites, and the mechanism of the reaction has been exhaustively studied by Werner,[10] but if a molecular equivalent of bromine is added to a urea solution of *M* to 10 *M* concentration, and the mixture kept almost neutral by addition of some pieces of calcium carbonate, oxidation proceeds slowly in the cold, with production of a ketonic compound. This ketone can be separated, when the reaction has gone on for some days, preferably in the dark, by distillation of the slightly acidified mixture. All the bromine is removed previous to distillation by acidifying the mixture with 0·1 *N* sulphuric acid and concentrating in a desiccator over sodium hydroxide. The ketone is a colourless liquid with a characteristic smell. It gives an immediate type B reaction with recently prepared nitro-ferrocyanide, and also gives a positive Reynolds reaction (Tognoli).[8] It is rapidly hydrolysed by warm alkalis, and polymerised by strong acids. Heated with barium hydroxide solutions above 60° C., the ketone is quantitatively hydrolysed into hydrazine and carbon dioxide, which implies the formula,  , or hydrazi-ketone.

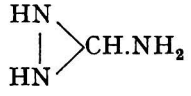
The details of the preparation and properties of hydrazi-ketone will be described elsewhere.

THE STRUCTURE OF UREA IN AQUEOUS SOLUTION.—To account for the oxidative production of hydrazi-ketone from urea the following cyclic formula is proposed, in which urea is represented as hydrazi-carbinol,  . This formula also offers an explanation of the properties of urea in aqueous solution, which no current formulae adequately defines. Thus, both the original carbamide formula, $H_2N–CO–NH_2$, and the amidine formula, $H_2N–C(NH)–OH$, indicate the possession of basic properties, which are not shown by solute urea. The dipolar formula first proposed by Werner,[10] $^+H_3N–C(NH)–O^-$, undoubtedly applies to urea in crystalline form (Clow[3]), and to the various reactions undergone by urea in presence of strong acids or alkalis, and appears in all the syntheses of urea so far investigated (Werner, 1923).

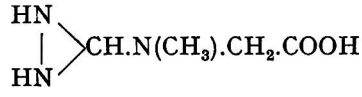
In neutral solution, however, urea does not display the properties of a dipolar ion (Wyman,[11] Sidgwick[7]). It has no buffering powers, it does not contain an ionised amino group, $–NH_3^+$, and will only react with nitrous acid in presence of acids strong enough to unmask the latent amino configuration. In 1905, Armstrong and Robertson[2] showed that nitrogen in conjunction with carbon has a preferential tendency to stabilise in three-membered rings, but up to the present time the hydrazi-structure does not appear to have been suggested for

urea, although the production of hydrazine when urea is carefully oxidised in alkaline solution has been reported by Schestakoff[6] and by Frankland,[4] and affords evidence of a di-imino linkage in the solute.

According to the theory now advanced, hydrazine arises from the alkaline hydrolysis of the hydrazi-ketone, which is the primary product of urea oxidation. The hydrazi-ring probably occurs in many other compounds containing the amidine system $-C(NH)-NH_2$, such as guanidine and creatine.



Guanidine



Creatine

Guanidine is a strong base, owing to the presence of the free amino group, but creatine is non-basic in aqueous solution, and thus differs from arginine, in which the amidine group is open. The non-basic character of the amidine group in creatine is inexplicable in terms of the current "open" formula (Hunter[5]). Only when the hydrazi-ring is unlocked by strong acids is its basic character revealed, as happens in the phosphorylation of muscle creatine or the precipitation of urea as the mono-nitrate, $HO-C(NH)-NH_2.HNO_3$.

## References


1. J. E. Andes and V. C. Myers, *J. Biol. Chem.*, 1937, **118**, 137.
2. H. E. Armstrong and W. Robertson, *J. Chem. Soc.*, 1905, **87**, 1286.
3. A. Clown, *Trans. Faraday Soc.*, 1937, **33**, 381.
4. E. P. Frankland, *Ann. Rep. Chem. Soc.*, 1905, **2**, 96.
5. A. Hunter, "Creatine and Creatinine" (London, 1928).
6. P. J. Schestakoff, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1.
7. N. V. Sidgwick, T. W. J. Taylor and W. Baker, "The Organic Chemistry of Nitrogen" (Oxford, 1937).
8. E. Tognoli, "Reagents and Reactions," trans. C. A. Mitchell (London, 1918).
9. C. J. Weber, *J. Biol. Chem.*, 1928, **78**, 465.
10. E. A. Werner, "The Chemistry of Urea" (London, 1923).
11. J. Wyman, *Chem. Rev.*, 1936, **19**, 212.



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# The Iodimetric Determination of Alkali

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

ALTHOUGH the formation of potassium iodide and iodate in the reaction between iodine and potassium hydroxide was discovered as early as 1815 by Sir Humphry Davy, it was not until 1896 that the reaction was applied in analysis for the determination of alkali. In that year Phelps[1] put forward a method for determining carbon dioxide by absorption of the gas in barium hydroxide, which was standardised iodimetrically. Shortly afterwards, in 1899, Walker and Gillespie[2] modified Phelps's procedure and showed how potassium and barium hydroxides might be determined directly, and hydrochloric and sulphuric acids indirectly. More recently an application of the method to the determination of lime in the presence of calcium carbonate has been described by Scott,[3] but most modern text-books of volumetric analysis ignore the method or its applications. It is, however, referred to by Beckurts,[4] and it appears in the 1911 edition of Sutton.[5] The methods of Phelps and of Walker and Gillespie are fully described and discussed by Gooch.[6]

In the method devised by Phelps an excess of $N/10$ iodine was added to a known volume of $N/10$ barium hydroxide solution in a flask fitted with a trap containing potassium iodide solution. After the solution in the flask had been heated to boiling, it was cooled, and the excess of iodine found by titration with $N/10$ arsenite solution. Carbon dioxide was determined by leading the gas into a similar quantity of barium hydroxide in the same apparatus and determining the unchanged hydroxide as before, on the assumption that no observable reaction occurs between barium carbonate and iodine.

The modification introduced by Walker and Gillespie consisted in the determination of the iodate produced by the reaction. The alkaline solution in a conical flask was treated with an excess of $N/10$ iodine solution and gently boiled until all the iodine not required had been expelled, and the volume of the solution had been reduced from about 100 ml. to 35 ml. The solution was then cooled, and, after addition of dilute acid, titrated with thiosulphate, starch being used as indicator. Since alkali carbonates reacted irregularly with iodine, the complete absence of carbonates from the solution was found to be essential to the accuracy of the method. The difficulty of achieving this in practice has undoubtedly interfered with the utility of the process.

The results given in the present paper show that the irregularities observed by Walker and Gillespie when carbonates are present are due to too short a period of reaction and that, by maintaining an excess of iodine in the system for a sufficiently long time, alkali carbonates and bicarbonates, as well as hydroxides, can be accurately determined. The complete transformation of barium carbonate into iodide and iodate is effected in a reasonable time if it has been freshly precipitated. A sample which had been filtered, washed and dried reacted much more slowly with iodine.

In the cold, sodium hydroxide solution dissolves iodine at once, giving a solution containing sodium iodide and sodium hypoiodite.[7]

$$2NaOH + I_2 = NaI + NaIO + H_2O.$$

On standing, but much more rapidly on warming, the hypoiodite is transformed into iodide and iodate.

$$3NaIO = 2NaI + NaIO_3.$$

The complete reaction is represented by the equation

$$6NaOH + 3I_2 = 5NaI + NaIO_3 + 3H_2O.$$

When acid in excess is added to the mixture of iodide and iodate, iodine is set free, exactly equivalent to the amount of sodium hydroxide that had previously reacted with iodine.

$$5NaI + NaIO_3 + 3H_2SO_4 = 3I_2 + 3Na_2SO_4 + 3H_2O.$$

A solution containing iodide and iodate reacts with free acid to give a solution having a *p*H approximately that of the turning-point of phenolphthalein. Kolthoff[8] states that if a solution containing only iodide and iodate is boiled, the reaction even becomes distinctly alkaline to phenolphthalein. If, therefore, sodium hydroxide in solution is completely transformed by iodine into iodide and iodate, the resulting alkalinity should correspond with that of a solution obtained on titrating mineral acid with carbonate-free sodium hydroxide to the phenolphthalein end-point. In actual fact, the alkalinity of the solution, after removal of iodine by boiling, is barely perceptible with phenolphthalein, and may be caused to disappear altogether by the addition of a few ml. of ordinary distilled water (containing carbon dioxide).

Some preliminary experiments on Walker and Gillespie's process were made, with the following results:

(1) 25 ml. of 0·1 *N* NaOH, reasonably free from carbonate, were treated with 25 ml. of water and 50 ml. of 0·1 *N* iodine in KI solution, the iodine was then boiled off, the solution cooled, dilute sulphuric acid added and the iodine liberated titrated with 0·1 *N* thiosulphate. Of this solution, 24·4 ml. were required, as against the theoretical 25 ml. This result was typical of a number obtained similarly. Whenever the solution, after removal of iodine by boiling, was tested with phenolphthalein, the reaction was strongly alkaline.

(2) 25 ml. of 0·1 *N* NaOH were treated with carbon dioxide in excess, the iodine solution was then added and the excess boiled off.
8·0 ml. of 0·1 *N* thiosulphate solution required.

(3) as in (2), except that the solution was boiled for 10 minutes to remove a great part of the carbon dioxide before addition of iodine.
12·1 ml. of 0·1 *N* thiosulphate solution required.

(4) 25 ml. of 0·1 *N* $NaHCO_3$ treated as in (1).
(*a*) 11·3 ml., (*b*) 12·1 ml. of thiosulphate solution required.

(5) 25 ml. of 0·1 *N* $Na_2CO_3$ treated similarly.
(*a*) 18·3 ml., (*b*) 18·3 ml. of thiosulphate solution required.

Much better results were obtained by repeated additions of iodine over two or three hours, water being added to the gently boiling solution from time to time. In order to avoid the accumulation of potassium iodide, solid iodine was used. Although rather troublesome, this procedure yielded excellent results with sodium carbonate and bicarbonate as well as with the hydroxide. Barium carbonate was found to react to a considerable extent.

The method found most satisfactory and free from difficulty was a reflux process in which benzene was used to prevent the escape of iodine from the reaction mixture. The use of a volatile solvent to retain the iodine in the system was suggested by a paper written by Buehrer and Schupp,[9] who used carbon tetrachloride in a method for determining phosphorus by means of potassium iodate.

The method is carried out as follows:—The alkaline hydroxide or carbonate solution, 2 or 3 ml. of pure benzene and an excess of sublimed iodine are placed in a flask of 150-ml. or 250-ml. capacity, fitted with a ground-in water condenser. The solution is boiled gently until the reaction is judged to be complete, after which the excess of iodine must be expelled. This is most simply effected by continuing the boiling after removing the cooling water from the condenser. Should this treatment cause the flask to adhere firmly, it may usually be removed quite simply by running a little cold water down the condenser to cool the inside of the neck of the flask. The contents of the flask are then cooled and the iodate is determined in the usual manner by means of 0·1 *N* thiosulphate solution, after the addition of potassium iodide and dilute sulphuric acid. Alternatively, without addition of any extra iodide, the acid (preferably about 0·1 *N*) may be added in two stages, the first portion sufficient to produce not more than about a third of the total iodine, which is then nearly removed by the standard thiosulphate, and the second in excess to complete the reaction, followed by titration to the end-point, with starch as indicator.

Some results obtained by this method are given below. The sodium thiosulphate solution was standardised against potassium iodate and potassium bromate. The alkali solutions were standardised against 0·1 *N* sulphuric acid, itself standardised against pure sodium carbonate. Phenolphthalein and rosolic acid were used as indicators in these neutralisation titrations, which were finished after complete removal of carbon dioxide. Incidentally, the use of rosolic acid can be highly recommended for titrations in boiling solution, as the end-point can be observed very accurately, even with 0·01 *N* solutions.

(1) *Sodium hydroxide.*—25·0 ml. of 0·1 *N* sodium hydroxide solution, refluxed for 20 minutes, required 25·0 ml. of 0·1 *N* thiosulphate solution. 50 ml. of 0·1 *N* sodium hydroxide solution, refluxed for 30 minutes, required 50·0 ml. of 0·1 *N* thiosulphate solution.

Identical results were arrived at when the time of refluxing was increased to one, two or three hours.

(2) *Sodium carbonate.*—25·0 ml. of 0·1 *N* sodium carbonate solution, refluxed for 2½ hours, required 25·0 ml. The reaction was never quite complete in 2 hours.

10 ml. of 0·01 *N* sodium carbonate solution, refluxed for one hour, required 9·7 ml. of 0·01 *N* thiosulphate solution.

(3) *Sodium bicarbonate.*—With 25·0 ml. of 0·1 *N* solution exact results were obtained, but only after about three hours.

(4) *Barium carbonate.*—(*a*) *Precipitated, filtered, washed and dried.*—The product was well mixed and similar amounts taken for the iodine treatment and for titration with standard acid. 0·2468 g. was found to be equivalent to 25·1 ml. of 0·1 *N* hydrochloric acid. The same quantity, after being refluxed for three hours with iodine, produced three quarters of the theoretical amount of iodate.

0·1 *N* thiosulphate solution required = 18·5 ml.

Another portion, refluxed for nine hours, required 23·9 ml.

(*b*) *Freshly precipitated.*—25·0 ml. of 0·1 *N* barium hydroxide solution were treated with carbon dioxide gas in excess, and after the addition of 50 ml. of water, followed by iodine and benzene, boiled under a reflux condenser. The solution remained cloudy, showing the presence of barium carbonate, for nearly two hours, when it became perfectly clear. The heating was continued for another hour, after which the iodine was expelled, the solution cooled, and potassium iodide and hydrochloric acid were added, and the iodine liberated was titrated with thiosulphate. The theoretical quantity (25·0 ml.) was required.

Barium hydroxide, treated in the same way, without carbon dioxide, gave the same result.

(5) *Calcium carbonate, precipitated, washed and dried.*—0·1251 g., equivalent to 24·7 ml. of 0·1 *N* hydrochloric acid, after being refluxed for five hours with iodine, required 17·8 ml. of thiosulphate solution instead of the theoretical 24·7 ml.

The method provides a direct comparison of standard alkali with standard thiosulphate solution. It may be mentioned that there is another method available for the direct comparison. This depends upon the titration of the acid liberated in the reaction between thiosulphate and mercuric chloride, and has been investigated by Wöber, by Bodnar and by Sander (references in Kolthoff[10]).

The excellent results obtainable with sodium carbonate would warrant the use of this substance as an iodimetric standard. Although the time required for complete transformation into iodide and iodate is somewhat long, the apparatus needs no attention.

A further development was achieved by determining the amount of iodide in the solution after the thiosulphate titration. It was found possible to titrate the iodide with 0·1 *N* silver nitrate solution, with the use of an adsorption indicator. For this purpose the thiosulphate titration was preceded by the addition of acid in two stages, so that, in the absence of an excess of potassium iodide, the free iodine should not separate from the solution. After the exact end-point with thiosulphate had been obtained the solution was neutralised (with dilute alkali and sulphuric acid) to methyl orange, a few drops of the adsorption indicator were added, and the iodide was titrated with silver nitrate. The volume of the silver solution required agreed, within 0·05 ml., with that of the thiosulphate previously used. As adsorption indicator a red writing ink diluted 10-fold was found suitable.[11]

Hence it is possible to use sodium carbonate as a standard in alkalimetry, iodimetry and argentometry.

DETERMINATION OF IODATE AFTER REMOVAL OF FREE IODINE BY MEANS OF PHENOL, AND ITS APPLICATION TO THE DETERMINATION OF ALKALI.—In the method described above the excess of iodine at the end of the reaction is removed by boiling. If only a slight excess of iodine has been added originally, a few minutes suffices for this operation, but as much as half-an-hour may be necessary at times. In any event, it is impossible to discover the extent of conversion after any given time unless the iodine can be removed by some means other than boiling. As an alternative, the possibility of using phenol to bind the iodine was considered.

Gardner and Hodgson[12] found that phenol might be quantitatively determined by means of iodine, if, after addition of excess of iodine, dilute alkali were added in amount just sufficient to decolorise the solution; then, after acidification of the solution, the excess of iodine was titrated with thiosulphate solution. They remarked that excess of alkali was injurious.

Under these conditions one atom of iodine is required for each molecule of phenol. The compound formed is colourless and soluble in water.

Cofman[13] also studied the reaction between phenol and iodine in the form of alkali hypoiodite. He found that if excess of phenol were added to an iodine solution previously treated with alkali, so that, in addition to hypoiodite, some iodate was present, the hypoiodite reacted, but not the iodate. The iodate could be determined by titration with thiosulphate after acidification with acetic acid. The use of a strong mineral acid was stated to be objectionable, since, before the hydroxide can be completely neutralised, the acid liberates iodine from some of the iodide and iodate, and this iodine is partly transformed into hypoiodite, which reacts at once with phenol and does not show in the subsequent titration.

Schulek[14] also emphasised the necessity for careful removal of hydroxyl ions before acidification. This may be done by means of carbon dioxide (*cf.* Batey[15]).

In acid solution no reaction occurs between phenol and free iodine, potassium iodide or potassium iodate; in neutral solution, moreover, phenol is incapable of liberating iodine from a mixture of iodide and iodate; in alkaline solution phenol is not attacked except by hypoiodite. In the experiments on which these conclusions are based sulphuric acid was used to acidify the solution prior to the titration, but the effect noted by Cofman was observed only when comparatively large amounts of alkali had to be neutralised. Under such conditions approximately correct results were obtained when acetic acid was substituted for sulphuric acid. For lower alkalinities, sulphuric acid may be used without introducing any error.

*Solutions used.*—Potassium iodate, 0·1 *N* solution; sodium thiosulphate, 0·1 *N* solution; potassium iodide, 10 per cent. solution; iodine, 4 per cent. in 10 per cent. potassium iodide solution; phenol, 5 per cent. aqueous solution; sodium hydroxide, approx. 0·5 *N* solution; sulphuric acid, dilute (sp.gr. 1·2).

*Procedure.*—The solution of the composition indicated in Table I was treated with 5 ml. of phenol solution, the specified amount of sodium hydroxide solution was added, followed, after a few seconds, by 10 to 15 ml. of dilute sulphuric acid, and the liberated iodine was titrated with thiosulphate solution, starch being used

as indicator. Potassium iodide was added, if necessary. The quantity of sodium hydroxide solution used was at least sufficient to decolorise the solution in those experiments in which free iodine was present. The volume of the solution before titration was approximately 100 ml.

TABLE I

| Composition of solution | | | Sodium hydroxide sol., 0·5 *N* | Thiosulphate solution required |
|---|---|---|---|---|
| Potassium iodate ml. | Potassium iodide ml. | Iodine ml. | ml. | ml. |
| nil | 10 | — | nil | nil |
| nil | 10 | — | 25 | nil |
| nil | — | 5 | 10 | nil |
| 25·0 | — | — | nil | 25·0 |
| 25·0 | — | — | 15 ml. of 5 *N* | 25·0 |
| 25·0 | 10 | — | nil | 25·0 |
| 25·0 | 10 | — | 5 | 25·0 |
| 25·0 | 10 | — | 10 | 24·5 |
| 25·0 | 10 | — | 25 | 23·6 |
| 25·0 | 10 | — | 8 ml. of 5 *N* | 22·5 |
| 25·0 | — | 5 | 2 | 25·0 |
| 25·0 | — | 5 | 5 | 25·0 |
| 25·0 | — | 5 | 10 | 24·5 |

The modification in the iodimetric determination of alkali suggested by the results given above is as follows:—After the alkaline solution has been refluxed

TABLE II

| Alkali | Volume of solution refluxed ml. | Duration of refluxing Minutes | Thiosulphate solution, 0·1 *N* | |
|---|---|---|---|---|
| | | | Calculated ml. | Found ml. |
| NaOH, 0·1 *N* | | | | |
| 20·0 ml. | 70 | 5 | 20·0 | 19·85 |
| 20·0 ,, | 70 | 10 | 20·0 | 19·9 |
| 20·0 ,, | 70 | 20 | 20·0 | 20·0 |
| 50·0 ,, | 70 | 30 | 50·0 | 50·0 |
| $Na_2CO_3$, 0·1 *N* | | | | |
| 25·0 ml. | 70 | 10 | 25·0 | 18·0 |
| 25·0 ,, | 70 | 45 | 25·0 | 21·6; 22·1 |
| 25·0 ,, | 70 | 60 | 25·0 | 23·7 |
| 25·0 ,, | 70 | 120 | 25·0 | 24·8; 24·9 |
| 25·0 ,, | 70 | 180 | 25·0 | 25·0; 25·0 |
| Borax | | | | |
| 0·3814 g. | 70 | 5 | 20·0 | 18·8 |
| Do. | 70 | 30 | 20·0 | 19·0 |
| Do. | 70 | 90 | 20·0 | 18·8 |
| Do. | 500 | 30 | 20·0 | 19·7 |
| 0·9538 g. | 70 | 30 | 50·0 | 45·4 |
| Do. | 70 | 45 | 50·0 | 37·5 |
| Sodium aluminate | 70 | 90 | 25·0 | 24·95 |
| Sodium silicate | 70 | 90 | 25·0 | 25·0 |

with iodine in benzene for a sufficient time, cool the solution, now containing iodide and iodate, add 5 ml. of 5 per cent. phenol, and run in 0·1 *N* sodium hydroxide solution, with shaking, until all trace of iodine colour is removed. Then add an excess of potassium iodide and dilute sulphuric acid and titrate with thiosulphate.

Some typical results, so obtained, are shown in Table II.

The sodium aluminate solution was obtained by dissolving 0·05 g. of aluminium in 25·0 ml. of 0·1 *N* sodium hydroxide solution.

The sodium silicate solution was a solution of the salt standardised by titration against 0·1 *N* sulphuric acid.

The figures confirm the previous results for sodium hydroxide and carbonate, and indicate that the alkali of sodium aluminate and silicate, but not that of sodium borate, may be quantitatively determined by the iodimetric process described.

## References


1. I. K. Phelps, *Z. anorg. Chem.*, 1896, **12**, 431.
2. C. F. Walker and D. H. M. Gillespie, *Z. anorg. Chem.*, 1899, **19**, 194; Abst., ANALYST, 1899, **24**, 80.
3. W. W. Scott, "Standard Methods of Chemical Analysis," 1926, Vol. I, p. 108a.
4. H. Beckurts, "Die Methoden der Massanalyse," 1931, p. 384.
5. F. Sutton, "A Systematic Handbook of Volumetric Analysis," 10th Ed., 1911, p. 131.
6. F. A. Gooch, "Methods in Chemical Analysis," 1912, pp. 70–73, 231.
7. R. L. Taylor, *J. Chem. Soc.*, 1900, **77**, 725.
8. I. M. Kolthoff, "Volumetric Analysis," Vol. II, 1929, p. 391.
9. T. F. Buehrer and O. E. Schupp, *J. Amer. Chem. Soc.*, 1927, **49**, 9; Abst., ANALYST, 1927, **52**, 171.
10. I. M. Kolthoff, *loc. cit.*, p. 148, footnote.
11. A. D. Mitchell and A. M. Ward, "Modern Methods in Quantitative Analysis," 1932, p. 11.
12. W. M. Gardner and H. H. Hodgson, *J. Chem. Soc.*, 1909, **95**, 1819; Abst., ANALYST. 1909, **34**, 371.
13. V. Cofman, *J. Chem. Soc.*, 1919, **115**, 1040.
14. E. Schulek, *Z. anal. Chem.*, 1925, **67**, 142.
15. J. P. Batey, ANALYST, 1911, **36**, 132.


166, WICKHAM CHASE
WEST WICKHAM, KENT

# The Micro-Determination of Gold

By W. B. POLLARD, B.A., Ph.D., F.I.C.

Introduction.—In previous papers[1,2] I have investigated micro and macro methods for the volumetric determination of gold, and in the present paper I have attempted to develop a technique for the determination of traces of gold in solution, similar to that which has long been used for ores.

The therapeutic use of gold preparations has led to a demand by the medical profession for micro methods for studying the elimination of gold. In the course of this investigation a "collector" has been found, by the use of which gold can be co-precipitated from very dilute solution; this acts in the "wet" assay as lead does in the dry. With this "collector" it has been found possible to recover almost spectroscopic amounts of gold from solution without recourse to evaporation.

Preparation of Gold Solutions for Titration.—The first step in the volumetric determination of gold is its conversion into chloroauric acid or the analogous bromine compound.

Precipitated gold, or gold resulting from "parting" an alloy in nitric acid, can be dissolved in bromine water acidified with hydrochloric acid, but gold that has been melted or strongly heated is more easily dissolved in *aqua regia*.

In whichever way the gold has been dissolved, the solution must be freed completely from nitrosyl chloride, chlorine or bromine before titration. Evaporation to dryness on the water-bath cannot be employed, owing to the partial loss of chlorine from chloroauric acid, but this does not occur when these substances are removed by the passage of a current of air through the liquid.

*Aqua-regia* solutions, obtained by dissolving small amounts of gold in 2 drops of nitric and 6 drops of hydrochloric acid in a porcelain crucible, are freed from gases by allowing a stream of air to impinge on the surface of the acid. This can be done by placing the crucible in a 150-ml. beaker which can be closed by a rubber cork, as shown in the diagram (Fig. 1). Through the centre of the cork passes a short length of glass tube, of about 1·5 mm. bore, down nearly to the level of the crucible. Another tube also passes through the cork and can be connected with the vacuum water-pump by means of a rubber tube.

On starting the pump air is drawn through the centre tube and impinges on the *aqua regia* contained in the crucible, and after two or three minutes the gases will have been removed. After this air treatment 50 ml. of water are put in the beaker, together with the crucible, and the solution is then ready for titration.

If gold is alloyed with more than twice its weight of a base metal, it can generally be "parted" by heating it in a test-tube with nitric acid of sp.gr. 1·2. The gold is then separated from the nitric acid solution by means of the filtering device shown in Fig. 2.

This consists of a piece of capillary tubing (1 mm. bore), with a double right-angle bend. At the end of the long arm a small bulb is blown. An opening is also blown at the top of the bulb, so as to form a small thistle-funnel, and into this is pushed a plug of asbestos wool to serve as a filtering medium. The short arm

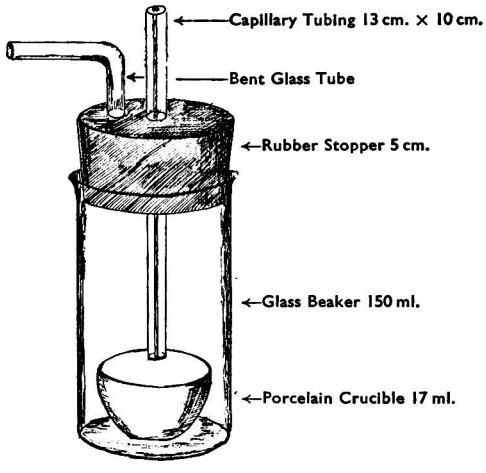
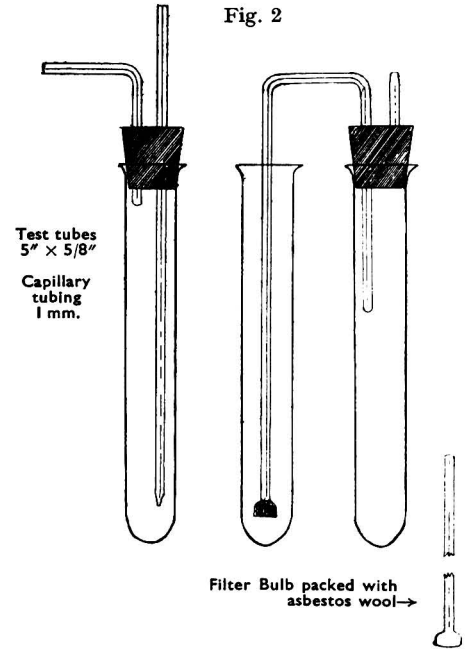



Fig. 1

Fig. 2




passes through a rubber cork which can be inserted in a test-tube. A short length of glass tube also passes through the rubber cork and can be connected by means of a rubber tube with the vacuum water-pump.

The filter is inserted down to the bottom of the test-tube containing the "parted" gold, and the nitric acid is drawn over into the second test-tube, which is connected with the water-pump. The sides of the first tube are washed down two or three times with water. The test-tube containing the nitric acid is then removed and replaced by an empty tube. Ten ml. of saturated bromine water and 2 drops of hydrochloric acid are added to the tube containing the gold and, when this has dissolved, gentle suction is applied, and the bromine water is transferred to the empty tube. Suction is increased, and the sides of the first tube are washed down two or three times with water. The tube, which now contains the gold as bromoauric acid with excess of bromine water, is disconnected from the filter.

To remove the bromine, a rubber cork, through which pass two glass tubes, is inserted in the test-tube, as shown in Fig. 2. The longer tube passes to within a centimetre of the bottom of the test-tube and terminates in a fine jet. The short tube is connected with the vacuum-pump by means of a rubber tube. When the pump is started a turbulent jet of air is drawn through the solution and the bromine is quickly removed. By adjusting the size of the jet at the end of the tube any danger of sucking over the gold solution is avoided. The time required to remove the bromine from 10 ml. of saturated bromine water is approximately $2\frac{1}{2}$ minutes. In actual practice double this time is always allowed. Under altered conditions the exit air can always be tested by passage through a second tube containing a little of the *o*-dianisidine indicator described below, which will show a pink colour with minute traces of bromine and chlorine. The gold solution is then transferred to a beaker and is ready for titration.

Gold can be separated from almost every impurity by precipitation with a suitable reducing agent. After precipitation of the gold in a test-tube, the asbestos micro-filter can be inserted, and the gold collected and washed. Precipitated gold dissolves very quickly in bromine water acidified with 2 drops of hydrochloric acid. By sucking the bromine solution slowly through the filter, the gold is almost instantly dissolved. The filter can be washed with distilled water, and the solution freed from bromine as described above.

THE MICRO-TITRATION OF GOLD.—The method previously described by me (*loc. cit.*) depended on the conversion of gold into the tervalent condition, followed by reduction to metallic gold by a standard reducing agent. At first *o*-tolidine was used as indicator, but this was afterwards replaced by *o*-dianisidine, which was found to be more reactive. Chloroauric acid forms an intense reddish compound with this substance in faintly acid solution. The addition of a standard hydroquinone solution precipitates metallic gold and at the same time discharges the colour.

The *p*H of the solution plays an important part in the titration. If it lies too much on the acid side, combination between the chloroauric acid and *o*-dianisidine is retarded, and it is necessary to wait for the re-formation of the colour before the titration can be continued. If the *p*H moves too far towards the alkaline side, a sparingly soluble compound tends to separate. Both these defects can be overcome by the use of acid potassium fluoride as a buffer.

The reduction of chloroauric acid with hydroquinone proceeds according to the equation:

$$2HAuCl_4 + 3C_6H_6O_2 = 2Au + 3C_6H_4O_2 + 8HCl.$$

The solutions required are prepared as follows:

*Standard Hydroquinone Solution.*—0·4186 g. of pure hydroquinone is dissolved in about 200 ml. of water, 10 ml. of hydrochloric acid are added, and the volume is made up to 500 ml. (1 ml. of solution ≡ 1 mg. of gold).

*Standard Gold Solution.*—0·5 g. of pure gold is dissolved in a 500-ml. flask by gently warming it with 2 ml. of nitric acid and 6 ml. of hydrochloric acid. Dissolved gases are removed from the solution by inserting a glass tube into the liquid and blowing in a strong current of air for about five minutes. Liquid adhering to the tube is washed into the flask, the tube is removed, and the volume is made up to 500 ml.

*o-Dianisidine indicator solution.*—0·5 g. of *o*-dianisidine is dissolved in 200 ml. of water and 2 ml. of hydrochloric acid and put in a 500-ml. standard flask, and the solution is made up to 500 ml.

The relation between the gold and hydroquinone solutions was determined as follows:

Various amounts of gold solution were transferred by means of a 2-ml. pipette into 50 ml. of distilled water, and 2 drops of strong hydrochloric acid were added. The solution was buffered with acid potassium fluoride, 1 ml. of indicator solution was added, and, without waiting, standard hydroquinone solution was run in from a micro-burette graduated in hundredths of a ml. until the red colour was just discharged.

The operation was then repeated, but this time the indicator was not added

until the hydroquinone solution had been run in to within 0·05 ml. of the amount used in the first titration. After a short delay for the colour to develop, the titration was finished as before. The results of the two methods of titration are recorded below:

| Gold solution taken ml. | Hydroquinone used with indicator at start ml. | Hydroquinone used with indicator at end ml. |
|---|---|---|
| 2·0 | 1·98 | 1·99 |
| 2·0 | 1·97 | 2·00 |
| 2·0 | 1·98 | 2·00 |
| 1·0 | 0·98 | 0·99 |
| 1·0 | 0·98 | 0·99 |
| 0·5 | 0·50 | 0·50 |
| 0·5 | 0·49 | 0·50 |
| 0·2 | 0·20 | 0·20 |
| 0·2 | 0·20 | 0·20 |

The slight difference in the two series of titrations is probably due to the gradual fading of the red colour, which occurs when solutions are left standing. The first method of titration is the one that would normally be adopted; the second can be used only when the results are known within narrow limits.

The strength of the hydroquinone solution remains unchanged for several months, but in time the solution develops a slight brown colour. Hydroquinone can be obtained in a sufficient degree of purity to enable a standard solution to be made up directly.

The method is essentially a micro one, and is most suited to quantities of less than 2 mg. of gold. If larger amounts of gold are taken, the second method of titration should be used. The indicator should not be added until less than 2 mg. of gold remain in solution.

THE EFFECT OF OTHER METALS ON THE TITRATION.—The effect of other metals was tested by dissolving 10 mg. of the metal in 2 drops of nitric acid and 6 drops of hydrochloric acid in a porcelain crucible. In the tests with lead and silver the metal was dissolved first in the nitric acid and afterwards the hydrochloric acid was added. The solutions were blown with air in the manner already described, and diluted with 50 ml. of water, and then 2 ml. of the standard gold solution were added. The solution was buffered with acid potassium fluoride, 1 ml. of indicator solution was added and, without delay, the liquid was titrated.

| Metal taken | Gold taken mg. | Gold found mg. |
|---|---|---|
| 10 mg. of copper | 2 | 1·99 |
| 10 mg. of silver | 2 | 2·01 |
| 10 mg. of iron | 2 | 2·00 |
| 10 mg. of nickel | 2 | 2·00 |
| 10 mg. of zinc | 2 | 2·03 |
| 10 mg. of cadmium | 2 | 2·03 |
| 10 mg. of aluminium | 2 | 1·97 |
| 10 mg. of tin | 2 | 2·07 |
| 10 mg. of lead | 2 | 2·54 |

The error that results when lead is present can be eliminated if the *aqua-regia* solution is diluted and a few drops of bromine water added, and the excess of

bromine removed by the passage of air through the solution. Correct values are then obtained in the titration. In strong *aqua-regia* solutions lead appears to form a higher chloride which breaks down on addition of water, with the liberation of free chlorine.

When large amounts of metallic impurities are present the gold should be separated before attempting the titration. A large number of reducing agents are available, but some of them are not very satisfactory when used in micro-determinations.

Stannous chloride gave excellent results with *aqua-regia* solutions. As nitric acid was converted into ammonia, it was not necessary to remove this substance before precipitating the gold—

$$2HNO_3 + 8SnCl_2 + 18HCl = 7SnCl_4 + (NH_4)_2SnCl_6 + 6H_2O$$

The reaction should be carried out just below the b.p. in strong hydrochloric acid solution, and under these conditions the gold is precipitated as metal and not as "purple of Cassius." The stannous chloride solution was prepared by dissolving 200 g. of the salt in 100 ml. of strong hydrochloric acid and was filtered through asbestos wool. It does not precipitate the platinum metals unless mercury, arsenic, tellurium or selenium is also present. By a second precipitation with "metol" or *p*-phenylenediamine hydrochloride, the gold can be obtained free from these impurities. Precipitants such as oxalic acid which react slowly, were not found as satisfactory as those with a high velocity of reaction. Direct precipitation is only advisable when dealing with small volumes of solution; when the gold has to be separated from metallic impurities in large volumes of solution, concentration by co-precipitation should be employed.

Co-precipitation of Gold with Tellurium.—Gold is known to precipitate with tellurium from solutions that contain from 10 to 42 per cent. by vol. of strong hydrochloric acid, and the passage of sulphur dioxide through such solutions precipitates the tellurium in a form in which it can be readily filtered. Large volumes of liquid can be passed through the most rapid filters while every trace of tellurium is retained.

Mercury, platinum, palladium and selenium, and small amounts of titanium, tin, antimony, bismuth, molybdenum, etc., are, as is known, carried down with the tellurium. Barium, strontium and lead would precipitate as sulphates, but could be removed before precipitating the tellurium.

To test the possibilities of tellurium as a "collector" for gold, a solution was prepared by dissolving 5 g. of powdered tellurium in 20 ml. of hydrochloric acid and 5 ml. of nitric acid in a beaker on the water-bath. Nitric acid was then removed by evaporating the liquid to a thick syrup after addition of hydrochloric acid. Twenty-five ml. of hydrochloric acid were added, and the volume was made up to 50 ml. with distilled water. Each ml. of solution thus contained 100 mg. of tellurium.

Blank tests were made first with 10 litres of tap water alone, and then with the addition of known amounts of a standard chloroauric acid solution. It was found necessary to add 1 litre of strong hydrochloric acid to each 10-litre sample, as sulphur dioxide failed to precipitate the tellurium when less was used. After acidification, 2 ml. of tellurium solution were added, the sulphur dioxide was

passed into the well-mixed solution, until there was a strong odour of the gas. The containing vessel was then left on the water-bath overnight.

The liquid was filtered through a Buchner funnel. The paper and precipitate were transferred to a 17-ml. porcelain crucible, charred at a low temperature, burnt off at a rather higher temperature, and finally heated strongly for a few minutes. During the burning most of the tellurium escaped, but a little dioxide was left in the crucible.

When the crucible was cold, 6 drops of hydrochloric acid and 2 drops of nitric acid were added, and any undissolved solid was broken up with a short piece of glass rod. The crucible and rod were then placed on the top of the water-bath for 15 minutes, and the gold was dissolved. The crucible was not placed directly in the steam, as this caused too rapid evaporation. After air-treatment the solution was diluted, buffered and titrated in the usual way. The following results were obtained:

Gold determined in 10 litres of tap water acidified with 1 litre of hydrochloric acid

| No. | Gold present mg. | Tellurium added mg. | Gold found mg. |
|---|---|---|---|
| 1 | none | 200 | none |
| 2 | none | 200 | none |
| 3 | 0·01 | 200 | 0·01 |
| 4 | 0·02 | 200 | 0·02 |
| 5 | 0·05 | 200 | 0·05 |
| 6 | 0·10 | 200 | 0·10 |

The method will therefore recover one part of gold in a thousand million parts of solution.

In order to test the effect of metallic impurities on the recovery of gold by co-precipitation with tellurium, a solution was made containing 1 g. each of the chlorides of calcium, magnesium, aluminium, iron, zinc, cadmium, bismuth and copper dissolved in 100 ml. of 10 per cent. hydrochloric acid. To this 1 ml. of standard gold solution and 1 ml. of tellurium solution were added. The tellurium and gold were then precipitated with sulphur dioxide and the gold was titrated. In two experiments 0·99 mg. of gold was recovered as compared with 1·00 mg. taken.

As palladium is carried down by tellurium and interferes with the gold titration, search was made for a reagent that would precipitate gold without also precipitating tellurium and palladium. "Metol" and *p*-phenylenediamine both seem to have the required properties. In the following test the gold was precipitated in dilute hydrochloric acid solution at the boiling-point. The gold was collected on the micro-filter, washed, dissolved in bromine, and titrated in the usual way.

| Gold taken mg. | Palladium mg. | Platinum mg. | Tellurium mg. | Gold found mg. | Precipitant |
|---|---|---|---|---|---|
| 1·00 | 1·00 | — | 20·00 | 0·99 | "Metol" |
| 2·00 | 1·00 | 1·00 | 20·00 | 1·98 | ,, |
| 0·50 | 1·00 | — | 20·00 | 0·49 | ,, |
| 0·50 | 1·00 | — | 20·00 | 0·50 | *p*-phenylenediamine hydrochloride |

Co-precipitation with tellurium was found to be a rapid method for the determination of gold in the urine of persons who were undergoing treatment with gold salts. The gold could also be completely recovered from solutions of the complex gold salts used in the treatment.

I wish to express my thanks to Sir Harold Carpenter for the facilities provided.

REFERENCES

1. W. B. Pollard, *Trans. Inst. M. M.*, 1923, **32**, 242.
2. —— *Id.*, 1932, **41**, 434.

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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.*

## A NEW COLORIMETRIC TEST FOR NOVOCAINE AND PRIMARY AMINES

NOVOCAINE, like all primary amines, gives an immediate colour when treated with a solution of paradimethylamino-benzaldehyde in presence of hydrochloric acid. A drop or a minute particle of the primary amine to be tested is treated on a slide with a drop of the aldehyde solution (prepared by dissolving 4 g. of the aldehyde in 380 ml. of absolute alcohol and 80 ml. of conc. hydrochloric acid). Primary amines generally give a yellow, greenish-yellow or orange colour, undoubtedly due to the formation of coloured dye (Schiff's) bases.

This test, which has obvious advantages over the diazo test for primary amines, should prove particularly valuable in analytical laboratories where hundreds of samples have to be tested every year for the presence of novocaine. One of the usual adulterants of cocaine in India is novocaine, and novocaine is at once indicated by the greenish-yellow colour obtained, whereas the other usual adulterants, such as acetanilide, aspirin, starch, eucaine, alypin, antipyrine, aconitine, apomorphine, atropine, caffeine, tropacocaine and scopolamine, and cocaine itself give no colour. Orthoform and anaesthesin give a greenish-yellow colour, but novocaine is easily distinguished from these compounds. Commercial novocaine (hydrochloride) is completely soluble in water, whilst orthoform and anaesthesin are insoluble.

During the last ten years several tests for novocaine have been suggested (*e.g.* Young, *Amer. J. Pharm.*, 1931, **103**, 709; Abst., ANALYST, 1932, **57**, 179; Wagenaar, *Pharm. Weekblad.*, 1932, **69**, 727; Abst., ANALYST, 1932, **57**, 579; Wagenaar, *Mikrochem.*, 1932, **12**, 143; Abst., ANALYST, 1933, **58**, 178; Sanchez, *Ann. Chim. anal.*, 1934, **16**, 249; Abst., ANALYST, 1934, **59**, 634), but none of these is so simple or definite as that we have described.

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## ANALYTICAL DATA ON PALESTINIAN OLIVES AND OLIVE OIL

THE analytical results obtained in the examination of samples of olives from ten trees, over a period of four years (1933–1936) may be summarised as follows:

| Years | 1933 | 1934 | 1935 | 1936 |
|---|---|---|---|---|
| Average weight of each olive (grams) | 1·74 | 2·60 | 1·98 | 2·07 |
| Proportion of seed to flesh (flesh = 1) | 0·41 | 0·27 | 0·33 | 0·33 |
| *Analysis of the flesh* | | | | |
| Water, per cent. | 41·9 | 42·6 | 39·9 | 37·7 |
| Oil, per cent. | 34·7 | 38·8 | 36·3 | 40·8 |
| Oil (calculated on dry sample), per cent. | 59·9 | 67·6 | 59·4 | 65·5 |
| Ash, per cent. | 1·56 | 1·20 | 1·46 | 1·15 |
| Protein ($N \times 6{\cdot}25$), per cent. | 1·59 | 1·78 | 1·94 | 2·07 |

*Experiments on the acidity of local olive oil.*

(*a*) Selected olives.

| | Per Cent. |
|---|---|
| (1) Picked by hand | = 0·3 |
| (2) Combed | = 0·3 |
| (3) Beaten in usual way | = 0·3 |

(*b*) Average whole sample.

| | |
|---|---|
| (1) Picked by hand | = 0·45 |
| (2) Combed | = 0·55 |
| (3) Beaten in usual way | = 0·90 |

(*c*) Acidity of oil pressed after keeping olives 10 days.

| | Per Cent. |
|---|---|
| (1) Picked by hand | = 1·4 |
| (2) Combed | = 1·65 |
| (3) Beaten in usual way | = 2·15 |

(*d*) Oil from local presses 3 to 10 per cent.

The acidity of local olive oil varies (as shown above) according to the methods of gathering, handling and pressing. The practice of gathering by beating the tree, stacking the olives in heaps for 10 days prior to pressing, and the use of primitive hand-presses all tend to increase the acidity by fermentation. The best unrectified edible oil on the local market has an acidity of 3 to 5 per cent., whilst that from some of the more primitive presses may contain 10 per cent. or more. Oil pressed in the laboratory from selected hand-picked olives contained 0·3 per cent. of acid. In the same olives after being kept for 10 days the acidity had risen to 1·4 per cent. In unselected olives, harvested by beating, an initial acidity of 0·9 per cent. rose in 10 days to 2·15 per cent.

The analytical values obtained by W. Zananiri in these laboratories on ten samples from different local presses were as follows:

| | Sp.gr. at 15°C. | Saponification value | Reichert–Meissl value | Iodine Value (Hübl) | $n_D^{25}$ |
|---|---|---|---|---|---|
| Minimum | 0·911 | 183·7 | 0·77 | 81·0 | 1·4670 |
| Maximum | 0·918 | 193·5 | 0·99 | 84·7 | 1·4680 |
| Average | 0·915 | 189·3 | 0·83 | 82·6 | 1·4675 |

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# Legal Notes

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

## ARTIFICIAL VINEGAR SOLD AS "TABLE VINEGAR"

SUTTON *v.* TAME

ON June 15th Mr. Eustace Fulton, Chairman of the County of London Sessions Appeal Committee, heard an appeal against a fine imposed by Sir Rollo Graham-Campbell, at Bow Street Police Court, for selling vinegar not of the nature, substance and quality demanded by the purchaser (see ANALYST, 1937, 384).

The respondents to the appeal were the Westminster City Council, who were represented by Mr. St. John Hutchinson, K.C., and Mr. Vernon Gattie. The appellant was represented by Mr. Kenneth Swan, K.C., and Mr. R. E. L. Parry.

In reply to the Chairman's enquiry, Mr. Swan said that the point to be decided was whether there was any significance in the term "table vinegar." It was his contention that that term had been applied to a substance for many years, and was a correct and proper description.

Mr. Hutchinson said that the Westminster City Council contended that for a substance to be called "vinegar" at all it should be brewed. The certificate of the Public Analyst showed that the substance in question consisted of 100 per cent. of artificial vinegar. The Council contended that vinegar must be a product brewed from malt, whereas the substance they complained of was really synthetic and was made up of acetic acid and water together with some colouring. It was not brewed at all, which, they were contending, was an essential feature of vinegar. There was a great difference in the process of manufacture and undoubtedly a great difference in taste. The general trade looked upon brewed vinegar as a different article. For over 300 years vinegar had been made by fermentation, and their contention was that one could not change the whole attitude of the people towards a substance by manufacturing it later in a synthetic manner. They felt that if people were going to get that sort of manufactured vinegar there ought to be some notice upon it, so that they knew what they were buying.

Mr. F. W. Edwards, Public Analyst for Westminster, said that, in his view, fermentation was an essential part in the manufacture of vinegar. Artificial vinegar did not contain any mineral salts, proteins or vitamins, and the odour and taste were utterly different from those of genuine vinegar.

In cross-examination the witness said that there were no chemical operations in the manufacture of brewed vinegar; they were all biological. He agreed, however, that malt vinegar had to be manufactured by a sequence of carefully controlled steps. Real vinegar could not be produced from wood, although for many years there had been a substance known in the trade as "wood vinegar." There were very few Public Analysts in this country who refused to condemn wood vinegar if sold as vinegar.

Dr. C. Ainsworth Mitchell said that, in his opinion, vinegar ought to be defined with reference to its source. He would accept "imitation vinegar" as a proper description of wood vinegar, but would not accept "vinegarine." From his knowledge of the trade he was of opinion that they accepted the definition put forward by Dr. Hamill (now of the Ministry of Health) in his Report to the Local Government Board. He did not consider that the word "table" defined wood vinegar.

In cross-examination the witness agreed that Dr. Hamill's recommendation to the Local Government Board had not been adopted by the Ministry of Health.

Dr. H. E. Cox, Public Analyst for Hampstead and for Cornwall, said that he agreed with the definition of vinegar that had been drawn up by the Society of Public Analysts (*cf.* ANALYST, **1935**, **60**, 3). He had not heard that any protest against that definition had been sent by any member of the Society. He would not accept "table vinegar" as a correct description of "wood vinegar"; there had been numerous prosecutions for the sale of artificial vinegar as "vinegar" or "table vinegar."

Evidence was then given by several representatives of large firms of grocers and provision merchants to the effect that they sold only brewed malt vinegar, and that if asked for "vinegar" they would not supply artificial vinegar.

For the appellant, trade evidence was called to prove that there was an extensive trade done in acetic acid vinegar, and that, although the product was made by different firms, it had for many years been sold as "table vinegar."

When the Court resumed on June 16th, Mr. Swan called scientific evidence on behalf of the appellant.

Dr. E. J. Parry said that, in his opinion, the word "vinegar" did not connote merely a brewed condiment, and "table vinegar" was to him an expression for pure vinegar. He regarded non-fermented vinegar as pure vinegar in the ordinary sense of the word. The vinegar to which he referred as "factitious" in 1910 was the imitation malt vinegar made by adding phosphates and proteins to diluted acetic acid and so deceiving the analyst.

In cross-examination, Dr. Parry said that he did not think that one in a thousand members of the public knew the difference between brewed and non-brewed vinegar, but he agreed that the public should know what they were buying.

Mr. William Lincoln Sutton, Public Analyst for Norfolk and Suffolk, said that the trade description of malt vinegar was generally "malt," but he had known the unbrewed product to be sold as "vinegar," and occasionally as "table vinegar." He thought that the definition of vinegar formulated by the Society of Public Analysts was too restricted.

Mr. A. J. Lickorish, Public Analyst for the City of London, who attended on subpoena, said that so long as vinegar was not labelled "malt vinegar" he saw no reason why the acetic type should not be sold as "vinegar" or "table vinegar."

In reply to the Chairman's question, whether a customer ought not to know what he was buying, the witness replied that he would know from the label; if the customer were having his own bottle filled, he would know by the flavour. If he (the witness) went into a shop and asked merely for "vinegar," he would expect to get synthetic vinegar.

Mr. Swan, addressing the Committee, said that there was no legal standard for vinegar, although various attempts had been made to get one. Bills had been promoted in Parliament to put the matter on a proper footing, but they had lapsed. During the last 25 or 30 years vinegar from wood and other synthetic sources had been evolved, and acetic acid had been produced in a state of great purity. He contended that the Statute was never designed to decide a question of this nature. A most extensive practice in non-brewed vinegar had been built up, and it was only in the past five or six years that the manufacturers had added words to inform the public whether it was brewed or non-brewed. The question his lordship had to decide was: "Does the expression 'table vinegar' necessarily mean malt or brewed vinegar?" It was essential in the case of a penal statute that it should mean "necessarily." An article demanded meant an article commercially known under that name. He asked the Committee to find as a fact that the public had, for a considerable number of years, asked for and bought this quality of vinegar by the name "vinegar" and by the name "table vinegar." The term "vinegar" might mean one of many things and, in his submission, if a customer asked for vinegar, it could not be suggested that he did not receive what was demanded if supplied with the non-brewed variety. There was abundant

evidence of a differentiation in trade terminology with regard to the description of non-brewed vinegar. It would be unfair to conclude that when a purchaser went to a shop and asked for table vinegar, by which name millions of bottles had been sold to the public, that he only meant that he wanted malt vinegar.

The Chairman, announcing the decision of the Committee, said: "The Committee desire to thank counsel on both sides and the expert witnesses on both sides for the very valuable assistance they have given them in arriving at a decision in this rather difficult case. The Committee cannot agree with Mr. Swan's contention that the words 'table vinegar' have become a term of art and are, by a custom of the trade, in this case used to denote what may be termed synthetic vinegar. The fact that a very large majority of manufacturers add such words as 'wood,' 'non-brewed,' or similar words of that description to the products, shows, in the opinion of the Committee, that the words 'table vinegar' are not considered by the custom of the trade sufficient to describe it. The Committee are satisfied on the evidence that to sell a substance as 'vinegar' or 'table vinegar' without any qualification or explanation as to its origin being given by the seller to the purchaser, implies that the substance sold is produced by a process of fermentation. The substance demanded by Mr. Gray was half-a-pint of table vinegar. The substance sold to him was admittedly a synthetic product, and it is not suggested that the seller gave him any information about the substance he sold as table vinegar. It follows that, for the reasons we have given, the article sold to him was not of the nature, quality or substance demanded, and, in our view, in such circumstances was clearly sold to him to his prejudice. The appeal must therefore be dismissed with costs."

The Chairman agreed to state a case if counsel on each side could agree a case together. An order for 75 guineas costs was made.

The Editor is informed that no appeal against this judgment has been lodged, and that the time for appeal has expired.

# Department of Scientific and Industrial Research

## METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY*

### I. HYDROGEN SULPHIDE

THIS is the first of a series of leaflets describing standard methods for the detection of toxic gases in industry.

The Foreword explains that a paragraph of the Chemical Works Regulations, 1922, made under Section 79 of the Factory and Workshop Act, 1901, prohibits entry by any person not properly protected into any place which might contain dangerous gas, until the air has been tested and found safe to breathe. To meet this requirement the question of simple and rapid chemical or other methods for determining low concentrations of dangerous gases, such as may occur in various circumstances in chemical works, was discussed by the Association of British Chemical Manufacturers with the Home Office, and, as a result, arrangements were made by the Department of Scientific and Industrial Research, at the request of the Home Office and with the financial and technical co-operation of the Association of British Chemical Manufacturers, for a series of tests to be developed by the Chemical Defence Research Department.

* Leaflet No. 1. London: H.M. Stationery Office. June 18th, 1937. Price 3s. 6d. net.

POISONOUS EFFECTS.—In concentrations of 1 in 1000 by vol. or higher, hydrogen sulphide will cause immediate unconsciousness, and will result in death unless artificial respiration is immediately applied. In such concentrations it is nearly as toxic as hydrogen cyanide and may act with equal rapidity by paralysing the respiratory centre of the brain. In weaker concentrations the effects may be summarised as follows:

| Concentration in air | | |
|---|---|---|
| Parts by vol. | Mg. per litre | Effects |
| 1 in 2,000 | 0·76 | Very dangerous if inhaled for 15 to 30 minutes. Causes severe irritation of the eyes and respiratory tract with risk of pneumonia or serious injury to the lungs, which may readily prove fatal. |
| 1 in 5,000 | 0·304 | Dangerous if inhaled for one hour. Causes severe irritation of the eyes and respiratory tract. Eyes are affected after 6 to 8 minutes. |
| 1 in 10,000 | 0·152 | Symptoms of local irritation of eyes and respiratory tract after *one* hour's exposure. |

METHODS OF DETECTION.—The lead acetate test has been adopted as a sensitive qualitative test readily adaptable as a quantitative method. Of the various methods of applying the lead acetate test, the only one that was considered satisfactory was that of drawing the atmosphere *through* the test-paper.

It is mentioned that the lead acetate test-paper method has been applied in a continuous automatic detector, in which the stain interferes with a ray of light directed on to a photo-electric cell, and causes a bell to ring (cf. *J. Soc. Chem. Ind.*, **1934**, **53**, 526T).

DETAILS OF THE LEAD ACETATE TEST.—The atmosphere to be tested is sampled by means of a hand exhausting pump with a barrel of approximately 1·25 in. bore and a capacity of 126 ml. To the inlet end of the pump is screwed a spigot with an external screw, 7/16 in. Whit., 14 T.P.I. on 0·437 in. diameter.

*Test-papers.*—These are made from Whatman No. 1 filter-paper, cut into strips, 2 in. × 4 in. The strips are impregnated with lead acetate solution (10 g. of lead acetate of analytical reagent quality in 100 ml. of water plus 5 ml. of glacial acetic acid), suspended vertically in an atmosphere free from hydrogen sulphide, and left to dry at the ordinary temperature. One inch is then cut off the top and bottom of each strip and discarded. Test-papers can be stored in a glass-stoppered, air-tight container, in which is a drying agent, such as a silica gel capsule. Papers that have been stored more than a fortnight must not be used for the test.

*Method.*—The lead acetate paper is clamped in a holder of special design (illustrated in the Leaflet), which is screwed into the pump. The apparatus having been tested for leaks by a technique described, a preliminary indication of the atmosphere to be tested is obtained by making two slow and steady strokes of the pump, and the paper is then removed from the holder and compared within 10 minutes with the standard colour chart provided with the Leaflet.* A concentration greater than 1 in 60,000 (0·025 mg. per litre) is thus indicated. If no stain has been produced, further tests are made with fresh lead acetate paper, 3 or 5 strokes of the pump being made and the concentration read off from the chart as before.

The stains obtained should be only on that side of the paper exposed to the gas entering the pump, and the back of the test-paper should remain white (or nearly so if the stain is very heavy).

* Further copies of the standard stains produced on lead acetate paper can be obtained from H.M. Stationery Office. Price 2s. 1d. post free.

A method is also described for sampling, from a distance, air in a space that is not readily accessible (*e.g.* in acid tanks).

FIRST AID.—A patient who has been gassed with hydrogen sulphide should be removed into fresh air and wrapped in a blanket to keep him warm. Artificial respiration with oxygen should be started at once and continued even after it may seem to have failed. In one case artificial respiration with oxygen was eventually successful after more than 5 hours.

# New Zealand

## ANNUAL REPORT OF THE DOMINION ANALYST FOR 1935

THE Sixty-ninth Annual Report of the Dominion Analyst (Mr. W. Donovan, M.Sc., F.I.C.) summarises the work undertaken for various Government Departments at the main Laboratory in Wellington and the Branch Laboratories in Auckland, Christchurch and Dunedin.

THE REDUCTASE TEST.—The experience of the laboratory, extending over twenty years, is that the reductase test is the most satisfactory method for controlling the bacteriological purity of milk supplies. The legal standard is at present three hours, but the experience of a number of years shows that this could be raised to five hours.

ZINC IN GLAZED EARTHENWARE.—Zinc, equivalent to 0·4 g. of the metal per 100 ml. of acid, was dissolved from a sample of glazed ovenware when treated for 30 minutes at cooking temperatures with *N* hydrochloric acid. Zinc oxide is used in glazes to give a matt effect, which was apparent in the sample.

ALKALOID OF RAGWORT.—An alkaloid with the empirical formula $C_{18}H_{25}O_6N$ was isolated from ragwort (*Senecio jacoboea*) growing in New Zealand. It is probably identical with the alkaloid, jacobine, isolated from Canadian ragwort by Manske. The acetate was very toxic; when injected subcutaneously into rats it produced cirrhosis of the liver.

FLUORESCENCE OF HUMAN HAIR.—According to a statement in an American journal it is possible to ascertain the race of an individual from the fluorescence of the hair in ultra-violet light. This assertion was investigated in connection with the identification of the body of a half-caste Maori woman. The most suitable arrangement for comparing the fluorescence of hairs was to mount them stretched side by side on a slide made of three-ply veneer stained with aniline black, and to examine them under a microscope in filtered ultra-violet light focused on to the stage by means of a flask, 6 inches in diameter, filled with distilled water; the light was reflected on to the specimens from the silvered inside of a spherical glass basin.

Light hairs fluoresce brightly and grey hair shows a brilliant fluorescence, but in the case under investigation the dark hairs were of particular interest. Specimens of dark brown and black hairs from various races were examined, including European, Chinese, Kaffir, American negro, Syrian, Red Indian, and Maori, as well as half-castes from these races. All the specimens were washed with warm soap solution, rinsed and dried before examination.

The results showed that there was no difference in fluorescence according to race, but that the differences observed simply corresponded with the visual classification of the hair into black and dark brown, black giving a dull blue fluorescence and dark brown a light blue. The method would therefore not be effective for distinguishing hair according to race.

CORROSION OF LEAD CABLE-SHEATHING.—The lead-sheathing of a submarine cable at the shore end was found to be extensively damaged by corrosion. Upon removal of the jute wrapping it was seen that very extensive corrosion of the lead had occurred. The corrosion product contained 78·8 per cent. of lead and 13·3 per

cent. of carbon dioxide (theoretical for basic lead carbonate 80·1 and 11·4 per cent., respectively). The absence of chlorides, sulphates, nitrates and lead peroxide indicated that the corrosion was not electrolytic, due to stray currents. After removal of the impregnating material from the jute by means of a solvent, the pitch obtained was tested for phenols by azo tests with sulphanilic acid and with *p*-nitroaniline; in each test pronounced positive results were obtained. Confirmation was afforded by Nellensteyn's test with freshly-prepared Millon's reagent (*Proc. World Petroleum Congress*, Vol. II, p. 577). The evidence, therefore, suggested strongly that the corrosion of the sheathing was due to the action of phenols, and was similar to the instances mentioned by the Dutch Corrosion Research Committee on Cables (see *Chem. and Ind.*, 1934, **53**, 565). An interesting sequel to the investigation was that information was sent that the cable concerned was of a new type in which a feature had been made of protecting it against the attack of white ants by impregnation with a preservative compound instead of the customary arsenious oxide; one of the ingredients of this preservative was anthracene oil, and it was from this that the phenols had emanated.

# New South Wales

## ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR 1935

THE Chemical Laboratory of the Health Department is under the control of the Government Analyst (Mr. S. G. Walton). Work is also done for other Government Departments, including the Police Authorities and the Pharmacy Board, and in connection with Coroners' inquiries. Among points of interest in the report are the following:

CHANGE OF FREEZING-POINT STANDARD FOR MILK.—As the result of a survey of genuine samples of milk collected in the milk-producing districts under the Milk Act it was found that occasionally the freezing-point of the mixed milk from a herd of cows gave a figure of −0·535° C. It was considered advisable, therefore, to alter the present freezing-point standard of milk from −0·55° C. to −0·535° C. This does not mean that in the past the vendor has been penalised in any way, for it has been the Departmental practice to allow a tolerance of 3 per cent.

BLEACHED TRIPE.—At the present time the practice of bleaching tripe has become almost general in the Metropolitan area. The treatment consists in (*a*) a preliminary scrubbing and boiling, (*b*) immersion in a peroxide bath, (*c*) washing the bleached tripe, either with or without the addition of acetic acid. To ascertain the effect of bleaching on the tripe, 56 samples of the untreated, and 21 samples of the treated substance were analysed. The following results were obtained:

| | Moisture | | | Alkalinity* | | |
|---|---|---|---|---|---|---|
| | Max. Per Cent. | Min. Per Cent. | Average Per Cent. | Max. Per Cent. | Min. Per Cent. | Average Per Cent. |
| Untreated tripe | 92·0 | 66·3 | 80·7 | 0·34 | 0·013 | 0·12 |
| Treated tripe | 92·6 | 83·0 | 89·1 | 1·17 | 0·18 | 0·63 |

* As $Na_2O$ on the water-free tripe.

The general conclusion arrived at was that the tripe undergoes a pronounced decrease in solid matter and an increase in soluble alkalinity during the process.

The *p*H of 12 samples of untreated tripe ranged from 7·0 to 7·1 and the *p*H of 24 samples of treated tripe from 9·4 to 10·8.

TOMATO PRODUCTS.—With a view to obtaining data for formulating standards for tomato purée and tomato paste, analyses of a number of commercial products were made, with the following results:

| | Mould* count Per Cent. | Total solids Per Cent. | Sugars Per Cent. | Ash Per Cent. | Sodium chloride Per Cent. |
|---|---|---|---|---|---|
| Concentrated purée .. | 22 | 30·2 | 13·0 | 10·2 | 3·5 |
| Double concentrated conserve | 25 | 44·1 | 15·5 | 8·7 | 0·6 |
| Triple concentrated conserve | 50 | 9·6 | 3·8 | 1·3 | 0·3 |
| Tomato purée .. .. | 50 | 10·9 | 5·1 | 3·2 | 0·3 |
| Triple concentrated purée.. | 50 | 19·5 | 7·3 | 3·4 | 1·3 |
| Concentrated purée .. | 30 | 16·4 | 8·1 | 2·5 | 0·27 |
| Concentrated purée, 8 to 1 | 13 | 35·3 | 17·1 | 4·4 | 0·72 |
| Concentrated purée .. | 44 | 25·3 | 11·4 | 4·9 | 0·35 |

* The mould count represents the percentage of fields, as determined by the A.O.A.C. official method.

*Tomato Pulp.*—Regulation 35 (2) of the Pure Food Act (N.S.W.) requires tomato sauce to be prepared from sound and ripe tomatoes. An examination of the mould-content of the proprietary brands of tomato sauce on the Sydney market indicated that a large proportion was made from unsound stock. The mould counts (by the A.O.A.C. official method) of tomato pulps showed that by the use of good stock and efficient sorting no difficulty should be experienced in producing tomato sauce the mould count of which does not exceed 25 per cent. positive. To allow for seasonal conditions, however, it is proposed to introduce a standard imposing a maximum mould count of 50 per cent. of fields positive.

LEAD ARSENATE POISONING.—In a case which formed the subject of a charge of murder a woman administered lead arsenate to her husband in his food. Death did not occur until four or five weeks later. The following results were obtained in the analysis of the exhibits:

| Material | Weight of material | Lead found | Arsenic found |
|---|---|---|---|
| Liver .. | 3 lb. 14 oz. | 5·6 mg. | 0·10 mg. |
| Hair .. .. | 2·0 g. | — | 4·0 mg. per 100 g. |
| Nails and cuticle | 2·0 g. | — | 3·0 mg. per 100 g. |
| Bones .. | 800 g. | 4 mg. per 100 g. | — |

STRYCHNINE POISONING.—In this case the deceased had several fits over a period of about 15 hours. The doctor diagnosed strychnine poisoning, and the patient was removed to hospital for treatment. Death took place in approximately 48 hours after the first fit. From a check of the hypodermic strychnine tablets kept on the premises occupied by the deceased it appeared that the maximum amount of strychnine that could have been taken was 0·4 grain. No trace of strychnine could be found either in the stomach or the organs, and it would seem that in the 48 hours between the taking of the strychnine and death the whole of the alkaloid had been eliminated or destroyed.

POLLUTION OF BEACH SANDS.—An investigation was made to ascertain the extent of pollution of beaches used by the public. The method of determining pollution was as follows:—A sample of the sand was shaken at frequent intervals with an equal amount of distilled water, the sand was allowed to settle, and the supernatant liquid was analysed as in water analysis. From the results obtained it is considered that the organic nitrogen figure for unpolluted beach sands should not exceed 0·02 part per 100,000 of wash water; the figure for slightly polluted sand

should not exceed 0·10 part; excessive pollution is indicated if the figure exceeds 0·20 part per 100,000.

DETERMINATION OF ALCOHOL IN HUMAN URINE AND BLOOD.—As the result of various coroners' inquiries it was found necessary to ascertain, from an examination of the urine or blood, the approximate alcoholic condition of persons concerned in accidents. In conjunction with the Medical Officer for Sydney, Dr. A. A. Palmer, an investigation was undertaken into the relationship existing between the amount of alcohol consumed and the amount contained in the urine and in the blood at definite intervals of time after consumption. Different types of alcoholic liquids were used, the subjects selected were of different ages, from 25 to 54 years, and their body weights ranged from 125 to 174 lb. The personal history varied from almost total abstainers to moderate drinkers.

The method of analysis used for urine was a modification of that of Southgate and Carter (*Brit. Med. J.*, **1926, 463**), and for the removal of proteins from blood prior to the determination of alcohol the method of Bock was used (*J. Biol. Chem.*, **1931, 93**, 645; Abst., ANALYST, **1932, 57**, 49). In experimental determinations it was found that the loss of alcohol in the process of distillation and determination in urine did not exceed 2 per cent. For the purposes of the investigation known quantities of various alcoholic liquors (wine, beer, whiskey, and rum) were consumed, the wine and beer being taken undiluted, the whiskey diluted with an equal volume of water, and the rum with an equal volume of milk.

From the results of the test experiments the conclusion is drawn that the amount of alcohol found in the urine and blood is a definite indication of the minimum quantity of liquor consumed and the alcoholic condition of the person.

The maximum elimination of alcohol in the urine takes place in 2 to 2½ hours. This opinion was based on the results of averaging the amount of liquor consumed and the time taken in the consumption. The factors given by Evans and Jones (ANALYST, **1929, 54**, 134) for the calculation of the amount of alcoholic liquor consumed from the alcohol-content of the urine at its maximum excretion apply reasonably well for a person weighing about 9 stone. For those weighing approximately 13 stone the factor should be increased in the ratio of 13 to 9. Of the alcohol consumed, approximately 2 to 3 per cent. is eliminated in the urine; apparently, persons of lower body weight eliminate a greater percentage for the same consumption of liquor. It is advisable to collect at least two samples of urine at approximately half-hourly intervals in order to form an opinion as to the minimum amount of alcohol consumed.

# British Standards Institution

## BRITISH STANDARD METHOD FOR THE DETERMINATION OF VISCOSITY OF LIQUIDS IN ABSOLUTE (C.G.S.) UNITS

This Standard Method (No. 188—1937), revised in May, 1937, has been approved by the Chemical Divisional Council and is published under the authority of the General Council. In earlier editions the term "viscosity" was used to connote "dynamic viscosity," but since the tube viscometers, described in this Standard, give indications of the kinematic viscosity rather than dynamic viscosity, it has become desirable that the results should be normally expressed in terms of kinematic viscosity. This is in agreement with a resolution carried at the World Petroleum Congress in London in 1933.

The Standard is published by the British Standards Institution, 28, Victoria Street, London, S.W.7. Price 2s. net, post free 2s. 2d.

## BRITISH STANDARD SPECIFICATION FOR GRADUATED PIPETTES AND STRAIGHT PIPETTES

The series of graduated pipettes (Type 1), calibrated for delivery from the zero mark to the graduation marks, includes the following sizes:

| | | | | | | |
|---|---|---|---|---|---|---|
| Total | capacity | 1 ml. | sub-divided | into | 0·01 ml. | intervals |
| ,, | ,, | 2 ml. | ,, | ,, | 0·02 ml. | ,, |
| ,, | ,, | 5 ml. | ,, | ,, | 0·05 ml. | ,, |
| ,, | ,, | 10 ml. | ,, | ,, | 0·10 ml. | ,, |
| ,, | ,, | 25 ml. | ,, | ,, | 0·10 ml. | ,, |

Capacity is defined as the volume of water at 20° C., expressed in ml., delivered by the graduated pipette at 20° C., when emptied, in the method specified, from the zero mark to the graduation mark.

British Standard Graduated Pipettes of Type 2, calibrated for delivery down to the jet, must conform with specified dimensions.

The specified method of emptying the pipette leaves a small quantity of water remaining in the jet, and no method of emptying, such as blowing out, which expels liquid completely from the jet, or increases the natural rate of delivery, should be used.

The pipettes in this series have a capacity of 1 ml., 9 ml. and 10 ml., and are calibrated for the delivery of water at 20° C.

Copies of the Specification can be obtained from the Publications Department, British Standards Institution. Price 2s. net, post free 2s. 2d.

## BRITISH STANDARD SPECIFICATION FOR DENSITY HYDROMETERS FOR USE IN MILK

This Specification (No. 734—1937) forms part of a series for scientific glassware. One basis of adjustment is adopted for these hydrometers, namely, that they shall indicate density, *i.e.* mass per unit volume, in g. per ml., at 20° C. in a liquid having a surface tension of 46 dynes per cm., instead of the customary practice of using hydrometers for testing milk adjusted to indicate sp.gr., S60° F./60° F. at 60° F. This brings the hydrometers into line with the B.S.I. Specification for Density Hydrometers No. 718—1936 (*cf.* ANALYST, 1937, 129).

Specifications are given for hydrometers of range 1·025 g./ml. to 1·035 g./ml. for use in normal milks, and for hydrometers of range 1·015 g./ml. to 1·025 g./ml. for use in milks of low density.

The following tables to be used in conjunction with hydrometers for use in normal milk are given in an appendix:—(1) Correction for scale errors in hydrometers. (2) Corrections to hydrometer readings to obtain density in g./ml. at the temperature of observation. (3) Corrections to obtain density of milk at 20° C. (4) Table for determination of percentage of total solids and percentage of non-fatty solids. (5) Use of the British Standard Hydrometers in the measurement of milk in bulk.

The Specification may be obtained from the Publication Department, British Standards Institution. Price 3s. 6d. net, post free 3s. 10d.

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

# Food and Drugs

**Colorimetric Determination of Lactic Acid in Milk and Milk Products.** **F. Hillig.** (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 130–140.)—The yellow colour produced in the reaction between ferric chloride and lactic acid (Williams, Muller and Neiderl, *Mikrochem.*, 1931, **9**, 268) may be used to determine the latter in milk and milk products. A serum is prepared by the addition of sulphuric and phosphotungstic acids and, although lactalbumin is not completely removed, the small amount present is not sufficient to cause foaming in the liquid extractor, which is of the type previously described (*J. Assoc. Off. Agr. Chem.*, 1933, **16**, 435), modified to take 50 ml. of liquid. Part of the citric acid in milk is extracted, but is completely removed by precipitation as barium citrate in an alcoholic medium. The extracted lactic acid is purified with active carbon which, under the controlled conditions, adsorbs only a constant small amount (about 7 per cent.) of the lactic acid present. The carbon used may be Nuchar W, Suchar, Darko G.60 or Carbex E, but not Norit A or animal charcoal, which adsorb greater amounts. Colour comparison may be made in Nessler glasses but, owing to the necessity for treating the standards with active carbon, the process is tedious, and measurement by means of a photometer is more rapid and accurate. The instrument recommended is that described by Clifford and Wichmann (*J. Assoc. Off. Agr. Chem.*, 1936, **19**, 130), used with a filter transmitting at about 450$m\mu$. A calibration curve is prepared by treating lithium lactate solutions, containing the equivalent of up to 12 mg. of lactic acid, with active carbon, as described in the process, and plotting the amount of lactic acid present against the photometer readings.

To prepare the standard lithium lactate, heat syrupy lactic acid, diluted with twice its volume of water, nearly to boiling-point, add lithium carbonate gradually until the solution is slightly alkaline to phenol red, re-acidify slightly, evaporate to crystallising point, add five volumes of alcohol and allow the liquid to stand over-night, after which the deposit is re-crystallised from water and dried at 100° C. The active carbon is purified by mixing 10 g. with 30 ml. of *N* hydrochloric acid and 200 ml. of water and agitating with a current of air on the steam-bath, after which the carbon is filtered off by suction and washed twice with 200-ml. portions of water. The ferric chloride solution used is a 1 per cent. solution in water containing 2·5 per cent. by volume of *N* hydrochloric acid. To 50 g. of milk (or 5 g. of dried milk with 50 g. of water, or 20 g. of cream or ice-cream made up to 50 ml. with water) add, with constant stirring, 6 ml. of *N* sulphuric acid, followed by 5 ml. (1 ml. for cream and 2 ml. for ice-cream) of a 20 per cent. phosphotungstic acid solution. Make the mixture up to 100 ml. with water, allow it to stand for several minutes and filter. Pipette 50 ml. of the serum into the inner tube of the extractor, add 0·5 ml. of dilute sulphuric acid (1 +1) and extract for two hours with 200 ml. of washed ether in which a thread is suspended to ensure even boiling. To the extract add 20 ml. of water and expel the ether on the steam-bath. Neutralise the aqueous residue to phenolphthalein with saturated

barium hydroxide solution, make up to about 90 ml. with alcohol, heat almost to boiling, cool, make up to 110 ml. with alcohol and filter. Evaporate 100 ml. of the filtrate to about 10 ml., add about 50 ml. of water and again evaporate to 10 ml. From a burette add 3·3 ml. of $N/10$ hydrochloric acid, make up with water to about 40 ml., add 200 mg. of active carbon and heat on the steam-bath for 10 minutes. After cooling the liquid, make up to 55 ml. and filter, pouring back until a bright filtrate is obtained. Transfer 10 ml. of the filtrate to a Nessler glass, add sufficient $N/10$ hydrochloric acid to bring the amount present to 3 ml., and make the mixture up to about 40 ml. with water. Place the Nessler glass in a jacket of black paper and add, from a burette, 5 ml. of ferric chloride solution, make up to 50 ml. with water and mix. Dilution is not permissible after the colour has developed. Fill a 4-in. cell, the walls of which have been painted black, with the solution, and read in the photometer. Determine the amount of lactic acid in the 10-ml. portion from the calibration curve and, if necessary, repeat the determination with an amount of solution which will not overstep the 12 mg. limit of lactic acid. If a photometer is not available, place 5 ml. of standard lithium lactate solution (1 ml. = 1 mg. of lactic acid) in a Nessler glass, add 3 ml. of $N/10$ hydrochloric acid, make up to about 40 ml. with water, wrap the glass in black paper, add 5 ml. of ferric chloride solution, dilute to 50 ml., and compare the colour with that of the 10-ml. portion of filtrate prepared as described above. If the colours do not match, repeat with a suitable amount of the standard solution. Having thus ascertained the approximate amount of lactic acid present, transfer a portion of the remaining filtrate, containing not more than 10 mg. of lactic acid, to a Nessler glass and produce the colour as described. Prepare a suitable series of standards, subjecting these to the active carbon treatment as described in the process.

To calculate the amount of lactic acid in the original sample, an allowance must be made for the volume of insoluble solids. For this purpose the sp.gr. of butter-fat is taken as 0·9 and that of casein as 1·3. If S is the volume of insoluble solids, A the aliquot portion taken for the final determination, and W the weight of the sample, the amount of material in the final aliquot part is

$$\frac{W}{100-S} \times \frac{50}{110} \times \frac{100}{55} \times A.$$

For butter, the general method is the same, but it is necessary to remove the fat. A 20-g. portion of butter is warmed on the steam-bath with 15 ml. of water and 0·5 ml. of $N$ sulphuric acid. The liquid is then neutralised with $N/10$ sodium hydroxide solution, and transferred with 15 ml. of water to a centrifuge tube. Ether (50 ml.) is added, the tube is gently shaken, and an equal amount of petroleum spirit is added. After centrifuging, the ethereal layer is removed by means of a siphon with a turned-up end, and the extraction is repeated with 25-ml. portions of the solvents. The aqueous layer is acidified with 3 ml. of $N$ sulphuric acid, warmed to expel ether, cooled and treated, drop by drop, with phosphotungstic acid solution. The mixture is made up to 100 ml. and filtered, and 50 ml. of the filtrate are transferred to the extractor. By this method the determination of 10 parts of lactic acid per million is possible. A. O. J.

**Colorimetric Determination of Lactic Acid in Tomato Products. F. Hillig.** (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 303–307.)—Bacon and Durbar (*U.S. Bur. Chem.*, Cir. 78) found that sound tomatoes contain little or no lactic acid, but that formation of this acid is associated in some instances with their spoilage. It may be determined by a modification of the author's method for the determination of lactic acid in milk (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 130; see preceding abstract). A 20-g. portion of tomato paste, catsup or chili sauce or a 40-g. portion of tomato juice is made up to 200 ml. with water and filtered. If filtration is slow, the liquid may be centrifuged and subsequently filtered with the aid of kieselguhr (Filtercel). A 50-ml. portion of the filtrate is transferred to a liquid extractor of the type previously described (*J. Assoc. Agr. Chem.*, 1933, **16**, 435) modified to take 50 ml., 1 ml. of dilute sulphuric acid (1 + 1) is added, and extraction with ether is continued for 3 hours. With catsup and other products containing acetic acid the extract, after removal of the ether, is made up to 50 ml. and distilled in steam until 250 ml. of distillate have been collected. The residue is then free from acetic acid. The extract after removal of the solvent is dissolved in 20 ml. of water, neutralised to phenolphthalein with saturated barium hydroxide solution, transferred to a 110-ml. flask with alcohol, and made up to the volume with alcohol, and 100 ml. are filtered. The procedure is then exactly as described (*loc. cit.*) with the exception that a filter transmitting at 460$m\mu$ is used in the photometer. To test the accuracy of the method, varying amounts ranging from 1 to 75 mg. of lactic acid as lithium lactate were added to tomato juices of good quality. By this method 93 to 99·9 per cent. of the lactic acid added was found. For catsup and other products containing acetic acid and necessitating steam distillation, the lactic acid found was 93·6 to 98·7 per cent. of that added. The lactic acid found in 13 samples of authentic tomato juice varied from 3·3 to 8·0 mg. per 100 g. In six samples of commercial catsup 23·6 to 28·4 mg. per 100 g. were found. Two samples of tomato paste gave 19·8 to 25·4, one sample of pulp 5·5, and two samples of chili sauce 21·2 and 27·2 mg. per 100 g. In the results quoted in the paper the small amounts of lactic acid, found in samples to which none had been added, are interpreted as material reacting as lactic acid under the conditions of the method of analysis. A. O. J.

**Chemical Composition of Avocado Fruits. A. R. C. Haas.** (*J. Agric. Res.*, 1937, **54**, 669–687.)—The acidity and contents of fat, sugar, and minerals in different parts of avocado fruits were determined. The acidity of the pulp decreases from *p*H 6·44 in the outer portion of the tip to *p*H 6·86 in the inner portion of the stem-half of the fruit. The fat showed no local accumulation and varied in fruits of different varieties and ages from 1·73 per cent. of the fresh weight to 28·87 per cent.; the fat-content increases with increasing maturity. The total and reducing sugar-contents of the stem-halves (0·65 to 2·05 per cent. of the fresh weight and 0·54 to 1·48 per cent., respectively) were slightly higher than those of the tip-halves (0·52 to 1·74 per cent. and 0·29 to 0·84 per cent., respectively) in unripe fruits and decreased with increasing maturity, the difference between the contents of tip- and stem-halves also decreasing with ripening. The percentage of dry matter on the fresh weight is usually higher in the tip-halves than in the

stem-halves, some figures for fruits of different varieties being 21·34, 12·37, 12·81, and 14·12 per cent. in the tip-halves, as compared with 20·74, 11·73, 12·03, and 13·24 per cent. in the stem-halves; the dry matter increases with increasing maturity. The ash (3·40 to 4·75 per cent. on the dry substance) is higher in the tip-halves than in the stem-halves. Potassium is the most abundant constituent of the ash. The percentages of potassium, manganese, copper, and nitrogen (including nitrates) are higher in the tip- than in the stem-halves, calcium, total sulphur and total chlorine being more abundant in the stem-halves. Sodium and iron are present but show no local accumulation. The content of sodium increases and the contents of inorganic phosphate and manganese decrease with increasing maturity. E. M. P.

**Sugar as an Inhibitor of Corrosion in Canning. H. C. S. de Whalley.** (*Chem. and Ind.*, 1937, **56**, 569–570.)—The Food Investigation Special Reports Nos. 40 (ANALYST, 1931, **56**, 315), and 44 (ANALYST, 1936, **61**, 193) of the Department of Scientific and Industrial Research showed that crude beet and cane sugars have greater inhibiting effects on the corrosion of iron than have the refined sugars, the effect being greater with raw beet sugar than with raw cane sugar. Inhibiting effects of different samples of some kinds of sugar varied considerably, which suggests that the inhibiting substances are breakdown products or other impurities. Refined sugars with inhibiting action usually gave pale yellow solutions. Treatment with alumina cream or decolorising carbons lessened inhibiting action; extraction of raw beet sugar with alcohol gave a dark brown sticky mass with a powerful inhibiting effect. The following are analyses of some raw beet sugars of good grade:

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Polarisation .. .. .. | 98·00 | 98·40 | 98·67 | 98·25 | 98·05 |
| Invert sugar, per cent. .. | — | — | — | — | — |
| Ash, per cent. .. .. .. | 0·36 | 0·27 | 0·29 | 0·41 | 0·37 |
| Moisture, per cent. .. .. | 0·95 | 0·79 | 0·72 | 0·85 | 0·88 |
| Undetermined .. .. | 0·69 | 0·54 | 0·32 | 0·49 | 0·70 |

Refined white sugar (Pure Gran from Tate & Lyle carton) gave the following results: Polarisation (or sucrose), 99·956; invert sugar, 0·006; ash, 0·006; water, 0·020; organic matter, 0·012.

The ash and undetermined substances in the raw beet sugars would include the inhibitor. Spectrographic analysis of the same sugars indicated the following amounts of metals in parts per million:

| | Raw beet sugars | | | | | Refined white sugar |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | |
| Copper .. .. | 4·0 | 3·6 | 4·2 | 5·9 | 4·1 | 0·1 |
| Lead .. .. | 3·2 | 2·4 | 3·2 | 4·5 | 0·4 | 0·1 |
| Manganese .. | 4·0 | 3·0 | 3·2 | 4·5 | 4·1 | 0·05 |

The inhibitive effect may be due to the presence of these traces of metals, which would be picked up by the sugar juices and liquors in contact with metallic apparatus. E. M. P.

**Physical and Chemical Properties of Casein Fat. S. G. Stevenson and A. L. Bacharach.** (*Biochem. J.*, 1937, **31**, 721–723.)—The fat in lactic-acid casein is between 1·0 and 2·5 per cent., and it may be extracted with hot 95 per cent. alcohol. The ethereal extract of the residue obtained by evaporating the alcoholic extract of a New Zealand casein was a yellow fat, which was examined in order to ascertain if hydroxystearic anhydride previously reported by Kon and Funk (*Biochem. J.*, 1924, **18**, 1238) was present. This compound was not found, and the results obtained indicated a slightly modified butter-fat. Although the gross difference between this fat and butter-fat was not great, it was found that the total unsaponifiable matter had increased threefold, and that the liquid portion had been even more concentrated than the sterol fraction. S. G. S.

**Fatty Acids Associated with Banana Starch. L. Lehrman and E. A. Kabat.** (*J. Amer. Chem. Soc.*, 1937, **59**, 1050–1051.)—Dried pulp from green bananas could not be used directly for the estimation, since some naturally occurring substance made the dried residue after hydrolysis difficult to pulverise. Banana starch was therefore isolated, and to make sure that any fatty acids found were not present extraneously, the starch was extracted with alcohol before use. The aqueous filtrate from the hydrolysis was tested for glycerol, and the result proved that glycerides were not the source of the fatty material. The amount of fatty acids liberated by hydrolysis of banana starch was then found to be 0·2 per cent. and consisted of a light yellow semi-solid with iodine value 59·4. The acids were a mixture of palmitic, oleic, linolic and linolenic, with a very small amount of phytosterol, this being the first time that phytosterol has been found combined in a starch. The bromination method was found more effective than oxidation for the detection of the small amounts of linolenic acid in the presence of oleic and linolic acids. D. G. H.

**Seeds of *Cichorium intybus*, Linn. R. N. Mistra and S. Dutt.** (*J. Indian Chem. Soc.*, 1937, **14**, 141–143.)—*Cichorium intybus* (chicory or Kasni in Hindustani) Nat. Order, *Compositae*, is found in north-west India and its seeds, reputed to be tonic, demulcent and cooling, are used in Indian medicine. The plant is prescribed very much as *Taraxacum* (dandelion) is in Europe. The seeds examined contained oil 4·7 per cent.; phlobaphenes 1·0; and tannin 1·0; also reducing sugars. They yielded 13·8 per cent. of ash (17·5 per cent. soluble and 82·5 per cent. insoluble in water), consisting mainly of potassium, sodium (traces), calcium, aluminium, sulphate, phosphate, chloride, carbonate and silica. The oil, as extracted with benzene, had the consistence of honey and gave the following analytical figures:—Sp.gr. at 22° C. 0·9229; $n^{30}$, 1·3795; solidifying pt., — 11° C.; saponification value, 193·1; iodine value, 95·6; acetyl value, 14·8; Hehner value, 93·9; unsaponifiable matter, 1·7 per cent. The fatty acids melted at 35 to 38° C. and had sp.gr. at 40° C. 0·8931; neutralisation value, 192·5; mean molecular wt. 291·4; iodine value, 104·8. They consisted of 21·7 per cent. of saturated and 78·3 per cent. of unsaturated acids. The unsaturated acids consisted of 42·8 per cent. of oleic and 57·2 per cent. of linolic acid, and the saturated acids after esterification and fractional distillation were shown to consist of palmitic and stearic acids. The unsaponifiable matter contained sterol. D. G. H.

**Philippine Curcas Nut Oil. A. O. Cruz and A. P. West.** (*Philippine J. Sc.*, 1936, **61**, 437–444.)—The Curcas or Physic nut is the seed of the small tropical American tree, *Jatropha curcas*, which is grown in other countries, including the Philippine Islands, as a hedge plant. The seeds are enclosed in rounded capsules. The general characters of the oil have been determined by various investigators, but data on the composition of the oil are meagre and contradictory. The present sample, collected from the Pampanga Province, Luzon, consisted of 34·3 per cent. of hulls and 65·7 per cent. of kernels. The kernels had a moisture-content of 20 per cent., and the yield of oil on extraction with ether was 38·2 per cent. of the dry seeds. After the crushed kernels had been cold pressed the resulting oil cake (which cannot be used as a cattle food owing to the presence of a toxic purgative substance) consisted of:—Moisture, 6·63; oil, 14·4; protein, 49·90; crude fibre, 3·45; ash, 8·87; carbohydrate (by diff.), 17·01 per cent. The fertiliser constituents in the cake were nitrogen, 8·23; phosphoric anhydride, 4·71; potash, 0·25 (moisture, 8·05 per cent.). The oil had the following characteristics:—Sp.gr. at 30°/4° C., 0·9082; $n_D^{30}$, 1·4665; saponification value, 192·4; iodine value (Hanus), 94·8; acid value, 5·1; unsaponifiable matter, 0·45 per cent.; saturated acids (corr.), 16·82 and unsaturated acids (corr.), 78·00 per cent., the latter of iodine value, 111·0. The unsaturated acids consisted of linolic acid, 22·9, and oleic acid, 77·1 per cent. The saturated acids, the proportions of which were calculated from data of analyses of the fractions obtained by distilling the methyl esters, were myristic, 2·56; palmitic, 67·14; stearic, 28·81; arachidic acid, 1·49 per cent. The percentage composition of the whole oil (as glycerides of the acids) was: oleic, 62·86; linolic, 18·65; myristic, 0·45; palmitic, 11·84; stearic, 0·26; arachidic, 0·26 per cent. D. G. H.

**Philippine Tobacco Seed Oil. A. O. Cruz and A. P. West.** (*Philippine J. Sci.*, 1936, **61**, 161–168.)—The tobacco seeds examined were a mixture of the Vizcaya and Espada varieties from plants grown in the Cabagan and Cagayan districts. The ground seeds were extracted with ether and the oil, after treatment with kieselguhr, Suchar and talcum powder, was of a light yellow colour. The yield was 39·92 per cent. of the dry seeds and the analytical figures were:—Sp.gr. at 30/4° C., 0·9130; $n_D^{30}$, 1·4714; saponification value, 190·5; iodine value (Hanus), 135·8; acid value, 16·8; unsaponifiable matter, 1·41 per cent. The saturated acids were (corr.) 9·99 and the unsaturated acids (corr.) 82·87 per cent. of the total fatty acids; the iodine value of the unsaturated acids was 153·6. The fatty acids were separated by the lead salt and ether method. Analyses of the fractions obtained by distillation of the methyl esters from the saturated acids showed the acids to consist of myristic, 0·49; palmitic, 67·08; stearic, 29·10; arachidic, 3·33 per cent. The unsaturated acids consisted of 69·55 per cent. of linolic and 30·45 per cent. of oleic acid. The oil is thus a semi-drying oil similar to kapok and cottonseed oils and appears to be suitable for the same purposes.

D. G. H.

**Green Turtle Oil. M. Tsujimoto.** (*J. Soc. Chem. Ind. Japan*, 1937, **40**, 185–186B.)—A specimen of green turtle oil from *Chelonia japonica*, Thunberg, from the Bonin islands, consisted of a mixture of body and liver oils, and was an

orange-yellow liquid, showing a deposit at ordinary temperature. Very little colour was given with the antimony trichloride test, and in the Tortelli–Jaffé test an orange-yellow colour developed without green fluorescence. The analytical figures for the oil were as follows, and agreed with those obtained by Lee for African turtle oil (ANALYST, 1935, **60**, 650): sp.gr. at 20°/4° C., 0·9150; $n_D^{20}$, 1·4662; saponification value, 205·8; iodine value (Wijs), 64·1; acid value, 1·36; unsaponifiable matter, 0·52 per cent. The fatty acids melted at 28–29° C. and had neutralisation value 211·4 and iodine value 65·8. The ether-insoluble (5.0 per cent.) and petroleum spirit-insoluble (7·6 per cent.) bromides were isolated and the proportion of bromine present determined. The fatty acids were converted into their methyl esters and fractionally distilled, and the fractions were examined for their component acids. The chief constituent was oleic acid, and myristic, palmitic and stearic acids were also present, with a small proportion of the highly unsaturated acids $C_{20}$ and probably $C_{18}$. The proportion of myristic acid was fairly large and lauric and possibly zoomaric (palmitoleic) acids were present. Dodecenoic and tetradecenoic acids were not identified with certainty. The oil differs from most marine animal oils in the comparative lack of $C_{20}$ and $C_{22}$ acids. The presence of cholesterol in the unsaponifiable matter was confirmed. D. G. H.

**Observations on the Chemical Determination of Adrenaline. J. Devine.** (*Biochem. J.*, 1937, **31**, 545–550.)—The variations in the estimation of adrenaline by the Folin method have been found to be due to the ascorbic acid present and to the *p*H at which the colour is developed. The ascorbic acid causes high values to be obtained, and an incorrect *p*H value may cause low values to be recorded. These sources of error may cancel one another, so that a determination may be in good agreement with the pressor assay. If the amount of ascorbic acid is determined and the Folin value corrected for this, the results agree well with those obtained in iodine determination of adrenaline and also with the pressor assay. The previously observed, but unidentified catechol compound, which is also present in the suprarenal gland, does not give a colour on oxidation, has little or no pressor activity, and does not affect the Folin reagent. Apart from this compound, the claim that an adrenaline precursor exists in the gland is not confirmed. S. G. S.

**Hydnocarpic and Chaulmoogric Acids and Ethyl Esters. H. I. Cole and H. Cardoso.** (*J. Amer. Chem. Soc.*, 1937, **59**, 963–965.)—Pure chaulmoogric acid may best be prepared from the oil of *Oncoba echinata* or *Hydnocarpus alcalae*, for these oils do not contain hydnocarpic acid, but since no oil is known that contains hydnocarpic but not chaulmoogric acid, to prepare hydnocarpic acid it must be separated from chaulmoogric acid. This may be done successfully by employing a combination of fractional vacuum distillation of the ethyl esters in a high-temperature fractionating apparatus, and fractional crystallisation of the free fatty acids separated from the esters. The free fatty acids from *Hydnocarpus Wightiana* oil were obtained, washed in hot water, solidified, re-melted, esterified with 99 per cent. ethyl alcohol and, after standing overnight, treated with an equal volume of water. The ester was extracted with ethyl ether and washed, and free

acids were removed with a 10 per cent. solution of sodium carbonate. The ethereal solution was washed with water, dried with calcium chloride, filtered and evaporated. The ethyl esters were distilled at 10 mm. pressure; one fractionation separated the ethyl hydnocarpate from the chaulmoograte, though not from the other solid and liquid acids. The fractions were separated and, after dilution with hot water, an excess of 15 per cent. sulphuric acid was added; the liberated fatty acids were washed four times with hot water, and crystallised to constant m.p. and optical rotation from 80 per cent. alcohol. The specific rotation of the crystals was found to be a more sensitive indication of purity than the m.p. Crystals of pure hydnocarpic and of pure chaulmoogric acids grow upward in branching forms from the melted acids as they solidify, and even a small proportion of impurity inhibits this growth, yielding instead a flat surface. Further re-distillation of the esters of the acids and crystallisation caused no change in the constants.

| | Hydnocarpic acid | Chaulmoogric acid | Ethyl hydnocarpate | Ethyl chaulmoograte |
|---|---|---|---|---|
| M.p. °C. .. .. .. | 60·5 | 68·5 | — | — |
| B.p. °C. (10 mm.) .. .. | — | — | 184 | 206 |
| $[\alpha]_D^{25}$ .. .. .. | 69·3 | 60·3 | 61·94 | 55·42 |
| Sp.gr. 20°/4° C. .. .. | — | — | 0·911 | 0·904 |
| 25°/4° C. .. .. | — | — | 0·907 | 0·901 |
| 30°/4° C. .. .. | — | — | 0·904 | 0·898 |
| $n_D$ 20° .. .. .. | — | — | 1·4597 | 1·4610 |
| 25° .. .. .. | — | — | 1·4578 | 1·4592 |
| 30° .. .. .. | — | — | 1·4558 | 1·4573 |
| Iodine value (Hanus) .. | 100·7 | 90·5 | — | — |
| Neutralisation equivalent | 251·8 | 280·9 | — | — |

Even a small percentage of palmitic acid lowered the m.p. of hydnocarpic acid to a surprising degree; the m.p. curve is given. Mixtures of the two pure acids (chaulmoogric and hydnocarpic) were made up and the m.p. curve was plotted; the mixture of lowest m.p. was not at the point of a molecular mixture, but the mixtures of the acids showed a very sharp drop in m.p. and a loss of the characteristic crystalline forms of the pure acids. The very high specific optical rotation makes this value a particularly useful means of determining the purity of the acids, and if an electric sodium lamp is used in conjunction with a precision polarimeter different observers can agree with each other to within ± 0·02°. Recorded values for $[\alpha]_D$ of chaulmoogric acid are often too high on account of admixture with a small proportion of the more optically active hydnocarpic acid.

D. G. H.

**New Colour Reaction for Morphine and its Derived Alkaloids. M. Pesez.** (*J. Pharm. Chim.*, **1937**, **25**, 504–508.)—The reactions of Froehde, Mandelin, Erdmann and Denigès and other reactions commonly used for the identification of morphine have the disadvantages that they are not absolutely specific for morphine and that they do not yield permanent colours. The following reaction, depending upon the action of nascent bromine, is free from these disadvantages. Morphine or one of its salts (0·1 to 0·2 g., or 3 or 4 drops of an aqueous solution) is added to 2 ml. of conc. sulphuric acid in a test-tube, and the

mixture is shaken until the solid matter is dissolved. Two drops (0·1 ml.) of a 10 per cent. potassium bromide solution are added, and the test-tube is placed in a boiling water-bath for 3 minutes. The yellow colour (due to free bromine) changes to yellowish-brown and finally to deep yellowish-green. When cold, the mixture is carefully diluted to about 20 ml. with water. A fine emerald-green colour is formed with 0·1 g. of morphine, and a paler green with smaller amounts. The colour is due to a green water-insoluble compound, which ultimately separates as a green precipitate, the separation being accelerated by boiling. The coloured substance is soluble in the following solvents, forming coloured solutions:—Xylene (blue), chloroform (bluish-green), ether (pale blue), benzene and ethyl acetate (violet-blue) and in methyl and ethyl alcohols and acetone (greenish-blue). It may be extracted by any of the above-mentioned solvents that are immiscible with water. By re-crystallisation from alcohol, fine needle-shaped crystals or stellate groups of needles are obtained. From its solution in acetone the compound separates as an amorphous powder. The bluish-green solution in chloroform exhibits a wide absorption band in the orange-yellow region of the spectrum. Saturated bromine water may be used instead of potassium bromide, but the reaction is not given when solutions of chloride, iodide, bromate or hypochlorite are used. Codeine, dionine and heroin give the reaction. Thebaine dissolves in cold sulphuric acid, giving an orange solution which, on the addition of potassium bromide and heating on the water-bath, changes to yellowish-brown and, on dilution, to a fine green. The solution obtained by extraction with chloroform is slightly different from that obtained with morphine, its colour being nearer blue. Narcotine gives a red colour before dilution, but the colour disappears on the addition of water. Narceine gives a golden-yellow solution changing to pale yellow and finally to orange-red, and this disappears on dilution. Apomorphine gives a solution of wine colour intensified by heating on the water-bath, but disappearing on dilution. Papaverine gives only the yellow colour of free bromine. The other alkaloids with an oxyphenanthrene structure, such as colchicine and hydrastine, do not answer to the test. Other alkaloids and glucosides which have been tested give colours ranging from yellow to brown before dilution and either colourless solutions or white precipitates on dilution. The reaction is given by the mixed alkaloids of opium (pantopon, etc.). Scopolamine, which gives a negative reaction and sometimes occurs with morphine in preparations for injection, does not interfere with the test. The reaction is affected by the presence of some compounds, and it is usually necessary to separate morphine by extraction with chloroform from a solution rendered alkaline by ammonia. The possibility of the adaptation of the reaction to the quantitative determination of opium and morphine is being investigated. A. O. J.

**Lipids of "Russian" Cantharides (*Lytta vesicatoria* Fb.). M. M. Janot and P. Faudemay.** (*Bull. Soc. Chim.*, 1937, **4**, 1149–1151.)—The constitution of the lipids of cantharides has scarcely been studied since Gossman's results (*Ann. Chem. Pharm.*, 1853, **86**, 317–330; 1853, **89**, 123–125) were published. Preliminary tests on five samples of *Lytta vesicatoria* of different origin, gave the following results:

| No. | Origin | Moisture Per Cent. | Ash Per Cent. | Lipids Per Cent. | Cantharidin Per Cent. |
|---|---|---|---|---|---|
| 1 | Russia | 6·8 | 6·5 | 13·5 | 0·70 |
| 2 | Russia | 6·4 | 9·9 | 3·5 | 0·46 |
| 3 | Russia | 9·3 | 9 | 4·2 | 0·40 |
| 4 | Spain | 9·3 | 5·5 | 12·7 | 0·45 |
| 5 | Roumania | 8·8 | 7 | 9·3 | 0·45 |

The lipids were extracted with petroleum spirit of b.p. 30–50° C. For a full analysis, for which only samples 1 and 2 were available in sufficient quantity, petroleum spirit of b.p. 50–70° C. was used. The residual fat was then extracted with ether. The fats from both samples consisted of free palmitic, stearic, oleic, linolic, and linolenic acids, their glycerides, and compounds of these acids with sterols. In the unsaponifiable matter the following were detected:—Cholesterol, a second sterol which was not identified, and two hydrocarbons, one of which was heneicosane $C_{21}H_{44}$. While Nos. 1 and 2 were qualitatively identical, quantitatively they differed greatly. In No. 1, the composition of the ethereal extract after separation of chlorophyll and cantharidin was practically the same as that of the petroleum spirit extract, and results for the whole derivatives, expressed as free fatty acids, were:—Palmitic, 37; stearic, 4; oleic, 32; linolic, 6, and linolenic acid, 3 per cent.; unsaponifiable matter, 10; undetermined, 8 per cent. The free acids form 65 per cent. of the total fatty matter. No. 2 gave the following results for the two extracts:—

| Petroleum spirit extract | Per Cent. | Ethereal extract | Per Cent. |
|---|---|---|---|
| Saturated acids .. .. .. | 36 | Saturated acids .. | 19 |
| Unsaturated acids .. .. | 29 | Unsaturated acids .. | 44 |
| Unsaponifiable and neutral products of saponification .. | 32 | Unsaponifiable .. | 16 |
| | | Chlorophyll .. .. | 12 |
| Undetermined .. .. .. | 3 | Undetermined .. | 9 |

These important quantitative variations indicate that this beetle cannot be classified physiologically by the fat constants or the percentage of lipids. Some of the methods of separation are described and the constants of the different constituents are given. E. B. D.

# Biochemical

**Chemical Composition of Teeth. V. Spectrographic Analysis. F. Lowater and M. M. Murray.** (*Biochem. J.*, 1937, **31**, 837–841.)—Spectrographic examination, particularly for "trace elements," has been made of human enamel and dentine, dog dentine and rats' teeth, over the range 210$m\mu$ to 620$m\mu$. Special consideration was given to the identification of fluorine, and the specimens analysed included "mottled teeth" from Maldon, Essex, and teeth from rats fed on a fluorine-containing diet. In addition to the major constituents known to be present in dental tissues, the following elements were found in all samples: sodium, silver, lead, strontium, barium, chromium, tin, zinc, manganese, titanium, nickel, vanadium, aluminium, silicon, boron, copper and iron. Teeth of normal dogs and rats do not contain fluorine, but in human teeth from London there was a "possible trace"; there was a definite trace in the human "mottled teeth" and a

considerable amount in the fluoride-fed rats' teeth. Potassium was present in the enamel and dentine of "mottled teeth" and in the teeth of rats fed on a diet containing fluorine, but was not found generally. The teeth of fluoride-fed rats contain less iron than those of the normal animal. S. G. S.

**Quantitative Method for the Isolation of *l*-Cystine from Keratin (Horsehair). A. Weidinger.** (*Rec. Trav. Chim. Pays Bas*, 1937, **56**, 562–564.)—The fat-free sample is heated for 8 hours on a sand-bath under a reflux condenser with a 4-fold volume of 20 per cent. hydrochloric acid, and most of the acid is then removed under reduced pressure at 60° C. A sufficient quantity of sodium acetate crystals is added to the warm solution to bring the *p*H to about 4·0, bromophenol blue being used as indicator, and after 4 days the resulting precipitate is separated by filtration and dissolved in 4 per cent. hydrochloric acid. This solution is decolorised with phosphate-free animal charcoal, which should previously have been boiled with 25 per cent. hydrochloric acid and washed well. The cystine adsorbed on the charcoal is extracted by boiling the mass three times with 4 per cent. hydrochloric acid. The extracts are filtered and evaporated to a small volume on the water-bath under reduced pressure, after which a warm 100 per cent. solution of sodium acetate and an equal volume of acetone are added. After 2 days at room temperature the precipitated cystine is collected in a weighed Gooch crucible, washed with cold water, dried at 95° C. and weighed. The important features of the method are:—(1) The period of initial hydrolysis, which is adjusted so as to obtain complete hydrolysis of the cystine without racemisation. (2) The complete removal of cystine from the activated carbon by heating it three times with acid. (3) The adjustment to the correct *p*H for precipitation. (4) The use of reduced pressure during evaporation to avoid decomposition of the cystine. (5) The use of acetone as an aid to precipitation. Horsehair was found to contain 12·5 per cent. of cystine ($[\alpha]_D$ — 206°; sulphur-content, 26·5 per cent.) as compared with the maximum value of 8 per cent. found by previous methods. Since the sulphur-contents calculated from the cystine-content and found in the horsehair were 3·32 and 3·45 per cent., respectively, the isolation of the cystine must have been almost complete. It has been stated recently that up to 5 per cent. of methionine occurs in wool and in the skin of cattle, but the above-mentioned results and the fact that the filtrate after hydrolysis is free from sulphur, indicate that this substance is not present in horsehair. J. G.

**Fat Metabolism in Fishes. XI. Specific Peculiarities in Depot Fat Composition. J. A. Lovern.** (*Biochem. J.*, 1937, **31**, 755–763.)—Specific peculiarities in the composition of fatty acids from the fats of certain species and families of fish have been reported from time to time. It has also been shown that the fats from fresh-water fish form a type distinct from those of marine fish. This difference is found to be due to the fat ingested by the species. In certain fish the degree of average unsaturation of one or more of the acid groups may be characteristically abnormal. In *elasmobranch* fish, for example, certain acids may be either unusually saturated or unusually unsaturated, and it is suggested that both types of peculiarity may be due to the appropriate modification of a reversible hydrogenation—dehydrogenation enzymic system. In some instances the acids

of the relatively saturated type are accompanied by chimyl, batyl and selachyl alcohols, and it is further suggested that these have been produced by different modifications of the hydrogenation system. The unsaturation aspect of the peculiarities is shown by halibut and turbot. Certain fish show a regular abnormality in the proportions of their various fatty acids. Acids having a lower molecular weight are either reduced or increased, with a corresponding increase or reduction of the higher acids. Instances of this type are certain *elasmobranch* fish, halibut and turbot. The molecular size may control this type of irregularity. Other fish may exhibit peculiarities of an irregular nature, the content of a certain acid or acids being increased or decreased without reference to other acids. Ratfish and catfish have a high content of $C_{18}$ acids and in the tunny $C_{14}$ acids are virtually absent. A compromise may occur when the two opposing sets of requirements are found in the same fish. In the brown trout, for instance, the characteristics of the *Salmonidae* family clash with the fresh-water habitat of the fish, and in the lampern, sea-feeding and fresh-water feeding by the same animal to some extent neutralise one another in their effect on the fat. S. G. S.

**Bromine Value of Urines. M. B. Drevon and J. Hagopian.** (*J. Pharm. Chim.*, 1937, **25**, 244–254.)—The bromine value of urine, first proposed by Bezssonoff, Vallette and Sacrez (*Bull. Soc. Chim.*, 1935, **17**, 1573) as an indication of a normal physiological condition, has been the subject of a critical investigation by the present authors. In a carefully controlled experiment the volume of urine excreted, the density, the bromine value, the dry residue, the total nitrogen, the nitrogen by formol titration and the ratio of the bromine value to the residue were determined, but no significant relationship was found. For a normal man, for a man after vaccination with typhoid-paratyphoid vaccine, for a normal guinea-pig and for a guinea-pig poisoned with benzene or dinitrophenol, the variation in the bromine value was comparable with that of the density or the dry residue. The authors therefore conclude that the bromine value has no apparent physiological significance. S. G. S.

**Carotene of Milk-fat. A. E. Gillam and M. S. El Ridi.** (*Biochem. J.*, 1937, **31**, 251–253.)—Early experiments on the chromatograph adsorption of carotene from milk-fat indicated that α- as well as β-carotene might be present. More recent work has shown that with repeated adsorption β-carotene changes into an α-carotene-like compound (*pseudo*-α-carotene). In the present investigation purified carotene from a mixed sample of colostrum and ordinary milk-fat has been found by analyses, melting-point, absorption spectra and optical rotation to be practically pure β-carotene. α-Carotene was either absent altogether, or was present in amounts less than 0·3 per cent. of the total carotene. S. G. S.

**Ascorbic Acid Content of a Number of Citrus Fruits. E. P. Daniel and M. B. Rutherford.** (*J. Agric. Res.*, 1937, **54**, 689–693.)—Ascorbic acid values were determined by the method of Bessey and King (*J. Biol. Chem.*, 1933, **103**, 687–698; Abst., ANALYST, 1934, **59**, 122) on the following freshly picked citrus fruits: 8 varieties of oranges, 3 of grape-fruit, 2 of tangerines, 8 of tangelos (grape-fruit-tangerine hybrid), and one each of tangor (tangerine-orange hybrid), lemon,

lime, limequat (lime-kumquat hybrid), orangequat (tangerine-kumquat hybrid), and Perrine lemon (lemon-lime hybrid). The results obtained were as follows:

| | Ascorbic acid content of juice, mg. per ml. |
|---|---|
| Orange (*Citrus sinensis*) | 0·32–0·62 |
| Grape-fruit (*C. grandis*) | 0·64, 0·33–0·38 |
| Tangerine (*C. nobilis deliciosa*) | 0·18–0·37 |
| Tangelo (*C. nobilis deliciosa* × *C. grandis*) | 0·18–0·64 |
| Tangor (*C. nobilis* × *C. sinensis*) | 0·40 |
| Lemon (*C. limonia*) | 0·33 |
| Lime (*C. aurantifolia*) | 0·22 |
| Limequat (*C. aurantifolia* × *Fortunella japonica*) | 0·17 |
| Orangequat (*C. nobilis* × *F. japonica*) | 0·23 |
| Perrine lemon (*C. aurantifolia* × *C. limonia*)— | |
| Fresh picked | 0·40 |
| Picked in ripe-yellow stage and stored in cold storage Oct. 23—Dec. 19 | 0·24 |
| Picked in light-green stage and stored in cold storage Oct. 23—Dec. 19 | 0·26 |

E. M. P.

**Ascorbic Acid Oxidase. W. Stone.** (*Biochem. J.*, 1937, **31**, 508–511.)—A number of vegetables and fruits have been examined for (*a*) their ascorbic acid content by extraction with 10 per cent. metaphosphoric acid, (*b*) the ascorbic acid of their expressed juices, before and after treatment with hydrogen sulphide, (*c*) the activity of the expressed juices in oxidising the ascorbic acid of orange juice, with a view to determining which, if any, contained an ascorbic acid oxidase. The vegetables which lost their indophenol-reducing power on mincing (banana, cabbage, carrots, cucumber, potato, string beans and vegetable marrow) were able to oxidise the ascorbic acid of orange juice, thus showing an ascorbic acid oxidase to be present. Those which retained their ascorbic acid content (cantaloupe melon, green peas, lettuce, lucerne, onions, spinach, and water melon) had no effect on orange juice and hence had no oxidase. The enzyme catalysed the reversible oxidation of ascorbic acid to dehydro-ascorbic acid, a recovery of 100 per cent. being obtained by hydrogen sulphide treatment, and acted equally well on the natural ascorbic acid of orange juice and on synthetic ascorbic acid. Dehydro-ascorbic acid was apparently not present in the intact vegetable, but was formed only when a cut or crushed vegetable containing the enzyme was exposed to air. The presence of a stabilising system for ascorbic acid, as proposed by McHenry and Graham, is not necessary, for those juices which retain their vitamin do not have any oxidase. The use of strong acids for the extraction enabled the true vitamin *C* content of the foodstuff to be obtained. If, however, the enzyme was given time to act before the acid was added, the vitamin was oxidised.

S. G. S.

**Crystalline Vitamin $D_4$. A. Windaus and G. Trautmann.** (*Hoppe-Seyler's Z. phys. Chem.*, 1937, **247**, 185–188).—Another antirachitic vitamin ($D_4$) has been prepared in the pure crystalline condition; the provitamin was 22-dihydro-ergosterol. Attempts to prepare this vitamin by hydrogenation of the

compound of calciferol with maleic anhydride were unsuccessful, but irradiation of 22-dihydro-ergosterol gave a mixture from which vitamin $D_4$ was isolated by means of its *m*-dinitrobenzoate. The authors believe that this vitamin is related to 22-dihydroergosterol in exactly the same way as calciferol is related to ergosterol. The dinitrobenzoate melted at 135° to 136° C. (uncorr.) and had $[\alpha]_D^{18°} = +94{\cdot}5°$ in acetone. The vitamin itself had m.p. 107° to 108° C. and $[\alpha]_D^{18°} = +89{\cdot}3$ in acetone, and showed a characteristic absorption band at $265m\mu$ with an absorption coefficient almost equal to that of calciferol. Ultimate analyses of the vitamin and its esters gave practically theoretical results. S. G. S.

# Toxicological

**Arsenic in a Well Water. J. Wyllie.** (*Canadian Public Health J.*, 1937, **28**, 128–136).—In 1922 a well was drilled to a depth of 94 feet through "red rock" (a sandy limestone stratum) to supply a farm near Madoc, Ontario, with water. As the result of drinking the water there have been several cases of chronic arsenic poisoning among the occupants of the farm. The original farmer was frequently ill and was treated for anæmia; even yet he has hyperkeratosis of the palms of his hands. In 1927 the farm was sold, and the new owner became ill, and in 1932 he was diagnosed to be suffering from nephritis, although signs of arsenic poisoning were present. He died two months later, and his brother took over the management of the farm. After two years both this brother and his sister-in-law, who had remained on the farm as housekeeper, became ill. The woman consulted a heart specialist, who diagnosed chronic arsenic poisoning, and in June 1935, the farmer underwent an operation for appendicitis. After a short period of convalescence he resumed work on the farm and very soon his former gastro-intestinal symptoms recurred. Becoming suspicious of the well water he sent samples to the Central Laboratory of the Ontario Department of Health for bacteriological and chemical analysis. The report showed that the water contained 7/10 grain of arsenic (as arsenious oxide) per gallon. An investigation of the probable source of arsenic was then made, and it was found that samples of the limestone stratum, through which the well had been drilled, contained up to 15 p.p.m. of arsenic (as $As_2O_3$). A thin section of the limestone, examined microscopically, showed interlocking granules of calcite with small brownish particles in the sutures between the granules, and at intervals small aggregates of similar brownish particles without definite boundaries between them and the calcite. These particles were found to consist of ferrous arsenate. Similar particles were observed in the scale from the household kettle, and a powdered sample of the scale contained 0·4 per cent. of arsenic. The clinical histories of the cases indicated that a period of approximately $2\frac{1}{2}$ years was necessary before definite signs of arsenic poisoning were produced by the use of the arsenical water.

# Agricultural

**Boron-Content of Plants Cultivated on the Same Soil. G. Bertrand and L. Silberstein.** (*Bull. Soc. Chim.*, 1937, **4**, 1147–1149.)—The work here described supplements that by Bertrand and de Waal (*Bull. Soc. Chim.*, 1936, **3**,

875), on the boron-content of plants grown on the same soil. The plants were grown alongside one another on a plot which had not been manured for a long time and was considered to be homogeneous in chemical composition. Ten species of agricultural plants were grown, and four weeds which occurred in the plot were also examined. All the plants were gathered just as flowering was beginning, washed, dried, and analysed as before. Some of the results were as follows:

| | Ash in dry substance Per Cent. | Method | Mg. per kg. in dry substance | |
|---|---|---|---|---|
| | | | $H_3BO_3$ | Boron |
| Onion .. | 8·0 | Colorimetric | 24·4 | 4·3 |
| Flax .. | 7·7 | Colorimetric | 40·3 | 7·1 |
| Celery .. | 19·4 | Colorimetric | 67·6 | 11·9 |
| | | | 85·2 | 15·0 |
| Potato .. | 14·4 | Colorimetric | 79·0 | 13·9 |
| | | | 85·2 | 15·0 |
| Bean .. | 8·9 | Colorimetric | 87·5 | 15·4 |
| | | | 99·4 | 17·5 |
| Tomato .. | 20·1 | Colorimetric | 85·2 | 15·0 |
| | | Volumetric | 108·0 | 19·0 |
| Lucerne .. | 13·0 | Colorimetric | 142·0 | 25·0 |
| | | Volumetric | 164·0 | 28·9 |

Celery of the same sowing as that in the table, in its first year, contained 17·5 mg. of boron per kg. All the results now obtained fall within the previous range (2·5 to 70 mg. of boron per kg. of dry substance), and confirm the previous conclusions. Some previous results, here repeated, were:—leek (3·1), pea (21·7), purple clover (36·2), soya (37·1), lentil (41·4), scarlet runner (43) and crimson clover (70). Cereals, with the leek and onion, contain not more than 5 mg. per kg., whilst leguminous plants contain from 16·5 to 70 mg. per kg. E. B. D.

**Losses of Organic Substance in the Spontaneous Heating of Alfalfa Hay. E. J. Hoffman and M. A. Bradshaw.** (*J. Agric. Res.*, 1937, **54**, 159–184.)—Samples of hay were exposed in a barn in containers made from nichrome wire-cloth, a thermocouple being inserted to register the changes in temperature. One sample of cured clover or dry timothy grass (*Phleum pratense* L.) and 6 of alfalfa (*Medicago sativa* L.) containing 28 to 70 per cent. of moisture were used, and some of the baskets were placed in selected places in the mow, all of the samples being weighed and analysed before and after storage for 1 to 7·5 months under various conditions. The following analytical values are tabulated:—*Moisture.*—Comparisons of the various suggested methods of determination were made; drying to constant weight under reduced pressure at 85° to 100° C. is preferred, as no decomposition was then observed. *Ether extract.*—Ten g. of the finely-ground sample, dried as described, are extracted for 20 hours in a Soxhlet apparatus, the residue left on evaporation of the extract being dried to constant weight at 100° C. *Total sugars.*—The residue from the ether extraction is analysed by the A.O.A.C. method (*Official and Tentative Methods of Analysis*, 1930, **1**, p. 281).

*Hemicelluloses.*—(*a*) The residue, after extraction of sugars, is boiled under a reflux condenser for 5 hours with 150 ml. of 2 per cent. (by weight) hydrochloric acid, capryl alcohol being added to prevent foaming. The residue is removed by filtration and washed with hot water, the combined filtrates being diluted to 250 ml. and neutralised, and aliquot portions used for the iodimetric determination of reducing sugars (*cf.* P. A. Schaffer and A. F. Hartmann, *J. Biol. Chem.*, 1920, **45**, 365). (*b*) As method (*a*) may also involve hydrolysis of the cellulose, the A.O.A.C. method (*loc. cit.*, **1**, p. 284), in which the original hay is distilled with 12 per cent. acid and the resulting furfural determined, was used, with the substitution of thiobarbituric acid for phloroglucinol to precipitate the furfural (*cf.* A. W. Dox and S. P. Plaisance, ANALYST, 1916, **41**, 384). This method is also open to the objection that uronic acids, certain aldehydes and lignin also yield furfural. A correction may be obtained, however, by applying a modification of the method of A. D. Dickson, H. Otterson and K. P. Link (*J. Amer. Chem. Soc.*, 1930, **52**, 775), in which the carbon dioxide evolved by treatment with the acid is passed through conc. sulphuric acid and then absorbed in weighed U-tubes containing ascarite; the weight of carbon dioxide, multiplied by 4, gives the weight of uronic anhydride, and, this divided by 6, gives the weight of furfural derived from uronic acids. The correction was found to be equivalent to about 25 per cent. of the total furfural. *Lignin and cellulose.*—The washed and dried residue from the previous determination (*a*) is treated by the method of Waksman and Stevens (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 167), except that the Schaffer and Hartmann method (*loc. cit.*) is used for the determination of the reducing sugars derived from the cellulose. *Nitrogen.*—The A.O.A.C. methods (*loc. cit.*, pp. 21 and 279) are preferred for the total organic, albuminoid, amino and ammoniacal nitrogen values. *Methoxyl value.*—Phillips's modification (ANALYST, 1932, **57**, 402) of the Zeisel and Fanto apparatus is recommended. *Alcohol and benzene extracts.*—The dried and weighed residue from the ether extraction is treated for 20 hours in a Soxhlet apparatus with a mixture of 32 parts of 95 per cent. alcohol and 68 parts of benzene (by vol.). The extracted material is dried for 2 days in air and then for 5 hours in the vacuum oven at 100° C., and re-weighed. *Alcohol extract.*—The dried residue from the previous extraction is re-extracted with 80 per cent. alcohol for 20 hours, and again dried and weighed. With some samples it was found preferable to use aliquot portions of the two extracts so obtained for the determination of total sugars (*cf. supra*), and portions of the alcoholic extract for the determination of lignin (*cf. supra*) and cellulose (by the method of Norman and Jenkins (*Biochem. J.*, 1933, **27**, 818). The moisture-content of the hay immediately surrounding the samples in the mows was 10 to 60 per cent., and the average moisture-content of the mows was 18 to 35 per cent. The losses in organic matter were 4 to 22 per cent. (average 13 per cent.), the highest losses being obtained when the moisture-contents of the sample and of the hay surrounding the mow were both high; variations occurred according to the position in the mow, and were probably occasioned by variations in resistance to the passage of air. When the samples had a normal moisture-content and most, or all, of the surrounding mow was relatively dry, the respective maximum losses were 8 and 8·6 per cent. (average 3·5 and 6 per cent.). The greatest losses occurred when moisture conditions favoured the production of

heat, *i.e.* when the highest temperatures were recorded. The use of 1·5 per cent. of salt to inhibit spontaneous heating was without effect on the losses. When hay undergoes such losses it deteriorates considerably in quality. With two exceptions there were losses of fat (6 to 47 per cent.), which spectro-photometric tests showed to be accompanied by the complete destruction of carotene. Losses of sugars ranged from 59·1 to 93·7 per cent., and hemicelluloses, as measured by the pentosan value, decreased by 13·9 to 52·1 per cent. (by the hydrolysis method), or 4·1 to 35·7 per cent. (by the uncorrected distillation method). The greatest losses were obtained when the total loss of organic matter was greatest, and this applied particularly to the cellulose, for which losses of 6·7 to 21·1 per cent. and some gains were obtained. The lignin-contents showed very little change, whilst both gains and losses are recorded for the various nitrogen values, although the latter were only of significance where the total losses were relatively large (*cf.* Hoffman, *J. Agric. Res.*, **1935**, **51**, 527). J. G.

**Determination of Rotenone. W. M. Seaber.** (*J. Soc. Chem. Ind.*, **1937**, **56**, 168–173T.)—A series of experiments showed that rotenone was not extracted completely from derris, timbo, and "barbasco" roots by carbon tetrachloride. Extraction with cold chloroform gave higher results than with any other solvent which was tried, except ethyl acetate (*cf.* Worsley, *J. Soc. Chem. Ind.*, 1936, **55**, 349T; Abst., ANALYST, 1937, **62**, 141). A cold process is considered preferable to a hot one, as changes may occur on long heating. Beach's chloroform process (*cf. Soap*, 1936, **12**, 109), which is preferable to Rowaan's (*Chem. Weekblad.*, 1935, **32**, 291; Abst., ANALYST, 1935, **61**, 483), was carried out as follows:—Thirty g. of ground root were shaken in a flask with 300 ml. of chloroform, allowed to stand overnight, and then shaken for one hour. The liquid portion was poured off as completely as possible into a large filter-funnel (with a glass tap in the leg), which was quickly covered with a clock-glass. The liquid was filtered directly into a 200-ml. measuring flask, up to the mark. Precautions were taken to reduce evaporation to a minimum. This filtrate was transferred to a suitable flask, about 150 ml. of chloroform were distilled off, and almost all of the remainder was evaporated on a water-bath. The residue was left for a time under reduced pressure on a water-bath, and 10 ml. of filtered carbon tetrachloride were then added. The carbon tetrachloride was evaporated off first on a boiling water-bath, then at a lower temperature with a vacuum pump. After this treatment had been repeated with 5 ml. of tetrachloride, the residue was dissolved in 15 to 25 ml. of carbon tetrachloride which had been saturated with rotenone at 0° C. Rotenone was crystallised from this solution as a complex with carbon tetrachloride by Jones's method (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 23). The factor 0·72 was used to convert the weight obtained into crude rotenone. The liquid was cooled, seeded with a crystal of rotenone complex, put aside in a cool place for two days and then in ice for three hours, collected on filter-paper in a Gooch crucible, and washed with the solution of rotenone in carbon tetrachloride until the washings were pale, after which suction was continued for ten minutes. After some time the complex was stirred with a platinum rod, then left overnight supported in a rack so that there was an air space beneath. It was then stirred again, left for one hour,

and re-weighed. The author does not consider any method of determination of the purity of the rotenone complex entirely satisfactory, but "pure" rotenone has been calculated approximately from the rotation of a solution of the complex in benzene, the rotation for a 5 per cent. solution of pure rotenone complex being taken as — 16·25°. When a mechanical shaker is not used for the extraction, the root may be shaken by hand with chloroform initially, then shaken occasionally throughout the next day, and on the following day before filtration. The very small error introduced into the above-described method by change of volume due to the solution of the root in the 200 ml. of chloroform tends to cancel that due to evaporation during filtration and measuring, and the resulting error is negligible. Extractions with other solvents are also described and discussed, and the results of numerous tests with various solvents are tabulated. E. B. D.

**Colorimetric Evaluation of Derris Root. A. Goudswaard and J. C. Timmers.** (*Pharm. Weekblad*, 1937, **74**, 630–634.)—The method of Jones and Smith (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 75) for the determination of rotenone is unsatisfactory, as the colour does not attain a constant value, and with small quantities of rotenone the results are inaccurate. The method of Danckwortt, Budde and Baumgarten (*Arch. Pharm.*, 1934, p. 561) is preferred. It is based on the observation of van Sillevoldt (*Ned. Tijdschrift Pharm., Chem. Toxicol.*, 1899, p. 246) that derris root dissolves in sulphuric acid, with the production of a blue-violet colour, and the method has been improved by Gross and Smith (ANALYST, 1934, **59**, 567) and by Goodhue (*id.*, 1936, **61**, 355). The following procedure is preferred, as it eliminates the objection noted by Danckwortt, namely, a change in the shade of the colour from yellow to brown in the first hour, and then to red-violet on standing for 24 hours. A solution of 100 mg. of the rotenone in 100 ml. of chloroform is prepared, and 0·1, 0·2, etc., to 0·5 ml. is pipetted into each of 5 similar tubes, which are then placed in the water-bath until the odour of chloroform is no longer perceptible (important). The tubes are then cooled, 10 ml. of ordinary conc. sulphuric acid (Dutch Pharmacopoeia, Ed. V) are added to each, and the colours are matched in a colorimeter. The colour ratios found for the pairs of tubes 1:5, 1:4, 1:3 and 1:2, were 8·2:40, 10:40, 14:45, and 21:45, respectively. Comparison of ordinary sulphuric acid with 0·01 per cent. solutions of a nitrate and nitrite in conc. sulphuric acid free from these impurities showed that the ordinary (Pharmacopoeia) sulphuric acid gave the best results. The others gave positive results, but the colour was not intensified by the use of larger quantities of nitrates or nitrites; additions of ammonium or iron salts were without effect. The colours obtained with extracts of derris root in chloroform also obeyed Beer's law, but the method is not considered sufficiently specific to enable the rotenone-content of derris root to be obtained (*cf.* Rowaan, *id.*, 1935, **60**, 483). The reaction may be used as a test for nitrites and nitrates if carried out with pure sulphuric acid and rotenone; it is more sensitive and more selective than the diphenylamine test. J. G.

**Evaluation of the Toxicity of Derris and Mundulea. R. R. Le Geyt Worsley.** (*J. Soc. Chem. Ind.*, 1937, **56**, 175–176T.)—Derris and mundulea samples can be separately evaluated from the amounts of optically active constituents in

each, as determined from the optical rotation of a benzene extract of the plant under certain standard conditions (*cf.* Worsley, *J. Soc. Chem. Ind.*, 1937, **56**, 15T), by reading off from a curve for pure rotenone the percentage corresponding with the rotation. Two groups of curves are obtained by plotting these results against toxicity, the munduleas being about 2·8 times as toxic as the derrises with equal contents of optical constituents. Toxicity is determined for sprays of various concentrations; ten tests, each on ten insects, are made for each concentration. The method advocated in the previous paper (*loc. cit.*), of taking the percentage of optical constituents (there called optical dehydro-compounds) in the ether extract does not hold in general. The "toxicity ratio," or TR value, is the reciprocal of the percentage of optical constituents in the sample of root or bark. It is directly proportional to the weight of derris or mundulea to be taken to give equal toxicity. The approximate factor 2·8 can be used to compare derris and mundulea with each other. Some tentative explanations of the greater toxicity of mundulea are given, but further research on this is required. E. B. D.

# Organic

**Direct Determination of Oxygen in Organic Compounds. P. Goodloe and J. C. W. Frazer.** (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 223–225.)—A modification of the hydrogenation method of Russell and Fulton (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 384) and Russell and Marks (*id.*, 1934, **6**, 381) is proposed, in which a nickel chromite catalyst is employed in the determination of oxygen in various compounds, including nitrogen and sulphur compounds. Low results were obtained with tartaric acid and sucrose. Further work is in progress on the application of the method to compounds containing halogen. S. G. C.

**Determination of Pentosans in the Analysis of Woods. I. The Gravimetric Determination of Furfuraldehyde. W. G. Campbell and L. H. Smith.** (*Biochem. J.*, 1937, **31**, 535–544.)—A critical study has been made of the gravimetric determination of furfuraldehyde by means of thiobarbituric acid, and this substance is compared with phloroglucinol as a precipitant for general use in the analysis of woods. Furfurylidene-malonyl-thiocarbamide cannot be collected and washed as easily as furfuraldehyde-phloroglucide, and when certain soft woods are examined the use of thiobarbituric acid gives rise to a granular precipitate which is readily peptised during washing with cold water and cannot be collected quantitatively by the ordinary filtration procedure. In addition, the results with this reagent are uniformly high, and its use as a general precipitant for furfuraldehyde is not recommended. It is suggested, however, that diphenyl-thiobarbituric acid may prove a suitable reagent. S. G. S.

**Identification of Dyes on Textile Fibres. E. Clayton.** (*J. Soc. Dyers and Colourists*, 1937, **53**, 178–197.)—In view of recent advances in dyestuff technology, the work of A. G. Green and his collaborators on the analysis of dyestuffs (*The Analysis of Dyestuffs*, 1915) requires revision. The present paper is intended to supply this need, and is based on the lines of Green's original tables, 14 schemes of analysis being given. These include prints and dyeings (*a*) on cotton and other

cellulosic fibres, and (*b*) on wool, silk and related fibres, each group having seven tables, *viz.* for red, orange and yellow, violet, blue, green, brown and black and grey colours. The reagents used are (1) 1 per cent. ammonia (by vol.); (2) 5 per cent. sodium hydroxide solution; (3) 5 per cent. sodium carbonate; (4) 5 per cent. ammonium chloride solution; (5) 3 per cent. hydrogen peroxide; (6) a vat-dye developer containing 8 g. of ammonium chloride and 2 g. of ammonium persulphate in 100 ml. of water; (7) a reducing agent prepared by mixing a solution of 20 g. of formosul in 75 ml. of hot water with 75 ml. of cold water and 50 g. of ethylene glycol (Formosul G); (8) commercial ethylene-diamine; (9) "developer O" (a solution of 1 g. of ammonium persulphate and 0·5 g. of ammonium dihydrogen phosphate in 100 ml. of water); (10) 1 per cent. sodium hydroxide solution. The tests are carried out in boiling-tubes on about 2 inches of the yarn or 0·5 sq. inch of cloth, and the following notes summarise the principal novel features of the tables. *Wool and Silk.*—Triarylmethane basic dyes which have been transferred from wool to cotton are readily reduced with Formosul-G (Reagent 7), and regenerated on warming with Reagent 9. Triarylmethane acid dyes, however, vary considerably in resistance to Reagent 7 and to subsequent oxidation by Reagent 9. Dyes of the Patent Blue type give most trouble in this respect, and they should be boiled for 1 minute in a 5 per cent. solution of sodium carbonate, and if the extract is deeply coloured, sodium hydroxide is added and boiling renewed until the tint is very pale; addition of glacial acetic acid then develops the original colour of the dye. Anthraquinonoid and azine acid dyes are easily reduced, the colour being restored by immersion in Reagent 5 and cold water, respectively. Most of the red and black "chrome" dyeings are distinguishable by their resistance to Reagent 7, whilst boiling 16 per cent. hydrochloric acid breaks up the lakes of azo dyes containing a co-ordinated metal, and the azo group may then be identified. Some dyes (*e.g.* Neolan Pink B) on silk require even stronger acid, and it is preferable to remove the dye from the fibre by means of warm Reagent 8, and to add sodium hydrosulphite, when permanent decolorisation takes place immediately. Almost all substantive dyes on wool or silk are detectable by boiling with Reagent 3 or 2, respectively, for 30 seconds in the presence of white cotton, which rapidly becomes stained and is then resistant to boiling Reagent 1. Exceptions to this Rule (azo dyes of the Coomassie Navy Blue and Black, or Sulphocyanine types) are identified by the dull yellow colour obtained on boiling with Reagent 10. Vat dyes change in colour in hot Reagent 7, but are regenerated by washing and aeration, or by treatment with Reagent 5. In some instances the action of Reagent 10 on a wool-dyeing forms the leuco-compound of the corresponding parent dye, which may be recognised by allowing a drop of the solution to oxidise on a filter-paper. Reagent 8 is convenient for the extraction of dyes of this type (especially indigo and its derivatives) or for the production of their leuco-compounds. The presence of azoic dyes is usually established "by difference," but unlike vat dyes, extracts of them in hot Reagent 8 are quickly and permanently decolorised by sodium hydrosulphite. *Cellulosic fibres.*—Basic dyes are best transferred to wool by boiling with 1 ml. of Reagent 2, and then adding 4 ml. of Reagent 4 and again boiling; the wool is introduced into this solution while it is cooling. Reagent 2 strips most substantive dyes which can be taken

up by mercerised cotton, the new dyeing being then resistant to hot Reagent 1. Some vat dye discharges on diazotised and developed dyeings require the addition of sodium hydrosulphite to the alkali, and in others stripping is aided by Reagent 7 or 8. Sulphur dyes are identified by boiling the pattern for 30 seconds with 16 per cent. hydrochloric acid and then adding magnesium chips to the cool extract, and testing evolved gases with lead acetate paper. The usual reduction tests (*supra*) generally give positive results, but the ease with which dyes of this class are decolorised by boiling sodium hypochlorite solution (sp.gr., 1·015) is a useful distinguishing feature. Reagent 7 (hot) or 8 (cold) reduces most azoic dyes, especially if alkaline, an exception being Naphthol AS–G, which requires alkali containing a little hydrosulphite. For viscose dyeings it is preferable to use a mixture of equal volumes of 10 per cent. sodium hydroxide solution and ethylene glycol monoethyl ether (*cf.* Rowe and Levin, *J. Soc. Dyers and Colourists*, 1924, **40**, 218). They are usually distinguishable from azoic dyeings and prints by their relatively slow reactivity in the presence of cold Reagent 8. Vat dyes may be detected by heating at 60° C. with hydrosulphite in Reagent 2, and then dyeing white cotton; the original colour may be regenerated by means of a suitable vat dye developer. Since commercial samples of ethylene-diamine vary in efficiency as a reagent, it is advisable to add glucose when testing for vat dyes on cotton. Reagent 8 is a particularly effective stripping agent, and will remove even fast co-ordinated chromium lakes or substantive dyes from wool or cotton. Basic-mordant dyes (*e.g.* gallocyanine derivatives) are easily broken up by hot 5 per cent. hydrochloric acid; if the solution is made alkaline with ammonia, excess being removed by means of solid magnesium sulphate, the resulting solution will dye white wool. Chromatographic adsorption (*cf.* Cook, *Chem. and Ind.*, 1936, **55**, 721) or filter-paper tests may be used for mixture dyeings. For the former the simplest apparatus is a small vertical tube containing an adsorbing agent (*e.g.* Brockmann's activated alumina), through which is drawn by suction a solution of the dyestuff mixture. The chromatogram is "developed" by means of a suitable solvent (*e.g.* water or the usual organic solvents) which serves to break the adsorbent-adsorbate complex. The individual dyes then travel down the column at different rates and form separate zones. J. G.

**Phenol Determination in Tars. E. Feil.** (*Chem.-Ztg.*, 1937, **61**, 549–550.) —The following empirical method is recommended. A 4-cm. square piece of drawing paper, free from salicylic acid, is fixed to a thin wire and then dried. A tin, 90 mm. in diameter and 45 mm. high, is filled to a depth of 30 mm. with the tar-asphalt mixture under examination, and the mixture is stirred with a thermometer and heated to 100° C. The paper is quickly dipped three times into the mixture at this temperature, allowed to drip at room temperature, and hung in 200 ml. of water at 20° C. contained in a 250-ml. beaker (height 90 mm. and diameter about 60 mm.), the wire being fixed to a cork which fits the beaker tightly. The paper is removed after soaking for 24 hours. Fifty ml. of the liquid are pipetted into an elongated 100-ml. volumetric flask and the phenol is determined as follows: —Exactly 1·5 ml. of 2 *N* nitric acid and 0·2 ml. of Millon's reagent are added to the liquid, which is then warmed until it just begins to boil and is kept hot, without

boiling, for 1 minute. The flask is filled almost to the mark with cold water, cooled, made up to the mark, shaken, and allowed to stand for 2½ hours. The colour developed is compared with water in a Pulfrich photometer, and the phenol-content is read from curves prepared by applying the same method of determination to a standard phenol solution containing 0·5 g. of phenol per litre. The figure obtained is multiplied by 4 to give the phenol-content of the tar-asphalt mixture. The influence, on the method, of the quantity of nitric acid, the quantity of Millon's reagent, the time of standing between making up the solution and comparing the colour, the temperature of soaking, the viscosity of the tar mixture, re-soaking of the paper in fresh water, and the exposure of the tar mixture to air has been determined. E. M. P.

# Inorganic

**Reduction and Electrolysis of Perrhenate. G. E. F. Lundell and H. B. Knowles.** (*U.S. Bureau of Standards J. of Research*, 1937, **18**, 629–637.)—Potassium perrhenate (16·6774 g.) was dissolved in 4 litres of 2·5 per cent. sulphuric acid, and aliquot portions were passed at 5° C. through an 18-inch Jones reductor (diameter 1 inch) filled with 20-mesh granulated zinc amalgamated with 5 per cent. of mercury. The solutions were previously boiled to expel air, and the operation was carried out in an atmosphere of carbon dioxide. The reduced solutions were titrated immediately with permanganate, or they were caught in excess of ferric sulphate or permanganate and then titrated. All the results indicate that the perrhenate is reduced to hydrorhenic acid: $HReO_4 + 8H = HRe + 4H_2O$. If the reduced solution, protected from oxygen, is warmed moderately and left to itself for 30 to 60 minutes, the reaction $HRe + H_2SO_4 = HReO + H_2O + SO_2$ appears to take place, with formation of hyporhenous acid.

Rhenium was deposited as such when a perrhenate solution containing 5 per cent. of sulphuric acid was electrolysed overnight between a sand-blasted platinum gauze cathode and spiral anode at 0·25 amp. per sq. dm. and 2·34 volts. The deposits were washed with water, alcohol and ether, and dried for 10 seconds at 105° C. Direct weighing of the deposit gave a positive error due to oxidation. The deposited metal does not oxidise appreciably in perfectly dry air, but it oxidises very rapidly in moist air, being quantitatively converted into perrhenic acid within 24 hours. The element can be determined by electro-deposition, conversion into perrhenic acid by exposure to moist oxygen, and alkalimetric titration of the perrhenic acid (phenolphthalein indicator). The small amount of rhenium that may escape deposition may be determined colorimetrically by Hurd and Babler's method (ANALYST, 1936, **61**, 500). W. R. S.

**Electro-deposition of Zinc from Citrate Solution. R. Winchester and L. F. Yntema.** (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 254–256.)—The zinc should be present in sulphate solution free from heavy metals, but aluminium, chromium and magnesium may be present. The solution, to which 1·5 g. of citric acid is added, is rendered neutral to methyl red—methylene blue indicator with sodium hydroxide. It is diluted to 200 ml. and electrolysed with a copper or copper-plated gauze cathode and a rotating platinum anode, the cathode current density

being about 1 amp. per sq. dm. After 1½ to 2 hours, a 1-ml. sample of the electrolyte is tested by the addition of 0·5 ml. of saturated hydrogen sulphide water. The electrolysis should be continued if more than a faint opalescence is produced. Finally the cathode is withdrawn and washed without switching off the current, dried and weighed. Practically quantitative results were obtained with 0·2 g. of zinc taken. Nitrate ions, dimethylglyoxime and urea interfere, also the following metals:—antimony, arsenic, bismuth, cadmium, copper, iron, lead, manganese, mercury, nickel and silver. S. G. C.

**Separation of Zinc from Cobalt by means of Hydrogen Sulphide. E. A. Ostroumow.** (*Ann. Chim. anal.*, 1937, **19**, 145–152.)—Zinc sulphide precipitated by hydrogen sulphide from buffered acid solution tends to be much contaminated with cobalt if that element is present. Under similar conditions the entrainment of iron, manganese and nickel was much less marked. The particular behaviour with cobalt is attributed to post-precipitation. The effect can be reduced by the presence of acrolein in the liquid, which is considered to become adsorbed on the zinc sulphide particles and to take the place, to some extent, of the active layer of adsorbed hydrogen sulphide which is held to be responsible for post-precipitation phenomena. It was further found that a slow current of hydrogen sulphide was desirable for minimising post-precipitation, the passage of the gas being continued only long enough to secure coagulation of the precipitate. A method suitable for a solution containing moderate amounts of zinc and cobalt (0·05 to 0·1 g.) is as follows:—The solution is neutralised approximately with dilute sodium hydroxide solution, and 10 ml. of chloroacetic acid (190 g. per litre) are added. To the clear liquid 10 ml. of sodium acetate solution (136 g. per litre) are added, and the solution is diluted to 150 ml. and heated (temperature not stated). Five ml. of acrolein solution (4 per cent.) are added, and a slow current of hydrogen sulphide (about 60 to 80 bubbles per minute) is passed into the solution until the zinc sulphide coagulates (about 25 to 30 minutes are usually sufficient). The zinc sulphide is filtered off, washed with dilute acetic acid (4 per cent.) saturated with hydrogen sulphide, and burnt off. The residue is converted into zinc sulphate in the usual way and weighed. Practically the theoretical recovery of zinc was obtained in test experiments, and the amount of cobalt in the zinc sulphate was found by colorimetric tests to be less than 1 mg. With small amounts of zinc in presence of moderate amounts of cobalt, difficulties were experienced, because the precipitate did not coagulate well and was difficult to filter off. The addition of paper-pulp suspended in water was satisfactory for collecting the precipitate, but was found to lead to serious contamination of the precipitate with cobalt. It was concluded that this partial precipitation of cobalt was due to a kind of post-precipitation on the paper fibres promoted by the fact that the water absorbed in the added paper gave locally too low an acid concentration. This drawback could be avoided by using pulp saturated with a buffered acid solution as follows:—Paper pulp prepared in the ordinary way is filtered off on a Buchner funnel, and then shaken up with 150 ml. of water containing 10 ml. of chloroacetic acid solution (190 g./litre), 10 ml. of sodium acetate solution (136 g./litre) and 5 ml. of acrolein solution (4 per cent.); quantities of this suspension are filtered off, as required, and

the impregnated paper is added for the purpose of collecting the zinc sulphide. With amounts of zinc of the order of 0·5 to 5 mg. in the presence of 0·1 g., of cobalt, it is desirable to pass hydrogen sulphide for about 15 minutes after the first signs of precipitation are seen; the impregnated paper pulp is added, and the passage of the gas is continued for a further 40 minutes, the determination being finished off as before. Quantitative results were obtained with zinc in amounts down to 0·5 mg. S. G. C.

**Separation of Beryllium in the Presence of Complex Tartrates. H. S. Miller.** (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 221.)—Beryllium may be precipitated from complex tartrate solution by the addition of a regulated quantity of ammonia. In this way it was possible to separate beryllium fairly quantitatively from elements, such as aluminium, iron, copper and chromium, that form complex tartrates from which the hydroxide is not precipitable by ammonia. No general directions for carrying out the method are given. The precipitate of beryllium hydroxide obtained is gelatinous and is stated to suffer from the disadvantage of readily adsorbing other substance from the solution, making repeated re-precipitation necessary. S. G. C.

**Phosphotungstate Colorimetric Method for the Determination of Vanadium. E. R. Wright and M. G. Mellon.** (*Ind. Eng. Chem. Anal. Ed.*, 1937, **9**, 251–254.)—The reaction on which the method is based involves the addition of sodium tungstate and phosphoric acid to an acid solution containing quinquevalent vanadium, whereupon a yellow or brownish colour is produced varying in hue and intensity with the vanadium concentration (*cf.* Willard and Young, *Ind. Eng. Chem.*, 1928, **20**, 764; Abst., ANALYST, 1928, **53**, 674). The preferred concentrations of reagents in the colorimetric solution are 0·025 *M* sodium tungstate, 0·5 *M* phosphoric acid and 0·6 *N* nitric, sulphuric, hydrochloric or perchloric acid; the concentrations are not critical; the amount of vanadium present in 100 ml. should be between 0·02 and 10 mg. Heating the solution to boiling is necessary for the full development of colour if more than 1 mg. of vanadium is present per 100 ml. The following substances were found to have no effect on the colour (in 100 ml. volume): sodium chloride (3 g.); sodium nitrate (5 g.); magnesium, calcium, strontium, barium, zinc, cadmium, mercury, aluminium, lead, arsenic, bromine, and acetate ion (0·5 g.); beryllium (0·025 g.); silver, lithium, chlorate ion, oxalate ion, citrate ion, tartrate ion (0·1 g.); silicate ion (0·05 g.); cyanide ion (0·02 g.). Ammonium and potassium give precipitates with the phosphotungstic acid and must not be present in more than traces. The following interfere by producing a precipitate: antimony, tin, titanium and zirconium, only small amounts of these being tolerable. Molybdenum tends to interfere, when present in fairly large amount, by forming a coloured compound. Ferric iron in the form of chloride gives a brown colour.

The following method is proposed for steel:—(*a*) *Chromium–Tungsten Steels containing* 0·7 *to* 2·0 *per cent. of Vanadium.*—A 150-mg. sample is dissolved, as far as possible, in 10 ml. of hydrochloric acid (1:1), by heating. Nitric acid is added, drop by drop, in amount sufficient to oxidise iron and tungsten. Perchloric acid (7 ml. of 60 per cent. acid) is added, and the liquid is evaporated until fumes of

perchloric acid are evolved, and kept boiling for 2 to 3 minutes after the orange-red colour, due to chromic acid, has appeared. After cooling, 40 ml. of water are added, the liquid is boiled, and 5 ml. of 0·5 *M* lead perchlorate solution are added. The precipitate of lead chromate and tungstic acid is filtered off from the cold solution, washed with a little cold water, and rejected (the small amount of vanadium occluded in the tungstic acid is ignored in this method). To the filtrate are added 10 ml. of nitric acid (1:1), 3 ml. of phosphoric acid (90 per cent.) and 5 ml. of 0·5 *M* sodium tungstate solution, the solution is heated to boiling, cooled, and diluted to 100 ml. The colour is compared colorimetrically with that of a solution containing 1·5 mg. of vanadium (as sodium vanadate), the same amount of reagents and about 60 ml. of water, which has been heated to boiling, cooled and diluted to 100 ml. (*b*) *Chromium–Tungsten Steels containing* 0·1 *to* 0·7 *per cent. of Vanadium.*—A 0·5-g. sample is dissolved, as far as possible, in 20 ml. of hydrochloric acid (1:1) by heating, 0·5 ml. of nitric acid is added, the liquid is evaporated to 10 ml., 5 ml. of hydrochloric acid are added, and the liquid is transferred to a separating funnel with not more than 5 ml. of water. The bulk of the ferric chloride is extracted by means of 30 ml. of ether. The aqueous layer is heated to remove dissolved ether and evaporated to fuming with 7 ml. of 60 per cent. perchloric acid, and the method continued as in method (*a*). S. G. C.

**Determination of Potassium in Soils and Silicates. J. E. Gieseking and H. J. Snider.** (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 232–233.)—A new flux is proposed for effecting the decomposition of soils, clays and similar materials when potassium is to be determined. It consists of a mixture of two parts of sodium carbonate with one part of lithium carbonate, and melts between 470° C. and 480° C. Potassium is finally determined by the cobaltinitrite method. A 1-g. sample of the 100-mesh material is first heated in a platinum capsule with perchloric acid in order to destroy organic matter. After removal of the perchloric acid by heating, the residue is mixed with 8 parts of the flux and covered with a layer of it. The mixture is fused at 500° to 600° C., with the capsule covered, until bubbling has ceased. The cooled melt is dissolved, as far as possible, in 75 ml. of 4 *N* hydrochloric acid; the liquid is evaporated to dryness, 10 ml. of conc. perchloric acid are added and evaporated to dryness. The perchloric acid treatment is repeated with the addition of 1 ml. of conc. hydrochloric acid, and 0·5 ml. of nitric acid to assist in dehydrating the silica and to decompose any traces of ammonium salts present. The residue is digested for a few minutes with 50 ml. of 5 per cent. hydrochloric acid, and the silica is filtered off, washed with 2 *N* hydrochloric acid, and ignited in the original crucible; the silica is volatilised with hydrofluoric acid and a little perchloric acid, and any residue is dissolved in a little dilute hydrochloric acid and added to the main solution, in which the potassium is now determined by the cobaltinitrite method, that described by Volk and Truog (*J. Amer. Soc. Agron.*, **1934, 26**, 537) being suitable. S. G. C.

**Determination of Rare Alkalis. J. C. Hillyer.** (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 236.)—The author discusses the applicability of Wells and Stevens' method (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 439) to the analysis of the mineral pollucite, which contains over 30 per cent. of caesium oxide. A modified

solvent-mixture is proposed for separating the alkali chlorides. It consists of 0·4 ml. of water and 10 ml. of alcohol, both saturated with hydrogen chloride, and will dissolve the following amounts of alkali chlorides at 25° C.:—potassium chloride, 0·0006 g.; rubidium chloride, 0·0027 g.; caesium chloride, 0·024 g. S. G. C.

**Analysis of Pollucite. R. C. Wells and R. E. Stevens.** (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 236–237.)—The authors concur in the necessity for modifying their original method in dealing with samples containing a high proportion of caesium and indicate a further procedure applicable to pollucite (*cf.* preceding Abst.). This mineral, which occurs at Tin Mountain, S. Dakota, is unique, as it is the only mineral compound of caesium found in nature. Caesium may replace potassium in minerals, but its amount seldom exceeds a few units per cent. and usually it is absent. S. G. C.

**Determination of Silicon in Aluminium and Aluminium Alloys. H. V. Churchill, R. W. Bridges and M. F. Lee.** (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 201–202.)—In order to examine the question whether silicon is lost as hydride when aluminium alloys are dissolved in acids, a number of representative aluminium alloys in different conditions of heat-treatment were submitted to three methods for the determination of silicon, involving attack with (*a*) sulphuric-nitric-hydrochloric acid mixture, (*b*) perchloric acid, and (*c*) sodium hydroxide. The results obtained by the tri-acid and sodium hydroxide methods showed satisfactory agreement for the silicon-contents of commercial aluminium, aluminium-manganese alloy (Mn, 1·25 per cent.), straight aluminium-silicon alloy (Si, 5 per cent.) and duralumin (Mn, 0·5; Cu, 4·0; Mg, 0·5 per cent.), irrespective of heat-treatment. Except with the material in the fully annealed condition, marked differences were found between the results of these two methods with aluminium alloys containing magnesium-silicide hardener* (*e.g.*, Mg, 0·6; Si, 1·0 per cent.). Examples of the results obtained with such an alloy are as follow:

| Heat treatment | Silicon, per cent. | | |
|---|---|---|---|
| | Tri-acid method | Perchloric acid method | Sodium hydroxide method |
| Fully annealed .. .. .. .. | 0·93 | 0·92 | 0·94 |
| "Solution heat-treatment" .. .. | 0·85 | 0·75 | 0·94 |
| "Solution heat-treated and aged at room temperature" .. .. .. | 0·89 | 0·84 | 0·94 |

There was a general trend towards low results with perchloric acid attack with all the materials tested. It was concluded that, whilst the tri-acid method is usually satisfactory, the sodium hydroxide method should be used when aluminium-magnesium silicide alloys are analysed for silicon. The following methods were found satisfactory at the American Aluminium Research Laboratories:

*Tri-acid method.*—A 1-g. sample, contained in a 250-ml. beaker, is attacked with 35 ml. of acid mixture (485 ml. of water, 115 ml. of sulphuric acid, 200 ml. of hydrochloric acid and 200 ml. of nitric acid). When no further action is evident, the liquid is evaporated until heavy fumes of sulphuric acid are evolved, the

* *Abstractor's Note.*—The alloy silmalec is a representative of this class of alloy in this country.

heating then being continued for 15 minutes. After cooling, 10 ml. of 1 : 3 sulphuric acid and 100 ml. of hot water are added, and the mixture is heated until the metallic salts are dissolved. Some paper-pulp is added and the residue is filtered off and washed with hot water. The filtrate is evaporated again as described above, in order to recover traces of silica, which are ultimately added to the first precipitate, the combined filters being ashed in a platinum capsule and the residue ignited. The residue is fused with 1 to 8 g. of sodium carbonate, and the cooled melt is dissolved in 50 ml. of 1 : 3 sulphuric acid. The solution is evaporated, and the residue is heated for 15 minutes while dense white fumes are evolved. The cooled residue is dissolved, as far as possible, in 100 ml. of hot water, prolonged digestion being avoided to minimise re-solution of silica. After the addition of paper-pulp, the silica is filtered off, and the filtrate is evaporated as before to recover traces of silica, which are then combined with the main portion. The filters are ashed in a platinum capsule, and the residue is ignited at 1000° C., cooled and weighed. It is moistened with a few drops of dilute sulphuric acid, hydrofluoric acid is added, the liquid is evaporated to dryness, and the residue is ignited and weighed. The difference between the two weights represents silica. A blank determination on the reagents is advised.

*Sodium hydroxide method.*—A 0·5 to 1·0 g. sample is dissolved, in a covered Monel-metal beaker, in 15 ml. of 30 per cent. sodium hydroxide solution. The liquid is then evaporated to 5 ml. If the solution is dark in colour, 2 to 3 ml. of 3 per cent. hydrogen peroxide are added, the liquid being then re-evaporated to 5 ml. The solution and any insoluble matter are transferred to a Pyrex beaker containing 65 ml. of 1 : 1 sulphuric acid and 20 ml. of 60 per cent. perchloric acid. The silica is recovered and determined in the usual way, with re-evaporation of the filtrate and use of the hydrofluoric acid volatilisation process. An alternative process is described involving acidification of the sodium hydroxide solution with hydrochloric acid, and evaporation with perchloric acid, as published by the Aluminium Research Institute (Standard Methods for Sampling and Analysing Aluminium and certain Aluminium Alloys, 1932). (*Cf.* Callender, ANALYST, 1933, **58**, 81.) S. G. C.

**Colorimetric Determination of Silicic Acid in the presence of Iron, Phosphorus and Fluorine. I. P. Alimarin and V. S. Sverev.** (*Mikrochem.*, 1937, **22**, 89–101.)—The Diénert and Wandenbulcke method (*Compt. rend.*, 1923, **176**, 1478; Abst., ANALYST, 1923, **48**, 398) which consists in comparing the yellow colour formed from silicic acid and ammonium molybdate with a standard solution has been tested under various conditions. For visual comparison the lowest concentration for accurate matching is about 1 mg. per litre, and the highest 50 mg. per litre. For the comparison, varying amounts of standard sodium silicate are treated with 2 ml. of a freshly prepared 10 per cent. solution of ammonium molybdate for every 5 mg. of silica present, and 4 drops of 50 per cent. (by vol.) sulphuric acid, to bring the *p*H to about 1·2–2·0. The solution is then diluted to 100 ml. The colour reaches the maximum in 10 minutes at room temperature. A more intense and constant colour is produced if the solution is heated on the water-bath for 5 minutes. The intensity obtained at 50° to 66° C. remains constant

for 24 hours. The acidity of the solution is important and should be maintained within the stated limits of *p*H 1·2 to 2. Excess of mineral acid may be eliminated by buffering with sodium acetate and acetic acid. Ammonium molybdate should be added before the acid; this is especially important in dilute solutions of silica. Iron, if not present in excess of 20 mg. per litre, does not interfere. To remove excess of iron the best results are attained by fusing the substance with sodium carbonate and leaching the melt with a sodium carbonate solution, all the iron remaining in the residue and all the silicic acid passing into solution. The yellow colour given by phosphates reaches its maximum at 60 mg. of $P_2O_5$ per litre, and disappears if the $P_2O_5$ content is increased beyond 100 mg. per litre. If oxalic, citric or tartaric acid is added after the colour formation the yellow colour due to phosphate is destroyed, whilst that from silicic acid persists for several hours. In the presence of phosphorus and iron it is proposed to add to the coloured solution an excess of phosphoric acid, which destroys the colour of phosphomolybdate without affecting that of silicomolybdate, and which also combines with the iron present to form a colourless undissociated phosphate. The procedure is as follows:—Sodium acetate is added to neutralise any mineral acid present, then 2 ml. of 98 per cent. acetic acid, and for every 5 mg. of silica, 10 ml. of 10 per cent. ammonium molybdate are added. The solution is heated to 50° to 60° C. for 5 minutes, and after cooling and dilution 1 ml. of phosphoric acid (sp.gr. 1·7) is added. The coloured solution is diluted to 100 ml. and compared with a standard solution of sodium silicate treated by the same method. The colour persists for 30 minutes. The influence of the fluoride ion is eliminated by introducing aluminium chloride into the solution. If the fluoride tested is insoluble in water it may be dissolved in 10 ml. of 10 per cent. aluminium chloride solution, after which the other reagents are successively added. J. W. M.

**Studies in Fluorine Distillation. D. Dahle and H. J. Wichmann.** (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 297–303.)—The authors' previous work on the influence of certain factors on the recovery of fluorine by distillation with sulphuric acid (*J. Assoc. Off. Agr. Chem.*, 1936, **19**, 313) is extended to include distillations with perchloric and phosphoric acids. The effect of the presence of the salts of non-volatile acids is also studied. To determine the effect of "input volume" (*i.e.* the volume of liquid present in the distillation flask when the temperature at which the distillation is to be made is reached), mixtures of perchloric acid with water giving different input volumes but containing the same amount of sodium fluoride were distilled at constant temperatures, *viz.* 125° C. and 135° C. to a constant output volume of 25 ml. The input volume was varied in two ways, *viz.* by increasing the amount of acid and by adding salts of non-volatile acids (sodium perchlorate and calcium monophosphate). The amount of fluorine present in each experiment was 0·5 mg. The effects of the two methods of changing input volume are compared, and a similar comparison is made for sulphuric acid with sodium sulphate and ammonium persulphate. From the data obtained the following conclusions are drawn. The fluorine recovery decreases with increasing input volume; the change in recovery decreases with increasing input volume; the presence of soluble salts of non-volatile acids causes a decrease in the fluorine

recovery by a greater amount than is indicated by the corresponding increase in input volume. This retarding effect of soluble salts becomes important when material low in fluorine-content is to be analysed and relatively large quantities of sample must be used. The effect of input volume is almost twice as great when perchloric or phosphoric acid is used as when sulphuric acid is used. This is of practical interest when complete recovery in the smallest possible amount of distillate is required. Perchloric and sulphuric acids cause a more rapid rate of volatilisation of fluorine than does phosphoric acid. Comparisons made at constant input volumes show that both sulphuric acid and perchloric acid are more efficient at 125° C. than phosphoric acid at 135° C. This is of practical interest in the problem of the removal of fluorine from commercial phosphoric acid, as well as in the substitution of this acid for the other acids in distillation. The effect of varying temperature is the sum of two effects working in the same direction, *viz.*, the decrease in input volume and the rise in temperature. By deducting the first-named effect, which can be estimated at least approximately, the second effect is found. Apparently the recovery is greater if the distillation is carried out at higher temperatures. The temperature effect per degree is greater when large volumes are present during distillation than with small volumes. The temperature effect at similar input volumes is about twice as great for perchloric acid as for sulphuric acid, whilst phosphoric acid occupies an intermediate position. As with fluorine distillations with sulphuric acid, the quantitative recovery varies with the amount of distillate collected in accordance with the following equation—

$$K = \frac{1}{t} \log \frac{c}{c - x}$$

where K is a constant, $t$ is the number of ml. of distillate collected, $c$ is the original concentration of fluorine, and $(c - x)$ is the concentration in the residue remaining in the flask after $t$ ml. has been distilled. If $c$ is taken as 100, $x$ becomes the percentage recovery in $t$ ml. of distillate. A. O. J.

**Hydrolysis of Rock-forming Minerals. A. Bramall and J. G. C. Leetch.** (*Bull. Inst. Min. and Met., No.* 391, April, 1937.)—Finely-divided powdered minerals are found to be very hygroscopic, and in the hydrolysed form many minerals are partly soluble in water; often alkali is leached out, and a mineral differing in structure from the original mineral may be obtained. A simple method of testing the solubility of a mineral to water is to grind it up very finely and test the reaction of the powder in water. Most of the common rock-forming minerals are reactive, *e.g.* various basic micas, hornblendes and other amphiboles (including asbestos); wollastonite, diopside, hypersthene, augite, aegirite, and other pyroxenes; olivine, apatite, sphene and some varieties of tourmaline; grossularite, melanite and some varieties of almandite; members of the chlorite and epidote groups; calcite, aragonite, magnesite, dolomite; brucite and chondrolite. Sericite, hydromuscovite and true muscovite are among the less reactive species. The reactivity and hygroscopic properties of the finely-divided dust may be explained from a knowledge of the crystal structure, and throw light on the problems of solubility of fine dust (*cf.* p. 645). J. W. M.

# Physical Methods, Apparatus, etc.

**Photographic Method for the Detection of Thorium Oxide in Lamp Filaments. J. A. M. Van Liempt and J. H. M. Van Uden.** (*Rec. Trav. Chim. Pays Bas*, 1937, **56**, 607–612.)—The method depends on the blackening of a photographic plate by radioactive thorium compounds in tungsten or molybdenum filaments (*cf.* Behrens-Kley, *Mikrochemische Analyse*, 1915, Pt. 1, p. 115). After removal of grease by treatment with hot sodium hydroxide solution the filament is wrapped once round a glass plate (9 × 12 cm.), and then secured on one surface so that the other glass surface is in contact with it. A photographic plate is placed on this surface in such a way as to make close contact with the wire, pressure being avoided in order to prevent damage to the plate. Hilger–Schumann plates gave the best results; after one day filaments containing 1 per cent. of thorium oxide produced no visible stain, whilst those with 2 per cent. produced a slight stain; in 5 days filaments containing 1 and 3 per cent. of the oxide produced a moderately dark stain and an intense stain, respectively. The next best results were obtained with ordinary sensitised plates (H and D, 4400), a slight darkening being obtained from 3 per cent. of oxide after 3 days. A metol-hydroquinone developer, or the developer recommended for the plates concerned, was used. Drawn filaments gave a greater degree of blackening than filaments which had been recrystallised by heating at 2200° C. for 1 hour, or than single-crystal filaments. This supports the authors' earlier conclusions (*Z. anorg. Chem.*, 1927, **168**, 107; 1930, **193**, 144) that the thorium in drawn filaments is held between the fibres, and also that a crystalline structure tends to enclose it. Recrystallisation by heating at 2900° C. for 8 hours produced no change in the degree of blackening, although an examination of the residue remaining after solution of the filament in a mixture of nitric and hydrofluoric acids showed that reduction to the metal had taken place. The phenomenon is therefore atomic in character. Moreover, filaments from pure thorium produced an intense darkening after 1 day, even when the ordinary sensitised plate was used and the diameter was only 150$\mu$. The sensitiveness is increased if the surrounding atmosphere is moist and if the diameter of the filament is relatively large; thus, a 300-$\mu$ filament containing 1 per cent. of oxide required 2 days to produce slight blackening, whilst filaments having diameters of less than 50$\mu$ required 18 days or longer in which to produce similar effects. The effects of low pressures (down to 0·1 mm.) are negligible.

J. G.

**Photometric Determination of the Colour of Cooked Potatoes. P. Bilham, A. E. Maunsell and L. H. Lampitt.** (*J. Soc. Chem. Ind.*, 1937, **56**, 165–168T.)—The colour of cooked potatoes depends on two factors. One is the normal potato colour, from white to yellow; the other is a grey tinge which may be normal or may develop, through some abnormality, on cooking. To obtain a grading system for potatoes which tend to blacken on cooking, a photometric method of determination of greyness is preferable to one with the unaided eye, as the yellow colour of some potatoes tends to mask the effect of blackening. The colour of the potato is matched against one of a series of standard yellow cards, and

greyness is measured by the diminution in the amount of reflected light from the card which is required in order to match that from the sample in intensity. Six cards, numbered from 1 to 6, cover the range from creamy white to deep yellow in approximately equal steps. Grading for greyness is as follows:

| Diminution in reflection, per cent. | 0 | 1–4 | 5–9 | .. | 55–59 |
|---|---|---|---|---|---|
| Grade No. .. .. .. .. | 0 | ½ | 1 | .. | 6 |

The Zeiss–Pulfrich instrument was used for this work. Two beams of light, obtained from the same lamp by means of mirrors, were focussed by means of lenses and directed at an angle of 45° on to the horizontal surfaces of the sample and card. Representative potato samples were prepared by hand and boiled in batches of six, one sample from each batch being included in the next batch in order to detect any abnormality in conditions of cooking. When the centres were soft, but before the outside began to break up, the potatoes were removed and mashed by forcing them through a grid with holes 2 mm. in diameter. After thorough mixing, a representative sample was packed in a Petri dish (95 mm. in diameter, 14 mm. in depth), the surface was smoothed with a knife, and the yellow colour was matched with a colour-card. The intensity of light from the card was then regulated by the drum of the photometer, and the grade number for greyness obtained. Four different parts of the surface of the sample were examined and the mean was taken. If the tint was between that of two yellow cards, four observations were made with each, the intensity was taken as the average of the eight, and the yellow grade number as half-way between the two card-numbers. Reproducibility of results was tested with mixtures of any two samples of white, white-grey, yellow, and yellow-grey potatoes in various known proportions by weight. Results of grading directly and by calculation are compared, and graphs for percentage composition against (*a*) percentage reflection and (*b*) yellow and grey grade numbers are given and discussed. These show that no mixture examined was placed in a grade that would theoretically be wrong by more than half a unit. E. B. D.

**Sampling of Industrial Dusts by means of the "Labyrinth". H. V. A. Briscoe, J. W. Matthews, P. F. Holt and P. M. Sanderson.** (*Bull, Inst. Min. and Met.*, No. 393, June, 1937.)—The "labyrinth" is an apparatus designed for the collection of comparatively large samples (of the order of 10 to 300 g.) of dust from the air of mines and factories. The apparatus consists of a long cylindrical or rectangular box containing baffles consisting of a series of polished copper plates, spaced and located by lengths of copper tube and held together in a single assembly by long brass bolts and wing nuts. In the rectangular shape the box is 36 in. × 6 in. × 4 in., and the baffles, which are spaced 1 in. apart, have an area 6 in. × 3¼ in., leaving a space 6 in. × ¾ in. above or below each baffle. The box can easily be taken apart, leaving the dust undisturbed. If required, dust from each section may be collected separately. The cylindrical model is stronger, the cylinder being a 14 s.w.g. copper tube, 36 in. long × 3 in. internal diameter. To permit of the easy removal of the collected sample, the baffle assembly is wrapped with an overlapping sheet of celluloid, held in place by woollen yarn. Connections

are made by short lengths of inner tube. In a test experiment, a labyrinth was connected with a 3-in. opening in the suction duct close to a high-pressure fan, ventilating a flint-grinding plant. To avoid the collection of many large particles, the entering air was drawn through an improvised elutriator made from an iron drum. After being left for 25 days (500 working hours), when the flow was of the order of 1000 $m^3$ per hour, a sample of about 100 g. of dust was collected. No attention was required except for setting up and dismantling. Several trials showed that over 50 per cent. of the dust was normally collected in the first sections, the last sections collecting less than 1 per cent. of the total weight. Samples of graded particle size are collected, the last sections consisting entirely of particles of 5$\mu$ and less. The efficiency of collection depends on the rate of flow, the faster rate being more efficient up to about 95 per cent. The advantages of the labyrinth, which is being used in an investigation of dangerous dusts, are that the dust is collected in an unchanged form without being heated or wetted. Sixteen photomicrographs are given showing the variation in particle size of various dusts collected in the different sections. J. W. M.

**New Properties of Certain Dusts. H. V. A. Briscoe, J. W. Matthews, P. F. Holt and P. M. Sanderson.** (*Bull. Inst. Min. and Met.*, No. 393, June, 1937.)—Samples of certain industrial dusts collected in the labyrinth (see preceding abstract) were examined for solubility in water under controlled conditions. The dusts were calcined flint, asbestos, cement and sillimanite; of these, the first two are extremely dangerous, the latter two, so far as is known, are innocuous to man and do not cause silicosis. The soluble silica, extracted by treating 1 g. of dust with 100 ml. of water at 100° C. for 5 hours, was as high as 12 mg. per 100 ml. for the flint dust of smallest particle size, 30 mg. per 100 ml. for the most soluble asbestos dust, and only 1 mg. per 100 ml. for cement and sillimanite. Experiments on pure graded quartz showed that the "solubility" increased with decreased particle size, increased with rise of temperature and time of extraction, and varied with variation in weight ratio of solid to solvent, so that no absolute solubility figure is obtainable, and to obtain comparative results the conditions must be strictly controlled. The effect of addition of various other substances on the solubility of silica is being investigated. The addition of lime or cement in equal weight to asbestos, quartz or flint dust decreased the solubility of the silica to a value equal to that given by cement alone (1 mg. per 100 ml.) or less. Of other calcium compounds tested, only calcium borate was at all efficacious, the soluble silica in asbestos being reduced from 42 mg. per 200 ml. to 8 mg. per 200. Magnesia behaves similarly to lime. Cryolite ($Na_3AlF_6$) diminishes the yield of soluble silica from flint and asbestos, but increases the yield from kaolin, felspar, cement and quartz. Sugar charcoal markedly depresses the yield of soluble silica from quartz, but has no effect on asbestos, flint, orthoclase and kaolin. Comparative solubilities of asbestos, flint (pure), quartz, felspar, sericite and kaolin showed that the largest amount of dissolved silica is yielded by asbestos and flint.

J. W. M.

# Reviews

THE SCIENTIST IN ACTION: A SCIENTIFIC STUDY OF HIS METHODS. By WILLIAM H. GEORGE, M.Sc., Ph.D., F.Inst.P., Royal Society Sorby Research Fellow, and Honorary Lecturer in Physics, University of Sheffield. Pp. 355. London: Williams & Norgate, Ltd. 1936. Price 10s. 6d. net.

The author defines scientific research as a form of human action which gives two typical products—facts, and the arrangement of facts.

Facts are observations regarding which general agreement can be attained—that is to say, that any person repeating the observation in the exact circumstances in which it was made will obtain the same result. The only class of observations which fulfil this requirement are coincidence observations—the coincidence of the end of the mercury column with a mark on the thermometer, of the liquid in a burette with a mark on the scale, of the colours of two coloured liquids, and so on.

Scientific classifications, laws or theories, are arrangements or "patterns" into which a number of facts will fit. Such "patterns" are said to "explain" the facts; but they are to be regarded as tentative, not necessary, for it is always possible that some other "pattern" may equally fit the known facts. Other facts may be discovered which will not fit into the pattern, and a new pattern may be devised into which all the facts may be fitted. To this process there can be no finality.

All research work must have the quality of "newness." The new theory or pattern must not be merely an extension of the old, but a new way of regarding the facts—the idea, for example, of looking at disease as due to the absence of some essential factor from food, instead of the presence of some disease-causing factor.

The scientific investigator must banish from his mind the idea of "absolute truth" as an end to be attained by research; he must make no statements about how things "should" or "ought to" behave, to which we are so prone in discussing the ordinary occurrences of daily life; nor must he give way to the habit of "assessing values" and assert that one "pattern" is "better" than another, or "the best."

Throughout, the observer is as much a part of the phenomenon as the observed; science has no concern with the question whether the things observed would or would not still remain were there no human race; and as all our observations depend upon our sensuous impressions, we must be alive to the imperfections of our senses.

These things are discussed in a series of chapters:—The eye-witness's observation; Scientific observation; Pattern; Are facts first seen in isolation?; Selection and abstraction; Order, laws, and classification; Pattern in action; The scientific theory; Some problems of theorising; Some factors in experimental technique; The future of experimental research. The book ends with a statement of the author's personal attitude, a summary of the contents, and a bibliography.

No adequate account of the book can be given in any short review; it must be read to acquire a knowledge of its contents. The present reviewer has found it a difficult book to read—a little prolix and repetitory—and feels that the presentation might have gained in clearness if made in considerably fewer words; but perhaps this is a personal idiosyncracy, and others may find the wealth of illustrative exposition a help to the understanding of the argument. It is a book that

has obviously been written because the author felt that he must write what he had thought, not think what he must write; and like all such books, it will excite thought in the reader. J. T. DUNN

ENZYME CHEMISTRY. By HENRY TAUBER, Ph.D. Pp. 243. New York: John Wiley & Son, Inc.; London: Chapman & Hall, Ltd. 1937. Price 15s. net.

The enzymes—the agents by which the living cell is able selectively to accelerate certain chemical reactions, hydrolytic, synthetic or oxidative-reductive, which are essential to the functional activity or well-being of the tissues—have a strong appeal to the imagination of chemists in virtue of their astonishing activity, and their study is obviously of fundamental importance if effective knowledge is to be obtained of both physiological processes and pathological changes occurring in living matter.

This joint appeal has led, during the past thirty years, to an ever-increasing amount of experimental activity in this field, and it is doubtful whether we have even yet reached the second inflexion of the curve. Whereas in 1907 the whole field of existing information regarding the enzymes could have comfortably been dealt with in a relatively few pages, in 1937 five thousand pages of "Oppenheimer" are needed to summarise our knowledge, and an annual volume of about 350 pages, "Ergebnisse der Enzymforschung," struggles manfully to keep biochemists and others abreast of the main lines only of advance.

To compress more than a small part of even the very recent developments in enzyme chemistry into some 240 pages, as has been attempted by Tauber, is a task which could only succeed by using what might well be called "review of reviews" methods, supplemented by copious references to original papers and to more specialised reviews, by rigid elimination of reference to most of the earlier work (with the tacit assumption that this work is probably known to the reader), and by abstaining from critical appraisal. The author indeed makes no claim to completeness, and has deliberately reduced theoretical considerations—such as those dealt with fairly recently in Haldane's monograph—to a minimum.

He has nevertheless succeeded in this volume in bringing together valuable, and in places even detailed, accounts of many of the recent significant researches in this field, and that in such a way as to provide a well-documented and very readable summary. The chemist with no specialised knowledge of enzyme work will be able to obtain from it an up-to-date account of the main experimental findings and ideas of the past few years. Work on crystalline enzymes and on specific co-enzymes is justly given considerable prominence, the chapter on the proteolytic and related enzymes being a particularly useful one. On the other hand, references to the *synthetic* action of the intra-cellular "lytic" enzymes (which in the cell almost certainly preceded a synthetic $\rightleftharpoons$ hydrolytic equilibrium) are somewhat scanty. There is evidence in places of rather hasty writing and the use of occasional chemical slang ("This is the theoretical yield on maltose"; "obtained by washing yeast with $H_2O$"; "50 per cent. of the theoretical $CO_2$"; "until free of $SO_4$"), which will doubtless be removed in a second edition.

This book is strongly recommended to every chemist interested in enzymic processes, and to all students of biochemistry and physiology who require an up-to-date summary of recent investigations and ideas in this field. H. D. KAY

CHEMISTRY OF NATURAL PRODUCTS RELATED TO PHENANTHRENE. By L. F. FIESER. American Chemical Society Monograph Series, No. 70. Pp. xii + 456. New York: Reinhold Publishing Corporation. 1937. Price 35s.

The first edition of this book was reviewed in THE ANALYST last September, and the fact that another edition has been called for scarcely a year after its first appearance is a proof of its utility. The work has not been re-written, and corrections and minor changes have been effected in such a way that no alteration in pagination has been required. The extra 98 pages of the present edition result from the inclusion of an appendix of 90 pages in which the order of the main portion of the book is followed, whilst the index has been necessarily expanded to include the newer work. The author has endeavoured to include complete references to papers published up to January 1st, 1937, and he dates his preface from Cambridge, Mass., on February 1st. Owners of the first edition seem able to bring the work up to date by obtaining the appendix separately, and it is to be hoped that Professor Fieser will continue to issue extra numbers at frequent intervals until it is necessary to re-cast the book on a more extensive scale.

Meanwhile Harvard University pursues its way in enlarging our knowledge of the phenanthrene group, not merely by the production of new derivatives, but also by considerations of structure (p. 3 of both editions) and of reaction conditions. Thus Price has recently concluded (p. 339 of Appendix) that the formation of phenanthrene dibromide proceeds by a chain mechanism, whilst Fieser and Price have investigated the effects of substituents on the phenanthrene-bromine equilibrium.

The arrangement of material in the Appendix follows that of the major portion of the work; thus Chapter I deals with the reactions of phenanthrene and the formation and properties of derivatives. The references are full, and those relating to the morphine alkaloids are given for the pharmacology as well as the chemistry of these compounds. New work on resin acids (Chapter II) needs a short appendix, and the carcinogenic hydrocarbons (Chapter III) a longer one, owing to the intensive study of these compounds by Cook and his co-workers. The reviewer of the first edition applied the term *pivotal* to Chapter IV (sterols and bile acids); its appendix accounts for a further 25 pages, and those to Chapters V (sex hormones) and VI (heart poisons) add 26 and 21 pages, respectively. Points in these chapters are the possible necessity of revision of the formulae of the unsaturated acids derived from cholic acid, the relationships of ergosterol, calciferol and vitamin *D*, stereochemical nomenclature, toad poisons and other matters of probably equal importance. The use of surface-film measurements by Askew, Farmer and Kon as a control on accepted formulae (*e.g.* sarsasapogenin, p. 427) is an example of the use of a physical method which is finding other applications.

Professor Fieser has dealt with a complicated subject in a masterly and interesting manner, and is to be warmly congratulated on his book. The printing is excellent and the representations of constitutional formulae leave nothing to be desired; even methyl and ethyl groups are printed as they should be, and not as Me and Et.

J. T. HEWITT