THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

THE Fourth Summer Meeting was held at the Imperial Hotel, Llandudno, from June 23rd to 26th. There was an attendance of fifty-nine, including many ladies.

Among those present were the following:—Past Presidents (Dr. B. Dyer, accompanied by Mrs. Dyer, and Dr. Dunn with Mrs. Dunn); Hon. Treasurer (Mr. E. B. Hughes with Mrs. Hughes); Editor of the ANALYST (Dr. C. A. Mitchell); Mr. E. M. Hawkins; and Miss Elliott.

On Saturday afternoon a paper, illustrated by lantern slides and photographs was given by A. Lucas, O.B.E., F.I.C., on "Ancient Egyptian Materials and Industries about 1350 B.C." Mr. Lucas gave a short account of the history of that period and of the objects found in the tomb of Tut-ankhamūn. The lantern slides were kindly lent by Dr. Howard Carter, the discoverer of the tomb. The materials described included alabaster (calcite), faience, glass, woven fabrics wool, pigments and varnish, copper, bronze, gold, silver, iron and jewellery; and the industries referred to were those connected with such materials.

The CHAIRMAN (Mr. John Evans), in extending a welcome to all present, spoke of the special pleasure felt by everyone at the presence of Dr. Bernard Dyer, who has been a member of our Society since its inauguration. Mr. Evans also mentioned the interesting fact that he himself, an examiner of the Institute of Chemistry in Branch E, his predecessor in that office (Professor W. H. Roberts), and his successor (Mr. S. E. Melling) were all examined by Dr. Dyer.

A resolution was passed conveying the greetings of the Section and declaring its continued loyalty to the Council of the Society.

Apologies for absence were received from the President (Mr. F. W. F. Arnaud), the Hon. Secretary (Dr. Roche Lynch), and Messrs. E. Hinks, H. M. Mason and J. W. H. Johnson.

The members engaged in various forms of recreation during the week-end. On Sunday afternoon the party motored through the Snowdon district and partook

of tea at the Waterloo Hotel, Bettws-y-Coed; in the course of the tour an inspection was made of the ruins caused by the bursting of the dam some years ago, at Dolgarrog.

Each lady present was the recipient of a handsome souvenir from the Chairman, for which he was thanked, on behalf of the ladies, by Mrs. W. H. Roberts.

A vote of appreciation was passed to the Hon. Secretary (Mr. J. R. Stubbs), on the motion of Dr. Dyer.

Note on the Use of Alkaline Pyrogallate Solution in Gas Analysis

By J. S. HALDANE, C.H., F.R.S., and R. H. MAKGILL, C.B.E., M.D.

Although alkaline pyrogallate has been for long in general use for absorbing oxygen in gas analysis, it has also been known for almost as long that a little carbon monoxide may sometimes be given off during the absorption, thus making the percentage of oxygen found somewhat too low. It was definitely pointed out by one of us, however,* that with a solution made by adding 10 grms. of pyrogallic acid to 100 c.c. of almost saturated caustic potash solution (sp.gr. about 1·54, and containing about 80 grms. of dry potassium hydroxide per 100 c.c. of solution) the formation of carbon monoxide is entirely avoided, so that the resulting analysis may be taken as correct to the second decimal place if the burette is corrected for errors in graduation and due care is taken. It is probably known, however, to many of those who use this solution that, if it is quite freshly made, it gives a result slightly low for pure air, instead of 20·93 per cent., the result which was invariably given afterwards and can thus be used as a convenient means of correcting the graduation of the gas-burette. This figure (20·93 per cent.) was obtained with a burette very carefully corrected by weighings, and with the inside wetted, as in actual use.

In connection with a recent paper (*Trans. Inst. Mining Engineers*, May, 1933), dealing with both the presence and absence of carbon monoxide in the residual gas, or "blackdamp," left in the oxidation of coal at an ordinary temperature, we made some experiments on the formation of carbon monoxide in various other sorts of oxidation of organic substances, such as wet sawdust, hay, or drying oil, and including alkaline pyrogallate. We have now extended the latter experiments, in so far as they bear directly on the use of pyrogallate in gas analysis. With the Haldane gas analysis apparatus it is easy to detect in the residual nitrogen, after a determination of oxygen in air, as little as 0·01 per cent. of carbon monoxide. With pyrogallate solutions made some time before in the proportions described above we have confirmed the fact that no carbon monoxide can be detected in the residual nitrogen—even with a solution which had already been used for over

* Haldane, *J. Physiol.*, 1898, **42**, 467, and *Methods of Air Analysis*, Second Edition, pp. 13 and 43.

200 analyses. Being suspicious, however, as to solutions quite freshly made, we tested one carefully, and found that immediately after the pyrogallic acid had been added to the potash as much as 0·13 per cent. of carbon monoxide was formed in an air analysis, and the oxygen was, as would be expected, considering that carbon monoxide contains half its volume of oxygen, 0·06 per cent. too low. During the next 38 hours the carbon monoxide formed dropped to 0·04 per cent. After 70 hours no carbon monoxide was found, and there was no deficiency in the oxygen percentage.

From these observations it seems to be necessary, when very accurate results are needed, to let the pyrogallate mixture stand for nearly three days before it is used. But, as this might sometimes be inconvenient, we have tried whether the delay cannot be avoided by heating the mixture directly after it has been made. We first tried heating the fresh mixture in a small flask in a bath of water, leaving the flask for half an hour in the water after it had been heated to boiling point. This had the effect of reducing the proportion of carbon monoxide formed to about half, with a corresponding diminution in the error of the oxygen percentage found. But the freshly-made solution was not yet right, though after 28 hours the carbon monoxide ceased to be measurable. We therefore, with another freshly-made solution, continued the heating in boiling water for an hour. The solution now gave no measurable carbon monoxide, and an exactly correct oxygen percentage for pure air. Accurate results can therefore be obtained with a freshly-made solution, if it has been heated for an hour at boiling point.

We have also made a number of experiments with weaker potassium hydroxide solutions. A solution made by adding 10 grms. of pyrogallic acid to a solution containing 20 grms. of potassium hydroxide per 100 c.c. produced 0·66 per cent. of carbon monoxide, with a corresponding reduction of 0·33 per cent. in the oxygen percentage. Three days later 0·4 per cent. of carbon monoxide was produced, and the oxygen was too low by about half of this percentage. It was thus evident that this solution is unsuitable for gas analysis. We had the curiosity to test solutions made with the same proportion of pyrogallic acid, and still lower percentages of potassium hydroxide; but, although the oxygen percentage obtained was always too low and the rate of its absorption became very slow, the percentage of carbon monoxide formed became less than with 20 per cent. potassium hydroxide solution.

We shall not attempt to discuss here the general question why carbon monoxide is sometimes formed, and sometimes not formed, in the oxidation of pyrogallate and various other substances, but must content ourselves with describing the facts, in so far as they bear on the use of pyrogallate in gas analysis. A very strong solution of pyrogallate and potassium hydroxide is extremely convenient on account of its great lasting properties and of the fact that, unlike comparatively dilute solutions used in gas analysis, it takes up hardly any gas in simple physical solution.

The Determination of Small Amounts of Pyridine in Nicotine

By N. STRAFFORD, M.Sc., F.I.C., and R. T. PARRY-JONES

The fact that pyridine is sometimes used as an adulterant in inferior grades of nicotine used for insecticidal purposes has long been recognised.

A search of the literature led us to the conclusion that comparatively little attention has hitherto been paid to the problem of detecting this adulteration of nicotine with pyridine. Whilst there are methods, such as the physico-chemical methods of P. J. and C. H. Fryer (Analyst, 1919, **44**, 363), which will determine approximately upwards of 1 per cent. of pyridine in nicotine, such methods are empirical and, in our experience, do not possess a very high degree of accuracy.

Spacu's copper-thiocyanate precipitation method (Analyst, 1925, **50**, 580; *cf.* Tallantyre, Analyst, 1931, **56**, 202) for pyridine proved ineffective when applied to the determination of small proportions of pyridine in nicotine, since nicotine was found to give a greenish-brown precipitate which masks the bright green pyridine complex.

An attempted direct determination of nicotine in a synthetic mixture of nicotine and pyridine containing about 10 per cent. of pyridine, by an adaptation of the picrate method of Pfyl and Schmitt (abst. Analyst, 1927, **52**, 728) was unsuccessful; in this case, the presence of pyridine apparently prevented the complete precipitation of the nicotine dipicrate.

The most promising method appeared to be a colorimetric one based upon the reaction of cyanogen bromide with the product of the interaction of pyridine and a primary aromatic amine. The coloured complex so produced is a derivative of glutaconaldehyde, *R*.NH.CH:CH.CH:CH.CH:N*R*.HBr, resulting from the rupture of the pyridine nucleus.

The reaction was described by Tallantyre (*loc. cit.*), and elaborated by Kulikow and Krestowosdwigenskaja (Analyst, 1930, **55**, 344), who used a solution of cyanogen bromide in specially purified *iso*-amyl alcohol, and a saturated aqueous solution of aniline as the primary amine. The colour produced is a bright yellow, slowly turning to orange on standing; the coloured complex is readily extracted from aqueous solution by amyl alcohol.

In our experience, the colorimetric method described by these authors gives very accurate results when applied to the determination of pyridine alone; furthermore, it is very much more sensitive than the copper thiocyanate precipitation method.

It was found, however, that nicotine, under like conditions, also gives a colour very similar to that given by pyridine, but that with nicotine the yellow compound is more soluble in water than in amyl alcohol; the colour in the latter solvent—a relatively faint yellow—corresponds with the apparent presence of about 4 per cent. of pyridine in the original nicotine.

Other bases, such as piperidine, diethylamine and ammonia, were found to give no colour, whilst homologues of pyridine behaved similarly to nicotine.

Further search was made for a reaction specific for pyridine, but without success, since in all cases the preponderance of nicotine present caused interference.

It therefore appeared likely that a solution to the problem might be found in the separation of the pyridine from the nicotine, followed by the colorimetric determination of the pyridine.

The difference between the boiling-points of the two bases has in the past been made the basis of a separation by fractional distillation (P. J. and C. H. Fryer, *loc. cit.*). This method, however, was not considered satisfactory for the present problem of determining very small amounts of pyridine. Attention was therefore directed to the possibility of destroying the nicotine by oxidation. It is known that nicotine is very readily oxidised to nicotinic acid, methylamine and malonic acid; homologues of pyridine are also readily oxidised to the corresponding pyridine carboxylic acids, whereas pyridine itself is relatively stable to oxidising agents.

Experiments conducted in this laboratory showed that nicotine and homologues of pyridine can be oxidised rapidly and completely by heating with an aqueous solution of potassium permanganate, whilst pyridine itself, under similar oxidation conditions, remains unchanged, and can be recovered quantitatively by steam-distillation.

When commercial nicotine, containing pyridine or pyridine bases, is similarly oxidised and steam-distilled, the resulting distillate contains only pyridine, together with any ammonia which might also have been present in the original sample. As previously stated, ammonia gives no colour with aniline and cyanogen bromide. It was found, however, that the presence of relatively large amounts of ammonia interferes considerably with the colorimetric determination of pyridine, (*a*) by promoting emulsification or retarding separation of the aqueous and alcoholic layers, and (*b*) by partially inhibiting the development of the yellow colour due to pyridine. On further investigation, however, it was found that the effect is negligible in actual practice, since, in amounts far in excess of those likely to be encountered in any commercial nicotine, ammonia shows no interference whatsoever.

The method ultimately evolved depends therefore on:

(*a*) Oxidation of the nicotine (together with homologues of pyridine) by potassium permanganate.

(*b*) Recovery of the unchanged pyridine by steam-distillation.

(*c*) Determination of the pyridine in the distillate by a colorimetric method based on the reaction of pyridine with cyanogen bromide and aniline.

RECOMMENDED PROCEDURE: REAGENTS REQUIRED.—*Potassium permanganate:* 6 per cent. aqueous solution; *sodium hydroxide:* 10 per cent. aqueous solution; *amyl alcohol:* specially purified as described below.

Ordinary commercial amyl alcohol is shaken for one hour with 20 per cent. of its volume of 5 per cent. sulphuric acid, the acid layer run off, and the amyl alcohol washed with distilled water until free from acid. It is then dried over

freshly-ignited sodium sulphate and distilled, and the fraction distilling between 129° and 134° C. is collected. The product should contain less than 0·025 mgrm. of pyridine per litre when tested by the colorimetric method described later.

Saturated Aqueous Solution of Freshly-distilled Aniline.—This must be prepared freshly as required.

Cyanogen Bromide in Amyl Alcohol.—Forty ml. of saturated bromine water are just decolorised by the gradual addition, in the cold, of a 10 per cent. aqueous solution of potassium cyanide (AR). The mixture is then shaken with 12 ml. of the purified amyl alcohol, and the alcoholic layer is separated.

Standard Pyridine Solution.—One grm. of redistilled pyridine is dissolved in distilled water and diluted to 1000 ml. (A). Ten ml. of this solution are then diluted to 1000 ml. (B).

One ml. of the dilute solution (B) = 0·00001 grm. pyridine.

METHOD.—From 0·25 to 0·3 grm. of the sample of nicotine is accurately weighed out from a Lunge-Rey pipette into a 250-ml. round-bottomed flask fitted with ground-in reflux condenser, and diluted with water to about 25 ml. Fifty ml. of 6 per cent. potassium permanganate solution are then added, and the mixture is heated on a sand-bath until it boils very gently, and is then maintained just below the b.pt. for thirty minutes.*

The mixture is then cooled and transferred to a 500-ml. bolt-head flask, the volume being kept as low as practicable. Ten ml. of 10 per cent. sodium hydroxide solution are added, and the mixture is steam-distilled, the distillate being collected in a 500-ml. receiver.†

The volume of the distillate (about 400-450 ml.) is then adjusted to 500 ml. (When pyridine is present in amounts greater than 5 per cent.—say, from 5 to 10 per cent.—it is more convenient to make the volume of the distillate up to 1000 ml.)

According to the amount of pyridine present (estimated by a preliminary test), a suitable aliquot portion (from 0·5 to 20 ml.) of the distillate is tested, and the colour obtained by the procedure subsequently described is compared with those obtained simultaneously with the standard pyridine solution.

Suitable standards are prepared from 0·5 ml., 1·0 ml., 2 ml., 3 ml., 4 ml., and 5 ml. of the standard pyridine solution (B).

PROCEDURE FOR COLORIMETRIC COMPARISON.—The aliquot portion of the distillate and the chosen aliquot portions of the standard pyridine solution are each diluted with water to 20 ml. in 100-ml. separating funnels. (This is most conveniently done by measuring the requisite amount of water first and pipetting the aliquot portions into the measured volume of water.) One ml. of the alcoholic cyanogen bromide solution is then added to each and the mixtures shaken. One ml. of saturated aqueous aniline solution and 15 ml. of purified amyl alcohol are then added to the respective solutions, and the mixtures are well shaken and allowed to stand for ten minutes. The aqueous layers are then run off, and the colours of the

* If the permanganate is completely decolorised, more should be added to ensure that a definite permanganate colour persists at the end of the oxidation.

† During the distillation, the flask itself should be heated to avoid excessive condensation of steam; towards the end, heating may be increased so as to reduce the final volume in the bolt-head flask to about 15 to 30 ml.

alcoholic solutions are compared directly in 20-ml. Nessler tubes without further dilution.

Let W represent the weight of the nicotine sample taken; V, the volume to which total distillate was diluted; v, the volume of the aliquot portion of distillate taken for colorimetric determination; and N the number of ml. of standard pyridine solution (B) required.

Then the percentage of pyridine in the sample of nicotine $= \frac{N \times 0{\cdot}001 \times V}{v \times W}$

The colorimetric method, described above, for the determination of the pyridine is extremely sensitive—0·00001 grm. of pyridine is easily detected—and the gradation of the golden-yellow colour produced is excellent for increments of 0·00001 grm. of pyridine up to 0·00005 grm. In our experience the colour beyond this limit is too deep for accurate comparison. The colours become redder on standing, but the reddening has no apparent effect on the gradation, and there does not seem to be any reason for allowing the coloured alcoholic solutions to stand, prior to matching, longer than the arbitrary period of ten minutes stipulated in the method.

The whole procedure is relatively simple, and involves no special technique; it is accurate to within ± 10 per cent. absolute. The extreme sensitivity of the reagent makes it possible to detect and determine as little as 0·05 per cent. of pyridine in 0·25 grm. of nicotine.

The method, as described, is suitable for the determination of quantities up to 10 per cent. of pyridine, but, if necessary, could readily be extended so as to be applicable to samples containing larger proportions of pyridine.

The following are typical results obtained by the given method on known mixtures of pyridine and nicotine:—

Pyridine present Per Cent.	Pyridine found Per Cent.
0·76	0·81
1·20	1·26
4·6	5·0
5·0	4·6
8·4	7·6

It must be emphasised that the method applies only to the determination of pyridine itself. It will, therefore, not detect the adulteration of nicotine with "heavy pyridine bases," which consist chiefly of the higher homologues of pyridine, and contain practically no pyridine.

In conclusion, we desire to thank Messrs. Imperial Chemical Industries Limited (Dyestuffs Group), in whose Research Analytical Laboratory the above investigation was carried out, for permission to publish this paper. We would also record our thanks to Dr. T. Callan for drawing our attention to the problem and for his interest in the investigation.

Notes on the Occurrence of Iron and Copper in Liver and Liver Extracts

By HENRY GEORGE REES, B.Sc., A.R.C.S., D.I.C., A.I.C.

(*Read at the Meeting, April* 5, 1933)

It is only during recent years that the importance of the mineral constituents of the diet has attracted the attention it merits. Iron and copper enter into the problem in very minute quantities, the normal daily requirement of iron for an adult being only 8 to 12 mgrms. This is used mainly for the formation of the haemoglobin of red blood corpuscles, and failure to supply the required amount may result in nutritional anaemia.

The following table, compiled from the series of papers by Elvehjem and Peterson (*J. Biol. Chem.*, 1927, **74**, 433; 1928, **78**, 215; Analyst, 1927, **52**, 650), and by Lindow, Elvehjem and Peterson (*J. Biol. Chem.*, 1929, **82**, 465; Analyst, 1929, **54**, 420), shows the distribution of iron and copper in various foodstuffs.

Iron and Copper in Foodstuffs

Expressed as mgrms. per kilo of fresh material

	Iron	Copper
Ox-liver	83	21·5
kidney	55	1·1
muscle	37–41	0·8–1·2
Milk	2·4	0·15
Egg	25·2	2·3
Fish muscle	3·4–9·6	1·4–4·1
Oyster	31·4	30·7
Wheat	37·2	12·7
Fresh fruits	6·6	1·0
Nuts	41·0	11·6
Roots and tubers ..	11·0	1·4
Vegetables (leafy) ..	69·0	1·2

A point of interest in this table is the large proportion of these metals present in meat products.

It was largely on account of its high iron-content that liver was chosen as a desirable substance for use in the experimental investigations of anaemia in the original work of Whipple. More recently, the theory that the therapeutic value of liver in pernicious anaemia may be, to some extent, due to the iron and copper present has attracted considerable attention, although it is by no means generally accepted. Some results put forward by Meyer and Eggert (*J. Biol. Chem.*, 1932, **99**, 265) induce us to publish figures obtained early in 1930 on the amount of iron and copper to be found in fresh ox-liver and liver extracts, and also to indicate our experiences in the method of determination of these metals in such products.

The results given by Meyer and Eggert deal with the iron and copper content of horse, dog, ox, and hog livers and the partition of these metals in various aqueous and alcoholic extracts of liver. As in this paper we are concerned only with aqueous extracts of ox-liver, the following figures may be quoted from their paper (*loc. cit.*).

	Quantity from 1 kilo. of fresh liver Grms.	Iron Mgrms.	Copper Mgrms.
Whole liver ..	—	61·6	16
Whole aqueous extract	33	11·9	3·96

It can be seen from these results that there is far from complete extraction of the metals by water. Calculating the results on the whole liver, we find that 19·3 per cent. of the total iron, and 24·7 per cent. of the total copper are extracted in the whole aqueous extract. If we assume, as Meyer and Eggert point out, that an extraction of only 60 per cent. was obtained, these figures become 32·2 per cent. and 41·2 per cent., respectively.

The details of our own experiments were as follows: Determinations were carried out on fresh ox-liver and on concentrated aqueous extracts of ox-liver, prepared in such a manner as to be free from external contamination with copper and iron. As it was found impracticable to ash the liver completely, this process was carried as far as possible and the solutions were made up by extracting the ash with dilute hydrochloric acid.

METHODS OF ANALYSIS.—*Iron.*—The method used was that of Elvehjem, Kemmerer, Hart and Halpin (*J. Biol. Chem.*, 1929, **85**, 92), with slight modification. The ashed material was taken up in dilute hydrochloric acid and oxidised with 5 drops of perhydrol, diluted and filtered. An aliquot portion was taken, 5 c.c. of 20 per cent. potassium thiocyanate solution were added, and the whole was made up to 100 c.c. The colour was then compared in a Duboscq colorimeter with that from a standard iron solution prepared from pure iron wire. It is suggested in the original method that the colouring matter be extracted with amyl alcohol, but some difficulty was encountered here owing to the alcohol layers being wet. A blank experiment, using blood albumin containing a definite added amount of ferric citrate, indicated that it is not necessary to extract the colouring matter, as determinations can be made directly.

Copper.—The Elvehjem and Lindow modification (1928) of the Biazzo method (*J. Biol. Chem.*, 1929, **81**, 435; ANALYST, 1929, **54**, 245) was used.

EXPERIMENTAL RESULTS:—Two liver extracts were used. In the first, for the determination of iron, 25 grms. of dry extract were obtained from 350 grms. of fresh liver, and, on analysis, the following figures were obtained:

	Total solid matter Per Cent.	Quantity from 1 kilo. of fresh liver Grms.	Iron Per Cent.	Iron Mgrms.
Fresh ox-liver	30·72	—	0·0080	80
Aqueous extract	—	71·5	0·0426	31·5

In this case it will be seen that the aqueous extract contained 38·1 per cent. of the total iron of fresh liver.

For the copper determination a concentrated fluid extract of liver was used, in which 1 kilo. of extract was equivalent to 3·6 kilos. of fresh liver.

	Total solid matter Per Cent.	Quantity from 1 kilo. of fresh liver Grms.	Copper Per Cent.	Copper Mgrms.
Fresh ox-liver	30·72	—	0·0024	24
Liver extract (dry)	—	109·6	0·00106	1·75

It will be seen that only 7·3 per cent. of the total copper has been obtained in the aqueous extract.

As in Meyer and Eggert's experiment, it must not be considered that a complete extraction of the liver has been obtained. In the first extraction (for the determination of iron) probably not more than 60 per cent. of extractable substances were obtained, judging by the relative proportions of total solids found in the extract and calculated to be present in the water left in the residue. In the extraction for the determination of copper the yield was probably higher, since the material was expressed in a filter press.

While our figures for the total iron and copper in fresh liver are in agreement with those of Meyer and Eggert and Elvehjem, we find that the amount of iron extracted by water is somewhat higher, whilst the copper is considerably lower.

In the preparation of their aqueous extract Meyer and Eggert heated the material to 85° C. In our experiments the temperature was not allowed to rise above 50° C., with the consequent retention of the major proportion of the coagulable protein. A further extract was then made and, before concentration, this was coagulated by boiling, the coagulum separated and well washed with hot water, and the two fractions worked up separately. The following table shows the iron content of these two fractions.

	Quantity from 1 kilo. of fresh liver Grms.	Iron Mgrms.	Iron extracted Per Cent.
Coagulable fraction ..	31·6	15·5	19·3
Coagulum-free fraction ..	46·6	8·7	10·9
Total extract	78·2	24·2	30·2

From these results it will be seen that a considerable quantity of the iron extracted by water is present in the fraction that is coagulated by heat, thus explaining the lower results of Meyer and Eggert.

It is interesting to note that these authors do not consider that their results lend much support to the theory that the therapeutic action of liver, as regards pernicious anaemia, is due, in part, to the metallic constituents, on account of the small amounts that are extractable in various anti-anaemic fractions. They state (*loc. cit.*): "It can be concluded from these results that the substance active in pernicious anaemia has no relation to the copper and iron content of the liver, whereas the value of liver in secondary anaemia may be at least partly due to the

presence of these metals." There is no doubt from the work of many investigators that iron and copper are of considerable value for the formation of haemoglobin, but whether the quantities present in liver contribute to the well-known therapeutic action of liver preparations in anaemia is a matter of some doubt; however, this is certainly not a point that can be settled on purely analytical data.

SUMMARY.—Determinations of iron and copper in ox-liver and liver extracts have been made, with a view to determining the proportion of these metals that can be extracted.

Fresh ox-liver has been found to contain 80 mgrms. of iron and 24 mgrms. of copper per kilo.

By extraction with water at 50° C. approximately 31·5 mgrms. of iron and 1·75 mgrms. of copper were extracted per kilo. of liver.

It is shown that extraction at a high temperature is less effective than at a relatively low temperature for the extraction of iron.

I wish to express my thanks to Messrs. Oxo Ltd., in whose Research Laboratories this work was carried out, for permission to publish the above results, and also to Dr. A. H. Salway for continued interest and guidance.

RESEARCH LABORATORIES
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DISCUSSION

The PRESIDENT pointed out that the amount of copper occurring in animal tissue depended very largely upon the food which the animal had consumed. For instance, in an orchard where the trees had been sprayed the copper-content of grass growing under the trees might amount to something in the region of ½ grain per lb. (dry weight), and it was not surprising that the organs of animals fed on such grass should contain large amounts of copper. There was some accumulation of copper in these animals. It was also significant that many linseed and other oil-cakes contained copper, which was also a constituent of straws and hays, having originally been derived from copper in the soil. Sheep, and especially ewes, were very susceptible to the toxic action of copper, and he had known them to die when turned into orchards where they had eaten fallen leaves containing copper derived from spray. The livers of such sheep had a metallic sheen and contained considerable quantities of copper. For these reasons it would be difficult to give representative figures for the copper-content of the livers of English animals.

Mr. A. L. BACHARACH asked whether, in the modification of Elvehjem's method, it had been found necessary to secure hydrolysis of the pyrophosphates.

Dr. R. H. SALWAY did not agree that the presence of copper in the liver was due to accidental contamination. The human liver contained copper, and he hoped that it was not due to eating sprayed vegetables. He did not think that the small proportions of metals invariably found in the human body were really poisons. Surely a certain amount of copper was necessary. Mr. Rees had shown that a considerable amount of the iron in the liver was removed with the coagulating substances, and this showed that in preparing a liver extract one must use a method which would retain the active principles—the vitamins, and the copper and iron.

Dr. G. ROCHE LYNCH stated that slices from the livers of persons who had died of pernicious anaemia gave a pronounced reaction when treated with hydrochloric acid and potassium ferrocyanide, showing that such livers contained

a considerable proportion of iron. On the other hand, in cases where the administration of liver had failed, strikingly successful results had been attained by giving enormous quantities of iron to the patients, although there was no proof that the iron was the effective agent.

Mr. T. McLACHLAN referred to the amounts of iron of copper in those liver extracts prepared for hypodermic injection. He presumed that they were not commercially prepared, as in that case they would be made in tinned copper pans, which might impart copper to them.

Mr. H. JENSEN called attention to the occurrence of cobalt in animal organs (*cf.* ANALYST, 1933, 340), and suggested that the action of that metal might also have to be taken into consideration.

Professor H. D. KAY pointed out that it was generally believed that there was more copper present in the foetus than in the adult. In the yolk of a hen's egg there was a fair amount of copper as well as of iron. Apparently, both were constituents of the protein, and the two could be separated.

Mr. REES, replying, said that the point which continually recurred in the discussion was the possibility of the iron and copper present in the liver being due to the method of feeding the animal. While admitting this possibility, it yet seemed rather remarkable that the figures which he had obtained with Argentine livers agreed to within 3 mgrms. per kilo. with those given by Elvehjem for North American livers; the results of the work of Myer and Eggert, which was carried out at Rockford, showed a difference of 20 mgrms. per kilo. He had no figures to cite as to amounts of iron and copper in hypodermic preparations, but as those preparations which he had examined had been made in glass vessels, there could be no question of contamination in these. Although cobalt had been found in the liver, it was only present in minute quantities, and he regarded it as supplementary to the iron and copper. In using the method of Elvehjem he had not taken the question of hydrolysis of pyrophosphates into consideration.

The Determination of Metals by Means of 8-Hydroxyquinoline

Part I. The Effect of p_H on the Precipitation of Magnesium, Zinc, Cobalt, Nickel, Copper and Molybdenum from Acetate Solutions

BY H. RONALD FLECK AND A. M. WARD, D.Sc., PH.D., A.I.C.

THE recent extensive studies on the determination of metals by means of 8-hydroxyquinoline ("oxine") show that the reagent possesses very many desirable analytical qualities. Precipitation is usually effected from acetate or tartrate solutions, but inaccurate results are sometimes obtained, and may arise from insufficient precision in the published account of the conditions. In acetate solutions, the effect of p_H on the extent of precipitation is presumably the cause, for, although general statements are given on the amount of acid or alkali to be added, yet exact studies of the range of p_H over which the metals are precipitated have not been made. In tartrate solutions additional factors, such as the formation and stability of complex metallic tartrates, probably are of significance. We propose to deal first with the simpler case of acetate solutions; results on the effect of p_H on the precipitation of six metal-oxine complexes are given in this communication.

In every instance the total volumes of solutions were 145 c.c. or 160 c.c., according to whether 10 c.c. or 25 c.c. of the standard solution containing the metal

were used. In each experiment 5 grms. of ammonium acetate and 10 c.c. of a 2 per cent. solution of oxine in *N* acetic acid were included in the total volume.

MAGNESIUM (Berg, *Z. anal. Chem.*, 1927, **71**, 23; Hahn and Vieweg, *ibid.*, p. 122; see also "Organic Reagents for Metals," Hopkin and Williams, Ltd., 1933, p. 41, bibliography):—A solution was used containing 13·9393 grms. of pure magnesium sulphate ($MgSO_4.7H_2O$) per litre, which corresponds with 13·75 mgrms. of magnesium, with 197·0 mgrms. of $Mg(C_9H_6ON)_2.2H_2O$, and with 45·22 c.c. *N*/10 potassium bromate solution per 10 c.c. of solution. Ten c.c. of the solution were found to contain 13·75 mgrms. of magnesium, determined as pyrophosphate. The weight of oxine precipitate, dried at 100° C., and the volumetric determination by means of potassium bromate, agreed with the composition $Mg(C_9H_6ON)_2.2H_2O$.

The following examples serve to illustrate the method used:—

(1) To 10 c.c. of the magnesium solution 25 c.c. of ammonium acetate (200 grms. per litre), 80 c.c. of water, 20 c.c. of *N* sodium hydroxide solution and 10 c.c. of oxine (2 per cent.) in *N* acetic acid were added. The solution was boiled for 3 to 5 minutes, and filtered at once through a sintered-glass crucible (1G3) into a dry flask. The undiluted filtrate was reserved for determination of p_H at room temperature. The precipitate was well washed with boiling water, dried to constant weight at 100° C., and weighed [obtained 175 mgrms. of $Mg(C_9H_6ON)_2.2H_2O$]. It was then dissolved in 2 *N* hydrochloric acid, and, after the addition of a small excess of *N*/10 potassium bromate and bromide, it was titrated with *N*/10 sodium thiosulphate in the usual way: 40·2 c.c. *N*/10 potassium bromate solution were required. The p_H was measured potentiometrically by means of hydrogen and calomel electrodes and a capillary electrometer: observed E.M.F., 0·762 volt; temp., 19° C.; whence p_H equals 8·91.

(2) To 10 c.c. of the magnesium solution, 25 c.c. of ammonium acetate (20 per cent.), 65 c.c. of water, 35 c.c. of *N* sodium hydroxide solution, and 10 c.c. of oxine (2 per cent.) in *N* acetic acid were added. Found: 197·0 mgrms. of complex: 45·2 c.c. of *N*/10 potassium bromate: E.M.F., 0·795 volt; temp., 18° C.; whence p_H equals 9·51.

TABLE I.

p_H	Complex Mgrms.	*N*/10 $KBrO_3$ c.c.	p_H	Complex Mgrms.	*N*/10 $KBrO_3$ c.c.
5·32	—	—	9·28	194·5	44·65
5·42	—	—	9·51	197·0	45·2
5·56	—	—	9·73	197·0	45·2
5·64	—	—	10·36	197·0	45·2
6·10	—	—	11·00	197·0	45·2
6·73	—	—	11·50	197·0	45·2
7·00	—	—	12·15	197·0	45·2
7·26	—	—	12·41	197·0	45·2
7·71	7·0	1·6	12·67	197·0	45·2
7·90	22·0	5·05	12·84	132·0	30·3
8·08	86·4	19·85	13·00	51·0	11·7
8·24	114·7	26·35	13·23	—	—
8·50	147·6	33·9	13·57	—	—
8·63	158·0	36·25	13·76	—	—
8·72	164·0	37·6	14·00	—	—
8·91	175·0	40·2	14·24	—	—
9·11	184·0	42·3	14·32	—	—

The complete results, using throughout 10 c.c. of magnesium solution, 5 grms. of ammonium acetate, 10 c.c. of oxine (2 per cent.) in *N* acetic acid, with varying quantities of *N* sodium hydroxide solution or *N* acetic acid in a total volume of 145 c.c., are given in Table I and Fig. 1 (p. 391). Between p_H 7 and 8, some co-precipitation of oxine took place; the precipitates obtained over this range were, therefore, dissolved in 2 *N* hydrochloric acid, and the pure magnesium-oxine complex was precipitated from alkaline tartrate solution.

Complete precipitation under the conditions specified takes place between p_H 9·44 and 12·66, the horizontal portion of the curve extending over the range 35–62 c.c. of *N* sodium hydroxide solution.

ZINC (Hahn and Vieweg, *loc. cit.*).—A solution of zinc (1·284 grm. per litre), dissolved in dilute acetic acid, was used. The oxine complex, dried at 120°–130° C., agrees excellently with the composition $Zn(C_9H_6ON)_2$, and, dried at 100° C., is the dihydrate, $Zn(C_9H_6ON)_2.2H_2O$. Twenty-five c.c. of the stock solution (32·1 mgrms. of zinc, equivalent to 173·4 mgrms. of $Zn(C_9H_6ON)_2$ and to 39·27 c.c. of *N*/10 potassium bromate) in a total volume of 160 c.c. were used for each determination, exactly as in the case of magnesium. The complex compounds precipitated from acid solution are well crystallised, and, to complete precipitation from the more strongly acidic solutions, these must be boiled for at least 5 minutes; the precipitates obtained from the solutions of highest p_H are apparently amorphous. The results are given in Table II, and are shown graphically in Fig. 2 (p. 393).

Complete precipitation, therefore, extends from p_H 4·58 to 13·4, which corresponds with solutions of total volume of 160 c.c. containing 5 grms. of ammonium acetate and from 80 c.c. of *N* acetic acid to 70 c.c. of *N* sodium hydroxide solution and 10 c.c. of oxine (2 per cent.) dissolved in *N* acetic acid.

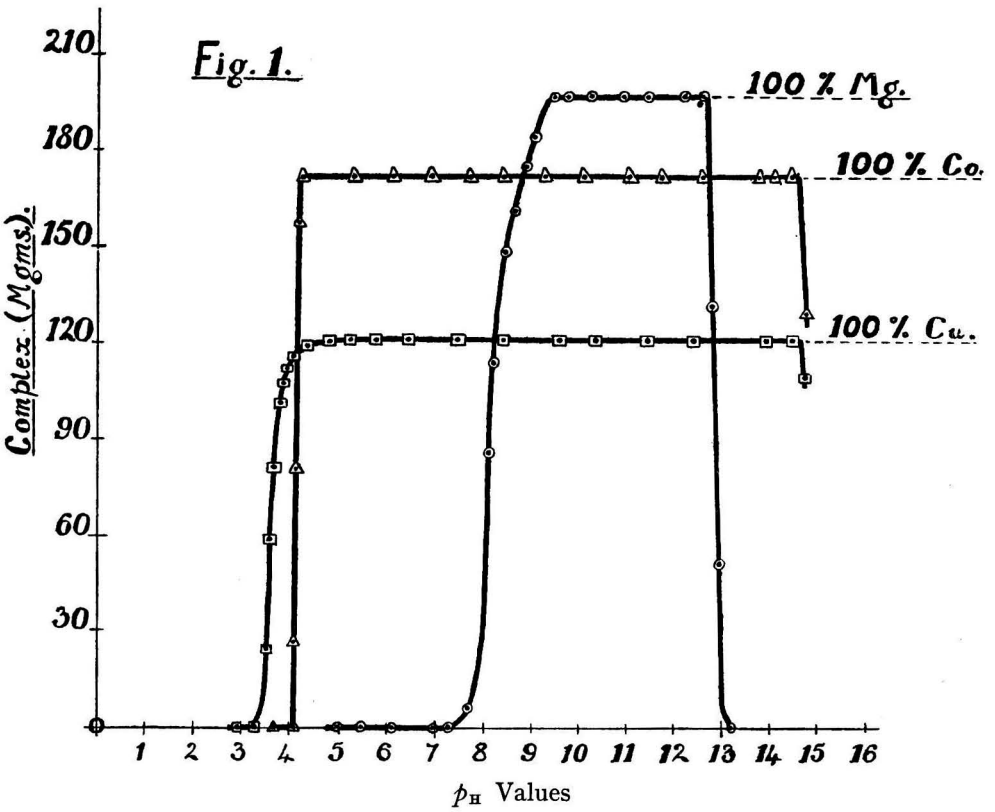
TABLE II

p_H	Complex Mgrms.	*N*/10 $KBrO_3$ c.c.	p_H	Complex Mgrms.	*N*/10 $KBrO_3$ c.c.
3·53	—	—	8·08	173·4	39·25
3·68	—	—	8·85	173·4	39·25
3·94	—	—	9·50	173·4	39·25
4·20	26·0	5·95	10·36	173·4	39·25
4·33	91·0	20·6	10·96	173·4	39·25
4·43	147·0	33·5	11·78	173·4	39·25
4·50	168·0	38·05	12·91	173·4	39·25
4·70	173·4	39·25	13·33	173·4	39·25
4·91	173·4	39·25	13·52	157·0	35·55
5·43	173·4	39·25	13·76	77·5	17·6
6·02	173·4	39·25	13·85	11·5	2·6
6·61	173·4	39·25	14·00	—	—
7·34	173·4	39·25	14·20	—	—

COBALT (Berg, *Z. anal. Chem.*, 1929, **76**, 196).—The solution used contained 14·104 grms. per litre of cobalt sulphate, $CoSO_4.7H_2O$, which corresponds with 29·56 mgrms. of cobalt, with 40·11 c.c. of *N*/10 potassium bromate, and with 173·9 mgrms. of $Co(C_9H_6ON)_2$ per 10 c.c. of solution. Determination by evaporation and ignition to $CoSO_4$, showed 10 c.c. of the solution to contain 29·53 mgrms. of cobalt. The gravimetric oxine method was not used, as the composition of the precipitate, dried at 120° C., was indefinite, corresponding approximately with $3Co(C_9H_6ON)_2.2H_2O$. The volumetric procedure gave excellent results, and the

TABLE III

p_H	Complex Mgrms.	$N/10$ $KBrO_3$ c.c.	p_H	Complex Mgrms.	$N/10$ $KBrO_3$ c.c.
3·68	—	—	7·80	173·9	40·1
3·86	—	—	8·50	173·9	40·1
4·03	—	—	9·32	173·9	40·1
4·10	27·1	6·25	10·15	173·9	40·1
4·17	81·7	21·15	11·15	173·9	40·1
4·23	158·9	36·65	11·80	173·9	40·1
4·27	173·9	40·1	12·68	173·9	40·1
4·55	173·9	40·1	13·80	173·9	40·1
5·42	173·9	40·1	14·15	173·9	40·1
6·16	173·9	40·1	14·53	173·9	40·1
7·00	173·9	40·1	14·80	128·8	29·7



titration figures are calculated also in terms of mgrms. of $Co(C_9H_6ON)_2$, for comparison with the other elements studied. The method used was as for magnesium, but for solutions containing more than 20 c.c. of N sodium hydroxide solution it was necessary to add the oxine before the alkali, otherwise precipitation of cobalt hydroxide took place.

The results given in Table III and Fig. 1 (*supra*) show the range for complete precipitation to be from p_H 4·33 corresponding with the presence of 11·5 c.c. of

glacial acetic acid to p_H 14·5 corresponding with 100 c.c. of 5 *N* sodium hydroxide solution per 145 c.c., the total volume of the solution.

NICKEL (Berg, *Z. anal. Chem.*, 1929, **76**, 191).—For these determinations, the solution contained 6·554 grms. per litre of nickel sulphate, $NiSO_4.6H_2O$, the calculated amount of nickel per 25 c.c. of solution being, therefore, 36·60 mgrms. Determination by means of dimethylglyoxime showed 25 c.c. of the solution to contain 36·38 mgrms. of nickel, which are equivalent to 49·60 c.c. of *N*/10 potassium bromate and to 214·9 mgrms. of $Ni(C_9H_6ON)_2$.

The procedure was exactly as for cobalt, and in this case, also, the gravimetric method was not used, as the precipitate dried at 120° C. corresponded in composition with $Ni(C_9H_6ON)_2.0{\cdot}23H_2O$.

The results are summarised in Table IV and Fig. 2 (p. 393). The range of complete precipitation is from p_H 4·33 (that is, 11·5 c.c. of glacial acetic acid) to 14·58 (that is, 115 c.c. of 5 *N* sodium hydroxide solution) in 160 c.c., the total volume of the solution.

TABLE IV

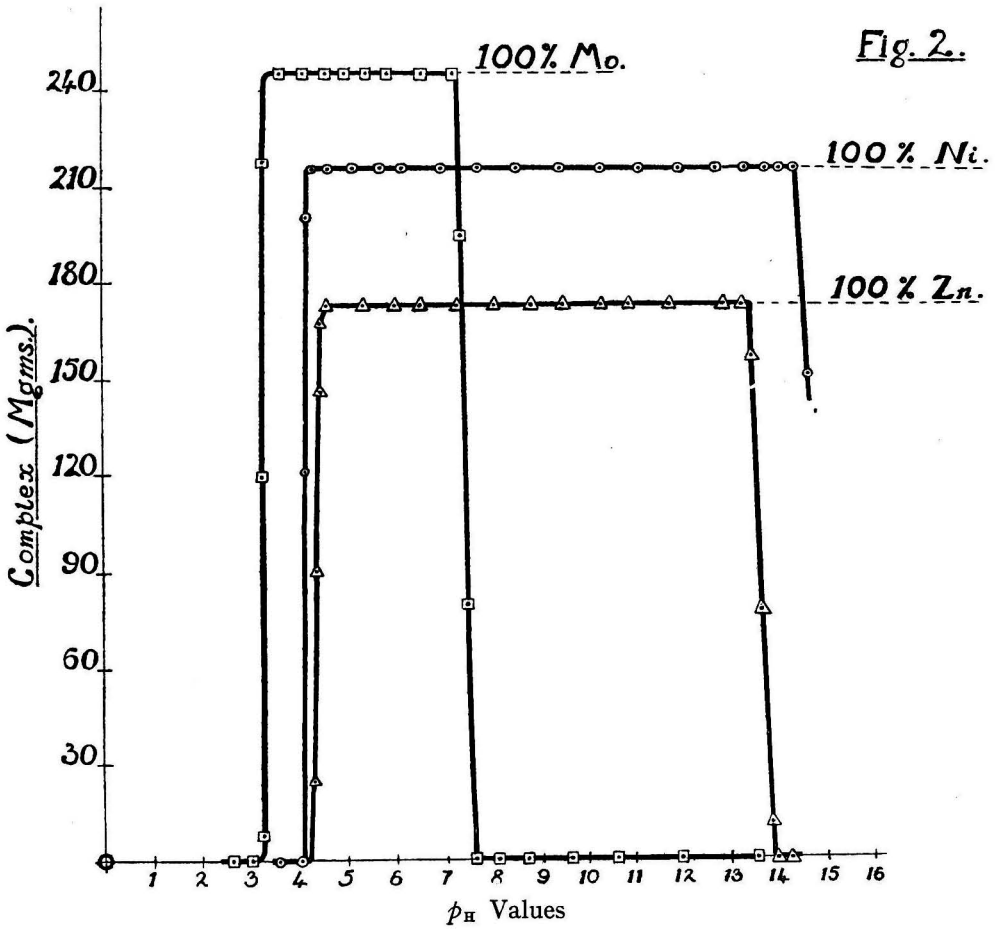
p_H	Complex Mgrms.	*N*/10 $KBrO_3$ c.c.	p_H	Complex Mgrms.	*N*/10 $KBrO_3$ c.c.
3·25	—	—	8·75	215·8	49·8
3·66	—	—	9·60	215·8	49·8
4·10	—	—	10·45	215·8	49·8
4·33	120·2	27·95	11·33	215·8	49·8
4·41	200·0	46·15	12·16	215·8	49·8
4·48	215·8	49·8	12·93	215·8	49·8
4·80	215·8	49·8	13·50	215·8	49·8
5·35	215·8	49·8	13·70	215·8	49·8
5·85	215·8	49·8	13·89	215·8	49·8
6·25	215·8	49·8	14·12	215·8	49·8
7·15	215·8	49·8	14·53	215·8	49·8
7·85	215·8	49·8	14·80	152·0	35·05

COPPER (Berg, *J. pr. Chem.*, 1927, **115**, 178; *Z. anal. Chem.*, 1927, **71**, 185).—A solution containing 3·443 grms. per litre of copper sulphate, $CuSO_4.5H_2O$, was used, corresponding with 21·93 mgrms. of copper per 25 c.c. of solution. Determination by means of potassium iodide and sodium thiosulphate showed 25 c.c. to contain 21·94 mgrms. of copper, which is equivalent to 121·3 mgrms. of $Cu(C_9H_6ON)_2$.

TABLE V

p_H	Complex Mgrms.	p_H	Complex Mgrms.	p_H	Complex Mgrms.
2·92	—	4·00	113·0	9·66	121·2
3·08	—	4·10	116·0	10·40	121·2
3·22	—	4·40	119·2	11·50	121·2
3·36	—	4·95	120·8	12·45	121·2
3·45	23·6	5·36	121·2	13·66	121·2
3·57	59·0	5·80	121·2	14·00	121·2
3·69	80·6	6·48	121·2	14·33	121·2
3·83	101·8	7·53	121·2	14·50	121·2
3·95	108·0	8·50	121·2	14·80	80·0

The method was exactly as for zinc. When working with copper in alkaline solution it is necessary to use a fine-mesh sintered glass crucible. The volumetric procedure is inapplicable in this case. Results are given in Table V and Fig. 1 (p. 391). The range for complete precipitation is from p_H 5·33, *i.e.* 10 c.c. of *N* acetic acid to p_H 14·55, *i.e.* 110 c.c. of 5 *N* sodium hydroxide solution in 160 c.c., the total volume of the solution.



MOLYBDENUM (Geilmann and Weibke, *Z. anorg. Chem.*, 1931, **199**, 347).—A solution of ammonium molybdate (10·435 grms. per litre) was used; 10 c.c. of this were found to contain 56·64 mgrms. of molybdenum (weighed as $PbMoO_4$) and 56·38 mgrms. of molybdenum by means of α-benzoin oxime (Knowles, *Bur. Stand. J. Res.*, 1932, **9**, 1). The latter precipitate was bulky and difficult to handle.

The procedure for the oxine precipitation was exactly as for magnesium. The complex was dried at 130°–140° C., and weighed as $MoO_2(C_9H_6ON)_2$; the calculated weight for complete precipitation is 245·4 mgrms. The volumetric process cannot be used, for it is remarkable that the complex after drying is insoluble in both acid and alkali, and is not dissolved even by *aqua regia*.

The results given in Table VI and Fig. 2 (p. 393) show that the range of complete precipitation is from p_H 3·60, corresponding with from 20 c.c. of glacial acetic acid, to p_H 7·33, corresponding with 9 c.c. of N sodium hydroxide solution. The total volume was 145 c.c.

TABLE VI

p_H	Complex Mgrms.	p_H	Complex Mgrms.	p_H	Complex Mgrms.
2·66	—	4·64	245·6	7·43	193·8
3·08	—	5·03	245·6	7·50	80·0
3·28	8·0	5·51	245·6	7·70	—
3·34	120·0	5·90	245·6	8·08	—
3·46	215·4	6·66	245·6	8·78	—
3·70	245·6	6·90	245·6	9·74	—
3·95	245·6	7·25	245·6	10·66	—
4·20	245·6	7·40	245·6	12·0	—

SEPARATIONS BASED ON THE FOREGOING RESULTS.—It does not necessarily follow that processes of separation can be based on the results given above, for complicating factors, such as the formation of mixed crystals, might cause co-precipitation of more than one complex at a p_H at which only one is precipitated, if alone. Not all the separations which appear to be possible from the curves have been tried, but all those which we have examined (see below) have proved to be entirely satisfactory. The method consisted in precipitating one metal at a p_H value approximating to the middle point of the horizontal portion of the curve, filtering off the complex, washing with some 25 c.c. of hot water, and adjusting the p_H of the filtrate and washings to a point definitely on the horizontal zone for the second metal. Both complexes were well washed with hot water and determined as described in the preceding sections.

On the basis of the results obtained the following binary separations should also be possible:—Magnesium from molybdenum, cobalt from magnesium, molybdenum from nickel, copper from magnesium, and copper from molybdenum, but it is obvious that zinc, cobalt, nickel, or copper cannot be separated from one another in acetate solutions.

SEPARATION OF MOLYBDENUM AND COBALT.—The aqueous solution (80 c.c.), containing molybdenum, cobalt, and ammonium acetate (5 grms.), was boiled and 60 c.c. of N sodium hydroxide solution and 10 c.c. of 5 per cent. oxine in 2 N acetic acid were added. The mixture was boiled for 5 minutes and the cobalt complex filtered off. The molybdenum complex was precipitated by the addition of glacial acetic acid (7·55 c.c.) to the boiling filtrate.

Taken		Found		Error, per cent.	
Mo Mgrms.	Co Mgrms.	Mo Mgrms.	Co Mgrms.	Mo	Co
56·68	14·78	56·56	14·81	−0·22	+0·20
56·68	29·56	56·73	29·48	+0·09	−0·27
70·85	22·17	70·68	22·17	−0·24	0·00
85·02	5·91	84·96	5·89	−0·07	−0·33
11·33	33·99	11·33	33·99	0·00	0·00

SEPARATION OF NICKEL AND MAGNESIUM.—The aqueous solution (80 c.c.), containing nickel, magnesium, ammonium acetate (5 grms.), and glacial acetic acid (5 c.c.), was boiled, and 10 c.c. of 5 per cent. solution of oxine in 2 *N* acetic acid were added. After being boiled for 5 minutes the nickel complex was filtered off. The filtrate was boiled, 30 c.c. of 20 per cent. sodium hydroxide solution were added, and after being boiled for 5 minutes the precipitated magnesium complex was filtered off.

Taken		Found		Error, per cent.	
Mg Mgrms.	Ni Mgrms.	Mg Mgrms.	Ni Mgrms.	Mg	Ni
2·76	21·92	2·77	21·91	+0·36	−0·05
3·43	7·61	3·43	7·63	0·00	+0·26
6·87	36·54	6·86	36·60	−0·15	+0·16
13·74	14·64	13·71	14·64	−0·20	0·00
16·50	25·02	16·53	25·04	+0·17	+0·08

SEPARATION OF MOLYBDENUM AND ZINC.—To the aqueous solution (80 c.c.), containing molybdenum, zinc, and ammonium acetate (5 grms.) were added 40 c.c. of 2 *N* sodium hydroxide solution. The mixture was boiled, and the zinc complex precipitated by the addition of 10 c.c. of 5 per cent. oxine solution in 2 *N* acetic acid. To precipitate the molybdenum complex from the filtrate, 8·5 c.c. of glacial acetic acid were added.

Taken		Found		Error, per cent.	
Mo Mgrms.	Zn Mgrms.	Mo Mgrms.	Zn Mgrms.	Mo	Zn
56·68	33·25	56·68	33·25	0·00	0·00
19·28	16·60	19·29	16·60	+0·05	0·00
29·03	27·30	29·03	27·32	0·00	+0·07
28·34	8·25	28·34	8·26	0·00	+0·12
9·62	15·52	9·61	15·52	−0·10	0·00

SEPARATION OF MAGNESIUM AND ZINC.—The aqueous solution (80 c.c.), containing magnesium, zinc, ammonium acetate (5 grms.) and glacial acetic acid (2·5 c.c.) was boiled, and 10 c.c. of 5 per cent. oxine solution in 2 *N* acetic acid were added to precipitate the zinc complex. To the boiling filtrate were added 30 c.c. of 17·8 per cent. (w/v) sodium hydroxide solution to precipitate the magnesium complex.

Taken		Found		Error, per cent.	
Zn Mgrms.	Mg Mgrms.	Zn Mgrms.	Mg Mgrms.	Zn	Mg
18·21	2·76	18·20	2·75	−0·06	−0·36
10·52	6·18	10·50	6·19	−0·19	+0·16
9·58	9·62	9·57	9·62	−0·10	0·00
6·43	12·37	6·44	12·36	+0·15	−0·09
3·32	15·11	3·32	15·13	0·00	+0·13

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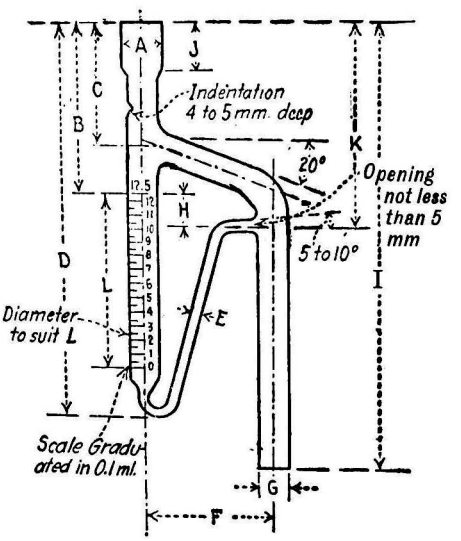
Notes

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.

APPARATUS FOR THE SEPARATION AND MEASUREMENT OF STEAM DISTILLATES

THE American Society for Testing Materials (*Proc.*, 1930, Part I, p. 1112) has recommended the use of a new piece of apparatus for determining the "dilution" with petrol of crank case lubricating oil, and, as the apparatus appears capable of very wide application, we think it should be more generally known. As will be seen from the accompanying figure (which is reproduced by the kind permission of its authors) the apparatus is extremely simple, and practically automatic in use. A weighed quantity of the substance under examination is mixed with 500 to



A	18 to 20 mm.,	inside diameter	G	11 to 15 mm.	
B	85 „ 90 „		H	15 „ 20 „	
C	70 „ 75 „		I	230 „ 250 „	
D	200 „ 225 „		J	25 „ 30 „	
E	4 „ 5 „	inside diameter	K	100 „ 110 „	
F	65 „ 75 „		L	90 „ 100 „	

800 c.c. of water in a large wide-necked round-bottomed flask which is attached by means of a cork to the bottom of the tube G. A vertical condenser is connected with A, and the contents of the flask are boiled. The solvent then collects above the condensed water in the graduated tube L, and its amount is read off. In practice it is found advisable to fill the tube L with water before commencing the distillation. We have used this apparatus, with entirely satisfactory results, in the determination of solvent in paint, polish, and spirit soap, as well as in other directions where steam distillation was required. One special advantage of the apparatus is that there is so little water in contact with the solvent that no correction is necessary for solubility of the solvent in water.

W. H. SIMMONS
C. A. HILLS

A CASE OF CHRONIC LEAD POISONING

THE man in this case, who died aged 58, in November, 1932, had been a stereotyper. In 1928 he had a seizure which was diagnosed as due to chronic plumbism, and he was thereupon pensioned by his employers. In the intervening four years he had, so far as could be ascertained, moderate health. The *post-mortem* (conducted by Dr. C. E. Jenkins, pathologist to Salford Royal Hospital) indicated that death was due to cardiac degeneration supervening on generalised arteriosclerosis. The pathologist described the conditions as consistent with natural causes or with chronic plumbism. The amounts of lead in parts per million found in the organs submitted were: Liver, 35; brain, 8; kidney, 8; right tibia, 27.

The interest in this case lies in the fact that four years elapsed between the last exposure and the time of death. Comparison of the amounts of lead found with those quoted by Thorpe (*Dictionary*, article "Lead") suggests that in chronic plumbism the lead in the body is held in extremely firm combination with the body tissues.

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THE DETERMINATION OF PECTIN IN DRIED APPLE POMACE

SOME pectin is present in pomace, but the main problem here is to produce the maximum of colloidally soluble pectin from insoluble pectocellulose, without demethoxylating it to insoluble pectic acid.

As the result of numerous experiments the following method is suggested:— Weigh 5 grms. of pomace into a 250-ml. beaker, add 74 ml. of water and 1 ml. of *N* hydrochloric acid. Boil for 30 minutes, keeping the volume approximately constant. Filter through a 9-cm. paper on a small Buchner funnel. Wash with boiling water, squeezing the pomace a little with a glass rod. Make the filtrate up to 100 ml., after cooling. With the help of the glass rod and boiling wash-bottle transfer the pomace again to the beaker, add 5 ml. of N hydrochloric acid, and make up to the same volume as before. Boil for 20 minutes and filter as before. Make up the second extract to 100 ml. For the third extraction use 25 ml. of *N* hydrochloric acid and 50 ml. of water. Boil for 10 minutes. Filter again, still using the same paper, and make the filtrate and washings up to 100 ml. Then mix the three extracts. Take 10 ml. for the determination, add 80 ml. of industrial methylated spirit (74 O.P.) and 9 ml. of *N* hydrochloric acid, mix and stir. Leave for one hour, filter off the pectin, wash with 80 per cent. acidified alcohol (*N*/10), and finally with strong methylated spirit. The pectin may be transferred to an evaporating basin with boiling water, and then dried. Weight × 600 = percentage of pectin. (Yield about 0·03 grm.) Here there are three extractions of decreasing time (30, 20 and 10 minutes) and increasing acidity *N*/75, *N*/15, *N*/3. With a single 30 minutes' extraction *N*/15 hydrochloric acid gives a higher yield than *N*/3 or *N*/75. With four successive treatments of 30 minutes each, however, *N*/3 acid still gives lower results than *N*/15 acid, although *N*/75 acid gives higher yields. The above triple-extraction method gives still higher results.

		N/15 acid Per Cent.			*N*/75 acid Per Cent.			Triple-extraction method	
I	30 minutes	10·10	I	30 minutes	8·72	I	*N*/75 acid for 30 minutes		
II	,,	5·26	II	,,	5·64	II	*N*/15 ,, ,, 20 ,,		17·97 per cent.
III	,,	0·48	III	,,	2·08	III	*N*/3 ,, ,, 10 ,,		
IV	,,	0·28	IV	,,	1·20				
		16·12			17·64				

Considerable variations were noted in the proportion of total pectin in the different samples, the amounts (calculated on the dry substance) ranging from 25·0 per cent. in the first, to 20·7 in the fourth sample. The first extract contained 46 per cent. of the total pectin, and the fourth extract 37 per cent.

D. W. STEUART

GAYMER'S LABORATORY
ATTLEBOROUGH

Official Appointments

THE Minister of Health has approved the following appointments:

RICHARD WILLIAM SUTTON as a Public Analyst for the County of Derbyshire, from July 1st, 1933, in place of John White, who is retiring on June 30th, 1933.

R. W. Sutton vacates the appointment of Additional Public Analyst for the County Borough of Leeds on June 20th, 1933 (June 8th, 1933).

CHARLES FREDERICK TURNER as a Public Analyst for the County Borough of Liverpool, in addition to William Henry Roberts (June 29th, 1933).

Bibliography on Heavy Metals in Food and Biological Material

(*From the beginning of the year* 1921 *to date*)

IX TIN

ANON. Tin in Canned Foods. ANALYST, 1923, **48**, 326. (Tinned asparagus containing 2·9 grains of tin per lb. referred to.)

BERTRAND and CIUREA. Tin in the Animal Organism. *Compt. rend.*, 1931, **192**, 780; ANALYST, 1931, **56**, 409. (Determined as stannic acid.)

BERTRAND and CIUREA. Lead in the Animal Organism. *Compt. rend.*, 1931, **192**, 990; *C.A.*, 1931, 5459. (Tin, as well as lead, a normal constituent of animal tissue.)

CLARKE. Metals in Foods. *J.A.O.A.C.*, 1921, **5**, 219; *C.A.*, 1922, 1812. (Method for tin discussed.)

CLARKE. Report on Metals in Foods. *J.A.O.A.C.*, 1922, **6**, 28; *C.A.*, 1923, 1511. (Tin determined by wet combustion and titration of stannous chloride with iodine.)

CLARKE. Metals in Foods: Determination of Tin. *J.A.O.A.C.*, 1923, **7**, 46; *J.S.C.I., Abs.*, 1923, 1040. (Iodimetric.)

CLARKE. Report on Metals in Foods. *J.A.O.A.C.*, 1924, **8**, 120; *C.A.*, 1925, 547. (The zinc-iron precipitation method for tin described.)

DAVIES. Detection in situ of Tin Solder causing Dark Discoloration in Cheese. ANALYST, 1932, **57**, 95. (Tin detected by the molybdenum blue test.)

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. Corrosion of the Tin-plate Container by Food Products. Special Report No. 40. ANALYST, 1931, **56**, 315.

DEUSSEN. Detection and Determination of Tin in Toxicological Cases. *Arch. Pharm.*, 1926, **264**, 360; *B.C.A.*, 1926, 872A. (Review of methods.)

DUTOIT and ZBINDEN. Spectrographic Analysis of the Ash of Blood and Organs. *Compt. rend.*, 1929, **188**, 1628; *B.C.A.*, 1929, 952A. (Tin found in some cases.)

DUTOIT and ZBINDEN. Spectrographic Analysis of the Ashes of Human Organs. *Compt. rend.*, 1930, **190**, 172; *C.A.*, 1930, 3552. (Tin abundant in all organs.)

DYER and TAYLOR. Tin in Cheese. *Report of the Essex County Analysts for the Fourth Quarter*, 1930; ANALYST, 1931, **56**, 251.

ELTEN. Tin-foil as a Packing for Rindless Cheese. *Chem.-Ztg.*, 1929, **53**, 586; ANALYST, 1929, **54**, 552. (Tin found in the cheese.)

GLASSMANN and BARSUTZKAJA. Volumetric Method for the Determination of Tin in Preserves and other Foodstuffs. *Z. Unters. Lebensm.*, 1928, **56**, 208; ANALYST, 1929, **54**, 110. (Volumetric, with dichromate.)

HOLWERDA. Tin Percentage of Canned Food in the Tropics. *Mededeel. Dienst. Volksgezondheid Nederland.-Indie*, 1925, 244; *C.A.*, 1926, 2027.

JÄRVINEN. Colorimetric Determination of Small Quantities of Metals in Foodstuffs and the Preliminary Destruction of the Organic Matter. *Z. Unters. Nahr. Genussm.*, 1923, **45**, 183; *J.C.S., Abs.*, 1923, ii, 655. (Method for tin given.)

LIDDEL. Report on [Determination of] Tin [in Foods]. *J.A.O.A.C.*, 1930, **13**, 423; *C.A.*, 1931, 358. (Iodimetric.)

MANICKE and LAUTH. Toxicological Determination of Tin. *Pharm. Zentr.*, 1927, **68**, 161; *B.C.A.*, 1927, 482A.

MANLEY. Occurrence of Antimony and Tin in Foil-wrapped Cheeses. ANALYST, 1930, **55**, 191.

MINISTRY OF AGRICULTURE AND FISHERIES. Causes of the Unusual Mortality in English Oyster Beds in 1920 and 1921. Part II. Chemical Reports, etc., 1924. ANALYST, 1924, **49**, 484. (Tin, as well as lead and copper, found in some cases; methods outlined.)

MISK. Tin in the Human Organism. *Compt. rend.*, 1923, **176**, 138; *J.C.S., Abs.*, 1923, i, 269. (Weighed as stannic oxide; tin normally present.)

MIX. Report on [Determination of] Tin [in Foods]. *J.A.O.A.C.*, 1931, **14**, 448; *C.A.*, 1932, 775.

NEWELL and MCCOLLUM. Spectrographic Analysis of Marine Products. *U.S. Dep. Comm., Bureau Fisheries, Investigational Report* 5, 1931, 1; *C.A.*, 1932, 1356. (Traces of tin found in some fish.)

OROSCO. Pneumonoconiosis in Bolivian Miners. *Semana Med.*, 1931, **38**, 601; *C.A.*, 1931, 5201. (Pulmonary tissue contains tin.)

OWE. Determination of Tin and Lead in Preserves and Containers. *Z. Unters. Lebensm.*, 1926, **51**, 214; *B.C.A.*, 1926, 606B. (Volumetric with iodine and thiosulphate.)

SPENCER. Report on [Determination of] Metals in Foods. *J.A.O.A.C.*, 1931, **14**, 434; *C.A.*, 1932, 774. (Tin referred to.)

WILLEY. Apparatus for the Estimation of Tin in Canned Foods. *J.S.C.I.*, 1924, **43**, 70T; ANALYST, 1924, **49**, 234. (Titration of stannous chloride with iodine.)

ZBINDEN. The Infinitely Small Quantities of Certain Elements in Milk and their Detection by the Spectrographic Method. *Lait*, 1931, **11**, 114; *C.A.*, 1931, 4032. (Tin found regularly in human and cow's milk.)

Notes from the Reports of Public Analysts

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

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1933

OF the 1480 samples submitted by the Food and Drug Inspectors during the quarter, 1392 were bought informally. Ninety-eight samples of food and 8 of drugs were returned as adulterated or incorrect.

COD-LIVER OIL AND MALT EXTRACT.—The 1932 B.P. requires this article to consist of 10 per cent. of cod-liver oil and 90 per cent. of malt extract. In addition, the malt extract should contain nitrogen equivalent to not less than 4·5 per cent. of protein. The extract used in one sample contained only 3·4 per cent. of protein, a deficiency of 24 per cent. The vendor was written to and the matter is still under discussion.

VITAMIN BEVERAGE.—Two samples consisted of a brown, coarse powder, with an odour resembling cocoa. It was directed to be mixed, for use, with boiling water or milk. The ingredients were stated to be nuts, malt, etc., vitamins *A*, *B* and *D*. It was also described as rich in vitamins. Analysis showed that about 83 per cent. of the sample was cane sugar and the remainder mainly cocoa. Nuts and malt, if present at all, were in very small amounts. Vitamin *A* was tested for by the colour test, but was entirely absent. Judging from the composition of the article, it was almost certain that vitamins *B* and *D*, if present at all, were in extremely minute quantities. The packers were communicated with and acquainted with the results of the analysis. They agreed not to use the leaflets, and to remove from the labels all the remarks relating to vitamins. They stated that the firm manufacturing the article for them had not kept to the original formula, and they sent a sample, taken from stock and alleged to be made for them by another firm, presumably to the correct formula. This sample, however, was of substantially the same composition as the original sample. Practically the whole of the claims made for this article were untrue and misleading.

PARRISH'S CHEMICAL FOOD.—Until last year there was no pharmaceutical standard fixed for this article, but, according to the B.P., 1932, the article must now contain 0·9 per cent. w/v of iron phosphate and 1·4 per cent. w/v of calcium phosphate, these being the two principal constituents of medicinal value. One sample contained only 0·25 per cent. w/v of iron phosphate, a deficiency of 72 per cent., and 0·35 w/v of calcium phosphate, a deficiency of 75 per cent. In addition to this, 10 per cent. of glucose syrup was present, which is not a constituent of the B.P. Parrish's Food at all. Apart from the serious deficiencies in the amounts of phosphates present, the label stated that one teaspoonful contained one grain of iron phosphate and 2½ grains of calcium phosphate, which quantities are equivalent to 1·3 per cent. w/v and 3·25 per cent. w/v, respectively. The deficiencies on this basis were, respectively, 80 and 89 per cent., and the label was, therefore, false. In consequence of these findings, a formal sample was taken during the present quarter. This proved to be of correct B.P. composition, but the same label, indicating the presence of a larger quantity of iron and calcium phosphate, was used, and the label was, therefore, still false. The vendor has arranged to have a new supply of labels printed, meanwhile to omit that portion of the old label which gives the quantities of phosphates present. Another sample contained only 0·76 per cent. w/v of iron phosphate (a deficiency of 15 per cent.) and 0·87 per cent. w/v of calcium phosphate (a deficiency of 38 per cent.). The vendor explained that the bottle must have been old stock which had been accidentally overlooked, all their recent stock being of 1932 B.P. quality.

TEA "FREE FROM TANNIN."—A sample of tea was labelled "Digestive Tea. Free from tannin." Tannin was actually present to the extent of 12·7 per cent. When their attention was called to this fact the firm concerned agreed to cover over the words relating to tannin on the packets and also to omit the words from the posters attached to the vans used for its distribution.

The label on another sample stated that the tannin was "minimised," but, actually, 13·9 per cent. (an average amount) was present. It is, of course, impossible to minimise the amount of tannin in tea by artificial means. The packers agreed to delete from their labels the words complained of, and were allowed a period of grace in which to dispose of their present stock of labels.

A third sample was stated on the label to be practically free from tannin. In this case 11·2 per cent. was present, which was obviously not in accordance with the label. The packers agreed to print new labels in which the word "tannin" did not appear.

H. H. BAGNALL

CITY AND COUNTY OF KINGSTON-UPON-HULL

REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR THE YEARS 1931 AND 1932

DURING the two years reviewed 9234 and 10,748 samples and specimens were examined. Of these, 1639 and 1628 were samples of foods and drugs received from inspectors, 115 and 169 were other food samples, 246 and 352 were miscellaneous samples, and 11 and 16 were fertilisers and feeding stuffs. The remainder were bacteriological specimens. In the year 1931 there were 54 adulterated and 31 suspicious samples, the corresponding figures for 1932 being 82 and 28.

DIRTY MILK.—No added preservatives or colouring matters were detected in milk during these two years. The percentage of dirty milk found was:—1931, 2·1; 1932, 0·5 per cent.—figures which are satisfactory. It is not contended that milk which is free from visible sediment is necessarily bacteriologically clean, but *dirty* milk is obviously unsatisfactory. It is very necessary that further steps be taken, without undue delay, to improve the cleanliness and purity of the whole milk-supply of the country. As urged in my Report for the year 1926 (p. 14), the greatest step forward will be the enactment that all ordinary milk shall be sold in sealed bottles. A bacterial standard will then be a practical basis for judging of its cleanliness. The recommendations of the Reorganisation Commission for Milk (Report to Ministry of Agriculture and Fisheries: Economic Series, No. 38, 1933) regarding the revision of the grades of milk, and a bacterial standard for all milk, are timely, and should be adopted by the Government.

PRESERVATIVES IN FOOD.—The percentages of preserved foods, calculated on the foods examined for such additions, for the two previous years (1929 and 1930) were 3·2 and 3·8, as compared with 3·2 and 2·4 for the years under review. The comparable figure for the year 1914, when butter, cream, margarine, confectionery (cakes), meats and other foods generally contained such additions, was 17·2 per cent.

Of the foods permitted under the Preservatives Regulations to contain chemical preservatives, there are few, if any, which contain, on the average, more than about half the permitted quantity, and many foods contain much less than this proportion. This matter might reasonably be re-considered by the Ministry of Health, with a view to the revision of the First Schedule of the Regulations, and a reduction of the permitted amounts of preservatives.

SUNLIGHT (ULTRA-VIOLET LIGHT) OBSERVATIONS.—The observation station for this work is now on the roof of the new City Laboratory. The tables below give the maximum and minimum averages for the City and six other areas:—

UNITS OF FADING

Daily Average throughout the months mentioned

	1931		1932	
	Maximum	Minimum	Maximum	Minimum
Hull (Central) ..	2·9 (July)	0·1 (Jan., Nov.)	3·2 (Aug.)	0·1 (Jan.)
Cleethorpes ..	4·1 (June)	0·2 (Nov.)	4·1 (Aug.)	0·5 (Feb.)
Lowestoft ..	9·1 (June)	1·0 (Nov.)	2·6 (Mar.)	0·4 (Dec.)
Prestatyn ..	5·5 (July)	0·9 (Jan.)	3·2 (June)	0·9 (Jan.,Feb.)
Scarborough ..	—	—	1·7 (July)	0·4 (Dec.)
Skegness ..	4·5 (June,Aug.)	0·7 (Jan.Feb.,Dec.)	5·5 (July)	1·1 (Nov.)
Southport ..	3·3 (July)	0·1 (Dec.)	3·6 (July)	0·2 (Feb.)

A. R. TANKARD

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.

THE SAMPLING OF MILK

GREENWOOD *v.* HANNAM

ON May 23rd an appeal was heard in a King's Bench Divisional Court (before the Lord Chief Justice and Justices Avory and Humphreys) against a decision of justices at Pateley Bridge, Yorkshire, who had dismissed two summonses against a farmer for the sale of milk alleged to be not of the quality demanded.

It was explained on behalf of the appellant (the sampling officer) that on the morning of November 1, 1932, a sample was taken from each of three churns in course of delivery. Summonses were issued in respect of two of the samples, but the analysis of the third sample gave average results for milk-fat and for solids-not-fat.

At the hearing of the cases it was contended on behalf of the farmer that, as the sale was in bulk, one sample of the whole should have been taken, and that each churn should not have been separately sampled. The justices upheld this contention, and dismissed the summonses.

Mr. Graham Mould, who appeared for the farmer in the appeal case, argued that had the contents of the three churns been sampled together, the deficiencies in fat and solids-not-fat would have been so small that no exception could have been taken to them. It was plain that one churn contained milk well above the standard, and that the milk-fat in another churn was extraordinarily high.

A further contention was that the fact that the inspector handed 3d. to the respondent in purported payment of the milk did not constitute a sale, since the milk had already been sold to a dairy company.

The Lord Chief Justice pointed out that, as the company had agreed to take as much milk as the farmer would sell them, there was nothing to prevent him selling a small quantity to the officer as a sample. In these cases there was evidence of a sale to the officer.

The Court, in allowing the appeal, held that there was a sale of milk to the sampling officer, and that it was right to issue the two summonses against the respondent. Since the justices had dismissed the information before hearing the respondent's evidence in support of his plea that the milk was genuine, the case would be remitted to them in order that they might hear that evidence if the respondent still wished to adduce it, and then adjudicate on the case.

At the re-hearing of the case, on July 1st, the justices accepted the ruling of the High Court, and, after hearing further evidence, fined the defendant £2, with £4 costs.

The National Physical Laboratory

REPORT FOR THE YEAR 1932*

THE Report of the Executive Committee notes the reduction of special investigations carried on for industrial firms and other bodies, and a falling off in the number of routine tests of instruments required, due in both cases to general trade depression. The General Survey of work followed by the Reports of the Superintendents

* Dept. of Scientific and Industrial Research. H.M. Stationery Office, Adastral House, W.C.2. Price 14s. net.

of the various Departments is on the general lines of the previous year's Report (ANALYST, 1932, **57**, 461–463). A comparison of the number of tests made in the departments during the year with those of 1931 and 1932 is included, together with a list of published papers.

Only a few details of the work done can be selected for notice.

WORK FOR THE FOOD INVESTIGATION BOARD.—*Heat transmission between metal pipes and an air stream.*—The general conclusion from the results of the continued work on the loss of heat from iron pipes, $1\frac{7}{8}$ in. diam., set horizontally and transversely to a stream of air, is that eddy flow set up in the air during its passage through the bank of pipes is a dominating factor. The heat loss per foot run was found to be much less when the pipe lay along the air stream than when it was transverse, and it was also observed that the heat loss per foot run diminished along the pipe, the first section losing most heat, and the fourth section least.

Thermal Properties of Foodstuffs.—In order to obtain data on the thermal properties of meat and the diffusion of heat through it, means have been devised for measuring separately the thermal conductivity, k, the specific heat, s, and the density, ρ, so as to calculate diffusibility ($k\rho s$). Thermal conductivity is found by totally immersing a miniature "plate" apparatus in acetone cooled with solid carbon dioxide. Specific heat is determined by weighing the amount of solid carbon dioxide sublimed when a known mass of meat at a given initial temperature is submerged in solid carbon dioxide. It was noticed that temperatures as low as −90° and −95° C. could be obtained locally in a mass of broken chips of solid carbon dioxide by forcing a rapid stream of air over the material.

SPECIAL INVESTIGATIONS.—*Determination of free water in fogs.*—As soon as weather conditions permit it is intended to find the amount of water present in vapour in fog particles, to deduct it from the total quantity present, and thus to ascertain the actual amount of free water present in the particles. Dew-point determinations have suggested that the vapour present is somewhat less than the amount necessary to saturate the air at the prevailing temperature.

Temperature Measurement.—A revised form of certificate is being introduced for precision thermometer tests, wherein the mean value of each observed correction is normally recorded to as close a degree of accuracy as is warranted by the degree of precision with which each column can be read. The probable degree of accuracy is indicated by plus or minus limits, which are also given in the certificates for each correction. As an example, in the case of a thermometer divided to 0·01° C., for which (under the old method) corrections were required "to the nearest 0·01° C.," an observed correction of +0·006° C. would have been recorded as +0·01° C. By the new method it would be given as +0·006 ± 0·005° C. A similar modification is being made in the reports dealing with pyrometers.

Precision Thermometers.—The apparatus for pressure tests on deep-sea thermometers is now installed; it is intended to work up to pressures of 4 tons per sq. in., and is fitted with a gauge which reads to 0·002 ton per sq. in. The thermometer to be tested is fitted between springs in a light metal cage which is inserted in the pressure cylinder, and the pressure is transferred through a connecting tube of flexible steel by means of transformer oil, the working parts being lubricated by a layer of castor oil. For a test at 0° C. under pressure the thermometer is fitted into the cylinder upside down, and the cylinder is inverted in the ice-bath. The pressure is adjusted, and, when temperature equilibrium is reached, the cylinder is withdrawn, quickly reversed, and the inverted thermometer removed, wiped free from oil and again immersed in ice for observation.

National Radium Trust and Commission.—The laboratory has rendered effective assistance on occasions in recovering radium containers from hospital incinerators. Containers tested two years ago have been re-tested to confirm

whether the radium supplied is free from mesothorium and its disintegration products.

X-Ray Tests.—The testing of protective materials, such as barium brick, lead rubber and lead glaze, and inspection of *X*-ray equipment in accordance with the International Recommendations have continued. Materials subjected to *X*-ray crystal analysis have included various forms of carbon, metals subject to season cracking (in which the internal strain was detected and its distribution determined) and various resinous materials. The nature of the extremely thin film on copper wire exposed to air was ascertained, and its approximate thickness determined.

Radium Tests.—A total quantity of nearly 6½ grms. of radium was submitted for test, and repairs to damaged containers were carried out. Twenty tubes belonging to a 4-grm. bomb were re-examined prior to being re-issued in units of 1 grm. to each of four London hospitals, and the mounting of the units was carried out at the Laboratory.

OPTICS.—*Colour Measurement and Standardisation.*—A re-determination of the properties of the light sources, established as standards by the resolutions of the 1931 International Commission on Illumination, has included a spectrophotometric study of filter B, with special attention to the influence of traces of impurities in the salts employed and to effects of temperature. To facilitate the work a new type of containing cell for liquid filters was developed, designed especially to ensure that the liquid layers should be of the specified thickness to a high degree of precision. The properties of the lamp-rating filter used to step up from the low temperature standards to the higher colour temperatures of gas-filled lamps were originally determined by general independent methods, and the results obtained from repetition of some of this work show that the Laboratory scale of colour temperature for gas-filled lamps is consistent to a degree of accuracy which is more than adequate for commercial requirements, so that any serious error in the absolute values can only arise from errors in the scale between 1800° K and 2400° K. Any uncertainty due to this cause should now be removable, preliminary work having already been done towards establishing a point on the colour-temperature scale by direct spectro- radiometric determination of spectral energy distribution in the visible spectrum.

Wave Length Determinations in the Infra-Red.—The spectrometer for these determinations has been completed, and, as a result of preliminary work, several improvements have been made, including a mechanism whereby the effect of stray radiation is taken into account. Greater steadiness has been attained, and sensitivity can be made to approach that of the moving magnet type of galvanometer. Certain persisting errors were traced to the grating used, and the testing of other types of grating is in progress.

Standards of Total Radiation.—Experience has shown that vacuum tungsten lamps with grid filaments of the type used for photometric standards are more satisfactory for providing radiation of the order of 20 to 100 micro-watts per cm.^{2} than the carbon filament lamps used heretofore. A systematic comparison of an Ångström pyrheliometer with the radio balance has been completed and shows that the former is less trustworthy as an absolute standard, and that in work for which its quicker response and greater sensitivity render it particularly convenient, it should be employed only as a working standard, its constant being obtained by exposure to radiation of known intensity.

Reports on the Electricity, Metrology, Engineering, Metallurgy, and Aerodynamics Departments, and on the William Froude Laboratory, are given.

D. G. H.

New Zealand

SIXTY-FIFTH ANNUAL REPORT OF THE DOMINION LABORATORY

In his Annual Report for 1931 the Dominion Analyst (Mr. W. Donovan) states that 5832 samples were analysed at the Wellington Laboratory, 2280 at the Auckland Branch Laboratory, 2278 at the Christchurch Branch Laboratory, and 1869 at the Dunedin Branch Laboratory. Of these, the greater proportion consisted of milks and other foodstuffs for the Health Department, and there were numerous specimens for the Police Department.

Department of Health.—A special feature of the work done for this Department was the examination of a large number of waters from the Hawke's Bay earthquake area. This was rendered necessary owing to the possibility of contamination of the town water-supplies from broken sewers. Using the analyses made in this Laboratory as a guide, the Medical Officer of Health for the district was enabled to take effective action for safeguarding the water-supplies.

Milk.—Of the 1644 samples taken in Wellington, 48 were adulterated, 15 were stale, and 4 were slightly deficient in milk-solids. A satisfactory feature of the milk supply in Christchurch City and suburbs was the absence of adulteration by added water. This is attributable to the greater regularity in sampling and the continued use, over a period of years, of the freezing-point test for the detection of added water.

The miscellaneous investigations included the following:

Iodine in Dried Seaweed and Seaweed Gels.—As seaweed and seaweed gels are used as a source of iodine in human nutrition, the iodine-contents of a sample of dried seaweed and of samples of seaweed gels were determined, with the following results: Seaweed (*Gigartina clavifera*), 120 parts per million; gel from *Gigartina clavifera*, 0·8 part, and gel from carrageen (*Chondrus crispus*), 1·2 part per million. Hercus and Roberts (*J. Hyg.*, 1927, **21**, 54) state that carrageen contains 480 parts per million.

Battery Acids.—Acid from a battery which was deteriorating rapidly and had lost a great deal of its capacity was found to contain 0·0017 grm. of iron per 100 c.c., and very little other impurity. But, according to Vinal ("Storage Batteries"), ten times this amount is permissible in used acid. However, scrapings from a negative plate contained 0·25 per cent. of iron, and from a positive plate 0·18 per cent. This result is interesting, as Vinal states that iron is not eliminated from the electrolyte. Lea and Crennel, in a paper in the Transactions of the Faraday Society, 1927, show that iron present in the electrolyte is absorbed by the positive plate, but there is no reference in the literature to absorption on the negative plate. If, for the purposes of a rough calculation, the weights of the positive plates, negative plates, and electrolyte are taken as 36 per cent., 31 per cent., and 19 per cent., respectively, of the total weight, and the active material as forming 50 per cent. by weight of the plates, then the amount of iron present originally in the electrolyte would be 0·4 grm. of iron per 100 c.c. This indicated that there had been considerable contamination of the electrolyte by iron, and this probably accounted for the deterioration of the battery.

In another case a sample of electrolyte was received from a new battery which after two months showed serious buckling and swelling of the plates. Several of the cells had suffered considerable loss in their capacity. The electrolyte contained 0·14 per cent. of acetic acid, and the origin of this was traced to the distilled water

used for making up the electrolyte. This water had been transported in wine casks, and it was evident that the acetic acid had been produced by acetification of the alcohol. A sample of water transported in a coconut oil cask contained 0·04 per cent. of dissolved and suspended organic matter and 0·01 per cent. of an organic acid.

SUBSTITUTES FOR ROUGE.—In an investigation, carried out on behalf of the Marine Department, with the object of finding a cheap substitute for rouge for polishing the lenses of lighthouses, two samples of well-known cleansing powders were examined. In practical tests on glass, it was shown that one of the powders (having felspar as abrasive) definitely scratched glass, though the other, which contained pumice as abrasive, was practically free from this defect. Recent researches have shown that the process of polishing glass is a complicated one, depending apparently less upon abrasive action than upon some little understood molecular reaction between the polishing medium and the glass, a certain amount of flow being induced in the latter. The powders which produce this polishing effect are the oxides of aluminium, iron, magnesium, and chromium. French chalk and other substances have been used, but give very inferior results. It was decided to recommend the continued use of rouge for polishing the lenses as being the safest.

CORROSION OF METALS.—At various times during the year the Laboratory was called upon to conduct investigations into the causes of the corrosion of metals in industrial use.

In two cases the tail shafts of oil-launches had been seriously pitted where they were in contact with sea-water. It was found in both these cases that the compositions of the metals used were such that they would not confer any anti-corrosive properties upon the shafts in sea-water. The corrosion in both cases was of the so-called "dezincification" type.

Corroded aluminium cables for use as electrical conductors were also examined. In this case the quality of the metal was found to be satisfactory, and was not a factor contributing to the corrosion, which was due to the action of salt solutions.

A fractured steel tail shaft was also examined to determine if segregation of phosphides or sulphides had been the cause of fracture. No evidence of such segregation was found.

DECIPHERING DAMAGED PARCHMENT DOCUMENTS.—The advice of the Department was sought in connection with the problem of making legible certain parchment deed documents, which had been damaged during the Napier earthquake. As a result of heat the documents had dried out, shrunk, and hardened to such an extent that it was not possible to separate them without cracking. The problem consisted therefore in restoring moisture without disintegration of the skin or destruction of ink. Water soaking had been previously tried, but was satisfactory only in the case of slightly damaged parchment. Advantage was taken of the fact that alkalis have a very powerful action in introducing moisture into the skin. Too strong an alkali would produce distortion, as well as solvent action on the fibres. A solution of about p_H 10·0 was found to give the best results. The parchments were therefore soaked in a solution containing 1·2 per cent. of boric acid and 0·4 per cent. of caustic soda per 100 c.c., and were finally stiffened with 10 per cent. formalin. This treatment was successful.

The International Standard for the Oestrus-Producing Hormone

THE following statement has been received from the Director of the Department of Biological Standards, Medical Research Council, with a request for its publication in an early issue of THE ANALYST:

In July of last year a Conference was held in London, under the auspices of the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations, with the object of discussing the possibility of securing international agreement on standards of reference and units of activity for the sex hormones. While the Conference agreed that knowledge of the male sex hormone, and of the hormones of the corpus luteum and the anterior posterior body, is at present insufficiently advanced to permit of a standard of reference being established, and a unit of activity defined for these substances, important decisions were reached in regard to the oestrus-producing hormone. This hormone has been prepared in pure crystalline form from the urine of pregnancy, in quantities sufficient to admit of chemical examination; it exists in two forms—a ketohydroxy form and a trihydroxy form—the first named being the more active, by the ordinary methods of testing, in producing oestrus in animals subjected to oöphorectomy.

The oestrus-producing hormone has been the subject of extensive investigations in recent years, and a state of confusion was developing in consequence of the adoption of different "units." As in the case of other substances exhibiting marked and specific biological activity, attempts to define units in terms of animal reaction had only served to show that units defined on such a basis lacked uniformity; the unit varied, not only from one species of animal to another, but, in the same species, was dependent upon the method of administration and the method chosen for interpreting the result of the administration of the hormone.

The Conference agreed that, as in other similar cases, the only safe basis for international agreement on a unit was the adoption of a standard substance, in terms of which the unit could be defined. The standard adopted by the Conference for international use is a quantity of the ketohydroxy form of the hormone in pure crystalline condition, which is preserved at the National Institute for Medical Research, London; and the unit of activity is defined as the specific oestrus-producing activity contained in $0{\cdot}1\gamma$ (= 0·0001 mgrm.) of this standard preparation.

In order to provide an adequate amount of material to serve as an International Standard, different countries have sent samples of the pure crystalline ketohydroxy form of the oestrus-producing hormone to the National Institute for Medical Research, London (acting for this purpose as the central laboratory on behalf of the Health Organisation of the League of Nations), where the final preparation of the standard has been completed, and arrangements have been made for the storage of the standard and for its dispatch to the central laboratories and institutions, in other countries, which have been nominated by the Health Organisation of the League of Nations, for local distribution.

Institutions or individual investigators in Great Britain and Ireland requiring the standard for the oestrus-producing hormone should apply to the Department of Biological Standards, the National Institute for Medical Research, Hampstead, N.W.3.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Arnold's Sodium Nitroprusside Reaction for Proteins and the Denaturing of Flesh Protein by Means of Concentrated Urea Solution. K. Beck and H. Urack. (*Z. Unters. Lebensm.*, 1933, **45**, 399–418.)—Arnold's nitroprusside reaction for urine (*Z. physiol. Chem.*, 1906, **49**, 397; 1913, **83**, 304) has been found to be applicable to all proteins or their derivatives containing a sulphydryl group which can be acted upon by the reagent. For example, egg albumin gives little, if any, reaction, whereas after the so-called denaturing process it reacts strongly (Arnold, *Z. physiol. Chem.*, 1911, **70**, 300; Harris, *Proc. Roy. Soc.*, 1923, **94**, [B], 426). The best method of applying the test is as follows:—Two c.c. of a 3 per cent. solution of the protein, dissolved at the ordinary temperature in a 50 per cent. solution of urea, are treated with 3 drops of approximately 2*N* ammonia, and then with a crystal (about 20 mgrms.) of sodium nitroprusside, or with about 0·2 c.c. of a freshly-prepared solution of sodium nitroprusside. A pink colour, gradually changing to raspberry-red and finally to yellowish-brown, is obtained. If the protein belongs to the class which reacts with nitroprusside only after treatment with a reducing agent, 2 drops of 10 per cent. potassium cyanide solution are added to the ammoniacal solution, and then, after two minutes, the crystal of sodium nitroprusside. A pronounced reaction was obtained with 0·02 grm. of egg albumin dissolved in 2 c.c. of a mixture of water and urea (1:1), treated with 3 drops each of 2*N* ammonia and 10 per cent. potassium cyanide solution, and then, after two minutes, with 40 mgrms. of solid sodium nitroprusside. The maximum intensity of colour was attained after 5 minutes, and the colour faded completely in 50 minutes. It was shown by Ramsden (*Nature*, 1931, **127**, 403) that nitroprusside solutions which have stood for some days will produce a pink coloration (pseudo-sulphydryl reaction), even in the absence of substances containing sulphydryl groups. Unlike the true sulphydryl reaction, however, the colour of solutions in which the pseudo-sulphydryl reaction appears is not discharged, or only slightly so, by the addition of hydrogen peroxide.

Application of the Reaction to Milk.—The intensity of the colorations obtained with raw, pasteurised and boiled milk varies with the degree of heating of the milk, but the differences are not sufficiently pronounced to enable a judgment to be formed as to the degree of heating. The addition of 0·1 per cent. of formaldehyde has no influence upon the reaction, but 0·5 per cent. prevents the appearance of the coloration. The presence of sufficient hydrogen peroxide also prevents the coloration for a period depending upon the time required for the peroxide to decompose. This decomposition proceeds slowly when the catalase activity of the milk has been weakened or destroyed by heating, whereas with raw milk the decomposition of corresponding quantities of hydrogen peroxide takes place in a relatively shorter time. On this principle has been based the following method of

estimating the degree to which milk has been heated. The sample of milk is treated with 30 per cent. hydrogen peroxide, so that the mixture eventually contains 0·1 per cent. (measured as accurately as possible), and, after standing for 24 hours, it is centrifuged. A mixture of 0·5 c.c. of the clear liquid with 1 drop of 2*N* ammonia and 1 drop of 10 per cent. potassium cyanide solution is saturated with urea and treated with about 20 mgrms. of solid sodium nitroprusside. The resulting coloration is rose with raw milk, brown with pasteurised milk, and yellow with boiled milk.

Application of the Test to other Proteins.—The nitroprusside test gave a pronounced bluish-pink coloration with cheese, and with the curd separated from raw milk on souring. The muscle fibres of the flesh of different animals, left after boiling, were also found to consist, in the main, of denatured proteins, but the albumoses of Liebig's meat extract (*i.e.* the compounds precipitated with zinc sulphate) did not give the distinctive coloration; the quantity of albumin (if any) in the meat extract was too small to be detectable by the nitroprusside reaction. On the other hand, precipitates obtained in the precipitin test gave the distinctive colorations with the nitroprusside reagent. The denaturing action of urea on various proteins, including egg albumin and the flesh of animals, was also studied, and the results showed that the protein obtained by extracting the muscular tissue of the ox with a concentrated solution of urea agrees in composition with the residual structural protein of the tissue.

Detection of the Neutralisation of Milk. K. Eble and H. Pfeiffer. (*Z. Unters. Lebensm.*, 1933, **65**, 435–439.)—At the present day very little sour milk is brought back to the normal acidity by the addition of alkali, but the acidity of fresh dairy milk is frequently slightly reduced (for prophylactic reasons) by the addition of a small proportion of sodium carbonate, and this cannot be detected with certainty by the usual methods. In experiments with dairy and creamery milks of various origin it was found that the addition of 30 c.c. of methyl alcohol to 20 c.c. of normal milk produced, at once or within a few seconds, a granular coagulum, whilst the serum showed only a slight opalescence. On the other hand, neutralised milk under the same conditions, formed an almost homogeneous mixture, which only after standing for some hours formed a finely flocculent coagulum, leaving a turbid serum not readily filterable. The p_H of the methyl alcohol serum of normal diary milk was between 6·5 and 6·3, whereas with partly neutralised milk it exceeded 6·5. For the detection of added alkali it is essential that practically the whole of the lactic acid in the milk should have combined with the alkali. If, however, very sour milk is treated with alkali, but not in sufficient quantity to reduce the acidity to a point near that of normal fresh milk, the method fails, since the free lactic acid causes more or less coagulation. Such milk, however, also lacks the distinctive characteristic of milk that has been altered by the addition of alkali, namely, the low acid value. For the detection of the addition of alkali to sour or very sour milks Tillmans' alizarin test (violet coloration) is preferable. Milk treated with excess of alkali yields a methyl alcohol serum containing alkali albuminate; the milk itself also shows some chemical change. Freshly-drawn milk occasionally behaves abnormally, no

coagulum being obtained until after the lapse of 5 to 20 minutes, and the serum then remaining turbid. This is attributed to such milks being exceptionally low in carbon dioxide. But, since the neutralisation process is not applied to freshly-drawn milk, but only to dairy milks, in which the normal lactic acidity has developed, this limitation does not affect the practicability of the process.

Detection of Eggs in Food Pastes. G. Bragagnolo. (*Giorn. Chim. Ind. Appl.*, 1933, **15**, 177–179.)—When eggs are heated for 10 minutes in water, shelled and mixed to a homogeneous paste, and when this is placed in contact at 40° C. with a pepsin-hydrochloric acid solution with p_H about 1·5 (that of human gastric juice), the acidity of the solution shows appreciable diminution within a few minutes. If wheat flour is used instead of the egg paste, the acidity of the liquid either remains constant or increases slightly. This difference in behaviour may be utilised to detect the presence of eggs in food pastes, the procedure being as follows:

Powdered pepsin (25 grms.) is dissolved in 0·05 *N* hydrochloric acid to give a solution of p_H between 1·4 and 1·7. The total acidity of this liquid is determined by titration with 0·05 *N* sodium hydroxide in presence of phenolphthalein. Fifty c.c. of the solution are then mixed in a small beaker with 10 grms. of the food paste to be tested and the beaker is placed in an oven at the ordinary temperature. The oven is next heated to 37° C., this temperature being maintained for 10 minutes. The beaker is then immersed in a freezing mixture in order to paralyse the action of the pepsin. The cooled liquid is filtered rapidly through a porous filter-paper, and the filtrate is titrated with 0·05 *N* sodium hydroxide as before. Diminished acidity denotes presence of egg in the paste, and increased acidity its absence.

The method indicates approximately the proportion of egg present. When a pepsin solution requiring 122·0 c.c. of 0·05 *N* sodium hydroxide per 50 c.c. for neutralisation was used, the titration results obtained with pastes containing proportions of egg varying from 1:1000 to 1:100 were as follows:

1:1000	1:500	1:333	1:250	1:200	1:150	1:125	1:100
119·2	107·3	104·6	103·0	95·2	89·0	86·1	90·2

T. H. P.

Action of Sodium Borate on the Reaction of Alkali Cyanides with Reducing Sugars. J. Bougault, Z. Hardy and A. Pinguet. (*J. Pharm. Chim.*, 1933, **17**, 462–469.)—The fixation of hydrogen cyanide by reducing sugars is, in general, sufficiently rapid to form the basis of a method for determining these sugars (*cf.* Bougault, ANALYST, 1917, **42**, 307), but with lactose it proceeds extremely slowly. To ascertain if the fixation of the cyanide is retarded by the increasing alkalinity of the solution, experiments have been made with various sugars in presence of sodium borate as buffer. The reactions cannot be followed polarimetrically owing to modification of the rotation by the borax, but determinations of the quantities of sugars combined, by determining the excess of unused cyanide show that fixation of the cyanide is accelerated by the presence of borate. The excess of cyanide cannot be determined by titration with ammoniacal silver nitrate, as this rapidly decomposes the nitrile-alcohols formed as the first products of the fixation of hydrogen cyanide by sugars. Titration of the cyanide with iodine gives more satisfactory results. T. H. P.

Colouring Matters of Butter. A. Loewy and G. Cronheim. (*Z. Unters. Lebensm.*, 1933, **65**, 450–451.)—Since petroleum spirit dissolves both the artificial and natural colours (including carotene) in butter, it is not recommended as a test for the former, and absolute alcohol is preferable. Filtered 20 per cent. extracts of natural butters in various solvents were matched against tincture of saffron (a 0·5 per cent. solution of which was taken as equivalent to 100 units), or against a 1 in 6000 solution of potassium dichromate (55 units). The values for ether and petroleum spirit were 29·6 to 53·5 and 37·2 to 48·7, respectively, whilst absolute alcohol gave zero results. The fact that the highest results were obtained with samples from mountainous districts supports the conclusion of Gabathulier (*Z. Vitaminkunde*, 1931, No. 16), who found that the milk of Davos cows was richer in vitamins than the milk of lowland cows. J. G.

Determination of Tannin in Wines. Astruc and Castel. (*Ann. Chim. anal.*, 1933, **15**, 196–199.)—Previous methods for determining tannins in wine are based either on the acidic properties of the tannins or on the reducing properties of their phenolic hydroxyl groups. The method now proposed makes use of the reducing properties of the glucose constituent of the tannin molecule.

The wine is diluted, if necessary, to bring its sugar-content below 3 grms. per litre. The reducing power of the wine (20 c.c.) towards Fehling's solution is first determined and calculated as mgrms. of copper (A) per litre. One hundred c.c. of the wine are then concentrated slightly by boiling to expel aldehydes, and potassium permanganate solution is added, drop by drop, and with shaking, until a copious precipitate forms and the wine turns brown. Basic lead acetate is next added in small amounts (about 5 c.c. in all), and the volume is made up to 100 c.c. either with water, or, if it is thought that excess of the lead acetate has been added, with saturated sodium sulphate solution. The liquid is filtered, and the copper-reducing power of the filtrate (22 c.c. $\equiv$ 20 c.c. of wine) determined as before and calculated as mgrms. of copper (B) per litre.

A 0·2 per cent. solution of tannin (oak) is prepared and its copper-reducing power determined and calculated as mgrms. of copper (C) for 1 grm. of tannin per litre. The tannin in the wine, in grms. per litre, is then given by (A—B)/C.

The accuracy obtainable is shown by the following results, expressed as grms. of tannin per litre; wine alone, 1·24; after adding 0·3 per cent. of glucose, 1·27; after adding 1 grm. of tannin per litre, 2·19; after adding 2 grms. of tannin per litre, 3·21. T. H. P.

Colorimetric Determination of the Preservative Value of Hops. J. M. Guthrie and G. G. Philip. (*J. Inst. Brewing*, 1933, **39**, 220–224.)—The method previously described (*cf.* ANALYST, 1930, **55**, 703, and French, *J. Inst. Brewing*, 1931, **37**, 436) has been simplified and improved as follows:—The sample is minced, and 10 grms. are shaken with 100 c.c. of distilled industrial methylated spirit for 10 minutes, 1 c.c. of the clear, filtered liquid being then added to about 50 c.c. of the methylated spirit and 0·5 c.c. of *N* acetic acid in a 100-c.c. flask. Ten c.c. of a 1 per cent. solution of uranyl acetate in methyl alcohol are then added, and, after dilution to 100 c.c. with methylated spirit, the colorimetric determination of α-soft resins is carried out as already described. Agreement is good both with

gravimetric methods (*cf.* Walker and Hastings, *ibid.*, 1928, **34**, 9; Ford and Tait, *ibid.*, 1932, **38**, 351) and with the earlier method in which petroleum spirit was used for extraction. A suitable 1 per cent. solution of uranyl acetate in alcohol will give a red colour with bromo-phenol blue similar to that obtained with the α-soft resin. Considerable latitude as regards the purity of the solvent alcohol is permissible, so long as the impurities present do not alter the p_H value appreciably; similarly, distilled technical methyl alcohol containing up to 5 per cent. of acetone may be used to prepare the reagent and colour standards. In the latter case 0·0238 grm. of the pure finely-divided lead α-soft resin is shaken gently with 3 c.c. of the alcohol and 0·5 c.c. of *N* hydrochloric acid. After one minute the lead compound becomes white, and 15 c.c. of the reagent and 0·4 c.c. of *N* sodium acetate solution are then added, and the mixture is diluted to 100 c.c. with methyl alcohol and filtered. Lovibond glasses are not suitable for colour standards, and Nessler cylinders or a suitable colorimeter may be used for matching purposes.

J. G.

Detection of the Colouring Matter of Paprika in Sausages. W. Plahl and A. Rotsch. (*Z. Unters. Lebensm.*, 1933, **65**, 452–454.)—The usual methods (*Codex alim. austriac.*, **2**, 123) of detecting colouring matters in sausages are not applicable to the colouring matter of paprika. This can be isolated, however, by extracting it, together with the fat, from 5 to 10 grms. of the sample by means of ether or petroleum spirit, saponifying the fat, converting the soap into the calcium salts of the fatty acids, washing these with hot water, and extracting them with 96 per cent. alcohol for 15 minutes on the boiling water-bath. On evaporation of the alcoholic extract the paprika colouring matter is left in the form of red droplets, which give the well-known blue coloration with concentrated sulphuric acid. After standing for one or two days the red colour fades, and the blue coloration with sulphuric acid can no longer be obtained. J. G.

Distinction between Lecithin Preparations of Animal and Vegetable Origin. B. Rewald. (*Chem.-Ztg.*, 1933, **57**, 373–374.)—The work of F. E. Nottbohm and F. Mayer (ANALYST, 1932, **57**, 322) is criticised on the grounds that no allowance is made for the difference in fat-contents between commercial animal and vegetable lecithins, and for the fact that lecithins from sources other than eggs may exist (*e.g.* from the liver, brain or flesh). The choline formula gave a value of 70·41 (instead of 98) per cent. for a sample of Merck's lecithin "ex ovo purissimum." The value of the N : P ratio is discussed, and it is considered that the cholamine-content is not a suitable means of evaluation; that the phosphorus-content must always be the basis of any such method, and appropriate allowances be made for variable factors; and that vegetable lecithin, although cheaper, is not necessarily inferior to the animal product. Suggestions are made for a revision of the nomenclature of the subject. J. G.

Determination of Phenacetin, Aspirin and Antifebrin. G. Weissmann. (*Z. anal. Chem.*, 1933, **93**, 31–33.)—Methods previously suggested for the determination of these compounds employ energetic reagents which may attack other constituents of antipyretic or analgesic medicaments. The method now described

is based on hydrolysis of the phenacetin, etc., by dilute hydrochloric acid, followed by titration of the acetic acid liberated. The material (0·3 to 0·35 grm.) is weighed in a dry, flat-bottomed flask and dissolved in 100 c.c. of water. After addition of 5 c.c. of *N* hydrochloric acid, the flask is connected with a reflux condenser through the cork. The flask is heated for at least an hour on a gauze, any crystals adhering to the wall being rinsed down by swirling. With the condenser water still flowing, the liquid is allowed to cool to 15° to 20° C., the condenser tube being then washed down with 5 to 10 c.c. of alcohol. The solution is then titrated with 0·1 *N* sodium hydroxide solution in presence of phenolphthalein. A blank experiment with 5 c.c. of *N* hydrochloric acid (from the pipette previously used) and 5 to 10 c.c. of the alcohol is carried out. One c.c. of 0·1 *N* alkali ≡ 0·01791 grm. of phenacetin ≡ 0·01351 grm. of antifebrin ≡ 0·09 grm. of aspirin. With the pure compounds, the results range from 99·6 to 100·3 per cent. The method has not yet been applied to mixtures containing other materials. T. H. P.

Biochemical

Practical Method for the Simultaneous Determination of Lactose and Glucose in Urine. I. S. Kleiner and H. Tauber. (*J. Biol. Chem.*, 1933, **100**, 749–754.)—A new rapid colorimetric method for the quantitative determination of lactose and glucose in urine is described. It is an adaptation of the colorimetric method of Tauber and Kleiner (*J. Biol. Chem.*, 1932–33, **99**, 249) for the determination of monosaccharides in the presence of disaccharides. By treatment with copper sulphate and barium hydroxide a filtrate is yielded free from pigments, proteins, uric acid, etc., and, at the same time, the urine is diluted to such an extent that other constituents give only minimal interference. The procedure consists in determination of the total reducing power and the monose-content of the filtrate; the difference between the two figures represents the lactose present. The cuprous oxide formed is treated with an acid molybdate solution, and the resulting blue colour is measured colorimetrically. The solutions required are as follows:—*Cupric sulphate :* 4 per cent. solution ($CuSO_4.5H_2O$). *Barium hydroxide :* 1 per cent. solution. *Monose reagent :* This is prepared as described by Tauber and Kleiner (*J. Biol. Chem.*, 1932-33, **99**, 249), except that 5 drops of 1 per cent. sodium bisulphite are added to each 25 c.c. of reagent just before use. This permits of the determination of "traces" of glucose. *Sodium bisulphite :* 1 per cent. solution. *Benedict's colour reagent :* This is prepared as described by Benedict (*J. Biol. Chem.*, 1931, **92**, 141), and is used in the determination of both the monose and total sugar. *Glucose standard :* Two standards, containing 0·2 and 0·4 mgrms. per 2 c.c. respectively, are used. *Alkaline copper reagent :* This is prepared as described by Benedict. Before use, 1 c.c. of 1 per cent. sodium bisulphite solution is added to each 20 c.c. of reagent. *Procedure :* To 1 c.c. of urine (diluted if the sp.gr. exceeds 1·025) in an accurately graduated 20-c.c. cylinder is added 1 c.c. of copper sulphate solution, then sufficient barium hydroxide (about 5 c.c.) to make the fluid faintly alkaline (approximately p_H 7·5 to 8), and water to give a total volume of 20 c.c. The whole is mixed, filtered, and re-filtered if a clear filtrate is not obtained immediately. If a faint opalescence

persists, the results will not be affected. The trace of barium present need not be removed. Two c.c. of filtrate are pipetted into a Folin-Wu sugar tube, and the glucose standards are placed in two similar tubes. The three tubes (after the addition of 2 c.c. of monose reagent to each) are heated in boiling water for 8 minutes, and cooled for 2 minutes. Another set is run with Benedict alkaline copper reagent simultaneously, with the same amounts of filtrate, standards and reagent, boiled for 6 minutes, and cooled for 2 minutes. Two c.c. of colour reagent are added to each of the tubes in both sets; the contents are mixed, left for 2 minutes, diluted with water to the 25 c.c. mark and mixed thoroughly; colorimetric comparisons are then made. A slight correction is necessary with the monose method (+0·02 per cent.). To obtain lactose values, the figure obtained by the monose method plus 0·02 per cent. must be subtracted from the total reduction (Benedict), and the result must be multiplied by 2·2. If the monose figure, plus 0·02 per cent., is about the same as the total figure, there is no lactose in the urine.

Calculation.

(A) Total reduction $= \frac{\text{Standard}}{\text{Unknown}} \times \frac{20\ (i.e.\ \text{degree of dilution})}{200\ (\text{or } 100 \text{ with strong standard})}$

(B) Monose reduction $= \frac{\text{Standard}}{\text{Unknown}} \times \frac{20\ (i.e.\ \text{degree of dilution})}{200\ (\text{or } 100 \text{ with strong standard})} + 0{\cdot}02$ per cent.

(C) Per cent. lactose $= (\text{A} - \text{B}) \times 2{\cdot}2$.

Tables including results showing the almost theoretical recovery of lactose added to pathological urines are given. Since, in a considerable number of obstetric cases, lactose may be found in the urine and the diagnosis of possible diabetes in such cases is of great importance, the value of the new method is obvious.

P. H. P.

Substances which Interfere with the Antimony Trichloride Test for Vitamin *A*. R. E. Corbet, H. H. Geisinger and H. N. Holmes. (*J. Biol. Chem.*, **1933, 100**, 657-666.)—The effect of refluxing certain acids with cod-liver oil in chloroform solution was determined. It was found that glacial acetic acid and *N* nitric acid lowered the blue value of the oil very slightly, but that *N* acetic, hydrochloric and sulphuric acids had no effect. Concentrated hydrochloric acid caused a decrease of about 60 per cent. of the value given by the control, 1 drop of concentrated sulphuric acid in 10 c.c. of the cod-liver oil solution immediately produced a purple colour which masked the antimony trichloride reaction, and 5 drops of concentrated nitric acid in 10 c.c. of the oil solution produced such an intense yellow that no blue could be observed in a subsequent reaction with antimony trichloride. The effect of adding various substances to a chloroform solution of halibut liver oil concentrate was also determined. Tabulated results show to what extent these substances interfere with the colour produced by reaction of concentrates of vitamin *A* with antimony trichloride. The maximum amounts of such interfering substances which may be present without masking the test are given.

The substances tested are grouped as follows:—(1) Substances which do not interfere with the vitamin *A* test, (2) substances which interfere slightly, but produce no colour alone with antimony trichloride, and (3) substances which interfere seriously, and produce a colour alone with antimony trichloride. The substances placed in group (i) are:—Glacial acetic, propionic, capric, lauric, palmitic, stearic and benzoic acids, bromoform, carbon tetrachloride, carbon disulphide, cyclohexane, benzene, toluene, coconut oil and cholesterol. Although benzene and toluene are in this group, yet xylene affects the test sufficiently to be placed in group (ii). The substances in group (ii) (consisting chiefly of the saturated alcohols and esters), unless diluted to one-fourth or less of the total volume, cause the colour produced by the vitamin concentrate to be weaker and to fade more rapidly. Coconut oil is in the first group, butter fat is in the second, but all the other oils tested, which contain a larger percentage of unsaturated fats, belong in the third class. Rancid oils have a much greater effect than fresh oils. Group (iii) is representative of more types of compounds than the other two groups. Some substances, *e.g.* quinone, affect the blue test given by a concentrate *only* if they produce a visible colour by themselves with antimony trichloride (obviously a masking of the blue of the vitamin chromogen by the yellow or red produced by the foreign substance). None of the substances tested directly with antimony trichloride showed any blue in the colour thus produced. The substances placed in group (iii) are:—Benzaldehyde, benzyl alcohol, allyl alcohol, amylene, cyclohexene, quinone, oleic acid, linolic acid, linolenic acid, ethyl oleate, olive oil, mazola, poppy-seed oil, lecithin, lanoline, pyridine, indole, scatole, limonene, pinene, geraniol, terpineol, and abietic acid. The extent of interference was found to increase with the degree of unsaturation, and to be modified by the configuration of the molecule. P. H. P.

Vitamin *A* Content of Naturally Coloured Nut Margarines. C. F. Poe and H. A. Fehlmann. (*Ind. Eng. Chem.*, 1933, **25**, 402–403.)—In November, 1930, the Bureau of Internal Revenue, U.S.A., ruled that unbleached palm oil might be used as one of the substantial ingredients of oleo-margarine; later a law was passed imposing a tax of 10 cents per pound on all naturally coloured oleo-margarines. The vitamin *A* content of a number of nut margarines coloured by the addition of palm oil has been determined. Rats, whose body store of vitamin *A* had been depleted, were fed on the basal diet plus different amounts of the nut margarines, and the experiment was continued for 8 weeks or until death. Sufficient vitamin-free cottonseed oil was given to each animal to make the total fat-constituent of the diet one grm. per day. Negative controls were run on a representative number of animals, and different daily levels of butter were added to the diet of a number of animals which were used as positive controls. Figures record the growth made by the animals. Samples from eight different manufacturers showed considerable variation in their vitamin content. The Sherman vitamin units per grm., which were calculated, ranged from 0·65 in one sample to 4·7 in another. It was shown that the vitamin *A* content is derived from the fat rather than from the added milk. The amount of vitamin *A* in the margarines was found to be low in comparison with that in butter. The fat-constituents of the nut margarines tested (so far as they could be obtained) are tabulated. None

of the fats listed contains any considerable amount of vitamin *A* except the palm oil; this is rich in carotene, the probable precursor of vitamin *A*. No colouring, other than that contained in the palm oil, was added in the manufacture of the margarines, which were made by churning the fats in milk. It is concluded, therefore, that palm oil shows promise as a source of growth-promoting substances in nut margarines. P. H. P.

Effect of Storage on Vitamin *A* in Dried Foods. G. S. Fraps and R. Treichler. (*Ind. Eng. Chem.*, 1933, **25**, 465–466.)—The effect of storage on vitamin *A* is of industrial as well as of agricultural importance, and certain dried foods have been tested to find the effect of storage on their vitamin *A* content. Units of vitamin *A* were determined on rats by the Sherman–Munsell method, as used by Fraps (*Tex. Agr. Expt. Sta., Bull.*, 1931, **422**). The materials were stored at room temperature in Mason jars, tightly closed except while portions were being removed for feeding purposes. The results obtained are summarised as follows:—There is a gradual loss during storage in the vitamin *A* content of alfalfa leaf meal, dried black-eyed peas, dried green sweet peppers, yellow maize, and powdered whole milk. Measured by the Sherman–Munsell unit method, alfalfa leaf meal lost about 50 per cent. of its vitamin *A* in 11 months, dried black-eyed peas 50 per cent. in 9 months, dried green sweet peppers 80 per cent. in 19 months, powdered whole milk 60 per cent. in 9 months, and yellow maize 30 to 50 per cent. in 6 months. The loss of vitamin *A* in dried samples stored in the laboratory should be taken into consideration in experimental work. It is possible that the loss would be less for goods stored in a cooler climate or in cold storage. The loss of vitamin *A* in stored food may be a factor of considerable importance in connection with the feeding of animals or man. The amount of destruction of vitamin *A* varies both with the length of the storage period and with the kind of material containing the vitamin. Grinding maize before storage does not seem to increase, to any noticeable degree, the loss of the vitamin *A* in yellow corn as compared with the whole grain. P. H. P.

Organic Analysis

The "Elaidin" Reaction. H. N. Griffiths and T. P. Hilditch. (*J. Chem. Soc.*, 1932, 2315–2324.)—The conversion of triolein into trielaidin in the presence of oxides of nitrogen has been investigated by numerous workers, including Poutet in 1819, Boudet (*Annalen*, 1832, **4**, 1), Varrentrapp (*ibid.*, 1840, **35**, 196), and Archbutt (*J. Soc. Chem. Ind.*, 1886, **5**, 303). Although Farnsteiner (*Z. Unters. Nahr. Genussm.*, 1899, **2**, 1) attempted to use the test to determine oleic acid in the mixed fatty acids of butter fat, little information as to the equilibrium of cis- and trans-forms in the "elaidin" reaction has been recorded, except that Jegorow (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 973; *J. pr. Chem.*, 1912, **86**, 539) observed that the transformation is brought about by relatively small proportions of the reagent and that addition products result from the use of larger proportions. A study of the action of oxides of nitrogen, prepared by different methods, on oleic acids, has shown that under the most favourable condition (minimal amounts of oxides of nitrogen approximating in composition to N_2O_3 at 10–20° C.) oleic

acid is converted at equilibrium into about 60 per cent. of its weight of elaidic acid. The reverse isomerisation of elaidic acid was brought about, to an extent equal to about 68 per cent. of the amount submitted to the process, by the use of Poutet's reagent (mercury dissolved in nitric acid of sp.gr. 1·42), whilst nitrous fumes from arsenious oxide and nitric acid, and from sodium nitrite and sulphuric acid, respectively, led to the recovery of 66 and 60 per cent. of the elaidic acid used in the isomerisation. Thus the proportions of unrecovered acids not reacting with Wijs solution, *i.e.* addition products, are greatest with oxides of nitrogen generated from sodium nitrite. It is seen from the tables that the yields of elaidic acid, starting from either oleic or elaidic acid, are closely similar when the same method of preparation of oxides of nitrogen is employed, and this is regarded as formal proof that the "elaidin" reaction is a reversible change, the same equilibrium being reached irrespective of whether the cis- or the trans-acid is the starting point. The composition of the final product is the same whether the cis- or trans-ethenoid acid is isomerised, and definite amounts of addition products accompany the mixture of cis- and trans-acids at equilibrium; the inference is that the isomeric change is effected by the addition of nitro- and nitroso-radicals at the ethenoid bonds, followed by reversion of the addition compound into nitrogen trioxide and the equilibrium mixture of cis- and trans-compounds. The action proceeds to quantitatively the same extent as in the free acid in the methyl or glyceryl esters of oleic acid; but, owing to the presence of three oleic groups in triolein, only about 30 per cent. of the latter is completely transformed into trielaidin. It is possible that semi-quantitative applications of the "elaidin" reaction may prove useful for the approximate estimation of oleic acid in mixtures of oleic with linolenic and other unsaturated acids in certain fats, particularly in "drying oils," and also for the isolation, by crystallisation from acetone, of mixtures of trielaidin and palmito-elaidins from different natural fats in characteristic proportions, and with characteristic equivalents and iodine values, thus giving a quantitative significance to what has so far been only a qualitative test, and work is proceeding on these lines. D. G. H.

Detection of *p*-Phenylene-diamine and other Diamines in Hair Dyes. C. Griebel and F. Weiss. (*Z. Unters. Lebensm.*, 1933, **65**, 419–428.)—*p*-Toluylenediamine and sulphonic acid derivatives of various amino compounds are increasingly used in hair dyes in place of the more toxic *p*-phenylene-diamine. These substances can be differentiated by the following reagents: Nos. 1, 2 and 4 are added to the aqueous solution of the hydrochlorides; No. 3 should be applied to the solid residue obtained by evaporating a few drops of solution of the hydrochloride on a crucible lid):—(1) Ferric chloride solution (1 : 40). (2) Excess of a fresh filtered solution of calcium hypochlorite (1 : 10). (3) A fresh solution of 0·05 grm. of vanillin in 1 c.c. of alcohol and 4 c.c. of 25 per cent. hydrochloric acid (*cf.* Griebel, *Apoth. Ztg.*, 1930, **45**, 318). (4) Small solid particles of lead dioxide. *p-Phenylene-diamine.*—(1) Dark green, turning violet. (2) Yellow-white needle- or hair-shaped crystals of quinone dichlorimide, which may be recrystallised from 70 per cent. alcohol; these darken at 120 to 123° C. and decompose into a tarry fluid at 129° C. (3) A yellow precipitate, turning brick-red, or in the presence of an

excess of water, purple-violet. (4) Blue-green, turning yellow-brown. *p-Toluylene-diamine.*—(1) As above. (2) As above, but 30 minutes are required for the separation, and the crystals are red; m.pt. 69° C., decomp. 126° C. (as above). (3) The yellow colour (*cf.* above) is permanent. (4) Blue-green, turning violet. *p-Amino diphenylamine.*—(1) Brown-red, turning green and then blue in 15 minutes. (2) An orange amorphous turbidity. (3) Bright orange, turning to brick-red droplets which are unchanged by an excess of water. (4) Blue-violet, turning to bright grey-blue. *m-Phenylene-diamine.*—(1) Red-brown after some time. (2) A yellow turbidity, and then an ochre-coloured precipitate. (3) Yellow, subsequently unchanged. (4) Negative. *p-Amino-phenol.*—(1) Violet. (2) A voluminous precipitate of fine bright-yellow needles, which are soluble in an excess of reagent. (3) Yellow aggregates. (4) Violet-brown. *Methyl p-amino-phenol.*—(1) A violet colour after 5 minutes. (2) Negative. (3) A yellow colour developing slowly. (4) Violet, turning brown. *Diamino-phenol.*—(1) Blood-red. (2) No precipitate, but a blood-red colour, which is destroyed by an excess of reagent. (3) Deep yellow, subsequently unchanged. (4) Red, turning brown. Mixtures of *p*-phenylene-diamine and *p*-toluylene-diamine give chlorimides whose melting and decomposition points are:—

		M. pt.	
p-Phenylene-diamine	*p*-Toluylene diamine	complete fusion °C	decomposition point °C
5	95	65	121
10	90	65·5	118·5
20	80	66	118
50	50	117	117·5

Quinone dichlorimide gives a reaction with vanillin which is similar to that obtained with *p*-phenylene-diamine. A procedure for the systematic examination of hair dyes is given. J. G.

Colour Reaction of Geranium Oil and of some Commercial Rhodinols. S. Sabetay. (*Ann. Chim. anal.*, 1933, **15**, 194–196.)—When 5 drops of geranium oil, dissolved in 2 c.c. of chloroform, are treated with 0·5 to 1 c.c. of a 10 per cent. solution of bromine in chloroform, an intense blue-green coloration appears after a few minutes. This reaction was shown by all samples of geranium oil examined and also by rhodinols which had been imperfectly purified. It is not due to any of the known constituents of geranium oil or to isopulegol, limonene, nerol, menthol, or citronellal. The same reaction was given by such Bulgarian, Anatolian and Grasse oils of roses as were available, but no sample of undoubted authenticity was tested. It is suggested that it may be of use in cases of adulteration by geranium oil or rhodinol. The question of the homogeneity of citronellol and rhodinol requires further investigation. T. H. P.

Acidity in Wool. S. R. Trotman and G. N. Gee. (*J. Soc. Dyers and Col.*, **1933, 49, 132–134.**)—The amount of acidity as sulphuric acid found in scoured knitted web by the sodium acetate distillation method was 0·28 per cent., and 0·22 per cent. by the magnesium carbonate method (*J. Soc. Dyers & Col.*, 1932, **48,**

321). After being treated with 10 per cent. Glauber's salt the figures were 0·26 and 0·22 per cent., respectively, thus showing that Glauber's salt does not affect the determination. The effect of dyestuff was found to be negligible. The acidity found in undyed web after boiling with 10 per cent. Glauber's salt and 2 per cent. sulphuric acid was 0·98 per cent. After boiling with the same proportions of salt and acid in the presence of Alizarin Delphinol SEN (which contains one sulphonic group per molecule), the acidity found was 1·04 for the 1 per cent. dyeing and 1·02 for the 3 per cent. dyeing. When Polar Red G (which contains two sulphonic groups per molecule) was used, a slight increase in acidity was found.

If oleic or stearic acids are steam-distilled with sodium acetate, acetic acid is liberated and will count as acidity. Wool containing fatty acids should be degreased with petroleum spirit prior to analysis by the sodium acetate method. The acidity of wool dyed in the presence of acetic or formic acid is about the same as when sulphuric acid is used. R. F. I.

Inorganic Analysis

Determination of Water of Crystallisation. Preparation of Anhydrous Oxalic Acid and Sodium Sulphate. V. Cerchez and C. Panaitescu. (*Bull. Soc. Chim.*, 1933, **53**, 243–248.)—Tests made by the Dean and Stark method (*cf.* Jones and McLachlan, ANALYST, 1927, **52**, 383) showed that the total water of crystallisation was recovered from the following crystalline salts: Sodium thiosulphate, barium chloride, sodium sulphate, ammonium molybdate, barium hydroxide, potassium ferrocyanide and sodium carbonate. The following salts, however, lost only a fraction of the water of crystallisation, as indicated: zinc sulphate, ferrous sulphate and magnesium sulphate, 6/7ths; copper sulphate, 4/5ths; cobalt chloride, 5/6ths. The principle of heating with an organic liquid was found to be effective for preparing large quantities of anhydrous oxalic acid and sodium sulphate. With oxalic acid, however, xylene is an unsuitable liquid, owing to the appreciable decomposition into carbon dioxide, carbon monoxide and water which occurs at the boiling point of xylene. By employing benzene instead of xylene, this decomposition is avoided. A 500-grm. quantity of oxalic acid dihydrate and 500 c.c. of benzene were heated in a flask fitted with a non-reflux condenser. When most of the benzene had distilled over, carrying with it a part of the water, the benzene layer in the receiver was returned to the distillation flask and the distillation continued; this process was repeated several times until no further water came over in the distillate, when the oxalic acid was found to be dehydrated. Anhydrous sodium sulphate may be prepared similarly, either benzene or xylene being employed. S. G. C.

Volumetric Determination of Uranium. Application to the Indirect Titration of Minute Quantities of Sodium. I. M. Kolthoff and J. J. Lingane. (*J. Amer. Chem. Soc.*, 1933, **55**, 1871–1876.)—Quadrivalent uranium may be titrated with potassium dichromate, diphenylamine or diphenylamine sulphonate being used as indicator, provided ferric iron is added to accelerate the change-point of the indicator. Potassium dichromate solution has an advantage over potassium

permanganate or ceric sulphate solutions, which have previously been proposed for titrating uranium, in that it can be kept indefinitely without change of strength. The method, which is as follows, involves the preliminary reduction of the uranium to the quadrivalent condition by the method of Lundell and Knowles (*J. Amer. Chem. Soc.*, 1925, **47**, 2637):—The solution (100 c.c.) containing sexavalent uranium in dilute sulphuric acid (5 per cent.) is passed through a "reductor" tube consisting of a 21-cm. column of 20-mesh amalgamated zinc (2 to 3 per cent. of mercury), gentle suction being used, at the rate of about 50 c.c. per minute. The tube is then washed through with three 30-c.c. portions of dilute sulphuric acid (5 per cent.), followed by three 35-c.c. portions of water. Air is bubbled through the combined liquids for 5 to 10 minutes in order to oxidise the tervalent uranium formed in the reduction process to the quadrivalent condition; quadrivalent uranium under these conditions was found to suffer no oxidation in half an hour. To the reduced solution the following reagents are added: 25 c.c. of ferric chloride solution (2 per cent.; 0·12 *N*), 15 c.c. of phosphoric acid (85 per cent.), and 10 to 12 drops of barium diphenylamine sulphonate indicator solution (0·2 per cent.), the final volume of the solution being 300 c.c.; it is titrated slowly with 0·1 *N* dichromate solution, and the titration is complete when one drop of the dichromate solution produces a strong violet colour which remains stable for at least 1·5 minutes. The colour-change is sharp. Good results were obtained in test experiments, taking from 25 to 5 c.c. of 0·1 *N* uranium acetate solution. Tests were also carried out with similar quantities of 0·01 *N* uranium acetate solution. In this case the initial volume before reduction was 25 c.c., a smaller "reductor" column (14 cm. long × 12 mm. diameter) was employed, less washing liquid was used, smaller volumes of reagents were added, *viz.* 5 c.c. of ferric chloride solution, 5 c.c. of phosphoric acid and 5 drops of sulphonate indicator solution, and 0·01 *N* dichromate solution was used for the titration, the volume of liquid titrated being 100 c.c.; an indicator correction of 0·15 c.c. was deducted from the volume of dichromate solution consumed in the titration. The results showed that as little as 6 mgrms. of uranium in 100 c.c. could be determined with an accuracy of 0·5 to 1 per cent.

Indirect Determination of Sodium.—The sodium is precipitated as sodium zinc uranyl acetate according to the directions of Barber and Kolthoff (*J. Amer. Chem. Soc.*, 1928, **50**, 1625; ANALYST, 1928, **53**, 456). The precipitate, after washing, is dissolved in dilute sulphuric acid (5 per cent.), and the solution is treated as above; 1 c.c. of 0·1 *N* dichromate corresponds with 0·383 mgrm. of sodium. In cases where less than 0·5 mgrm. of sodium was present, a special method of filtration was adopted to deal with the very small precipitate. The filter used was a Pyrex tube, 6 mm. in diameter, closed at one end by a fused-on disc of fritted Pyrex glass; the other end was connected with a suction flask by rubber tubing. In filtering, this filter is dipped into the liquid, which is drawn up the tube by suction, and by manipulation the precipitate is caused to collect on the under side of the disc. In washing the precipitate, 1 to 2 c.c. of the precipitating reagent is added to the precipitation vessel and drawn off, followed by 5 or 6 portions of alcohol (95 per cent.) saturated with the triple salt, and finally by 2 small portions of ether. During the entire washing process the suction should be maintained, with the bottom of the filter-tube resting on the bottom of the

precipitation vessel; in this manner a rapid and thorough washing of the precipitate can be effected. The filtration tube is then disconnected from the rubber connections, and the precipitate is dissolved in dilute sulphuric acid (5 per cent.); to assist in dissolving it from the pores of the disc, several successive 1 to 2 c.c. portions of the acid are delivered from a jet into the filter-tube and forced through the disc by pressure from the mouth. For the titration of these small quantities, 0·01 *N* dichromate solution is used, and the results obtained by the authors with quantities of sodium down to 0·16 mgrm. show a maximum error of 7·5 per cent.

S. G. C.

Nephelometric Determination of Chloride. I. M. Kolthoff and H. Yutzy. (*J. Amer. Chem. Soc.*, 1933, **55**, 1915–1922.)—The work of previous authors is referred to and the numerous factors affecting the light-reflecting power of suspensions are discussed. The following method has been developed, in which the chloride solution is added to a relatively large excess of silver nitrate solution containing alcohol:—A stationary Klett nephelometer with a plunger and movable cup was used. To one of two solutions containing 25 c.c. of ethyl alcohol, 1 c.c. of 0·5 *N* silver nitrate solution and 5 c.c. of 0·5 *N* nitric acid are rapidly added, and with just sufficient shaking for thorough mixing, 10 c.c. of the test solution, which should be neutralised; to the other are similarly added 10 c.c. of a standard chloride solution. The resulting solutions are kept at room temperature in a dark room for one hour, again shaken a little, and then compared in the nephelometer. Provided that the ratio of the chloride concentration in the test solutions and in the comparison solution is between 1·5 and 0·7, the concentration of the unknown may be calculated on the basis of an inverse proportion between the concentration and the depth measured in the nephelometer. The procedure can be applied over a concentration range between 0·08 and 42 mgrms. of chloride ion per litre, with an accuracy of approximately 2 per cent. Potassium nitrate and barium nitrate in concentration up to 0·06 *N* were without influence. Sodium sulphate had an appreciable effect; thus with a concentration greater than 0·3 *N*, flocculation of the suspension occurred, rendering comparison impossible, but with concentrations between 0·001 *N* and 0·065 *N*, a fairly fixed decrease in the turbidity was found, and it is recommended that when such small proportions of sodium sulphate are present in the test solution, sodium sulphate in concentration of the order of 0·01 *N* should be added to the comparison solution.

S. G. C.

Reagent for Lithium in Presence of other Alkali Ions. Separation of Lithium from Magnesium. Determination of Lithium. Separation of Arsenites from Arsenates. T. Gaspar y Arnal. (*Ann. Chim. anal.*, 1933, **15**, 193–194.)—Lithium may be detected in presence of other alkali ions by means of a reagent prepared by adding to 5 per cent. sodium arsenate solution, first ammonia solution in excess and then ethyl or methyl alcohol until a persistent precipitate forms; this is either filtered off or re-dissolved by addition of a small quantity of water. When about 0·5 c.c. of the solution to be tested is added to 3 or 5 c.c. of this reagent and the mixture is heated, a pale pink precipitate is formed if lithium is present. To separate magnesium from lithium, the former is first precipitated by adding sodium arsenite, and removed, and the lithium then

precipitated by the reagent described. To separate arsenites from arsenates, the latter are precipitated by addition of an ammoniacal solution of lithium chloride; the liquid is then treated with alcohol, heated, and filtered, the arsenite in the filtrate being precipitated by adding a solution of a magnesium salt. Lithium may be determined by precipitation with the above reagent, washing the precipitate with aqueous alcoholic ammonia, drying and weighing. T. H. P.

Determination of Fluorine and Phosphate in Presence of Silica and Aluminium. T. Millner and F. Kunos. (*Z. anal. Chem.*, 1933, **92**, 253–264. Part I: ANALYST, 1933, 54.)—(vi) Fluorine was determined in presence of silica and aluminium by the colorimetric method of de Boer and Basart (*Z. anorg. Chem.*, 1926, **152**, 213), based on the decolorising effect of fluorides on the zirconia lake obtained from sodium alizarinsulphonate and zirconyl chloride. For small quantities (1 to 10 mgrms.) of fluoride the high acidity of the solutions prescribed in the original directions had to be considerably reduced. (vii) For the determination of fluorine in solutions containing phosphate, the latter must first be removed by the usual precipitation as silver phosphate, since phosphates, as well as fluorides, decompose the zirconia lake. If aluminium is present in the solution together with phosphate, the silver phosphate precipitate occludes a considerable amount of alumina as well as fluoride, and should be dissolved in dilute nitric acid and re-precipitated by neutralisation. Even so, the results are only moderately accurate. (viii) For the determination of phosphoric acid in solutions containing also fluorides, silica, and aluminium, the liquid was evaporated twice with hydrofluoric acid for the complete removal of silica. Phosphoric acid was determined in the residue by the standard molybdate method. W. R. S.

Microchemical

A Simple Tapless Micro-burette. K. Schwarz. (*Mikrochem.*, 1933, **13**, 1–5.)—A tapless micro-burette constructed on the wash bottle principle is described. It is suitable for discharging amounts of liquid of 0·5 c.c. and less, with an accuracy of 0·1 to 0·2 per cent. The burette consists of narrow bore glass tubing bent to form a U tube, with an extension from one arm bent horizontally, then vertically downwards, and drawn out to a fine capillary through which the liquid is discharged. The other arm of the U tube is attached to a mouthpiece through a rubber stopper. The mouthpiece is conveniently bent into the horizontal position. For a burette to hold about 9 c.mm. the tubing is of such a bore that the height occupied by 9 c.mm. is about 10 cm. The volume is measured by means of a graduated scale divided in 200 divisions, fixed behind the arm of the burette attached to the mouthpiece. The burette does not drip, neither does air enter if the bore of the capillary is adjusted so that the force balances the difference in heights of the liquid in the burette. For a titration the tip of the capillary is placed in the liquid, and the titration liquid is gently blown out through rubber tubing attached to the mouthpiece. When the titration is at an end the rubber tube is clipped in the fingers and the tip of the burette raised above the liquid again. J. W. B.

Use of Polarographic Methods in Microanalysis. J. Heyrovsky. (*Mikrochem.*, 1933, **12**, 25–65.)—The method depends on the reproduction of current potential curves given by the intermittent passage of a current of regularly increasing potential (0 to 2 or 4 volts) through a solution of an electrolyte. The current is passed intermittently through the electrolyte by using a dropping mercury cathode. The increasing potential is obtained by using a 2 or 1 volt accumulator with the poles connected through a resistance consisting of 20 windings of resistance wire round a rotating wheel. The dropping mercury cathode is connected with a small contact which passes along the resistance wire as the wheel rotates. The curves are registered by means of a highly sensitive mirror galvanometer focused on a slowly rotating cylinder covered with light-sensitised paper, which rotates once for the 20 revolutions of the wheel resistance (Polarograph obtained from V. and J. Nejedlý, Prague XIX, Husová 76). As little as 0·1 c.c. of liquid may be used in the micro-electrolysis apparatus, or as much as 20 c.c. in the larger types. The anode potential remains constant and unpolarised during the electrolysis and may be measured against a normal calomel electrode, so that the cathode readings can be calibrated from it. The concentration of a substance and its reduction potential are read from the magnitude and position of the depression it causes in the potential curve. The relation of degree of depression to the concentration must be determined by calibration, as it depends on the rate of dropping of mercury, on temperature, and other factors. A typical reading is a 0·5 cm. depression representing a 10^{-4} N concentration, with a galvanometer sensitivity of $5 \cdot 10^{-9}$ amp. per 1 mm. scale. Concentrations of suitable substances as low as 10^{-8} or 10^{-9} N may be determined with an error of 20 per cent., and at 10^{-5} N with an error of 5 per cent. While the current is broken the substance deposited on the cathode redissolves, so that the concentration of the solution remains constant during the electrolysis. Only in irreversible reduction is this not the case, and the determination is less accurate. Many elements may be determined in the same solution, such as small amounts of copper, lead and cadmium in the presence of excess of zinc. However, traces of cadmium, zinc, iron or alkali metals cannot be determined in the presence of large amounts of heavy metals, such as copper, bismuth, thallium or lead, though sometimes the interference may be decreased by complex ion formation. As no complex salts of the alkalis are formed, a separation of sodium, potassium, rubidium and caesium is impossible, though lithium may be separated. Only certain anions are suitable for polarographic measurement; these are NO_3', BrO_3', IO_3', NO_2', SO_3'', and anions of the amphoteric and complex metal salts. Soluble organic substances (in water or methyl or ethyl alcohol) which show a change in the potential curve may also be measured polarographically. Examples of the use of the method include the determination of traces of bromates or iodates in chlorates, the detection of traces of niobium in tantalum, and of aldehydes in ether, vinegar, rectified alcohol and alcoholic beverages, the determination of hydrogen peroxide, and peroxide compounds in the presence of oxygen, the determination of barium in the presence of radium, traces of nitrites in nitrates, fumaric acid in the presence of maleic acid, traces of platinum in water, and traces of protein in solution (sensitive to 0·0001 per cent. solutions). For larger-scale work a less sensitive galvanometer and a larger electrolysis apparatus are used. J. W. B.

Use of the Micro-Dumas Method for Substances of Low Nitrogen Content. F. Vetter. (*Mikrochem.*, 1933, **12**, 102–108.)—The Pregl micro-Dumas method decreases in accuracy for substances containing less than 3 per cent. of nitrogen, and is unsuitable for substances containing less than 1 per cent., for the maximum weight of 4 mgrms., recommended by Pregl, gives a reading of little more than 0·03 c.c., which is the first marking on the nitrometer. If a larger amount of material is used, the conditions of the experiment (size of tube and rate of flow of carbon dioxide) must be altered; otherwise combustion will be incomplete. The initial weight may be increased up to 50 mgrms. by using a combustion tube, 80 cm. long and 1·2 cm. in diameter, passing through it carbon dioxide at a speed of 1 bubble per second, and increasing the time of combustion from 15 to 50 minutes. Larger initial weights are unsuitable, as the time of combustion must be still further increased and the blank errors become large and variable. By using a more accurate tapless capillary nitrometer (obtainable from P. Haack, Vienna IX, Garelligasse 4) very small volumes may be measured. The total volume which can be measured in this nitrometer is about 100 c.mm., and accurate results can be obtained with compounds containing as little as 0·01 per cent. of nitrogen, an initial weight of up to 50 mgrms. being taken. The method has been used for the determination of nitrogen in coals and oils. J. W. B.

Micro Method for Detecting and Determining Laevulose in Presence of Dextrose, Other Aldoses, or Sucrose. F. Fischl. (*Chem.-Ztg.*, 1933, **57**, 393–394.)—When sugar solutions are treated under definite conditions with a faintly alkaline copper and Rochelle salt solution containing phosphate, the reduction effected by sugars other than laevulose is negligible in amount. As little as 1 mgrm. of laevulose in presence of 49 mgrms. of dextrose is thus detectable and determinable.

The reagents used are as follows: (1) 1·5 grm. of anhydrous sodium carbonate, 5 grms. of crystallised copper sulphate, 300 grms. of Rochelle salt and 100 grms. of disodium phosphate ($+12H_2O$) are dissolved in water in a 1-litre measuring flask to form a volume of about 900 c.c. Solution is carried out as far as possible at room temperature, and is completed on a water-bath. The flask is left in the bath for an hour and, when cold, the liquid is made up to 1 litre, mixed with two teaspoonfuls of active charcoal, and filtered. It should be stored in a dark glass bottle with glass or rubber stopper, and should not be kept too long. (2) $N/100$ iodine solution; 1 c.c. corresponds with about 1 mgrm. of fructose. (3) $N/100$ thiosulphate. (4) About N hydrochloric acid (42 c.c. of the concentrated acid, d 1·19, in 500 c.c.).

The laevulose solution to be tested should be neutralised and diluted to contain about 0·5 per cent. of sugar. If it has been cleared with lead salts, the lead must be removed from the filtrate by means of sodium sulphate (not by alkali or sodium phosphate). Ten c.c. of the sugar solution and 30 c.c. of the copper solution (1) are placed in a 150-c.c. Erlenmeyer flask, which is fitted with a cork carrying an accurate thermometer and channelled at the edge to prevent development of pressure during the heating. The flask is then placed in a water-bath at 70° C. and its contents are swirled gently until they reach 65° C.; this temperature and the

swirling are maintained for exactly five minutes, after which the liquid is cooled as rapidly as possible in cold water to room temperature. The appearance of a turbidity or a precipitate of cuprous oxide shows the presence of laevulose.

For the determination, the thermometer is washed into the flask with 20 c.c. of water. About 15 c.c. of the *N* hydrochloric acid and then a few c.c. of the *N*/100 iodine solution are poured carefully down the wall of the flask, without mixing. The whole is then mixed and a further quantity of the iodine solution is added to give an excess (30 to 60 c.c., depending on the amount of cuprous oxide formed, are required in all). The flask is stoppered and the iodine allowed to act for exactly two minutes, with occasional shaking. After addition of starch solution, the liquid is titrated with the thiosulphate solution. Unless more than 0·5 c.c. of the iodine solution has been used up, the presence of laevulose cannot be assumed, since 50 mgrms. of dextrose require about 0·3 c.c. of the iodine solution.

The method allows of the determination of laevulose, not only in mixtures of sugars, but also in sweet wines, fruit juices, honey, and the like, and is suitable also for physiological chemical purposes. T. H. P.

Physical Methods, Apparatus, etc.

Action of Light on Fats. C. H. Lea. (*J. Soc. Chem. Ind.*, 1933, **52**, 146–148T.)—Light is one of the factors accelerating oxidation in fats, and direct sunlight may increase the rate in its initial stages by anything up to about 10,000 times. The effect of light is not proportional to its intensity, and once rapid oxidation has started, removal of the exciting source will not stop it. Both ultra-violet and visible light accelerate the oxidation, the former probably the more effectively. Of the visible spectrum, light in the yellow-orange region at about 6000–6500 Å is the most active, and green between 5000 and 5500 Å and the far red are the least active. Coloured wrappers used to protect foodstuffs should, therefore, have their light-transmission curves determined to ensure the cutting out of the most active wave-lengths. Curves are given demonstrating seasonal fluctuations in the ultra-violet components of sunlight through increased atmospheric absorption at low sun altitudes. D. G. H.

Reviews

GAS ANALYSIS BY MEASUREMENT OF THERMAL CONDUCTIVITY. By H. A. DAYNES, D.Sc., F.Inst.P. Pp. viii+357; 76 figures. Cambridge University Press. Price 16s. net.

Although this method of gas analysis has been in technical use for many years, and a number of instruments employing the principle have appeared on the market, its scope has not yet been fully appreciated, owing largely to the paucity of the literature on the subject. It is as fitting as it is gratifying, that the authoritative and detailed treatise for which technical chemists have been waiting, should come from England, where Professor Shakespear and Dr. Daynes himself

have done such pioneer work. Few people are as well qualified to write such a book as Dr. Daynes, whose contributions to gas analysis have not been confined to this method alone.

For the benefit of those who have not had occasion to become acquainted with the thermal conductivity method of gas analysis, the principle may be roughly outlined. In many gaseous mixtures of practical importance, the thermal conductivities of the constituent gases differ considerably, and the thermal conductivity of the mixture is a sensitive measure of its quantitative composition. A wire heated by an electric current loses heat in proportion to the thermal conductivity of the gas which surrounds it; hence, for a given current, its temperature (and consequently its electrical resistance) is a function of the composition of such gas. One of the great advantages, for technical purposes, of this method of analysis is that it lends itself to continuous-flow analyses and to automatic indicating and recording.

Among the uses of the method which are described in this book, perhaps the most important is the testing of flue-gases; in view of the great economic importance of furnace control, it is surprising that automatic flue-gas analysers are not yet a universally fitted part of boiler-house equipment. The general treatment of this subject is admirably clear and succinct. Other applications described are the testing of fuel gases, control of the gases in ammonia synthesis, the determination of carbon dioxide in fruit stores, of methane and other gases in mine-atmospheres, and of sulphur dioxide, water vapour and organic solvents in air. Another application is the analysis of the gases obtained from the fractionation of liquid air, which, since they contain both nitrogen and argon, make physical methods such as this almost essential. Among the technical uses in aeronautics are the determination of the purity of hydrogen and helium, and the testing of the permeability of balloon fabrics to these gases, for which purpose the Shakespear permeameter was of great service during the war.

The greater part of the book is taken up with technical details of the various forms in which the method can be used, and with its industrial and scientific applications. In the more general part, a particularly interesting and valuable section is that which deals with the precise quantitative relation between the thermal conductivities of mixtures and the pure constituents.

Data and statements are well documented; the references alone, many from relatively obscure and inaccessible publications, would make the book valuable. The information given in the text will, however, make reference to original publications unnecessary except to the very few. The indexing also is full and clear, the subject index occupying eighteen columns.

The book is an essential volume for all analytical, technical and engineering libraries. H. R. AMBLER

LUBRICATING AND ALLIED OILS. By ELLIOT A. EVANS. Second Edition. Pp. xiv+175. London: Chapman & Hall, Ltd. 1933. Price 9s. 6d. net.

The first edition of this book was published in 1921, the object of the author being to provide a "non-too-technical" book, to "assist chemists in compiling specifications and examining lubricating oils; also to give engineers an insight into

the application and properties of such oils and the interpretation of their specifications."

The new edition has been enlarged by some 47 pages, and a considerable part of it has been re-written. The first twelve pages are devoted to three short chapters on History of Petroleum, Oil Refining, and Occurrence of Fatty Oils. Under Oil Refining there is a brief reference to hydrogenation, but, in view of recent developments, it appears regrettable that more space has not been devoted to this important subject, and the Fatty Oils merit more attention than can be given in rather less than 2½ pages. Only three vegetable oils are said to be now used extensively in lubrication—rape, castor and coconut oils—and it is surprising to find no reference here to animal lubricating oils—lard, tallow, and neatsfoot oils—though marine animal oils have their share of the chapter. Neither in this chapter nor throughout the book is there any reference to the useful results of adding a small proportion of fatty acids to a mineral oil.

The next two-thirds of the book are concerned with the physical and chemical testing of lubricating oils; and, as the author was also a member of the Lubricants Sub-Committee of the Institution of Petroleum Technologists, engaged on the preparation of "Standard Methods of Testing Petroleum and Its Products" (two editions of which have appeared since 1921), it is only to be expected that these sections should now have been brought into line with "Standard Methods." The tests included are not confined, however, to those official in the Institution's book, among the new ones described being the Cleveland Open Cup, commonly used in the United States for determining flash-point, the Barbey ixomètre, which measures fluidity instead of viscosity, and has been largely used in France, the British Admiralty's method for determining demulsification value, and the method recently devised by the American Society for Testing Materials for determining the dilution with petrol of used oils. The author rightly points out the tendency nowadays to attach more importance to the open, rather than to the closed, flash-point, and the increasing popularity of potentiometric methods for determining the acidity of lubricating oils. It might, perhaps, have been well to include the Conradson method for determining demulsibility, as this test requires no special or complicated apparatus, and gives very useful results. Under "Determination of a Fatty Oil in a Compound Oil by Estimating the Glycerol-content" (p. 87) there is a slight slip, the amount of glycerol yielded by a fatty oil being approximately 10 (not 5) per cent.

The remainder of the book includes chapters on Decomposition of Petroleum (by heat and oxidation, with formation of carbon and other deposits), Oleography (dealing with the theory of lubrication), Selection of Lubricants, and Oils Employed. This portion of the book has been brought well up to date and very greatly improved, the chapters on Decomposition and Oils Employed being particularly useful.

Whilst, as the author says in the Preface to this edition, "since 1921 a vast amount of literature has appeared upon the subject," this book still appears to fulfil a purpose accomplished by no other one with which the reviewer is acquainted, and it should prove useful to those who require a general knowledge of lubricating oils and their examination, without going too deeply into the subject.

W. H. SIMMONS

UNTERSUCHUNGSMETHODEN FÜR ARZNEISPEZIALITÄTEN. Speciality Commission of the International League of Pharmacists, pp. 85. Fédération Internationale Pharmaceutique, Leyden.

This work represents the report of the International Speciality Commission, a body composed of eight of the leading Continental pharmacists under the chairmanship of Dr. L. van Itallie, who succeeded the late Dr. H. Thoms. The absence of any British representative on the committee illustrates the lack of interest in the subject of the sale of medical specialities in this country, where there are practically no restrictions on the import and sale of preparations of this class.

In several continental countries declaration of the composition of medicinal preparations is required before permission to import them is granted, and the analyst is required to examine samples at intervals to see if their composition tallies with the declaration. It is, therefore, desirable that the analysts on both sides should be in agreement with regard to working methods.

This report, which is written throughout in German, consists of two parts. The first, which discusses the determination of physical constants, is merely a draft which, as stated in the Preface, "appears a peculiar mixture of positive recommendations and vaguer points for discussion." The second part contains a number of recommended methods of analysis, including the determination of nitrogen, arsenic, phosphorus, and iron in organic combination. A section on the examination of tablets includes methods for the determination of organically-combined bromine and iodine, the bromometric determination of unsaturated ureides, the determination of acetylsalicylic acid, antipyrin and nitroglycerin, and the analysis of compounds of the veramon type (amidopyrin + a barbituric acid derivative). A useful table gives methods of extraction and assay suitable for a number of synthetic drugs in the form of tablets. Finally, there are given a number of methods for the examination of tablets containing alkaloids.

The book offers little assistance to the analyst in this country, who most frequently requires to identify the constituents of an unknown preparation—a purpose for which the book is not intended. But by the time (if ever) that the sale or importation of medical specialities in this country is controlled by law, it is to be expected that the work of the Commission will be complete, when it will form a useful guide to the analyst concerned.

G. MIDDLETON

VITAMINS AND OTHER DIETARY ESSENTIALS. By W. R. AYKROYD, M.D. Pp. viii+218. London: Heinemann. 1933. Price 7s. 6d. net.

The kind of work being done by men like Dr. Aykroyd should receive the most hearty support of all members of the Society of Public Analysts, for they will naturally desire to see scientific knowledge spread among the general public. The author is a popular writer in the best sense of the phrase, and combines a grasp of his subject with a fully developed sense of scientific accuracy, a combination of characteristics that is, to the highest degree, scarce in association. So well has his task been achieved that even those primarily engaged on problems of nutrition and

food chemistry may possibly learn facts from it, and so felicitous is his pen that they will quite certainly learn methods of exposition.

The few matters over which anyone could disagree with Dr. Aykroyd are either those that are entirely questions of opinion, or those upon which Dr. Aykroyd himself has admittedly expressed only tentative views. He has, for example, fallen into the common fallacy of assuming, on the basis of animal experiments alone, that carotene can replace vitamin *A* for the human subject. Very likely it can, but the case has not yet been proved. On the other hand, the statement that mammals convert carotene into vitamin *A* in the liver is an under-statement, since it has been shown that birds can do the same. Again, to say that "vegetable fats, *e.g.* margarine, are devoid of it" (vitamin *A*) is only correct if qualified by the statement that certain oils, such as soya bean, appear to contain appreciable quantities, either of vitamin *A* or of carotene, and that one oil, red palm oil, is relatively rich in carotene. Once or twice Dr. Aykroyd has used, without explanation, terms that might have warranted a parenthesis or footnote; the sudden introduction of the hyphenated "amino-nitrogen" on page 80 might to some readers be a little frightening, and is quite unnecessary. There appear to be very few misprints in the book, and none of importance.

The author, as he indicates by his title, deals with the chief dietary constituents; he also devotes considerable space to discussing the nature and incidence of the commoner deficiency diseases. In addition, he considers at some length the nature of, and the conditions making for, an ideal diet. Such a rough summary, however, cannot in any way do justice to the extent of the field covered by Dr. Aykroyd, or to the skill and charm with which he takes us over it. It can honestly be said that his book is bound to give entertainment with instruction to all intelligent readers, whatever their previous knowledge of the subject-matter.

A. L. BACHARACH

TABELLEN ZUR BERECHNUNG VON MINERAL- UND GESTEINANALYSEN. By H. VON PHILIPSBORN. Pp. xvi + 310. Akademische Verlagsgesellschaft m.b.H., Leipzig. 1933. Price 26.50RM., bound 28.00RM.

This book should save petrologists and geo-chemists much monotonous and time-taking calculation. Four series of logarithmic tables are presented in form comprising some three hundred quarto pages, and including all common, and most rare, rock-constituents.

Table I enables the molecular proportions of the constituent oxides to be read off from their percentage composition by weight, *e.g.* 6·97 per cent. MgO = 0·1729 molecular proportions. The various oxides and elements are arranged in alphabetical order. Proceeding to Table II, the percentages of the corresponding standard minerals of the norm* can be read off from the re-sorted molecular proportions—an operation which is facilitated by arranging the tables in the standard order of the norms.

A possible slight disadvantage arises from the tables having been calculated from the latest accurate atomic weights, rather than from the "rounded" molecular

* *Standard Minerals of the Norm.*—Ideal, standard minerals, potentially present in any rock, as computed from the chemical analysis of it—as distinct from "modal" minerals which actually appear in the rock.

weights used in the C.I.P.W.* tables. The differences are slight, as shown for the following olivine-nephelinite, chosen at random. Table I refers to norms calculated with rounded molecular weights, whilst Table II is calculated by means of Philipsborn's Tables.†

	I.	II.
Or	6·64	6·58
Ab	2·26	2·57
An	14·61	14·68
Ne	24·32	27·10
di	27·92	10·13
ol	10·23	10·66
mg	5·83	5·84
il	4·42	4·44
ap	1·18	1·19

Henceforward it will be necessary to state if the norm has been calculated by the Philipsborn Tables.

Table III (vol. per cent. by sp.gr.) enables the weight of a known percentage volume of a given mineral to be read off; and, in conjunction with Table IV, which gives the theoretical composition in percentages by weight of rock-forming minerals, including all mixtures of AbAn,‡ readily provides the composition of a rock or mineral aggregate, once the percentage volumes of the minerals present are known. These latter two sets of tables are especially adapted for use with the Leitz-Wetzlar integrating stage.

The preface, which includes a short set of illustrative examples of the use of the tables, is written in both English and German.

The tables have been printed by photochemical processes, and are extremely clear to read. The ordering of the constituents is logical, and devices to aid in the reverse use of the tables are provided.

JANET W. BROWN
AUSTIN EDWARDS

* C.I.P.W.—Abbreviation for "Cross, Iddings, Pierson and Washington," inventors of the Normative Classification of Rock Analyses.

† *Abbreviations.*

Or = orthoclase
Ab = albite
An = anorthite
Ne = nephaline
di = diopside
ol = olivine
mg = magnetite
il = ilmenite
ap = apatite

} Standard abbreviations of mineral names used when quoting their normative percentages.

‡ AbAn.—Abbreviation to designate the plagioclase mix-crystal felspars.

Erratum:—CATALYSIS AND ITS INDUSTRIAL APPLICATION. By E. B. MAXTED, D.Sc. The price of this book was incorrectly stated on p. 374. It is 36s., not 30s.