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Obituary.

ALFRED ASHBY.

It is with great regret that we record the death, on January 7th, of yet another of our earlier members.

Dr. Ashby was born at Staines in 1844. He studied medicine at Guy's Hospital and qualified as L.S.A. in 1869. Subsequently, he became F.R.C.S. (1871), and graduated M.B. (London) in 1872. He was elected a Fellow of the Institute of Chemistry in 1887. In 1879 he was appointed Medical Officer and Public Analyst for Grantham; in 1883 for Newark; and in 1888, Medical Officer, Public Analyst and Gas Examiner for Reading. It is not two years since he resigned his appointment as Medical Officer for Reading, while continuing to act as consultant to that Borough, but he retained his three appointments as Public Analyst until his death.

Although Dr. Ashby was a "medical" Public Analyst, he was not satisfied with acquiring merely sufficient knowledge to examine certain foods, but took an active interest in the development of this branch of his dual office.

He was a frequent contributor to the pages of our journal, his first paper on "The Estimation of Phosphoric Acid" being published in 1882 (ANALYST, **6**, 108), and his last, on "The Detection of Methylated Spirits in Tinctures, etc.," in 1895 (ANALYST, **19**, 265). He was also associated with Mr. Otto Hehner in an investigation of the so-called "previous sewage" contamination (ANALYST, 1884, **8**, 58).

Handicapped by deafness, it is remarkable that Dr. Ashby should have achieved the results he did. He was known personally to only a small proportion of the present members of the Society, for, owing to his physical defect, and, more recently, advanced age, he had not attended the meetings for many years past. But his kindly disposition was felt by everyone who met him, even casually, and his genial personality will be remembered by all his friends.

EDITOR.

The Separation of Aluminium from Beryllium. Part III.

By HUBERT T. S. BRITTON, M.Sc., A.I.C.

Ammonium Chloride Method.

The first reference to Berzelius' method which the author has found appears in H. Rose's *Handbuch der analytischen Chemie*, 1851, Vol. II., p. 61. The method is to suspend the hydroxides of aluminium and beryllium, precipitated by means of ammonium hydroxide, in a concentrated solution of ammonium chloride, and to boil until the free ammonia has been evolved, as indicated by placing a glass rod moistened with nitric acid in the issuing steam. It is stated that by so doing the beryllium hydroxide will be completely dissolved, whereas the aluminium hydroxide will remain unattacked. Weeren (*Pogg. Annalen*, 1854, **92**, 101) considered the method to be quantitative and to be the best of the methods put forward, provided that care was taken to prolong the boiling sufficiently. Joy (*Amer. J. Sci.*, 1863, [ii.], **36**, 84) agreed that correct results could be obtained by this method, although it was tedious and entailed much digestion with ammonium chloride solution of the correct concentration. The latter he did not give. Klatzo (*J. prakt. Chem.*, 1869, **106**, 227) apparently employed the method successfully in the analysis of beryl. On the other hand, Penfield and Harper (*Amer. J. Sci.*, 1886, [iii.], **32**, 110) stated that long boiling caused the liberation of acid, which dissolved some aluminium hydroxide. Hence, from the observations of previous investigators, the impression is obtained that under certain conditions a quantitative separation may be effected.

Experimental.—I.—An aqueous solution of about 400 c.c. of aluminium sulphate was made up containing about 0·1 grm. of alumina. The aluminium hydroxide was precipitated by means of a little ammonium hydroxide, after which the solution was saturated with ammonium chloride. A few drops of litmus were added, and the solution boiled until all free ammonia had been driven off. Just over an hour was required, although the solution had become acid to litmus some time before. On filtering, not a trace of aluminium hydroxide was found to have passed into solution.

II.—The previous experiment was repeated, a beryllium sulphate solution containing about 0·1 grm. of beryllia being used. After boiling for half an hour, the beryllium hydroxide had passed completely back into solution, which had become slightly acid to litmus.

III.—From each of several solutions of beryllium sulphate, each 10 c.c. in volume and containing 0·063 grm. of beryllium oxide, beryllium hydroxide was precipitated by the addition of 5 c.c. of 6 *N*-ammonium hydroxide. To each solution 100 c.c. of ammonium chloride solution were added of concentrations varying from 1 *N*- to 4·5 *N*- (*i.e.* nearly a saturated solution). In every case the beryllium hydroxide had completely dissolved after a half hour's boiling, the

last to dissolve being that to which the *N*-ammonium chloride had been added. Although the solutions were slightly acid to litmus, ammonia had not ceased to be given off.

From these experiments it appears that the hydrogen ion concentration of the hydrochloric acid liberated by hydrolysis of boiling ammonium chloride solutions is insufficient to produce the solution of aluminium hydroxide, but sufficient to cause the solution of beryllium hydroxide. This agrees qualitatively with Hildebrand's conclusions drawn from determinations of the hydrogen ion concentrations required for the precipitation of these hydroxides. (*Cf.* ANALYST, 1921, **46**, 361.) These experiments also show that, if no other difficulties occur when the two hydroxides are precipitated and subsequently treated together, ammonium chloride might be employed to effect a quantitative separation of the two hydroxides. It should be borne in mind, however, that the actual separating reagent is exceedingly dilute hydrochloric acid. In consequence of its very small concentration it becomes clear why any beryllium hydroxide which gets surrounded with aluminium hydroxide will stand a poor chance of being dissolved. The chances appear greater when the solution in which the precipitates are suspended is boiled vigorously, there being a greater tendency by the more frequent collisions for the precipitate to be more completely broken up.

Trial separations were carried out thus. Weighed quantities of the two sulphates were dissolved in about 25 c.c. of water, and from this solution the hydroxides were precipitated by the addition of a slight excess of ammonium hydroxide. To thus 200 c.c. of saturated ammonium chloride solution were added. The solution was then boiled for over two hours, the initial volume being maintained by the occasional addition of water. In each case the solution became acid to litmus, although ammonia could be detected in the issuing steam. The remaining precipitate was filtered by suction and estimated.

Results.

BeO taken. Grm.	Al_2O_3 taken. Grm.	Al_2O_3 found. Grm.	Extra = BeO undissolved. Grm.
0·0651	0·3418	0·3781	0·0363
0·1769	0·2152	0·2561	0·0409
0·2636	0·0737	0·1200	0·0463

It will be observed from these data that, although the conditions as shown by the preliminary experiments had been satisfied, in every case some beryllium hydroxide had not been dissolved. The amount which was unattacked appeared to depend upon the weight of alumina and also the weight of the beryllia. If boiling had been further continued, no doubt more, and perhaps all, of the beryllium hydroxide would have passed into solution. However, as the method stands, it is obviously unsatisfactory.

It seemed feasible that if a less voluminous precipitate of the hydroxides, one preferably composed of fine particles, could be obtained, there would be less chance of any beryllium hydroxide being completely surrounded by the aluminium

hydroxide. Consequently the amount of beryllium hydroxide which would dissolve in the ammonium chloride solution would be considerably increased. If the two hydroxides are precipitated from a large volume of solution when boiling, the precipitates are somewhat finer than those obtained from more concentrated solutions in the cold. To ascertain if such precipitates were more efficacious, the following separation was attempted. A solution of 500 c.c. of weighed quantities of the two sulphates was boiled, during which process the hydroxides were precipitated by adding a little ammonium chloride and ammonium hydroxide. Complete precipitation of the aluminium hydroxide was ensured by boiling until nearly all the ammonia had been driven off. Solid ammonium chloride sufficient to render the concentration of the mother liquor about twice normal was then added, and the solution boiled, its volume being kept constant, until ammonia could not be detected in the issuing steam. Just over two hours were required. The remaining precipitate was estimated.

Result.

BeO taken.	Al_2O_3 taken.	Al_2O_3 found.	BeO undissolved.
Grm.	Grm.	Grm.	Grm.
0·1644	0·1064	0·2536	0·1472

This treatment had had the effect opposite to the one desired, it appearing that beryllium hydroxide precipitated from a boiling solution is much less soluble in ammonium chloride solution than when it is precipitated in the cold.

In conclusion, the method is unsatisfactory, as no means has been found by which the occlusion of beryllium hydroxide by aluminium hydroxide can be eliminated.

Sodium Carbonate Fusion Method.

A method was described by Wünder and Wenger (*Zeitsch. anal. Chem.*, **1912, 51,** 470) which depends upon the fact that on fusing a mixture of aluminium and beryllium oxides with excess of sodium carbonate for two to three hours in a platinum crucible, the alumina combines to form sodium aluminate, and the beryllia is unattacked. The beryllium oxide can therefore be separated by treating the fused mass with water, the aluminate and sodium carbonate being dissolved.

The author has confirmed the truth of the principle underlying this separation in the case of fusions of sodium carbonate with the oxides separately.

Much difficulty was experienced in obtaining iron-free sodium carbonate, even the "A.R." grade was found to contain sufficient to render any results by this method valueless. Fortunately, sodium carbonate made by heating "A.R." sodium bicarbonate was found to be free from iron oxide.

From some preliminary separations in which the oxides had been taken in amounts greater than 0·2 grm., and fused with about 5 grms. of sodium carbonate for three hours over a Bunsen flame, it was found that some of the alumina had not been converted into sodium aluminate, proving that one fusion was insufficient. This was evidently found to be sometimes the case by Wünder and Wenger, for

they state that, in order to be quite sure that all alumina has been attacked, the unattacked oxides should be subjected to another fusion. Thus the time required to carry out a reliable separation is exceptionally long.

Consequently a series of separations was attempted, one fusion only being employed, in which the oxides were taken in varying proportions, and the amount of each oxide was not more than 0·15 grm.

It should also be stated that if fusion is carried out at a temperature higher than that just required for the fusion of sodium carbonate, the platinum crucible will be appreciably attacked. The following separations have been effected by single fusions of three hours of the oxides which had first been strongly heated, and then ground so as to form a fine layer on the bottom of the crucible. For each fusion about 5 grms. of sodium carbonate were employed. Heating by means of a good Bunsen burner was found to be sufficient to keep the sodium carbonate immediately above the oxides in the fused state, thus enabling interaction to take place. After extracting the sodium carbonate and the sodium aluminate with boiling water, it was found more convenient to allow the unattacked oxide to settle and then to decant as much of the clear liquid as possible. The remaining solution, when diluted, could be filtered easily and the oxide estimated. In this way the difficulty experienced in filtering sodium carbonate solutions, due to their attacking the filter paper, was eliminated. The alumina in solution was estimated as usual after acidification with hydrochloric acid and boiling.

If the amount of water used in the extraction was small, *e.g.* about 250 c.c., the solution was observed to be cloudy, and the beryllium oxide took some time to settle. When 500 c.c. or more, of water were used, the solution was clear, and the oxide settled more rapidly. As it was often more convenient to allow the solution to stand overnight, it was advisable to know the stability of sodium carbonate solutions of aluminium hydroxide. Some experiments were carried out to ascertain how the solubility of aluminium hydroxide varied in solutions of sodium carbonate of different concentrations at room temperature. These experiments showed that the amounts of aluminium hydroxide which dissolved were very nearly those required (within one per cent.) by the quantities of sodium hydroxide liberated by hydrolysis for the quantitative formation of sodium aluminate. (*Cf.* Part I., ANALYST, 1921, **46**, 363.) Hence, as diluting a sodium carbonate solution has the effect of enhancing hydrolysis, the power to dissolve aluminium hydroxide is therefore proportionately increased. Furthermore, sodium carbonate solutions, made at room temperature, of aluminium hydroxide did not show any sign of decomposition after standing for two days. On the other hand, solutions which were saturated when boiling with aluminium hydroxide deposited alumina on cooling and standing. This, no doubt, explains why aqueous extracts in which too little water had been used were cloudy. As a general rule, to prevent such a separation, at least 500 c.c. of water should be used to extract the mass from a fusion of about 5 grms. of sodium carbonate with not more than 0.15 grm. of alumina.

Each of the following sets of data were obtained by means of a single fusion.

BeO taken. Grm.	BeO found. Grm.	Al_2O_3 taken. Grm.	Al_2O_3 found. Grm.
0·1416	0·1414	0·0527	0·0525
0·1451	0·1449	0·1163	0·1166
0·1430	0·1424	0·1559	0·1563
0·0178	0·0176	0·1783	0·1788

From these results, it will be observed that the method is capable of yielding satisfactory separations by the use of a single fusion, when sufficiently small amounts of the two earths are present and care has been taken to keep the temperature of fusion as low as possible. In order to make sure that a complete separation has been obtained, a second fusion is advisable, as recommended by Wünder and Wenger. In attempted separations in which fusion had been effected by too drastic heating, especially when a blow-pipe had been employed, the unattacked oxide was somewhat brown, due to contamination with platinum. Contamination was also noticed when large amounts of alumina were present, evidently due to fused sodium aluminate behaving like fused sodium hydroxide towards platinum. In each of the above cases the separated beryllium oxide was white, contamination, if any, being insufficient to affect either its colour or weight.

Sodium Thiosulphate Method.

This method is based on Chancel's method (*Comptes rend.*, 1858, **46,** 987) for the estimation of alumina, in which an excess of sodium thiosulphate is added to a neutralised solution of alumina in either hydrochloric or sulphuric acid, and boiled until the evolution of sulphur dioxide has ceased. By so doing, the thiosulphuric acid which is liberated decomposes immediately into sulphur and sulphurous acid. On boiling, the concentration of the sulphurous acid becomes so small, that its hydrogen ion concentration is inadequate to keep the aluminium hydroxide in solution. If a beryllium salt were present, this concentration would, however, be just enough to prevent the precipitation of beryllium hydroxide, and thus a complete separation theoretically appears to be just possible. Such a case would be, in effect, a modification of the method suggested by Berthier (*Ann. Chim. Phys.*, 1843, [iii.], **7,** 74), who proposed the use of sulphurous acid. Joy (*Amer. J. Sci.*, 1863, [ii.], **36,** 83) was the first to apply this principle, but without success. Zimmermann (*Zeitsch. anal. Chem.*, 1888, **27,** 61) investigated this method, and stated that he could only get satisfactory results when the amounts of the oxides were about equal. Fifteen to twenty hours' boiling was sometimes necessary. In 1906 a paper appeared (*Ber.*, **39,** 3366), in which Glassmann claimed to have found a new method, which in reality was the one in question. It is interesting to note that in each of the five sets of data which he gave, the two oxides were taken in nearly equal quantities.

Preliminary Experiments.—(1) One c.c. of 0·5 *N*-aluminium sulphate (=0·0085 grm. Al_2O_3) had to be added at room temperature to 25 c.c. of saturated sodium

thiosulphate solution before any aluminium hydroxide was precipitated. On boiling for a short time all the aluminium hydroxide separated out.

(2) When 0·5 *N*-aluminium sulphate solution was added to 25 c.c. of boiling saturated thiosulphate solution, aluminium hydroxide was precipitated on the addition of one drop. A few c.c. were added, and the solution allowed to stand for several days. Not a trace of alumina passed into solution.

(3) These experiments were repeated with 0·5 *N*-beryllium sulphate solution; no beryllium hydroxide was precipitated.

These experiments show that the method may possibly yield quantitative results. In each case, however, much sulphur was precipitated, which had a great tendency to remain in colloidal solution, but, on continued boiling, became granular.

Separations were attempted by the use of saturated solutions of thiosulphate, the liquid being boiled until all sulphur dioxide had been expelled. The amounts of alumina found were too high, due to some beryllia having been precipitated with the alumina. Once again, it was decided to see if the desired separation could be obtained by employing larger volumes of solution. Weighed amounts of the two sulphates were dissolved in water to which about 600 c.c. of approximately *N*-sodium thiosulphate solution were added, and then boiled vigorously, the volume being maintained by the addition of water until no more sulphur dioxide could be detected in the issuing steam. Five hours were required in each case. The aluminium hydroxide, together with much sulphur, was filtered off by suction, washed with a hot solution of sodium thiosulphate and ignited. After the adsorbed sodium salts had been extracted from the ash with boiling water containing hydrochloric acid, and the solution rendered ammoniacal, the alumina was estimated.

BeO taken. Grm.	Al_2O_3 taken. Grm.	Al_2O_3 found. Grm.	Extra. Grm.
0·0564	0·1214	0·1504	0·0290
0·0859	0·0444	0·0720	0·0276

Here again, much beryllium hydroxide has been rendered insoluble under the peculiar influence of aluminium hydroxide. Thus the method appears unsatisfactory.

Ether-Hydrochloric Method.

Iron may be separated from aluminium by taking advantage of the insolubility at ordinary temperatures of crystalline aluminium chloride ($AlCl_3.6H_2O$) in a mixture of equal volumes of concentrated hydrochloric acid and ether saturated with hydrogen chloride, ferric chloride being soluble. Working under the guidance of Gooch, Havens (*Amer. J. Sci.*, 1897, **4**, [iv.], 111) found that beryllium chloride when taken in quantities of about 0·1 grm. in about 20 c.c. of ether-hydrochloric acid mixture was also soluble. On this principle he devised the following method:—Dissolve the hydroxides of aluminium and beryllium, corresponding to about 0·1 grm. or less of each of the

respective oxides, in the minimum volume of concentrated hydrochloric acid and evaporate to about 10 c.c. Cool, add an equal volume of ether, which will be miscible or nearly so, then carefully saturate with hydrochloric acid gas, care being taken to keep the vessel cooled. This will cause the complete precipitation of aluminium chloride. Filter through a Gooch crucible and wash the precipitate with a solution containing ether and concentrated hydrochloric acid in equal volumes and saturated with hydrogen chloride. The aluminium chloride can be quantitatively converted into aluminium oxide by covering it with a layer of mercuric oxide, drying the mixture at 150° C. for half an hour, and then carefully igniting it. The beryllium oxide in the filtrate may be estimated either by (*a*) evaporating the liquid in a platinum vessel until nearly all the hydrogen chloride has been driven off, and then adding a few drops of concentrated nitric acid and igniting; or (*b*) treating the solution with ammonium hydroxide and igniting the precipitate. By this method he obtained quantitative separations.

Pollok (*Trans. Roy. Soc. Dublin*, 1904, [ii.], **8,** 138) found that most of the aluminium chloride was precipitated simply by saturating a concentrated hydrochloric acid solution with hydrogen chloride. Havens' method has since been found by Parsons and Barnes (*J. Amer. Chem. Soc.*, 1906, **28,** 1589), and also by Noyes, Bray and Spear (*ibid.*, 1908, **30,** 481), to give quantitative results. The latter workers state that they obtained quantitative separations, even when large amounts of alumina were present, provided that a sufficient proportion of ether had been employed, and that the solution had been thoroughly saturated with hydrochloric acid gas.

Experimental.—As the author's pure salts were the sulphates, it was first resolved to take weighed quantities, dissolve them in concentrated hydrochloric acid and carry out the separation as described, thereby omitting the conversion into chlorides. The figure obtained for alumina was too high and the one for beryllia correspondingly low. This led to the investigation of the effect of adding ether to hydrochloric acid solutions of weighed amounts of beryllium sulphate. It was found that beryllium sulphate crystallised out in quantities depending on its concentration. Hence, in the following separations, the sulphates were converted into hydroxides, and then dissolved in concentrated hydrochloric acid. The separations were carried out in accordance with Havens' instructions. The total volume of the mixture, through which the hydrogen chloride was passed, was about 20 to 30 c.c.; cooling the mixture while saturating with gas below room temperature was found unnecessary. It was more convenient to estimate the beryllium oxide by precipitation.

The following method of saturating the mixture with hydrogen chloride was adopted:—A bell jar was placed over mercury. On the mercury inside the jar a crystallising dish was floated, on which was placed a glass cylinder of about 50 c.c. capacity, to contain the ether-hydrochloric acid solution. Through the stopper of the bell jar passed two tubes, one through which the hydrochloric acid was led into the solution, and the other serving merely as an exit for gas. The end of the tube, which dipped just below the surface of the solution, was opened

out in the form of an elongated funnel. Dry hydrogen chloride was generated by dropping concentrated sulphuric acid on to common salt and passed through concentrated sulphuric acid.

If the solution was homogeneous, the time required for saturation was about an hour. In some cases where the ether and acid solution were not completely miscible, there seemed to be some delay in the crystallisation of the aluminium chloride, which, however, could be hastened by occasional stirring. The following results were obtained.

Al_2O_3 taken. Grm.	Al_2O_3 found. Grm.	BeO taken. Grm.	BeO found. Grm.
0·1224	0·1220	0·0699	0·0696
0·0858	0·0864	0·1081	0·1078
0·0148	0·0150	0·0991	0·0987

The method is therefore satisfactory. The separation is easy to carry out, and has none of the difficulties usually encountered in beryllium-aluminium separations.

Other Methods.

No other methods have been investigated. Of the remaining methods, it is probable that only two are quantitative. The methods referred to are those of (*a*) Kling and Gelin, which involves the distillation of the basic acetate of beryllium under reduced pressure; and (*b*) Renz, depending upon the fact that ethylamine precipitates beryllium hydroxide alone from either a nitric or hydrochloric acid solution of the two earths. The former requires considerable manipulation and time, whereas the latter involves the use of an expensive reagent. Moreover, in Renz's method the beryllia is precipitated as the gelatinous hyhroxide, which will adsorb much alumina from the mother-liquor unless it is very dilute. Hence, as Renz suggested, a "large excess" of ethylamine is necessary.

In order to complete these studies, brief outlines of these two methods and of the remaining methods which have been proposed will now be given.

Basic Acetate Method.—Urbain and Lacombe (*Comptes rend.*, 1901, **133**, 874) isolated a basic beryllium acetate of the formula, $Be_4O(CH_3COO)_6$, by the action of glacial acetic acid on beryllium hydroxide. This work was continued by Lacombe (*Comptes rend.*, 1902, **134**, 772), who was successful in preparing a series of well-defined basic salts, in which there may be formate, propionate, isobutyrate, butyrate, or isovalerianate, instead of the acetate radicle. Among many other properties investigated, he found that the basic acetate, when heated under 19 mm. pressure, sublimed. Haber and Van Oordt (*Zeitsch. anorg. Chem.*, 1903, **40**, 465) took advantage of the solubility of the basic acetate in chloroform. Hence they converted the hydroxides of aluminium and beryllium by means of glacial acetic acid and extracted the basic acetate of beryllium with chloroform. Kling and Gelin (*Bull. Soc. Chim.*, 1914, **15**, 205) pointed out that Haber and van Orrdt's method usually gave an error of about 10 per cent. They also described a method which they found was capable of giving results within two per cent.

Apparently the method depends upon the observation of Lacombe that the basic acetate of beryllium sublimes under 19 mm. pressure. Briefly the method is as follows:—Evaporate a solution of the two hydroxides in nitric acid on a water-bath. Treat the residue with glacial acetic acid and expel excess of acetic acid on an air-bath. Distil the residue of the acetates under 19 mm. pressure in a current of acetic acid vapour, first at 160–170° C. for four hours, and finally at 250° C. for one hour. The beryllium basic acetate will be deposited on the cool part of the condenser. Dissolve the deposit in nitric acid, evaporate the solution, and ignite the residue. For alumina, ignite the residue which has not distilled over. Kling and Gelin say, however, that a second treatment may be necessary to remove the last traces of beryllia.

ETHYLAMINE METHOD.—The method described by Renz (*Ber.*, 1903, **36**, 275) is to dissolve the hydroxides in dilute nitric acid, and to concentrate and treat the solution with a large excess of ethylamine. The mixture is shaken to effect the precipitation of beryllium hydroxide, which is afterwards filtered and estimated. The alumina in the filtrate is also estimated.

AMMONIUM PHOSPHATE METHOD.—Rössler (*Zeitsch. anal. Chem.*, 1878, **17**, 148) found that if an excess of ammonium phosphate were added to a solution of beryllia in hydrochloric acid which had been neutralised with ammonium hydroxide, a gelatinous precipitate first appeared, which became crystalline on boiling. According to Rössler, this precipitate on ignition yields beryllium pyrophosphate, and the beryllia may be estimated as such. Austin (*Amer. J. Sci.*, 1899, [iv.], **8**, 206) showed that the quantities of so-called beryllium pyrophosphate obtained were greater than those required by theory. If a little alumina happens to be present it may be kept in solution by carrying out the precipitation in presence of citric acid. Should the amount of alumina be large, the greater portion must first be removed. To do this, Rössler suggested evaporating to dryness a solution of the two oxides in hydrochloric acid, mixing the residue with an excess of potassium sulphate equal to twelve times the amount of alumina present, and placing it in a tube with sufficient water to dissolve the potassium sulphate when heated after the tube had been sealed. After being heated for 15 minutes the tube is cooled and opened, and its contents extracted with water. The residue is basic aluminium sulphate. The solution is then ready for treatment with ammonium phosphate as described. It is extremely improbable that this process is satisfactory.

GENERAL NOTE ON THE REMAINING METHODS.—The following is a brief account of the remaining methods which have been proposed. There appears no doubt that any one of them is sufficiently quantitative for analytical determinations. Debray's method (*Ann. chim. phys.*, 1855, [iii], **44**, 1), which depends upon the fact that beryllium sulphate, if rendered basic, may still be soluble, whereas aluminium sulphate on becoming basic is precipitated, presents the difficulty that if a basic beryllium sulphate solution is rendered too basic, some beryllia will be precipitated as well. The process was carried out by digesting a solution of the sulphates with zinc. This was dissolved in the sulphuric acid which had been

in combination with the alumina and the beryllia and precipitated the former. According to Scheffer (*ibid.*, 1859, [iii.], **56**, 112) the treatment with zinc required several days, after which the zinc in solution had to be separated from the beryllium. An electrolytic method was described by Classen (*Ber.*, 1881, **14**, 2782), in which the separating agent is, in reality, ammonium carbonate. If a solution of alumina and beryllia in ammonium oxalate be electrolysed, care being taken to have a suitable current, etc., the ammonium oxalate is reduced to ammonium carbonate, and consequently precipitates the alumina. The data given by Classen show that the method, at best, is only approximate. In all probability, it has the same defects as the simple ammonium carbonate method. (Cf. Part II., ANALYST, 1921, **46**, 437.) A method was proposed by Wolcott Gibbs (*Amer. J. Sci.*, 1864, [ii.], **37**, 356) by which alumina could be approximately separated from beryllia, and, moreover, could be employed for the preparation of pure beryllium salts. In order to obtain beryllium oxide free from alumina, he fused the oxides with twice their weight of potassium hydrogen fluoride, and extracted the fused mass with boiling water containing a little hydrofluoric acid. Under these conditions, the nearly insoluble salt, $AlF_3,3KF$, remained on the filter, and the beryllia was dissolved, and from supersaturated solutions it could be crystallised as the double fluoride, $BeF_2.2KF$. Gibbs also stated that it was probable that the addition of sodium fluoride to a solution of beryllia and alumina as fluorides would precipitate all the alumina as cryolite. This method, besides being troublesome, is not quite quantitative, on account of the slight solubility of the double fluoride of sodium and aluminium. Nevertheless, it is important, as it is the basis of the recently described process of obtaining beryllia from beryl by fusion at 850° C. with sodium silicofluoride. (Copaux, *Comptes rend.*, 1919, **168**, 610.) Pollok (*Trans. Roy. Soc. Dublin*, 1904, [ii.], **8**, 139) carried out a separation from a dilute solution by precipitating the alumina as the double fluoride of aluminium and potassium, using hydrofluoric acid and a concentrated solution of potassium hydrogen fluoride. If the dilution is insufficient, the beryllia will also be precipitated as the double fluoride. The slight solubility of the double fluoride of aluminium and potassium prevents this method from being completely quantitative. These fluoride methods have, of course, the serious drawback that only platinum vessels, or glass vessels which have been carefully coated with wax, can be used. In concluding, mention should be made of the suggestion of Wyrouboff (*Bull. Soc. Chim.*, 1902, [iii.], **27**, 73), that the double oxalate of beryllium and potassium is so slightly soluble that it is possible that the beryllia could be separated as this salt. Wyrouboff did not actually work out this method, but suggested that the precipitation might be made from a concentrated solution in hydrochloric acid by the addition of potassium hydrogen oxalate, in presence of either sodium acetate or sodium hydroxide. The author has prepared the double oxalate, $K_2C_2O_4.BeC_2O_4$ (C_2O_4 found = 67·0%; calc'd = 66·85%). The salt was not well defined, and its crystallisation was sluggish. A separation involving this salt would therefore probably be unsatisfactory.

GENERAL CONCLUSIONS ON THE METHODS.

SUMMARY.—(1) The ammonium chloride method is unsatisfactory; no method having been found to prevent the occlusion of beryllium hydroxide by aluminium hydroxide.

(2) The method of Wünder and Wenger is satisfactory.

(3) Sodium thiosulphate does not give quantitative separations, owing to adsorption of beryllia by the aluminium hydroxide which is precipitated.

(4) Havens' method is quantitative.

(5) The remaining methods have been discussed.

Of the many methods which have been investigated, only four have been found to be capable of giving quantitative results, viz.: (1) Decomposition by boiling of sodium hydroxide solutions (Part I., ANALYST, 1921, **46**, 361); (2) Parsons and Barnes' method (Part II., ANALYST, 1921, **46**, 442); (3) Wünder and Wenger's method; and (4) Havens' method. In the opinion of the author, methods (1) and (4) are the most satisfactory. They are both fairly quick, and, if the necessary precautions are taken, will give accurate results. In order to get reliable results by the method of Wünder and Wenger, two fusions are necessary, which makes the time required for an analysis somewhat long. Parsons and Barnes' method is the most difficult, as it involves the elimination of adsorption effects.

The author desires to record his appreciation of the interest shown by Professor Allmand in these investigations, and to thank the Chemical Society for a grant from its Research Fund, which was obtained by Professor Allmand for work on beryllium salts.

UNIVERSITY OF LONDON,
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Notes on the Analysis and Use of Red Squill in Rat Poisons.

BY C. L. CLAREMONT, B.Sc., F.I.C.

(*Read at the Meeting, December* 7, 1921.)

RED squill has recently come into prominence as a rat poison, and the question of its recognition, estimation and toxic value becomes of some importance.

This plant is similar to, and, in fact, is usually considered to be identical with the officinal plant, which is described as consisting of yellowish white or pinkish scales. It is described more or less indiscriminately under the names *Urginea scilla* or *Scilla maritima*.

It belongs to the genus *Urginea*, the fact being that it was classified as *Scilla* by Linnæus, and subsequently re-classified by Steinheil as *Urginea*, and according to the Vienna convention in use among botanists is correctly described as *Urginea maritima*. It is a large bulbous plant somewhat like an onion, covered with reddish scales, the interior varying from light yellow to deep purple. The plant bears a flowering stem and leaves at different periods of the year.

The use of squill both as a medicine and as a raticide dates from very early times, but nevertheless it has not attracted much attention from the chemical point of view. Abderhalden describes a sugar-like substance, sinistrin or scillin, and a glucoside scillain which is stated to have toxic properties. Merck states that there are three glucosides, scillipicrin, scillitoxin and scillin.

The more recent work on this subject is contained in a paper by Kopaczewski (*Comptes rend.*, 1914), who describes a glucoside, scillitin, and a paper by Buschmann (*Archiv. der Pharm.*, 1919). This latter authority gives a good resumé of the earlier work, and describes a substance of glucosidal character which he calls xantho-scillid, and states that Merck's scillin is impure xantho-scillid. He also appears to have obtained choline and various phytosterols. There is, however, no information as to the physiological action or toxicity of these substances, and in no case is it stated whether the plant used was red or white squill. In a paper by F. W. Smith (ANALYST, 1921, **46**, 178) reference is made to the difficulty of distinguishing red from white squill.

Red squill is used as a rat poison in various forms—the raw bulb chopped up fine may be used, or it may be pulped and the juice expressed, in both cases, of course, being mixed with suitable ingredients to form an attractive bait; the bulb can also be dried and powdered, and this powder used instead. Another method is to prepare an aqueous extract from the chopped bulbs by maceration, with or without the addition of a trace of hydrochloric acid.

In the case of solid rat poisons, containing either bulb or powder, it is possible to obtain results indicative of its presence and rough estimations of the amount. The raw bulb contains about 80 per cent. of moisture, so that the dry powder represents about a fifth of the bulb contents.

TABLE I. RED SQUILL POWDERS. PERCENTAGE COMPOSITION.

		Calculated on Dry Material.									
No.	Moisture	Ash	SiO_2	CaO	Fibre	Extract to water	Reducing Sugar	Total Sugar after inversion	Non-reducing Sugar	Toxicity Mgrms. per kilo. body weight	Remarks
1	4·00	3·50	0·5	1·4	5·2	72·91	10·31	24·58	14·27	600	Made in laboratory, own bulbs.
2	6·20	2·65	0·07	—	4·3	81·55	4·63	51·54	46·91	450	Made in laboratory from sample submitted.
3	4·05	4·7	0·05	—	5·8	72·91	8·12	64·58	56·46	850	,, ,, ,, ,,
4	6·19	6·75	0·59	2·72	7·9	59·16	9·22	50·66	41·44	600*	Prepared from own bulbs.
5	4·2	3·40	0·04	1·12	6·5	67·85	6·99	54·91	47·92	1400	Made in laboratory, Algerian bulbs.
6	3·8	4·7	0·44	1·56	—	80·04	6·59	59·78	53·19	600	Made in laboratory, own bulbs.
7	3·8	4·18	0·14	1·48	3·6	77·96	6·79	60·90	54·11	Not toxic at 1800	Selected very purple bulb.
8	4·55	3·92	0·16	1·34	—	74·91	3·32	73·73	70·41	900	Selected colourless bulb.
9	1·2	4·76	0·22	1·74	—	73·38	6·14	69·39	63·25	555	Toxicity somewhat variable.
10	6·15	5·60	0·5	1·9	9·6	55·40	7·99	31·16	23·17	360	Purchased.
11	8·4	10·40	0·8	2·1	8·2	56·77	9·50	40·39	30·89	800	,,
12	8·0	10·70	0·7	1·9	7·9	55·98	10·45	46·59	36·14	550	,,
13	3·5	12·80	1·16	5·66	21·9	17·62	4·28	6·94	2·66	260	Outer scales only, own bulbs
14	1·7	2·70	0·10	0·46	5·93	73·24	5·26	48·58	43·32	870	Growing centre of bulb, own bulbs.
15	2·4	7·66	0·54	2·28	8·9	50·72	5·14	30·79	25·65	420	Bases only, own bulbs.

* After re-heating to 60° C. for 2 hours.

Table I. gives the results of analysis and the toxicity of a number of red squill powders, all of which were genuine and some of which were prepared in the laboratory from the actual bulbs, the outer dry scales and bulb bases being usually previously removed.

The bulbs do not grind well, unless the moisture content is reduced to at most 5 per cent. A drying temperature of about 60° C. appears to produce a satisfactory powder, but the influence of the temperature of drying is curious, as in one case (No. 4, Table I.) I had a powder which was of low toxicity, but on heating to about 70° or 80° C. its toxic power greatly increased, and I afterwards found that the powder had been dried in a vacuum apparatus at a temperature of about 40° C. Temperatures somewhat over 100° C. do not appear to be detrimental, as in practice our rat poisons, both with raw bulb and powder, are in the form of biscuits which are baked at about 350° F.

It will be seen that the results obtained are very variable. The chief points of interest are the aqueous extract and the reducing and hydrolysable sugar substances; in order to have comparative results these three figures have been calculated on the basis of dry substance, and the sugar in all cases calculated as dextrose. The toxicity is expressed as mgrms. of powder per kilo. body weight; most of the experiments were done on tame rats, wild rats being used when available for confirmatory purposes; if anything, the latter appear rather more susceptible to this poison than tame ones. I should explain that the absolute minimum toxic amount was not, in every case, worked down to, since for practical purposes a toxicity of under 1,000 is satisfactory.

There does not appear to be any obvious relationship between toxicity and the sugar content.

Another point of importance, which is not recorded in the table, is the colour of the extract; this is nearly always distinctly reddish, and is increased on the addition of traces of hydrochloric acid, as is readily noted on adding acid for the inversion.

If, therefore, in a rat poison supposed to contain squill, a considerable aqueous extract is found giving comparable sugar figures, I think it is reasonable to presume its presence. This can sometimes be confirmed by microscopic examination, although the structures of squill unfortunately do not present any specific features, with the exception of a very large number of raphides. In the "teased" bulb the main features are large polygonal parenchyma cells with a few spiral vessels and small thicker walled cortical cells of a yellowish red colour; in a very deeply coloured bulb the red colouring matter is diffused throughout the tissue; the raphides occur in bundles of acicular crystals and also as large isolated prisms. The powders present similar appearances, but the crystals are often much broken and harder to find.

White squill, as used for the B.P. preparations, is similar, and, save for the absence of colour, is indistinguishable from red squill.

Table II. gives some figures obtained with samples of white squill powder; these are similar to those obtained from red squill, though there is a tendency for the reducing sugar to be lower. In the case of these the extract was

invariably colourless, and in no case was a toxic result obtained, though No. 3 was stated to have been used successfully as a rat poison.

TABLE II. WHITE SQUILL POWDERS. PERCENTAGE COMPOSITION.

						Calculated on Dry Material.					
No.	Moisture	Ash	SiO_2	CaO	Fibre	Extract to water	Reducing Sugar	Total Sugar after inversion	Non-reducing Sugar	Toxicity Mgrms. per Kilo. body weight	Remarks
1	2·95	7·25	0·95	1·90	—	68·78	—	—	—	Not tested.	Made in laboratory from own bulbs.
2	5·0	4·39	0·45	0·92	—	65·26	4·63	24·00	19·37	1500 neg.	Submitted as red squill.
3	6·6	10·8	2·08	3·78	8·3	79·23	4·60	26·34	21·74	2300 neg. 3400 ,, 9000 ,,	Purchased; stated to have been used successfully as a rat poison.
4	7·0	4·0	0·20	1·28	2·6	88·71	3·31	86·65	83·34	5000 ,,	Purchased.
5	6·45	3·5	0·20	1·4	2·7	80·17	1·45	57·07	55·62	3300 ,,	,,

In Table III. figures given by three samples of a South African squill, *Urginea Burkei*, are recorded. The non-reducing sugars are distinctly lower, and the extract is highly coloured, being a deep cherry red. These bulbs contain very much more mucilage than ordinary red squill, and the extract is very difficult to filter. Even if toxic they would be useless for the preparation of extract by simple maceration, as an extract of the strength used is a jelly-like mass and almost unfilterable.

TABLE III. *URGINEA BURKEI* POWDERS. PERCENTAGE COMPOSITION.

						Calculated on Dry Material.					
No.	Moisture	Ash	SiO_2	CaO	Fibre	Extract to water	Reducing Sugar	Total Sugar after inverson	Non-reducing Sugar	Toxicity Mgrms. per Kilo. body weight	Remarks
1	15·60	3·28	0·26	0·62	—	65·17	9·95	27·49	17·54	2000 pos.	Dried scales. *Note*: Eight months later the toxicity was *nil*.
2	11·45	4·02	0·20	—	—	62·11	6·85	19·25	12·40	1400 neg.	Dried scales.
3	1·7	5·24	0·34	1·2	—	34·08	6·51	11·49	4·98	3000 neg.	Bulbs supplied by S.A. Govt. Botan. Dept.

Of these three samples examined only one appeared to be toxic, and the toxicity of that was low. I understand, however, that the plant is of the nature of a pest in South Africa, as stock eat it and die, although in that case it is apparently the leaves which are taken.

TABLE IV. COMPOUND SQUILL POWDERS. PERCENTAGE COMPOSITION.

						Calculated on Dry Material.					
No.	Moisture	Ash	SiO_2	CaO	Fibre	Extract to Water	Reducing Sugar	Total Sugar after inversion	Non-reducing Sugar	Toxicity Mgrms. per Kilo. body weight	Remarks
1	8·45	5·07	0·24	0·22	—	21·84	2·35	6·06	3·71	4000 neg. 8000 ,,	Contained about 25% of powder No. 2, Table II., and wheat starch as bulk.
2	10·15	4·30	0·96	—	7·8	32·27	7·23	15·14	7·91	3300 pos.	Genuine red squill 20%, cereal meal 80%.
3	9·38	11·88	2·88	—	3·8	20·5	3·9	9·0	5·1	3500 ,,	French sample contd. 3·25 $BaCO_3$, wheat present.
4	9·5	9·52	1·58	—	3·8	33·0	6·9	14·96	8·06	1800 ,,	French sample contd. 3·63 $BaCO_3$, wheat present.

In the above table the analyses of four samples of compound squill powders are given.

In the case of No. 1, which was not toxic, the extract was quite colourless, and I inferred that it was prepared from white squill. This I afterwards found was correct. Both the French samples contained a little barium carbonate, and I estimated the squill powder to be approximately 20% and 30% respectively. As the excipient in all cases was wheat flour, the major part of the extract and sugar is due to the squill, and a rough estimate of the amount present can be deduced.

So far as my experience goes up to the present, the excipients used are not such as will interfere with the detection of squill based on the above data.

TABLE V. SQUILL PASTE POISONS. PERCENTAGE COMPOSITION.

No.	Moisture	Ash	Ether Extract	Aqueous Extract	Reducing Sugar	Sugar after inversion	Non-reducing Sugar	Fibre	Meal by difference	Toxicity	Remarks
1	25·9	1·0	2·50	43·66	25·0	40·0	15·0	0·5	26·9	Toxic.	Made with juice from pulped bulb.
2	3·05	12·43	55·0	9·51	1·2	7·7	6·5	—		Toxic.	French, made with powder contained 9·68% $BaCO_3$; squill, and undetermined vegetable matter.
3	6·35	1·88	30·33	20·05	2·24	15·20	12·96	—	50·0	Toxic.	Squill powder No. 9, Table I., 20%, meal 50%, fat 30%.

In Table V. the results obtained with three samples of squill pastes are recorded. In the case of the last sample, which was made in my own laboratory, the figures agree well with those given by the powder used in the manufacture; the French sample probably contained about 10 per cent. squill powder; in the case of No. 1 the interpretation is difficult, as expressed juice was used, but the excessive reducing sugar suggests that glucose syrup may have been used as the binding material, since no fat sufficient for the purpose was present.

In the case of squill extracts the results are more difficult to deal with, as they vary with the method of preparation, and sometimes substances, such as glycerin, glucose syrup, meat broth and flavouring oils, etc., are added with a view of either improving their keeping qualities or enhancing their attractiveness. Frequently, however, these extracts as supplied to the public require diluting with milk, meat-broth, gruel or bread and milk before being used, the aqueous extract itself being unpalatable to the rodents.

Table VI. gives some analyses of various extracts of red squill.

Numbers 1–6 were prepared in my laboratory, and do not exhibit much variation. The process is a simple cold maceration for 24 hours, using one part of bulb and two parts of water by weight with a trace of hydrochloric acid (1/500 part); all were toxic.

Numbers 7–20 are various samples from outside sources and prepared by a similar method, except that in some cases hot maceration was used. The results are similar, except for a tendency for the reducing sugar to be higher; the toxicity

TABLE VI. RED SQUILL EXTRACTS. PERCENTAGE COMPOSITION.

No.	Sp. Gr. 15/15	Total Solids	Reducing Sugar	Total Sugar after inversion	No.	Sp. Gr. 15/15	Total Solids	Reducing Sugar	Total Sugar after inversion
1	1·020	4·04	1·58	4·96	16	1·02	5·2	3·86	4·00
2	1·017	4·28	0·96	2·58	17	1·02	5·1	4·25	4·31
3	1·019	4·50	1·06	3·65	18	1·02	5·9	5·10	5·15
4	1·023	6·0	0·68	4·36	19	1·045	11·0	5·9	6·8
5	1·014	3·44	0·50	3·28	20	1·05	12·48	5·68	7·9
6	1·017	4·32	0·54	3·99	21	1·124	63·0	2·14	13·78
7	1·023	5·94	0·31	5·01	22	1·07	23·5	0·5	2·3
8	1·05	10·74	5·38	10·06	23	1·054	13·46	7·8	13·6
9	1·02	4·62	3·03	3·51	24	1·04	9·30	2·75	3·7
10	1·02	4·56	3·03	3·38	25	1·03	7·80	2·30	3·9
11	1·02	4·88	2·95	3·25	26	1·03	6·94	2·02	3·5
12	1·02	5·92	3·17	4·82	27	1·02	6·60	2·02	3·5
13	1·02	5·8	2·40	3·71	28	1·03	8·22	2·27	3·63
14	1·01	5·7	4·10	4·30	29	1·04	8·90	1·84	1·97
15	1·02	5·0	3·34	4·13					

varied. Samples 21 and 22 both contained about 10 per cent. of glycerin, while No. 23 contained some other saccharine matter, possibly malt extract; it is at any rate ready for use, merely requiring the addition of bread. It was quite toxic, and I believe has been very successful in practice.

Numbers 25–29 are from a French source. I do not know the process used, but the solid matter is high in relation to the sugars.

I might add that all my own samples were a bright cherry red in colour, and the others varied from reddish to reddish brown, many were very turbid, and in one or two cases, known to be old samples, were almost black; the latter were not necessarily non-toxic.

I have only examined one alcoholic extract, and that was a thick sticky substance and was not toxic. I have reason to know it was made from white B.P. powder.

With regard to the active principle present in red squill the information at present available is conflicting. No reference is made in any report to the colour, but I presume the samples were the red variety, as I believe this is generally used on the continent as the official drug. It appears to be fairly stable, as I have had extracts known to be six months old retain their toxicity,—and the powder keeps reasonably well if kept in air-tight containers.

It is possible that the bulb varies in toxicity according to the stage of growth, but this point has not yet been investigated. One series of experiments referred to in Table I. indicates that the scales and bulb bases are at least as toxic as the mass of the bulb, and undoubtedly individual bulbs vary, and apparently the most coloured bulbs are not necessarily the most toxic.

A few experiments have been made to see what effect varying conditions have on the extract. In each case 125 grms. of chopped bulb were taken, treated with about 400 c.c. of water, strained, pressed and made up to 500 c.c.

These results are recorded in Table VII.

TABLE VII. SQUILL EXTRACTS. PERCENTAGE COMPOSITION.

No.	Method of preparation	Sp. Gr.	Total Solids	Reducing Sugar	Sugar after inversion	Toxicity c.c. per Kilo. body weight
1	Cold, 24 hours. HCl.	1·016	3·94	0·31	2·37	19
2	Cold, 24 hours. No HCl.	1·009	3·24	0·34	3·04	19
3	Cold, 48 hours. HCl.	1·02	4·42	0·41	3·72	18
4	Boiled 4 hours, left 20 hours. No HCl.	1·013	4·50	0·33	4·49	15

The results explain themselves; there was apparently some slight advantage in boiling the extract, but this, on a manufacturing scale, was probably not comparable with the additional cost of plant and steam; the trace of acid present does not appear appreciably to increase the reducing sugar.

A few experiments have also been made to test the effect of alcoholic extraction, as the glucosides supposed to be present are stated to be soluble in alcohol.

TABLE VIII. PERCENTAGE COMPOSITION.

	Alcoholic Extracts.					Powders after Extraction.					
							Calculated on Dry Powder.				
No.	Total Solids	Reducing Sugar	Total Sugar after inversion	Toxicity quantity 3000 mg/Kilo.	Toxicity quantity 6000 mg/Kilo.	Moisture	Extract to Water	Reducing Sugar	Total Sugar after inversion	Non-reducing Sugar	Toxicity Mgrms. per Kilo. body weight
1	7·0	2·76	3·0	+	+	14·85	56·0	4·4	37·0	32·6	1250
2	7·8	3·9	6·8	±	+	13·55	55·5	7·4	36·1	28·7	1350
3	3·35	1·36	1·76	−	±	15·97	63·0	4·5	17·8	13·3	2000 negative

REMARKS.—No. 1 Corresponds to No. 10, Table I.
No. 2 Corresponds to No. 1, Table I.
No. 3 Corresponds to No. 1, Table III.

Note.—+, toxic; ±, symptoms produced but complete recovery; −, no result.

Three powders were extracted three times with 90 per cent. alcohol in the cold, and the alcoholic extract evaporated down, taken up in water, and given to rats. The extracted powder was then dried and tested on rats. The toxicity was undoubtedly reduced, but the extraction of toxic principle was by no means complete, and it does not seem that alcoholic extraction offers any particular advantage for practical purposes.

To summarise the general results, it appears that, though the presence of squill can be recognised, and its quantity roughly estimated, there is not any certain method of distinguishing red squill from white, and, in any case, the toxicity cannot be inferred from the analytical results and can only be determined by actual experiments on rats.

In conclusion, I have to acknowledge the help of my assistant, Mr. A. W. Ling, and also the courtesy of the Ministry of Agriculture and Fisheries in allowing me to make this use of results which have been obtained in the Ministry's laboratory.

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DISCUSSION.

Mr. W. PARTRIDGE drew attention to the fact that in the case of two of the samples of white squill analysed the ash exceeded the 5 per cent. allowed by the British Pharmacopoeia.

Mr. CLAREMONT, in his reply, stated that the squill used for rat poisoning was red squill, white squill being that used medicinally; that large animals, so far as was known, were not readily killed by it, but in the case of the rat it was most effective. With regard to the recorded eruption on the skin of those engaged in gathering the bulbs, he could confirm this, and always took the precaution of wearing thick gloves when handling the material.

Notes.

The Editor desires 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.

ACTION OF GLASS BOTTLES ON SOFT WATER.

Owing to a number of samples of water being kept some time before analysis, suspicions were raised that the bottles had altered the alkalinity of the water. The bottles in question were new green glass corbyn quarts. A number were filled with tap water and the total alkalinity was determined at various periods, by boiling half a litre with methyl red and titrating with 0·1 *N* HCl. The contents of many bottles showed no change in alkalinity, but the results obtained with others were striking.

Two were filled with water the alkalinity of which was equal to 1·8 parts of calcium carbonate per 100,000, and five days later the alkalinity had risen to 2·8 and 3·0 respectively. Another bottle was filled with water, the alkalinity of which was 1·95. Two months later the alkalinity was 1·6, and after another two months 1·3.

Two stoppered Winchester quarts were filled with water on December 2nd, and the alkalinity of the water determined after keeping for various periods :—

Days	0	75	200	293	383
I. Alkalinity	1·9	2·7	2·85	3·2	3·2
II. ,,	1·9	1·7	1·8	1·9	1·9

After standing in these green glass bottles some of the waters became more alkaline, some became less alkaline, and others, after losing alkalinity, regained it. (*Cf.* Mitchell, ANALYST, 1921, **46**, 133.)

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DILUTION OF ACIDS TO A DESIRED STRENGTH.

In the December issue of THE ANALYST (p. 488) Mr. A. E. Johnson calculates the amount of water to be added to a strong nitric acid solution in order to reduce

it to a desired strength. He finds that the quantity of water which should be added to one litre of nitric acid sp. gr. 1·42 (69·8 per cent. HNO_3), so that the resulting solution shall have sp. gr. 1·20 (32·36 per cent. HNO_3), is 1552 c.c. Mr. Johnson himself suggests that, owing to possible contraction on mixing, this figure may not be the volume actually required.

It should be observed, however, that whilst the volume of a mixture is not necessarily the sum of the volumes of the constituents, its *weight* is strictly equal to the sum of the weights of the constituents. On this latter basis it is possible, without using other data than those employed by Mr. Johnson, to calculate the *actual* amount of water to be added in the special case considered.

Thus, one litre of the strong nitric acid solution weighs $1000 \times 1{\cdot}42 = 1420$ grms., and contains

(*a*) $1420 \times \frac{69{\cdot}8}{100} = 991$ grms. HNO_3,

(*b*) $1420 \times \frac{30{\cdot}2}{100} = 429$ grms. H_2O.

After dilution the nitric acid forms only 32·36 per cent. of the solution, and hence the total weight of water in the diluted solution is $991 \times \frac{67{\cdot}64}{32{\cdot}36} = 2072$ grms. Of this quantity, however, 429 grms. were already present in the one litre of the strong solution; hence the correct amount of water to add is 1643 grms., or (say) 1645 c.c. This is nearly 100 c.c. greater than the figure given by Mr. Johnson, and it is clearly therefore of little value to use a purely volume basis for the calculation in such a case.

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Notes from the Reports of Public Analysts.

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

REPORT OF THE KENT COUNTY ANALYST FOR THE QUARTER ENDED SEPTEMBER 30, 1921.

The total number of food and drug samples examined was 664, of which 21 were found to be adulterated.

MILK.—The milk samples, formally taken, were 229, and of these 10 were adulterated. The abnormally dry weather and absence of early summer rain affected the milk throughout July, whereas in normal years the effect is not produced until August or September.

BORIC ACID IN BUTTER AND MARGARINE.—Boric acid was present in 52·8 per cent. of the 78 samples of butter examined, the smallest and largest amounts being 0·10 and 0·34 per cent., and the average 0·23 per cent. All but 4 of the 37 margarines examined contained boric acid, the amounts varying from 0·12 to 0·34 per cent., and averaging 0·21 per cent.

CREAM AND PRESERVED CREAM.—One of the five samples of unpreserved cream contained only 16·7 per cent. of fat, whilst another contained 60·9 per cent. Preserved cream must contain 35 per cent. of fat, but it is strange that no standard for the unpreserved product has been fixed.

F. W. F. ARNAUD.

REPORT OF THE KENT COUNTY ANALYST UNDER THE FERTILISERS AND FEEDING STUFFS ACT, FOR THE QUARTER ENDED SEPTEMBER 30, 1921.

During the quarter 154 samples of fertilisers and 12 of feeding stuffs were examined, and 28 of the former and two of the latter were unsatisfactory.

Of 62 shoddies examined 17 were deficient in ammonia, whilst two contained 50 per cent. of water.

A poultry manure composed of dried hen manure and litter contained two per cent. of ammonia, 2·8 per cent. of phosphates and nearly one per cent. of potash. A sample of clean feathers contained 15·8 per cent. of ammonia, and many samples had been mixed with dirt, and this fertilising material should be purchased with a guarantee.

POND MUDS.—A sample, presumably sun-dried, contained 25 per cent. of water, but in two other cases the water amounted to 60 per cent. The organic matter varied only from about 12 to 14 per cent., but the calcium carbonate ranged from 0·6 to 14·0 per cent. The muds also contained about 0·25 per cent., each of ammonia and phosphates.

NAURU ISLAND PHOSPHATE.—This is usually sold mixed with basic slag and is recommended by the Ministry of Agriculture. A sample contained 52 per cent. of total phosphates and 18·2 per cent. of citric-soluble phosphate. As the Ministry has every confidence that this rock phosphate will act as well as basic slag, particularly on old grass land, it is somewhat strange that it should be thought necessary to mix it with basic slag containing a much smaller proportion of phosphate, and thereby increasing the cost of carriage.

FEEDING STUFFS.—Two samples which were alleged to be poisoning cattle contained 0·8 and 7·0 per cent. of castor meal respectively. Even castor meal made from beans from which the oil has been removed at a high temperature must be regarded as suspicious.

F. W. F. ARNAUD.

MINISTRY OF HEALTH. SALE OF FOOD AND DRUGS ACTS.

EXTRACTS FROM THE ANNUAL REPORT FOR 1920–21, AND ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR 1920.*

APPOINTMENT OF ANALYSTS.—During the year the Department approved 51 appointments in England.

PERCENTAGE OF ADULTERATION.—The total number of samples purchased for analysis under the Acts in 1920 was 111,797, of which 7903 were reported not to be genuine. In 1919 the number of samples was 101,140, of which 8313 were reported as not genuine. The proportion of samples reported against shows a decrease, from 8·2 per cent. in 1919 to 7·1 per cent. in 1920.

MILK.—Of the 62,463 samples submitted for analysis, 5797 were reported as adulterated or not up to standard—a proportion of 9·3 per cent., as compared with 11·1 per cent. in 1919. In the Metropolis the proportion of adulterated milk samples was 6·7 (760 out of 13,184), as compared with 7·7 per cent. in 1919, and 8·9 per cent. in 1913. In the 38 largest provincial towns the proportion was 9·0 per cent., and in the remainder of the country 10·8 per cent. A considerable number of samples contained colouring matter, usually annatto.

* Published by H.M. Stationery Office, Kingsway, London, W.C.2. Price 1s. 6d. net.

BUTTER.—The number of samples examined was **7346**, of which **266** (3·62 per cent.) were not genuine. One sample, purchased in Anglesey, was rancid, and contained 11·7 per cent. of salt.

CHEESE.—Only 20 of 1019 samples were reported as adulterated. Opinions have been received from Public Analysts in favour of establishing a standard for cheese. A sample, sold as "cheese," examined by the Public Analyst for West Hartlepool had been made from skimmed milk; it contained 52 per cent. of water, and only 7·27 per cent. of fat.

COFFEE.—Thirty-nine of **2554** samples examined were adulterated. Apart from two samples containing small amounts of Epsom salts and cocoa (presumably through accidental contamination) the adulterant was chicory.

VINEGAR.—The number of samples examined was **2345**, of which **190** (8·1 per cent.) were reported as not genuine.

SELF-RAISING FLOUR AND BAKING POWDER.—Ten of 1095 samples of self-raising flour, and 29 of **1147** samples of baking powder were reported as not genuine. A few contained a slight excess of calcium sulphate or insignificant traces of arsenic, but the more usual complaint was insufficiency of available carbon dioxide. The difficulties of dealing with such cases are discussed by the Public Analyst for Oldham, who points out that investigation into the methods of packing, conditions under which the material is kept, etc., is advisable before framing even a commercial definition, and that at this stage it is hardly justifiable to return samples as adulterated when fraudulent intent on the part of the manufacturer, by substitution, or in other ways, cannot be maintained.

EGG POWDERS, SUBSTITUTES, ETC.—During the year **551** samples of egg preparations were analysed, and eight reported as not genuine. Complaints are still being received as to misleading advertisements of such articles, and attention is directed to the remarks of the Public Analyst for Birmingham on the subject. (*Cf.* ANALYST, 1921, **46**, 451.)

FRUIT CORDIALS.—Various fruit beverages, such as lemon squash or lime juice cordial have been found to consist of solutions of phosphoric acid, with the addition of sugar and flavouring and colouring substances. A sample of lemon squash submitted to the Public Analyst for Surrey contained 13·1 grains of salicylic acid per pint, and 1·20 per cent. of phosphoric acid. The case was dismissed on the production of a warranty, but the vendor was convicted under the Merchandise Marks Act and fined £20, with £10 10s. costs.

DRUGS.—Of **5353** samples examined **453** (8·5 per cent.) were reported to be not genuine.

BORAX.—The number of samples analysed was **182**, of which **56** were reported as not genuine. In most cases the drug contained small quantities of arsenic. Two samples submitted to the Public Analyst for Liverpool had been sold respectively as "refined" and "purified" borax; they were found to contain 50 parts per million of arsenic. In the former case the dealer was cautioned and withdrew the article from sale, and the vendor of the latter sample was fined.

CREAM OF TARTAR.—Of **425** samples examined **32** were reported as not genuine. A few contained traces of lead or arsenic, and others (sold as substitutes) contained excessive proportions of calcium sulphate. Not infrequently substitutes composed of a mixture of an acid phosphate with a diluent such as maize starch have been sold. An instance of the kind occurred in Lancashire, where a dealer, who was asked for cream of tartar, supplied the inspector with a mixture of acid phosphate of sodium and 12 per cent. of maize starch. A fine of £5 was imposed with £4 4s. costs.

STATUTORY RULES AND ORDERS, 1921, No. 1883.

FOOD CONTROL.

Order dated 14th December, 1921, made by the Board of Trade under the Ministry of Food (Continuance) Act, 1920 (10 & 11 Geo. 5, c. 47), and the Ministry of Food (Cessation) Order, 1921, amending the Sale of Food Order, 1921. (*Cf.* ANALYST, 1921, **46**, 426.)

In exercise of the powers conferred upon them by the Ministry of Food (Continuance) Act, 1920, and the Ministry of Food (Cessation) Order, 1921, and of all other powers enabling them in that behalf, the Board of Trade hereby order that the Sale of Food Order, 1921 (hereinafter called the Principal Order), shall be amended as follows :—

1. The following shall be substituted for Part I. of the Principal Order:—
"PART I.—BREAD.—1. (*a*) A person shall not sell or offer for sale any bread otherwise than by weight, except in the case of a sale or offer for sale for consumption on the premises of the seller. (*b*) A person shall not sell or offer or expose or carry for sale or deliver under a contract for sale any loaf of bread, unless its weight be 1 lb. or an even number of lbs. (*c*) The preceding provisions of this Clause shall not apply to fancy bread or rolls. 2. Every person selling, offering, exposing or carrying for sale, or delivering any bread under a contract of sale shall, if so requested by an Inspector of Weights and Measures or by any person duly authorised in that behalf by a Local Authority, weigh the bread in the presence of such Inspector or person, or permit such Inspector or person to weigh the bread."
2. The provisions of Part III. of the Principal Order shall not apply to lard.
3. Part IV. and Part V. of the Principal Order are hereby revoked, but without prejudice to any proceedings in respect of any contravention thereof.
4. This Order shall come into operation on the 2nd January, 1922.

By Order of the Board of Trade,

FRANK. H. COLLER,

14th December, 1921. *Secretary to the Food Department.*

BRITISH ENGINEERING STANDARDS ASSOCIATION.

STANDARD SPECIFICATION FOR CREOSOTE FOR WOOD PRESERVATION.

A COMMITTEE of the Association, under the chairmanship of Mr. W. W. Grierson (engineer-in-chief G.W. Railway) has investigated the question of creosote for the preservation of timber, in co-operation with the War Office, Air Ministry, Government Laboratory, National Physical Laboratory, General Post Office, Institute of Chemistry, Association of British Chemical Manufacturers, Royal Aeronautical Society, and several railway companies. As the result of the report the Association has published the following specifications:

GENERAL SPECIFICATION.—The material shall consist essentially of a distillate of coal tar, and shall be free from any admixture of petroleum or similar oils. The sp. gr. shall be not less than 1·015, and not more than 1·07 at 38° C. (100° F.) when compared with water at the same temperature. The material shall become completely liquid on being slowly warmed to 38° C. (100° F.) with stirring, and on cooling down shall remain completely liquid after standing for two hours at 32° C. (90° F.). The amount of water in the creosote shall not exceed 3 per cent.

When 100 c.c., measured at 38° C. (100° F.), of the dry creosote are distilled from a 250 c.c. distillation flask at such a rate that the distillation is complete in about twenty minutes, there shall distil at 760 mm. pressure: Up to 205° C. (401° F.), not more than 7 c.c.; up to 230° C. (446° F.), not more than 40 c.c.; up to 315° C. (599° F.), not more than 78 c.c., the volumes of all fractions being measured

at 38° C. (100° F.). The residue above 315° C. (599° F.) shall be soft and not sticky, and its weight shall be not less than 22 grammes.

The amount of tar acids shall be not less than 5 per cent. and not more than 16 per cent. by volume. The amount of matter insoluble in benzol (benzene) shall not exceed 0·4 per cent. by weight.

ALTERNATIVE FOR SCOTCH CREOSOTE.—Scotch creosote shall conform to the above specification, with the following exceptions: The sp. gr. shall be not less than 1 at 38° C. (100° F.). In the case of the blast-furnace oil the sp. gr. may be lower, but shall not be less than 0·940 at 38° C. (100° F.). The distillate at 315° C. (599° F.) shall be not more than 85 c.c., and the residue not less than 15 grammes. There shall be no upper limit to the amount of tar acids.

DETERMINATION OF SPECIFIC GRAVITY.—Care shall be taken to ensure that the creosote is completely liquified and homogeneous before the sample is taken. In the event of the temperature at which the determination is made not being exactly 38° C. (100° F.), the observed specific gravity (d) at the temperature $t°$ shall be converted to "corrected" specific gravity D by means of the formula: $D = d + 0{\cdot}00075\ (t - 38)$ if t be in degrees centigrade, or $D = d + 0{\cdot}00042\ (t - 100)$ if t be in degrees Fahrenheit.

ESTIMATION OF WATER CONTENT.—The material shall be made completely liquid and homogeneous by warming to 38° C. (100° F.). 100 c.c. of the liquid measured at 38° C. (100° F.) shall be mixed with 50 c.c. of xylol, previously saturated with water, and the mixture distilled from a distillation flask at a rate of about 3 c.c. per minute, 50 c.c. of distillate shall be collected in a cylinder of suitable size, graduated in 1/5 c.c., and the volume of water determined at room temperature. The condenser used in this test shall be either a straight vertical condenser, or of such construction that it will readily drain completely.

DISTILLATION.—The creosote shall be dried over calcium chloride, plaster of Paris, or other suitable material, and 100 c.c. of the dried creosote, measured at 38° C. (100° F.), placed in a tared standard 350 c.c. Wurtz distillation flask, the neck of which is approximately 12 cm. long, with outlet tube emerging approximately half-way up the neck. The flask shall be furnished with a standardised thermometer, the top of the bulb of which is just below the outlet tube. The distillation shall be carried out over a free flame. When a temperature of 315° C. (599° F.) has been reached, the distillation shall be stopped, the flask and contents allowed to cool and then reweighed.

The number of degrees C. (dt) to be added to the observed thermometer reading $t°$ C. shall be calculated from the following formula: $dt = 0{\cdot}000143\ (t - t')\ N$, where N is the number of degree divisions of thread exposed above the cork, and t' the air temperature half-way up the exposed thread. When Fahrenheit thermometers are used, the formula shall be $dt = 0{\cdot}0000794\ (t - t')\ N$.

For every 25 mm. above or below 760 mm., 0·8 gramme (0·6 gramme in the case of Scotch oils) shall be subtracted from or added to the observed weight of residue in the flask.

ESTIMATION OF THE TAR ACIDS.—The tar acids shall be determined by complete extraction of the total distillate below 315° C. (599° F.) with caustic soda solution of specific gravity 1·18. The tar acids shall be separated from the soda solution by neutralising with sulphuric acid (specific gravity 1·35 at 15° C. (59° F.) —i.e. one volume of 1·84 acid mixed with two volumes of water) and their volume determined.

The specification can be obtained from the Secretary of the British Engineering Standards Association, 28, Victoria Street, London, S.W.1, price 1s. 2d. post free.

BRITISH CHEMICAL STANDARD STEEL "A2."

(ANALYTICALLY STANDARDISED SAMPLE.)

There is now ready for issue a new steel which is of special value both as a dead mild analytical standard very low in impurities and also as a "pure iron" sample for standardising bi-chromate and other volumetric solutions.

The standard figures are as follows:—CARBON STEEL, "A2":—Carbon (combined), 0·039; silicon, 0·036; sulphur, 0·020; phosphorus, 0·008; manganese, 0·043; arsenic, 0·031; nickel, 0·06; chromium, 0·013; copper, 0·065; oxygen, 0·04; and iron (by difference), 99·64 per cent.

The standard turnings may be obtained in 500, 100 or 50 grm. bottles either direct from Organising Headquarters, 3, Wilson Street, Middlesbrough; or through any of the leading laboratory furnishers at a price just sufficient to cover the cost. A certificate giving the names of the Analysts co-operating, the types of methods used, and a detailed list of the results, will be supplied with each bottle.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Alkaline Hydrolysis of Casein. M. A. Griggs. (*J. Ind. Eng. Chem.*, 1921, **13**, 1027–1028.)—The maximum yield of amino nitrogen (60 per cent. of the total nitrogen) is obtained when casein is heated under pressure at 150° C. for five hours with 10 per cent. sodium hydroxide solution. W .P. S.

Detection of foreign Starch in Meal. K. Amberger. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 181–182.)—Wheat, rye, barley and oat starches are readily saccharified by diastase at a suitable temperature, whereas maize, potato and bean starches remain unaffected, and may be detected microscopically among the fragments of tissue in a flour; the small rice starch granules may also be revealed in this way. The best temperature for the action of the diastase is 58–59° C., and 60° C. must not be surpassed. The procedure is as follows: The sifted flour (0·5 grm.) is mixed intimately with 0·3 grm. of diastase and 10 c.c. of water in a dish, the mixture being introduced into a 100 c.c. Erlenmeyer flask, into which also the residue is washed after being triturated with water; about 50 c.c. of the latter are used. The flask is now heated, with frequent shaking, in a water-bath so that the temperature of its contents is 58–59° C. After being left for an hour in the bath, the flask is allowed to cool, and the contents brought gradually into a centrifuge tube, the clear liquid being poured away after each period of centrifuging; before the final centrifuging the residue is mixed thoroughly with the liquid. The ultimate residue consists of two layers, which may both contain foreign starches, and is conveniently sampled at different depths by means of a small pipette with a moderately wide opening. The samples are examined with a magnification of about 218, but, for recognising rice starch, higher magnification (560) is required. By the above procedure as little as 4 to 5 per cent. of maize starch is detectable with certainty. T. H. P.

Detection and Estimation of Diluents in Flour and Bread. E. Vogt. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 145–173.)—Methods have been investigated for the detection and estimation in bread and bread flour of barley flour, maize flour, prepared oat flour, wheat offals, potato starch, and potato flour in its various forms. For the microscopic detection of these diluents use is made of the shape and size of the starch granules and natural admixtures, either in their original condition or as altered by the baking process; their recognition is facilitated by differential staining by means of a dilute solution of Congo-red in Indian ink. Steamed potatoes are difficult to detect microscopically owing to the profound conversion of their cell-contents into an amorphous mass soluble in water. Estimation of the diluents on the basis of microscopic counting and measurement is impracticable. Chemically the diluents may be detected by determining the "true alkalinity" of the ash of the flour or bread prepared in presence of a known volume of approximately 0·1 *N* sodium carbonate solution. This true alkalinity, which represents the total alkalinity of the ash towards methyl orange less the alkalinity of the phosphates present—determined by titration with alkali hydroxide solution—is expressed as the number of c.c. of *N* alkali per 100 grms. of dry matter. Its average value lies between −5 and −15 for wheaten flours, and increases in absolute value with the degree of extraction of the wheat; for barley, oat and maize flours the average value is −20, for wheat offals −31, for potato starch −5, and for potato flocks and rolled potato flour, +20 to +25. With mixtures, the alkalinity of the ash agrees with the value calculated from those of the constituents. In many cases, qualitative microscopic investigation, in conjunction with a determination of the alkalinity of the ash, permits of approximate estimation of the component flours employed in making a particular bread. T. H. P.

Estimation of Starch in Sausage. J. Grossfeld. *Zeitsch. Unters. Nahr. Genussm.*, 1921, **42**, 29–31.)—Twenty-five grms. of the finely minced sausage are digested on the water-bath with 50 c.c. of 8 per cent. alcoholic potassium hydroxide solution for several hours, until all meat and fat are dissolved. The contents of the flask are then filtered and washed with alcohol until the filtrate is colourless. After the crude starch has been allowed to drain well, it is transferred, by the aid of a glass rod and 25 per cent. hydrochloric acid, to a 100 c.c. flask, and made up to the mark with the 25 per cent. hydrochloric acid, and a little kieselguhr added. When the starch has dissolved, the solution is passed through a dry filter and polarised. In a 200 mm. tube each angular degree is equivalent to 0·99 per cent. of starch. H. E. C.

Modified Babcock Method for Determining Fat in Butter. N. W. Hepburn. (*Cornell Univ. Agric. Station*, Memoir **37**, 669–690.)—When the ordinary 18 grm. Babcock cream bottle is used for the estimation of fat in butter a maximum quantity of 9 grms. can be used, and the resulting experimental error is too large. A special type of bottle has been devised for use with the ordinary centrifuge which takes the Babcock bottle. Two sizes suitable are (1) the

9-inch, 9-grm. 90-per cent. bottle; height 223·5 mm., length of graduated neck 139 mm., and diameter of neck 9·07 mm. (2) the 6-inch, 6-grm., 90-per cent. bottle; height 165 mm., length of neck 93·5 mm., diameter of neck 9·04 mm. To carry out the test, 9 grms. or 6 grms. are weighed into the 9-inch or 6-inch bottle, 9 c.c. (or 6 c.c.) of lukewarm water are added, then 17·6 c.c. (or 12 c.c.) of sulphuric acid are run in, in small portions at a time, with thorough mixing. Water is now added to fill the bottle to the base of the neck, and, after centrifuging for five minutes, more water is added to bring the fat into the graduated part of the neck. After a further four minutes' centrifuging the bottle is warmed in water at 125° to 130° F., and the percentage of fat read off. Glymol may with advantage be added to remove the meniscus. H. E. C.

Glycerides of Goose-fat. C. Amberger and K. Bromig. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 193–218.)—A specimen of fresh goose fat gave the following values:—M. pt., 29°–31° C.; acid value, 0·62; saponif. value, 192·6; Reichert-Meissl value, 0·4; and iodine value, 72·77. It was fractionated by the usual methods and found to consist mainly of tri-olein, with small amounts of stearodipalmitin (in the form of two isomerides), palmitodiolein, and oleodipalmitin. The last-mentioned mixed glyceride has only been found in fresh goose-fat.

The Villavecchia Reaction for the Detection of Sesame Oil in Olive Oil. J. Prax. (*Ann. Falsif.*, 1921, **14**, 270). Olive oils from certain sources, particularly Tunisian olive oils, yield a red coloration with Villavecchia's reagent, the test thus giving a false indication of the presence of sesame oil. If, however, these olive oils are shaken with their own volume of 90 per cent. alcohol containing 10 per cent. of ammonia, and the mixture is then heated on a water-bath to expel alcohol and ammonia, the red coloration does not develop when the Villavecchia test is applied, unless, of course, the oil is actually adulterated with sesame oil. W. P. S.

Estimation of Sugar by Titration with Alkali Hydroxide of the Cuprous Oxide obtained from Fehling Solution. A. Hanak. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 248–250.)—The material containing the sugar is freed from all disturbing admixtures, clarified, inverted and diluted until the content of invert sugar does not exceed 0·5 per cent. Twenty-five c.c. of the solution are treated with 50 c.c. of Fehling solution in the usual way, and the precipitated cuprous oxide collected on an ashless filter and washed with hot water, any adhering precipitate being left in the precipitating vessel. The filter and precipitate are restored to this vessel and moistened with sufficient *aqua regia* for complete solution of the cuprous oxide, this being effected by heating the vessel for a few seconds on a water bath. The copper solution thus obtained is filtered quantitatively, the filtrate diluted with 250–300 c.c. of distilled water free from carbonic acid, and the cold liquid rendered deep pink with methyl orange, nearly neutralised with concentrated alkali hydroxide solution, and brought with 0·5 *N* alkali

hydroxide to a faint greenish-yellow, which represents the neutral point in presence of copper; the exact attainment of this point is of the utmost importance. After subsequent addition of phenolphthalein, standard alkali solution is run in until the liquid assumes a red colour, the solution being heated and the titration continued until, after three minutes' boiling, the red colour is still perceptible in the supernatant liquid, 1 c.c. of 0·5 *N* potassium hydroxide solution corresponds with 0·0159 grm. of copper. From the amount of copper thus determined the corresponding quantity of sugar is ascertained with the help of the usual tables.

T. H. P.

Researches on the Formation of Osazones. H. van Laer and R. Lombaers. (*Bull. Soc. Chim. Belg.*, 1921, **30**, 296–301.)—By mixing 10 c.c. of a hot five per cent. sugar solution with an equal volume of a hot freshly-prepared aqueous solution of 10 per cent. of phenylhydrazine and 10 per cent. of glacial acetic acid, filtering the liquid at intervals of 15 minutes, and washing the precipitate with water and 20 c.c. of methyl alcohol and finally drying and weighing it, it was found that the formation of the osazone of laevulose proceeded three times as rapidly as that of dextrosazone. This result is attributed to the oxidation of the primary alcohol group taking place in one-third of the time required for the oxidation of the secondary alcohol group. Observation of the rotatory power at brief intervals of similar solutions, mixed when cold, showed that with both laevulose and dextrose the rotation diminished within one minute to a small minus value, and afterwards slowly approached zero, thus indicating that the formation of the hydrazones is practically instantaneous. Application of the usual equation to the results obtained shows the formation of osazones from hydrazines to be trimolecular reactions.

T. J. W.

A Simple Test for Technical Invert Sugar in Honey with Resorcinol or β-Naphthol. F. M. Litterscheid. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 88–90.)—A modification of Fiehe's and Bruhn's tests (*Cf.* ANALYST, 1908, **33**, 397): about five grms. of honey or syrup are macerated for a short time with two successive 5 c.c. portions of ether, which should preferably be dry, and the mixed ether extracts poured into two test tubes, one containing about 10 mgrms. of resorcinol, and the other a similar quantity of β-naphthol. Into the first tube is run one c.c. of fuming hydrochloric acid, and into the other one c.c. of 80–90 per cent. sulphuric acid, the tubes being then corked and set aside for about 15 minutes. A positive reaction in the case of the resorcinol test is indicated by a red ring. With the β-naphthol test a dark cherry-red or violet-red ring is formed, with a deep blue ring underneath, and in the negative case a deep yellowish green colour appears.

H. E. C.

The Bee's Body as a Carrier of Formic Acid. T. Merl. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 250–251.)—The statement often made that honey is flavoured and preserved by means of formic acid derived from the body of the bee is at variance with the facts, no trace of this acid having been obtained from 500 honey bees.

T. H. P.

Estimation of Acetone in Potable Spirits by means of Hydroxylamine Hydrochloride. G. Reif. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 80–87.)—Many processes for the estimation of acetone in spirits are reviewed, and a modification of Meyer's method (*Zeitsch. Physiol. Chem.*, 1919, **104**, 220) is recommended. The method depends on the formation of acetoxime by acetone and hydroxylamine, and subsequent titration of the product with standard alkali. The presence of acetone is first established by the nitroprusside test, then 100 c.c. of the sample are acidified with 10 c.c. of *N* sulphuric acid and distilled into a stoppered receiver cooled in ice. To this distillate are added 15 c.c. of 0·5 *N* sodium hydroxide and 10 c.c. of 30 per cent, hydrogen peroxide, and the mixture gently warmed on the water bath under a reflux condenser to decompose aldehydes. The mixture is now distilled again into an iced receiver, about 5 c.c. being collected. Two 0·5 grm. quantities of hydroxylamine hydrochloride are dissolved in 30 c.c. of water and neutralised with 0·1 *N* alkali, methyl orange being used as indicator. One portion serves as a colour standard, and to the other is added a measured volume of the distillate; after standing for about an hour it is again titrated with 0·1 *N* sodium hydroxide to the same colour as the standard—the end point should not be judged until the mixture has stood for about 15 minutes. Each 1 c.c. of 0·1 *N* alkali is equivalent to 0·0058 grm. of acetone, and the percentage by volume is easily calculated. H. E. C.

Replacement of Morphine in the Detection of Methyl Alcohol in Potable Spirit. B. Pfyl, G. Reif and A. Hanner. *Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 218–225.)—The passage (in Germany) of the Opium Act of December, 1920, having rendered it difficult to obtain morphine for use in chemical laboratories, the authors have investigated other possible reagents for the detection of methyl alcohol in potable spirit. The results obtained show that the morphine may be replaced by guaiacol, apomorphine, or gallic acid, the reactions with which are more sensitive and rapid than with morphine and are, furthermore, free from certain undesirable secondary reactions. The use, for the detection of traces of methyl alcohol, of processes requiring oxidation of this alcohol to formaldehyde by means of permanganate is open to the objection that higher alcohols, methyl ethers, and other methyl derivatives may give rise to small quantities of formaldehyde. Ten c.c. of the spirit are distilled from a flask, preferably of only 25 c.c. capacity, through a tube 70 cm. long, bent twice at right angles (25+20 +25 cm.), the middle portion of the tube falling somewhat sharply towards the efflux, and the lower end of the part passing through the cork being flush with the bottom of the cork. The distillation is carried out slowly with the help of a small luminous flame, so that the descending part of the tube is not heated. This part of the tube is immersed as far as possible into the measuring glass in which the 1 c.c. of distillate is collected, the glass being surrounded with ice-water. Thorough cooling with ice-water is necessary also during the oxidation with permanganate, 1 grm. of the latter being finely ground and added in four or five portions to the distillate mixed with 4 c.c. of 20 per cent. sulphuric acid solution. The entire

oxidation occupies at least 15 minutes, the strongly cooled mixture being filtered through a small dry filter, and the pale pink filtrate left at the ordinary temperature until decolorised. A tenth of a c.c. of this solution, well cooled, is added slowly in drops to 0·5 c.c. of a cold, fresh (at most three days old) solution of 0·02 grm. of guaiacol in 10 c.c. of pure concentrated sulphuric acid, contained in a watch glass on a white surface. In presence of formaldehyde the liquid assumes immediately a moderately stable red coloration, corresponding in intensity with the amount of the aldehyde; in absence of the latter, a pale yellow coloration at most is obtained.

The reaction is carried out similarly with apomorphine or gallic acid; the former must be freshly dissolved in the sulphuric acid, whilst the acid solution of the latter may be kept for 2–3 days. These compounds give respectively deep grey-violet and intense yellowish green colorations with formaldehyde, in absence of which only faint colorations are obtained. With these two compounds the reaction is rendered more definite by the gradual formation of a precipitate in the form of a ring, if 0·5 c.c. of water is introduced in drops on to the middle of the liquid in the watch glass and the mixture then left undisturbed. T. H. P.

Occurrence of a Magnesium Salt in the Clove, and its Detection. W. Plahl. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 246–248.)—Magnesium occurs in all parts of the clove with the exception of the anthers, where the indications are uncertain, and may be detected as follows: After the cloves have been left in a moist chamber for two to three days and thus rendered flexible, sections of the different organs are cut and are soaked for 5–10 minutes in 96 per cent. alcohol, and then for about five minutes in 1 per cent. potassium hydroxide solution, at the ordinary temperature. The liquid is shaken from the sections, and the latter washed with distilled water until colouring matter is no longer given up, mounted in water and examined under the microscope. The presence of magnesium in the tissues is shown by brown patches; each of these stretches over several cells, and each of the latter contains a brown body. If a mineral acid is added, part of the cell content dissolves, the residue consisting of a finely granular, grey, brown or greenish-brown substance. The magnesium salt also becomes illuminated in the dark field of a polarising microscope and may be distinguished from calcium oxalate since it forms no drusy aggregates, often shows more or less marked striation, sometimes completely fills the cells and usually forms groups of crystals. T. H. P.

Detection of Incipient Putrefaction in Meat. J. Tillmans, R. Strohecker and W. Schütze. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 65–75.)—Three methods are described for detecting incipient decomposition in meat, based respectively on the facts that dissolved oxygen is all absorbed from water in four hours, nitrates are reduced to nitrites in a similar period, and methylene blue is decolorised. The oxygen method is a modification of that of Tillmans and Mildner (*Zeitsch. Unters. Nahr. Genussm.*, 1916, **32**, 65). Into each of two Winkler oxygen flasks are put 5 grms. of the minced meat, and the flask filled with water at 23° C. (air bubbles being carefully excluded) and incubated at that temperature for two

and four hours respectively, after which times manganese chloride and sodium hydroxide are added and the dissolved oxygen estimated. If there is incipient putrefaction all oxygen will have disappeared in the four hours. For the nitrate test 10 grms. are placed in each of two stoppered bottles, which are then completely filled with solution of potassium nitrate at 37° C. and incubated for two and four hours at that temperature, and their contents then tested for nitrate by the diphenylamine reaction. The nitrate solution contains 3·5 mgrms. of N_2O_5 per litre. For the methylene blue test, which is not quite so sensitive, 5 grms. of the sample are put in a stoppered bottle, which is filled with water at 40° C., and, after the addition of 1 c.c. of methylene blue solution, is warmed in a water bath at 45° C. for one hour, by which time the colour will be discharged by a meat which is unfit for human consumption. The methylene blue solution is prepared by diluting 5 c.c. of a saturated alcoholic solution with 195 c.c. of water. H. E. C.

Microchemical Reactions of Dulcin (*p*-Phenetolecarbamide). G. Denigès and R. Tourrou. (*Comptes rend.*, 1921, **173**, 1184–1186.)—If a fraction of a mgrm. of dulcin is moistened on a glass slide with a small drop of pure nitric acid (sp. gr. 1·39) it gives an immediate coloration, and soon dissolves in the acid. If then a fine stirring rod moistened with water is brought into contact with the drop, the surface of contact between the two liquids becomes turbid and rapidly deposits a brick-red or orange precipitate composed of microscopic crystals of ethoxy-*p*-phenetolecarbamide; the latter is soluble in concentrated, but insoluble in dilute nitric acid. Concentrated sulphuric and glacial acetic acids form excellent solvents for dulcin, which is deposited in a microcrystalline form when the solutions obtained are diluted with water or with an alkaline liquid. T. H. P.

Bacteriological, Physiological, etc.

Relation Between the Observed and Calculated Heat Values of Foodstuffs. J. König and J. Schneiderwirth. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 3–23.)—When the heat values of different classes of foods are calculated on the basis of the calorific value of protein (5710), fats (9300), and carbohydrates (4000), and compared with the values obtained by the calorimeter, it is found that if the foodstuff is composed almost entirely of one or all of these three principal food-substances there is close agreement between the observed and calculated values. Some error is, however, necessarily introduced by the differences in constitution of the fats, proteins or carbohydrates. In the case of milk-powders, eggs, butter, edible fats, breadstuffs, potatoes and such foods there is good agreement. In the case of meat, meat extracts, fat cheeses, and fish products there is a larger error due to the fact that the crude protein contains more or less amides, meat bases, and other nitrogenous compounds which have smaller heat values than pure protein. This may be corrected by allowing pure protein the value 5710 and the non-proteins (crude protein – pure protein) proteoses, etc., a value of 4700 grm./cal. Fruits and vegetables also show considerable differences between the observed

and calculated values by reason of their content of crude fibre, which may contain carbon compounds of higher heat value than cellulose, and the differences in the composition of their carbohydrates. Moderate agreement may be obtained by giving crude fibre the value 4292, starch 4182, and sugar 3950, but fruits also contain organic acids of varying heat values, so that good agreement is not obtained.

Experimental feeding of a man on a coarse diet rich in fibre and on a similar diet containing but little fibre gave results in agreement with the calculated values; more of the coarse diet is consumed and excreted, while the food value absorbed is approximately the same. The lowest efficiency is given by crude fibre, protein, and pentosans, and the highest by carbohydrates, while fats are in the intermediate position. The expression "foodstuff − faeces = digestibility" is not always correct, as much nitrogenous matter in the faeces is derived from the biliary and digestive juices. H. E. C.

Micro-Estimation of Nitrogen and its Biological Applications. M. Polonovski and C. Vallée. (*Ann. Chim. anal.*, 1921, **3**, 363–366.)—In the estimation of small quantities of nitrogen by Folin's method a quantity of the sample equivalent to 1–2 mgrms. of nitrogen is digested for 10 minutes with 1 c.c. of sulphuric acid, and 1 grm. of potassium sulphate (in presence of a fragment of quartz), the ammonium sulphate is then decomposed, and the ammonia carried over in a current of air into a known volume of 0·02 *N* acid and titrated. Unsatisfactory results were obtained by this method, and it was found:—(1) That the digestion with sulphuric acid must be continued for at least fifteen minutes after the liquid is colourless, in order to convert all nitrogen into ammonium sulphate; (2) That the direct addition of 3 c.c. of sodium hydroxide solution to the acid by means of the narrow tube used for the air current frequently leads to the production of dense crystals of sulphate which obstruct the tube; (3) That the passage of a current of cold air for 10 minutes is insufficient to carry over all the ammonia; (4) That sodium hydroxide is carried over by the rapid air current; and (5) That the apparatus employed is too fragile. A modified apparatus has therefore been made of Pyrex glass, and a method devised in which these drawbacks are remedied. Thus the air current is drawn through a small flask containing hot water acidified with sulphuric acid, which serves to remove any traces of ammonia from the air, and to heat the regulated air-current before it passes, by means of a glass-tube with a perforated bulb, through the alkaline liquid, which is in the test tube in which the digestion with sulphuric acid was previously carried out. This tube is fitted to a cork bearing the tube for the air-current and a tube (with two small splash-bulbs) which carries the ammonia over to another test-tube (of the same size, containing a known volume of the standard acid, whilst a bulb on the connecting tube prevents sucking-back of acid. The air current is used to draw the sodium hydroxide solution into the previously partly neutralised liquid from the digestion, and a current of warm air is drawn through the apparatus for 20 minutes. In applying the method to the estimation of albumin the total nitrogen in 1 c.c. of the sample is estimated as described, the albumin in 2–3 c.c. is then coagulated

by heating the liquid to 90° C. with two drops of acetic acid and a little sodium chloride in a graduated tube. After cooling, the liquid is made up to the original volume and centrifuged, the nitrogen in 1 c.c. of the clear liquid is then estimated, and the albumin obtained by difference. The method gives more accurate results than the usual methods for albumin. R. G. P.

Enzymes of the Abdominal Adipose Tissue of the Turkey. J. S. Hepburn. (*J. Amer. Chem. Soc.*, 1921, **43**, 1963–1965.) Aqueous extracts of the abdominal fat from turkeys were kept for several days at 0° C. and then showed the presence of catalase, lipase, and esterase. Most samples contained reductase and an oxidase acting upon phenolphthalein, but negative results were obtained on testing for oxidases acting upon *a*-naphthol and on tricresol. Some samples showed the presence of aldehyde reductase and peroxidases. In all cases control experiments were made on the boiled aqueous extracts to eliminate effects not due to enzymic action. Tricresol in 0·2 per cent. solution was used as an antiseptic in several tests. T. J. W.

Estimation of Vitamin Contents of Rice by the Yeast Method. W. D. Fleming. *J. Biol. Chem.*, 1921, **49**, 119–122.) Extracts prepared by treating rice at various stages of milling and polishing with 0·1 per cent. acetic acid, whether used without further treatment, or after boiling almost to dryness with 10 per cent. sodium hydroxide solution, and neutralising and diluting the liquid to the original volume with 0·1 per cent. acetic acid, gave similar results in the stimulation of yeast growth when added to cultures containing inorganic nitrogen only. Since the treatment with alkali destroyed any vitamin *B* present, the observed stimulation was due to other factors, and further experiments indicated that the organic nitrogen contained in the extracts added was the cause of the accelerated growths. T. J. W.

Bacteria as a Source of Water-Soluble B Vitamin. S. R. Damon. (*J. Biol. Chem.*, 1921, **48**, 379–384.)—Cultures of *B. paratyphosus B*, *B. coli* and *B. subtilis* were grown in solutions containing asparagine and various salts, then killed by heating them to 120° C. in an autoclave for 15 minutes, evaporated on a steam bath to a small volume, absorbed in starch and dried under reduced pressure. The starch thus treated was substituted for an equal weight of untreated starch in a basal diet, which was given to young rats. The diet contained casein, starch, sugar, lard, butter fat, and a mixture of salts and was adequate in all essentials, with the exception of the absence of *B* vitamin. In no case was the decrease in weight of the rats affected by the addition of the bacteria to the diet, thus indicating that the organisms examined do not produce the water-soluble *B* vitamin.

(*Abstractor's Note.*—It is not unlikely that the prolonged heating of the cultures in a salt solution gradually concentrating to about 60 per cent. of solids may have destroyed any vitamin originally present.) T. J. W.

Effect of Stimulants upon the Invertase Activity of Yeast. E. W. Miller. (*J. Biol. Chem.*, 1921, **48**, 329–346.)—The invertase activity of yeast was determined by shaking a known weight with water and a little toluene for eight hours at 30°C., adding 20 per cent. sucrose solution, a small quantity of 0·1 *N* hydrochloric acid solution, diluting the mixture to a definite volume and keeping it at the ordinary temperature for seven hours. At the end of this period 50 c.c. were removed, and treated with two drops of ammonium hydroxide solution (sp. gr. 0·90) and a small amount of talc, the mixture being then filtered and its optical rotation read in a 2 dm. tube. Extracts of yeast were prepared by means of alcohol, benzene, fuller's earth, and phosphotungstic acid precipitation, and an alcoholic extract of wheat germ was also made. These extracts were added to the synthetic yeast culture medium adopted by Williams, the mixture sterilised for 15 minutes by heating at 10 lbs. pressure, cooled, inoculated with yeast and incubated at 30° C. for twenty-four hours. After filtration, the invertase activity of the yeast was determined as above, 0·2 grm. portions being used. The results obtained confirm the presence in alcoholic and aqueous yeast extracts of a substance accelerating the formation of invertase. This substance is distinct from vitamin, since it may be separated by extraction with benzene, adsorption with fuller's earth, or by precipitation with phosphotungstic acid. The substance is concentrated in the gummy precipitate obtained on allowing the hot alcoholic extract of yeast to cool. Since the addition of yeast extract does not appear to have any effect upon the action of the invertase itself, the substance does not appear to be of the nature of an activator or co-enzyme. Extracts of wheat germ, which greatly accelerate the growth of yeast, have no effect upon the formation of invertase.

T. J. W.

Characteristics of Certain Pentose-Fermenting Bacteria. E. B. Fred, W. H. Peterson, and J. A. Anderson. (*J. Biol. Chem.*, 1921, **48**, 385–412.)—Twelve varieties of lactic acid bacteria were isolated from sauerkraut and maize silage and divided into two classes: Group I., including the species coagulating milk, but not forming mannitol from lævulose, and Group II., containing the forms which do not coagulate milk but break down lævulose into mannitol. None of the species examined was capable of decomposing hydrogen peroxide. Unsatisfactory and feeble growths were formed on a peptone-phosphate medium and meat infusions, but good results were obtained in yeast water, and this medium was adopted for use in the experiments described. From the results obtained on growing the various members of Group I. in solutions containing different sugars, etc., these bacteria were sub-divided into Strain A (which exerted no action upon dulcitol), Strain B (the members of which converted this alcohol into acid), and Strain C (which contained the only members of this group capable of fermenting melezitose). Owing to the similarity in size and form of these organisms, morphological characteristics are of little use in differentiating the various species. Arabinose and xylose are fermented by all the species, with the exception of Strain C, which exerts no action upon xylose. Analysis of the products of

fermentation showed that 85 to 97 per cent. of the sugar is broken down into lactic and acetic acids, and a small proportion of carbon dioxide, the two former acids being produced in the ratio of equal molecules of each. Tables are given showing the action of the various species of bacteria upon glucosides, polyhydric alcohols, hexoses, and disaccharides. T. J. W.

Flora of Maize Meal. C. Thom and E. Le Fevre. (*J. Agric. Research,* 1921, **22,** 179–188.)—A close correspondence has been observed between the flora of deterioration in unground maize and the flora of the milled product. The following species of moulds were characteristic of many species of cultures: *Fusarium* sp., *Aspergillus repens, A. flavus, A. tamari, A. niger, Citromyces* (or *Penicillium* section *Citromyces*) sp., *Penicillium oxalicum, P. luteum* varieties, *Mucor* sp., *Rhizopus nigricans,* and *Syncephalastrum* sp., together with various yeasts and yeast-like fungi. Among bacterial groups, the colon-aerogenes group and lacto-bacilli were most abundant in fresh meal. Aerobic spore-formers and micrococci were always present and persisted in the stored product. No bacterial activity was detected within the range of composition of merchantable meals. Only one grade of unbolted meal showed signs of mould development below 13 per cent. of moisture. Between 13 and 15 per cent. of moisture, varying with the form of milling, *Aspergillus repens* begins to be a destructive agent, whilst several other species of mould are active in meal containing 16 per cent. of moisture; and numerous forms, including some bacteria, develop when 18 to 20 per cent. of moisture are present.

Estimation of the Gases of the Blood. D. D. van Slyke and W. C. Stadie. (*J. Biol. Chem.,* 1921, **49,** 1–42.)—An apparatus for removal and analysis of the gases contained in 1 c.c. of blood, modified from a similar form described by van Slyke (*J. Biol. Chem.,* 1917, **30,** 374), consists of a graduated tube of 2·7 mm. bore divided in such a manner that the volume of gas may be read to 0·001 c.c., and connected above with a glass cup through a stopcock, and below with a bulb attached by indiarubber tubing to a levelling bulb containing mercury. The graduated tube is fixed to a vertical board, and the whole may be shaken by means of an eccentric connected with a small electric motor. Exhaustive details are given for the testing and manipulation of the apparatus, necessary precautions, and the methods adopted for the estimation of carbon dioxide, oxygen both in the free state and combined with haemoglobin, nitrogen, carbon monoxide and methæmoglobin. The reagents used are those commonly employed, with the exception that lactic acid is used instead of sulphuric acid to liberate the carbon dioxide from the blood bicarbonates. The results obtained are concordant and agree closely with those obtained by other methods requiring larger quantities of blood. T. J. W.

Colorimetric Estimation of Uric Acid in Blood. Grigaut. (*Compt. Rend. Soc. Biol.,* 1921, 1273; *Ann. Chim. anal.,* 1921, **3,** 370.)—Plasma or serum is shaken with an equal volume of trichloracetic acid (20 per cent.) and filtered, and

2 c.c. of Folin and Denis' phosphotungstic reagent are added to 5 c.c. of the filtrate. The reagent is prepared by boiling under a reflux condenser 100 grms. of sodium tungstate with 80 c.c. of phosphoric acid (85 per cent.) for one hour, and cooling and making up the liquid to one litre. The blue colour obtained on adding 15 c.c. of sodium carbonate solution (40 per cent.) is compared in a colorimeter with the colour obtained with 5 c.c. of a standard uric acid solution to which sodium carbonat-solution has been added at the same time. A stock solution of uric acid is prepared by dissolving 0·2 grm. of uric acid in 400 to 500 c.c. of warm water containing 9 grms. of di-sodium phosphate and 1 grm. of mono-sodium phosphate, adding 1 c.c. of glacial acetic acid to the cooled solution, and making it up to one litre (5 c.c. of chloroform are added as a preservative and should be renewed every 15 days). For use this solution is diluted to one quarter strength, and an equal volume of tri-chloracetic acid is added (20 per cent.), so that 5 c.c. of this standard solution correspond with 0·05 part of uric acid in one litre of the original blood sample. It is essential that the standard solution containing trichloracetic acid should not be kept for more than two days. The results indicate the amount of uric acid, together with alloxan and alloxantin, but exclude xanthine bases. The amount of uric acid in normal human serum estimated by this method is 0·045–0·05 grm. per litre compared with 0·02–0·03 grm. estimated by precipitation as silver-magnesium urate. R. G. P.

Agricultural Analysis.

Relation between the Clay Content and Certain Physical Properties of a Soil. B. A. Keen and H. Raczkowski. (*J. Agric. Sci.*, 1921, **11**, 441–449.)—The air-dry soil which has passed a No. 100 sieve is packed by hand, with tapping, into a brass box, of known volume, two inches square and one inch deep, having a number of small holes in the bottom with a piece of filter paper over them. The soil is levelled off with the top of the box, and the whole weighed, then it is left overnight in a basin with water one quarter of an inch deep. The box is wiped dry and again weighed; the soil which has expanded is levelled off and weighed, then the surplus soil and the box are dried separately for 24 hours in the water oven, and weighed again. From these figures the following quantities are calculated, allowance being made for the moisture in the air-dry soil and for the water absorbed by the filter paper. (1) The weight of unit volume (100 c.c. of air dry soil; *i.e.* the apparent specific gravity. (2) The amount of water taken up by unit weight of the soil. (3) The pore space. (4) The specific gravity of the soil. (5) The volume expansion of unit volume of soil when saturated. It is found that (1) and (4) vary inversely as the percentage of clay, whilst (2), (3) and (5) vary directly with the clay percentage. H. E. C.

Absorption of Copper from the Soil by Potato Plants. F. C. Cook. (*J. Agric. Research*, 1921, **22**, 281–287.)—Potato plants grown in soil treated with insoluble copper compounds contained more copper in the leaves than in the stems, whilst very little was found in the roots, and the tubers showed only traces of

copper. The average amounts, as compared with those of plants in the control plot, were: Leaves, 0·0107 (control, 0·0069); stem, 0·0030 (control, 0·0027); root, 0·0081 (control, 0·0012); and tubers, 0·0002 (control, 0·0002) per cent. The roots of plants treated with copper sulphate solution were injured, and subsequently contained more copper than the leaves. Samples of soil from sprayed potato fields showed only minute amounts of copper.

Report of the Fertiliser Research Committee. (Method for the Estimation of Nitric and Nitrous Nitrogen.) H. Neubauer. (*Chem. Zeit.*, 1921, **45**, 1077–1078.)—The following method has been adopted for the estimation of nitric and nitrous-nitrogen: A neutral or only slightly acid solution of the nitrate (0·5 grm. of potassium or ammonium nitrate, 1 grm. of mixed nitrate fertilisers) is diluted to about 300 c.c., 5 grms. of copper-magnesium alloy, in fine powder, and 10 c.c. of magnesium chloride solution are added, and the mixture slowly distilled into standard acid until all the ammonia has been driven off, which is usually accomplished in one hour. The alloy contains 50 per cent. of copper and 40 per cent. of magnesium; it should be powdered to pass a 1 mm. sieve and preserved from oxidation in a well-stoppered bottle. Magnesium chloride solution is prepared by dissolving 200 grms. of the crystals in a litre of water, adding three grms. of calcined magnesia and a fragment of pumice and evaporating the liquid twice to about one-third its volume. The solution is then made up to a litre and filtered. A blank test should be carried out on the materials and any correction applied. The presence of quantities up to three grms. of the chlorides of potassium, sodium, calcium, or magnesium, or of soluble sulphates does not interfere, but if much sulphate is present the amount of magnesium chloride solution should be increased to 50 c.c. Caustic alkalis interfere with the reaction, and free acid, if present in more than traces, should be neutralised with calcined magnesia. The total nitric and nitrous nitrogen to be estimated should not exceed about 100 mgrms. H. E. C.

Organic Analysis.

New Method of Preparing Formaldehyde Hydrosulphite. P. Malvezin, C. Rivalland and L. Grandchamp. (*Comptes rend.*, 1921, **173**, 1180–1182.)—Methanalsulphurous acid, $OH{\cdot}CH_2{\cdot}SO_3H$, obtained by Malvezin in 1906 from sulphur dioxide and 40 per cent. formaldehyde solution and suggested as a mould preventive, may be better prepared by passing the sulphur dioxide through the walls of a Chamberland candle into the 40 per cent. formaldehyde. The product thus obtained exhibits enhanced reducing properties, which are attributed to the formation of a certain amount of formaldehyde hydrosulphite. If zinc dust is suspended in the formaldehyde, and the temperature during the reaction is prevented from rising, the result is a concentrated zinc-formaldehyde hydrosulphite solution. Various mixtures of sulphites, finely divided metals and stabilisers of hydrosulphite have been examined, and one of these preparations, which readily decomposes in contact with moisture, yielding reducing agents in considerable proportion, gives promising results when applied to the reduction of indigo and dyes of the helindone, indanthrene and ciba classes, etc. T. H. P.

Iodine Values of Unsaturated Hydrocarbons and Cracked Gasolines. W. F. Faragher, W. A. Gruse and F. H. Garner. (*J. Ind. Eng. Chem.*, 1921, **13**, 1044–1049.)—The following are the iodine values found for the various hydrocarbons examined, the figures in brackets being the calculated values:—Amylene, b.p., 36·3°–37·3° C., 354 (362); amylene, b.p., 28·8°–31·8° C., 367 (362); isoprene, b.p., 29·3°–33·8° C., 382 (741); *n*-hexylene, b.p., 66°–68° C., 295·5 (302); isohexylene, b.p., 64°–65° C., 309 (302); hexadiene, b.p., 75°–78° C., 426 (620); cyclohexene, b.p., 81°–82° C., 298 (310); cyclohexadiene, b.p., 82°–83° C., 204 (630); heptylene, b.p., 96°–98° C., 260 (254); heptadiene, b.p., 100°–105° C., 253 (518); octylene, b.p., 122°–124° C., 210 (226); cetene, b.p., 125°–145° C./10 mm., 105 (113). The Hanus and Wijs reagents gave the same results with the olefines and with cracked gasolines when the amount used was less than 0·1 grm. per 25 c.c. of reagent. Diolefines may be qualitatively recognised by the shape of the time and quantity curves; on very largely increasing the excess of iodine present, iodine values approaching the theoretical values are obtained. *n*-Heptene behaves like an olefine, only one pair of halogen atoms being added; this is probably typical of the acetylenes in general. The Hanus reagent does not cause any appreciable substitution of hydrogen in the molecule of simple paraffins, cycloparaffins, or aromatic hydrocarbons, or of straight, branched-chain, or cyclic olefines, of diolefines, acetylenes, or cracked gasolines. All gasolines appear to contain diolefines.

W. P. S.

Estimation of *H*-Acid. H. R. Lee. *J. Ind. Eng. Chem.*, 1921, **13**, 1049–1051.)—The use of *p*-diazotoluene is recommended in the estimation of the coupling value of *H*-acid and other naphthol- and aminonaphthol-sulphonic acids, the rate of coupling being more rapid than that of diazobenzene, and secondary coupling being slight. The rate of decomposition of diazobenzene is approximately eight times more rapid in acid solution, and one and a half times more rapid in alkaline solution, than that of *p*-diazotoluene. The *p*-diazotoluene solution used is prepared by dissolving 10·7082 grms. of *p*-toluidine hydrochloride in 40 c.c. of concentrated hydrochloric acid and sufficient water to make one litre; 100 c.c. of this solution are frozen in a flask immersed in a mixture of ice and salt, and 102 c.c. of 0·1 *N* sodium nitrite solution are added; the ice in the flask maintains the temperature of the mixture below 2° C. After forty minutes, the mixture is diluted to 250 c.c. with ice-water, mixed, protected from light, and kept at 0° C. This solution is titrated against *H*-acid as follows:—Five grms. of dry *H*-acid are dissolved in sodium bicarbonate solution and diluted to 500 c.c.; 25 c.c. of the latter solution are then mixed with 200 c.c. of ice-water, 2 grms. of sodium bicarbonate are added, the mixture cooled at 0° C., and the diazo solution is run in from a burette provided with a jacket containing ice. When the titration is almost completed, 2 grms. of sodium carbonate are added, followed by 10 grms. of sodium chloride, and the titration is continued until a drop of the mixture placed on a filter paper gives a faint purple ring with a drop of *H*-acid solution. If the purple colour develops again after the solution has stood for five minutes, the titration is complete.

W. P. S.

Colour Reactions of Certain Nitro Compounds. O. Rudolph. (*Zeitsch. anal. Chem.*, 1921, **60**, 239-240.)—On dissolving a trace (0·5 to 1 mgrm.) of one of the nitro compounds specified below in about 10 to 15 c.c. of alcohol or acetone, and then adding 2 to 3 c.c. of dilute sodium hydroxide or ammonia solution, the following results are obtained, either immediately, or, after heating the mixture and allowing it to stand:

Compound.	Alcoholic Solution with NaOH.	Acetone Solution with NaOH	Alcoholic Solution with NH_3.	Acetone Solution with NH_3.
o-Dinitrobenzene	colourless	(cold) colourless	colourless	colourless
m-Dinitrobenzene	colourless	intense red-violet	colourless	pink to purple
p-Dinitrobenzene	colourless	intense yellow	no distinctive colour	pale yellow
1·3·5-Trinitrobenzene	intense yellow-red	blue-red	yellow-red	blue-red
2·4-Dinitrotoluene	deep blue	deep blue	colourless	colourless
2·4·6-Trinitrotoluene	deep yellow-red	pink to purple-red	light red	light red
1·8-Dinitronaphthalene	yellow-red	yellow-red	reddish	reddish

Quantitative Estimation of Phenanthrene. A. G. Williams. (*J. Amer. Chem. Soc.*, 1921, **43**, 1911–1919.)—The material most suitable for the estimation consists of anthracene oil hydrocarbons containing 30 per cent. or more of phenanthrene, less than 10 per cent. of carbazole, and not large amounts of anthracene oil constituents boiling above 360° C. Into a 50 c.c. flask fitted with an air condenser is introduced 0·25 grm. of the material, together with 0·75 grm. of iodic acid and 20 c.c. of glacial acetic acid. The mixture is boiled for 2½ hours, cooled for several hours, filtered through a Gooch crucible, and the residue washed with the minimum quantity of glacial acetic acid. The filtrate and washings are distilled together to a volume slightly less than 25 c.c. and diluted, while slightly warm, to this volume by the addition of glacial acetic acid. One grm. of 3·4-tolylene-diamine is added to the cooled liquid, and the flask rotated until this added substance is completely dissolved, and then allowed to stand overnight in water at about 20° C. The precipitate of toluphenanthrazine is collected on a weighed Gooch filter, washed with 25 c.c. of 50 per cent. acetic acid saturated with toluphenanthrazine, and finally with 200 c.c. of cold water, and dried and weighed, an addition of 0·053 grm. being made for the quantity remaining dissolved in the mother liquor. The total weight multiplied by 0·6052 gives the weight of phenanthrene contained in the sample taken for estimation. Concordant results were obtained with the same sample by three different analysts. A method is also given for the qualitative detection of phenanthrene. T. J. W.

The Tetrabromide Method for Estimating Rubber Hydrocarbon. H. L. Fisher, H. Gray and R. Merling. (*J. Ind. Eng. Chem.*, 1921, **13**, 1031–1034.)—The precipitated tetrabromide obtained in the method described by Lewis and McAdams (ANALYST, 1920, **45**, 339) occludes bromine, which is removed only very slowly during the subsequent titration. The authors, therefore, recommend that, after the addition of the potassium iodide, an excess of standard thiosulphate solution should be added, the mixture shaken thoroughly, then treated with a slight excess of bromine solution, and this excess at once titrated with thiosulphate solution. The quantity of potassium iodide prescribed by Lewis

and McAdams is too small; 15 c.c. of a 20 per cent. solution should be used. When vulcanised rubber is treated with alcoholic sodium hydroxide solution, in addition to the acetone extraction, the residue is not soluble in tetrachlorethane. This appears to be due to the presence of moisture, and the residue may be dissolved within twelve hours' heating by adding a small quantity of calcium oxide to the mixture of residue and solvent. The method does not always give concordant results, and requires further investigation. W. P. S.

Leather Substitutes and their Examination. V. Froboese. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 113–125.)—Leather substitutes should be free from ingredients, such as phenol or cresol, which may affect the skin of the user. Similar diseases have been caused by linings containing lead chromate and by a finish containing zinc (from the zinc chloride used as catalyst for the coumarone resin). The methods of manufacture and composition of various artificial leather linings are described. The examination of such substitutes should include: (A) Tests for phenol or cresol; (B) Solubility of the product in water: A:—Two hundred sq. cm. of the finely-divided sample are heated for two hours on a water bath with 75 c.c. of 10 per cent. sodium hydroxide solution until the coating has completely dissolved from the fabric. The liquid is filtered, and the residue washed with about 25 c.c. of warm water. The filtrate is saturated with carbon dioxide so as to convert the whole of the hydroxide into carbonate (any phenol present will be indicated by its odour), and is then shaken with an equal volume of ether, a few drops of sulphuric acid (but not sufficient to make the liquid acid) being added to facilitate the separation, if necessary. The ethereal extract is washed with water, without shaking, and evaporated, care being taken to remove the last traces of ether. It is then heated with about 40 c.c. of water on the water bath and the solution filtered, if necessary. The following tests are applied to this solution:—(1) Bromine water, which gives characteristic microscopic crystals of tribromphenol; (2) Ferric chloride solution, which is capable of detecting 0·5 per cent. of phenol; (3) Lex's test, in which 5 c.c. are heated with 2 c.c. of ammonia solution and a freshly-prepared solution of bleaching-powder, a blue coloration (or green if the original solution was yellow) indicating phenol or cresol; (4) *Nitrite reaction*: The solution is shaken with strong sulphuric acid until hot, and a crystal of potassium nitrite then introduced. In the presence of phenol or cresol red streaks are formed, and, on shaking, the whole liquid becomes red (yellow if only traces of phenol are present); (5) Zone reaction with formaldehyde and sulphuric acid; (6) Minute traces of phenol are best detected by the red coloration obtained with a freshly-prepared alcoholic solution of ethyl nitrite and sulphuric acid.

B. *Solubility in water*:—The artificial leather (200 sq. cm.) is cut into thin strips, mixed with 75 c.c. of water in a corked flask and left for 24 hours in an oven at 40° C. The resulting solution must be colourless, clear and transparent, without odour of glue or camphor when heated at 18° C., and must not be acid or alkaline. The soluble constituents are estimated by evaporating 50 c.c. of the

solution. The best products examined left a residue of 83·3 and 94·3 mgrms., but amounts up to 120 mgrms. are permissible. R. F. I.

Occurrence of Calcium Oxalate in Gidgee Wattle. T. Steel. (*Linn. Soc. New South Wales*, 1921, **46**, [2].)—The presence of a large amount of calcium and a small amount of potassium in a commercial sample of gidgee ash suggested the probability of unusual quantities of calcium oxalate being present in the timber and bark of the plant, *Acacia Cambegii*. This was found to be the case, the outer bark of the tree examined containing 18·82; the outer wood, 5·81; and the inner wood, 3·81 per cent.; average 4·77 per cent. of calcium oxalate calculated on the dry substance. Much smaller proportions were found in the barks of other species of *Acacia*.

Inorganic Analysis.

Determination of Hydrogen Ion Concentration in Water by means of Indicators without Buffer Solutions. L. Michaelis. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 75–80.)—Into each of six tall test glasses are put 40 c.c. of 0·02 *N* sodium hydroxide freshly diluted from *N* solution, and 0·25, 0·29, 0·33, 0·38, 0·45, 0·50 c.c. of a standard solution of *m*-nitrophenol (0·3 grm. in 300 c.c., diluted 1:10 for use). To 40 c.c. of the water to be tested is added from a graduated pipette a sufficient quantity of the indicator solution to match the colour of one of the standard alkali tubes. Let F denote the volume of the indicator solution in the particular standard colour tube which is matched, divided by that added to the water tube, then P_H is calculated from the equation $P_H = P_k + s + g + \phi$, where P_k is the constant for the indicator ($= 8{\cdot}33$ for *m*-nitrophenol), s is the salt correction (for sea-water $= -0{\cdot}16$, and for fresh water a negligible quantity), g is the temperature correction, which is negligible at ordinary temperatures, and $\phi = \log \frac{1-F}{F}$. Curves are given which show the last named quantity at a glance. H. E. C.

Buffer Solution for Colorimetric Comparison. T. C. McIlvaine. (*J. Biol. Chem.*, 1921, **49**, 183–186.)—A series of buffer solutions giving a range of P_H values from 2·2 to 8·0 was obtained by mixing solutions of 0·2 molar di-sodium phosphate and 0·1 molar citric acid in varying proportions to give a final volume of 20 c.c. Both substances were recrystallised from water two or three times, and separate solutions standardised by titration. The strength of the sodium phosphate solution was determined by titrating against hydrochloric acid, with methyl orange as indicator, and the citric acid solution by means of sodium hydroxide solution free from carbonate. The P_H values of the mixed solutions were determined electrometrically, calomel and hydrogen electrodes being used, and the results plotted on a curve from which the table given was interpolated. The following is an abridgement of the above table.

P_H value	3·0/	4·0	5·0	6·0	7·0	8·0
Sodium phosphate, 0·2 *M* solution	4·11	7·71	10·30	12·63	16·47	19·45
Citric acid, 0·1 *M* solution	15·89	12·29	9·70	7·37	3·53	0·55

T. J. W.

Direct Iodimetric Estimation of Lead Peroxide. S. Glasstone. (*J. Chem. Soc.*, 1921, **120**, 1997-2001.)—Lead peroxide (0·2 grm.) or red lead (0·5 grm.) is shaken for a few minutes in a stoppered bottle with 100 c.c. of water, 20 c.c. of hydrochloric acid (36 per cent.), 20–25 grms. of sodium chloride, and about 1 grm. of potassium iodide; when the lead oxide has dissolved, the liberated iodine is titrated with 0·5 *N* thiosulphate solution, starch being added towards the end. The addition of the sodium chloride prevents the formation of a coating of lead iodide on the oxide, and solution is rapid; no lead iodide separating out, the end-point is sharp. The method may be applied to the general estimation of lead: The solution is digested at the boiling point with excess of sodium hydroxide and bromine water for one to two hours, so as to convert any sesquioxide first formed into the dioxide. The solution is filtered hot, and the precipitate washed with boiling water until free from hypobromite (potassium iodide-starch test). To test for complete conversion into the dioxide, the precipitate may be digested with hot dilute acetic acid, and the filtrate made alkaline and again treated with bromine water. Filter and precipitate are transferred to a stoppered bottle, and the estimation is carried out in the manner described. W. R. S.

Highly Sensitive Reagent for Copper: the Kastle-Meyer Reagent. P. Thomas and G. Carpentier. (*Comptes. rend.*, 1921, **173**, 1082–1085.)—Alkaline phenolphthalein solution forms an extremely sensitive reagent for copper, giving, after some minutes, a perceptible pink coloration with a solution containing one part of the metal in 100,000,000 parts of water. If the liquid contains one part of copper per 10,000,000, the pink coloration appears in 15–20 seconds, whilst with one part per 1,000,000 the coloration is immediate and changes to bright red in a few seconds. In applying the test use must be made of water distilled in glass apparatus and of test-tubes washed with acid, and rinsed with tap water, and then with pure distilled water. The reagent is prepared by boiling a solution of 2 grms. of phenolphthalein and 20 grms. of potassium hydroxide in 100 grms. of water with 10 grms. of zinc dust until it is completely decolorised. Ten c.c. of the solution to be tested are treated with four drops of the reagent and one drop of hydrogen peroxide (5–6 volumes). It seems probable that many of the peculiarities and contradictory results observed with this reagent are to be attributed to its sensitiveness towards copper salts. T. H. P.

Estimation of Available Sulphur in Golden Sulphide of Antimony. B. D. W. Luff and B. D. Porritt. (*J. Soc. Chem. Ind.*, 1921, **40**, 275–278 T.)—The usual method of estimating free sulphur in antimony sulphide consists in extracting the sample with carbon disulphide. This method does not give a certain indication of the amount of "available sulphur" (*i.e.* that which is present in the free state at temperatures commonly employed for the vulcanisation of rubber), as amorphous sulphur, which may be present, is insoluble in carbon disulphide; further, antimony pentasulphide may undergo partial decomposition at vulcanisation temperatures, whilst certain brands of pigment show pronounced fixation of free sulphur at 120°–150° C. In order to overcome these uncertainties,

it is proposed to estimate the "available" sulphur by sealing up the weighed sample in a glass tube, the upper portion of which carries a small asbestos wad wetted with one drop of aqueous ammonia. The tube is heated for five hours to 150° C. in an oil bath, cooled, and broken, and the contents extracted with carbon disulphide for five hours; the solvent is distilled off, and the residue heated at 100° C. for one hour previous to weighing. The carbon disulphide used should be re-distilled over sulphur from a flask fitted with a rod-and-disc fractionating column. Heating in an atmosphere of ammonia converts amorphous sulphur into a form soluble in carbon disulphide; the heat treatment also allows any decomposition of pentasulphide and fixation of sulphur to take place under conditions closely approximating those obtaining in vulcanisation practice. W. R. S.

Estimation of Zinc as Pyrophosphate. D. Balarew. (*Zeitsch. anal. Chem.*, 1921, **60,** 442–448.)—The cold, feebly acid zinc solution containing 5–10 grms. of ammonium chloride and a moderate excess (2–3 grms.) of diammonium phosphate is carefully treated with ammonia till slightly alkaline to litmus. The amorphous precipitate of zinc ammonium phosphate is left to stand several hours in the cold, with occasional stirring, heated for half-an-hour on a water bath to complete the change into the crystalline modification, filtered off, washed, and ignited to pyrophosphate. If the precipitation is carried out in hot solution, the precipitate contains an admixture of tertiary zinc phosphate, and results are low. Glass vessels may be used. W. R. S.

Analysis of White Pigments. M. Lombard. (*Ann. Falsif.*, 1921, **14,** 261–268.)—A method described for the analysis of pigments of the zinc white type consists essentially in treating a portion of the sample with ammonium carbonate solution and an excess of ammonia; this dissolves the zinc oxide and leaves all the other constituents insoluble. Another portion of the sample is treated with acetic acid and alcohol to obtain the zinc sulphide, calcium carbonate and lead carbonate in solution, and a third portion is treated successively with nitric acid and ammonium carbonate in order to convert all the metals into compounds readily soluble in dilute acid, barium sulphate, however, if present, being left as an insoluble residue. Eight samples purchased as zinc white or zinc oxide were examined by the author; of these, only two consisted of zinc oxide, the others containing barium sulphate (4·8 to 71·3 per cent.), calcium carbonate (2·15 to 13·61 per cent.), calcium sulphate (5·46 to 20·99 per cent.), lead carbonate (0·56 to 45·22 per cent. lead sulphate (1·1 per cent.), and zinc sulphide (9·34 to 28·22 per cent.). All six adulterated samples contained zinc sulphide. W. P. S.

Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis. G. L. Kelley and E. W. Evers. (*J. Ind. Eng. Chem.*, 1921, **13,** 1052.)—Granular sodium hydroxide, which passes a 5-mesh sieve but is retained by a 20-mesh sieve, is a satisfactory absorbent for carbon dioxide and answers much better for the purpose than do soda-lime or "soda-asbestos." W. P. S.

Estimation of Chromium in Ferrochromium by Electrometic Titration. G. L. Kelley and J. A. Wiley. (*J. Ind. Eng. Chem.*, 1921, **13**, 1053–1054.)—Twenty grms. of sodium carbonate are fused in a nickel crucible and, during cooling, the crucible is rotated so as to form a lining on its interior surface; 16 grms. of sodium peroxide and 1 grm. of the finely-divided ferrochromium are placed in the crucible, mixed, fused, and kept in a state of fusion for three minutes. The lining of the crucible should not be fused or the crucible will be attacked. When cold, the contents of the crucible are dissolved in 300 c.c. of warm water, the solution is boiled for thirty minutes, cooled, treated with 80 c.c. of sulphuric acid (sp. gr. 1·58), boiled for five minutes, filtered through asbestos, and the filtrate diluted to one litre. One hundred c.c. of this solution are then acidified with 25 c.c. of sulphuric acid and titrated with ferrous ammonium sulphate and potassium dichromate solutions. The end-point of the titration is taken as the point of greatest change in the oxidation-reduction potential during the titration of the chromic acid with ferrous ammonium sulphate solution. Apparatus suitable for use in the titration has been described previously by Kelley, Adams and Wiley (ANALYST, 1917, **41**, 373). W. P. S.

Separation of Iron and Manganese. M. Carus. (*Chem. Zeit.*, 1921, **45**, 1194.)—Co-precipitation of manganese in the basic acetate process is due to a partial conversion of the manganous salt into a higher oxide by dissolved oxygen. In order to prevent the formation of the higher oxide and secure a quantitative separation in one precipitation, the dilute, feebly acid solution is treated with a few c.c. of 3 per cent. hydrogen peroxide, followed by sodium acetate as usual. The liquid is heated to boiling, left to settle, again treated with a little hydrogen peroxide, and filtered without delay. The precipitate is washed with hot water containing a little acetic acid, sodium acetate, and hydrogen peroxide, and the latter reagent removed from the filtrate by boiling, followed by the addition of a little sulphurous acid. W. R. S.

Volumetric Estimation of Aluminium. E. J. Kraus. (*Chem. Zeit.*, 1921, **45**, 1173.)—The neutral or feebly acid solution of aluminium sulphate, free from interfering substances, is titrated at boiling heat in a porcelain dish with a solution of disodium phosphate of known strength (*e.g.* 132·2 grms. $Na_2HPO_4 \cdot 12H_2O$ per litre; 1 c.c. = 0·01 grm. Al)—$Al_2(SO_4)_3 + 2Na_2HPO_4 = 2AlPO_4 + 2Na_2SO_4 + H_2SO_4$. A few drops of strong silver nitrate solution are added to the liquid. When all the aluminium has been precipitated, the yellow tinge, due to formation of silver phosphate, becomes permanent. The end point is sharper if the liquid is heated, as silver phosphate precipitated from hot solutions has a deeper colour than that produced in the cold. Iron, if present, is first separated by boiling the liquid with excess of sodium hydroxide. The filtrate is acidified with sulphuric acid and treated with ammonia; the washed precipitate is transferred to a porcelain dish, dissolved in a minimum of sulphuric acid, and the hot solution titrated as directed. W. R. S.

Tantalum, Columbium, and their Mineral Associates: *I. Use of Tartaric Acid in the Analysis of Natural Tantalocolumbates; II. Separation of Zirconium from Tantalum and from Columbium.* **W. R. Schoeller and A. R. Powell.** (*J. Chem. Soc.*, 1921, **120**, 1927–1935.)—I. In the usual method of analysis—fusion of the mineral with bisulphate followed by hydrolysis of the solution of the fused mass—the precipitate of earth acids is contaminated with a number of other elements, the removal of which is troublesome and not always effective. A preliminary account is given of a process which eliminates several interfering elements. The mass from the bisulphate fusion is treated with a solution of 10 grms. of tartaric acid in 50 c.c. of water, which dissolves everything except silica, gangue, cassiterite, and lead sulphate. The filtrate is saturated with hydrogen sulphide, and the precipitate (antimony, copper, tin, etc.) filtered off. The filtrate is digested with ammonia and ammonium sulphide to throw down iron and uranium, manganese being incompletely precipitated. Tantalum and columbium remain in solution, still accompanied by tungsten, titanium, zirconium, rare earths, and base metals; further work on the separation of these constituents is in progress. II. The mixed oxides are fused with 10 parts of potassium carbonate in a platinum crucible over a strong blast burner; the fused mass is treated with hot water, the residue washed with 2 per cent. potassium carbonate solution, ignited, and fused as before (in the separation of zirconium from tantalum a third fusion was made). The combined filtrates from the fused mass are acidified with hydrochloric acid and boiled with filter pulp and a slight excess of ammonia; the precipitated tantalic (columbic) acid is filtered off, washed with ammonium nitrate solution, ignited, and weighed. It contains a little platinum, and possibly silica; these are estimated by fusion with bisulphate, extraction with strong tartaric acid solution (see I.), treatment with hydrogen sulphide, and ignition of the precipitate; the weight of the precipitate is deducted from that of the first. The final zirconia residue is fused with bisulphate, the solution freed from platinum by hydrogen sulphide, and the zirconia precipitated by boiling the filtrate with sodium thiosulphate. The separation of zirconium from columbium was found to be quantitative; with tantalum, the results after three fusions showed a positive error of 2–8 mgrms. for zirconia, and a corresponding negative error for tantalum pentoxide.

W. R. S.

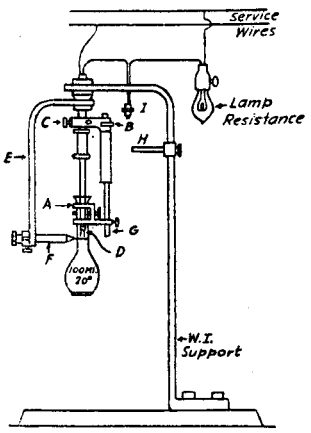
Sensitiveness of Tests for Barium. O. Lutz. (*Zeitsch. anal. Chem.*, 1921, **60**, 209–223.)—The most sensitive reagent for barium is the sulphate ion, whilst the chromate ion is almost as sensitive. The detection of barium by means of hydrofluosilic acid is about 200 times less sensitive. The following limits for the sensitiveness of various reagents were observed:—Sodium arsenate, 1:175; sodium phosphate, 1:6200; hydrofluosilicic acid, 1:7200; sodium carbonate, 1:160,000; sodium sulphate, 1:160,000; ammonium chromate, 1:1,200,000; and sulphuric acid, 1:1,600,000.

Sensitiveness of Tests for Strontium. O. Lutz. (*Zeitsch. anal. Chem.*, 1921, **60**, 433–441.)—The following precipitation reactions were tested as to their

sensitiveness: Phosphate (1 part Sr in 9500), sulphite (1 : 12,000), oxalate (1 : 50,000), carbonate (1 : 250,000), and sulphate (1 : 125,000). In presence of an equal volume of alcohol, the sensitiveness of the sulphate reaction is very much greater (1 : 1,400,000). With the exception of the flame spectrum, there are no colour tests or characteristic reactions. W. R. S.

Physical Methods, Apparatus, etc.

Flask Calibrating and Marking Device. G. L. Spencer. (*J. Ind. Eng. Chem.*, 1921, **13**, 1058–1059.)—The flask is filled from a calibrating burette with the desired quantity of water containing 0·1 per cent. of sulphuric acid; the neck of the flask is varnished or waxed in a broad band at the probable position of the mark, and the flask is then clamped in the apparatus shown in the illustration. The point of the graving tool, F, is adjusted previously at exactly the level of the electrodes, D, the latter are connected with a source of electricity, and the flask is raised very gradually by means of the micrometer screw, B. As soon as the electrodes touch the surface of the liquid, a distinct sound is made by the evolution of gases. The current is then cut off, the engraving tool brought into contact with the neck and the arm is rotated, a mark being thus made in the wax or varnish; the glass is then ready for etching. W. P. S.



Photomicrography of Opaque Crystals. M. François and Ch. Lormand. (*Bull. Soc. Chim.*, 1921, **29**, 1056–1059.)—The crystals are placed upon a small opaque disc of such a size as just to fill the field of the objective employed, and are illuminated by an incandescent electric lamp and lens situated axially beneath the microscope stage, the light from which is reflected upon the crystals by a small concave mirror (Lieberkuhn reflector) fixed just below the objective. To prevent deformation of the image of brightly reflecting facets of the crystals the objective is used without an eyepiece, and the illumination is reduced as far as possible consistent with a reasonable time of exposure. When photographing crystals having a brilliant metallic lustre, *e.g.* chromium silicide, with an objective of 17 mm. focal length, magnification ×25 and using Jougla panchromatic plates, the authors obtained satisfactory results with an exposure of seven minutes. Under the same conditions the exposures required for crystals of other colours may be determined approximately by using the following factors: Artificial cinnabar red ×4; dull black, similar to pyridine potassium irido-chloride, ×6; metallic black, as iron silicide ×18; and dark garnet red ×30. T. J. W.

Stereoscopic Photomicrography of Crystals. M. François and Ch. Lormand. (*Bull. Soc. Chim.*, 1921, **29**, 1059–1063.)—Stereoscopic pairs of

negatives may be obtained with an ordinary single tube microscope by making two exposures, one with the object slightly to the right and one to the left of the microscope axis, but, owing to the small separation required, careful and accurate adjustment is necessary. A second method consists in the use of a binocular microscope fitted with two objectives and a small camera fixed at the opposite end of each tube. Another apparatus, especially devised for this work, comprises a microscope in which the tube is capable of oscillation from right to left, the axis of rotation being situated in the plane of the stage. In conjunction with this, a small camera about 6 cm. from back to front, modified to allow the necessary movement of the microscope tube, and to allow the two pictures to be photographed upon one plate, was employed. The angular separation required between the positions of the microscope tube for the two exposures was determined by experiment, and was adjusted to show correct relief when the resulting transparencies were viewed through a Richard stereoscope. Since the concave mirror (see previous abstract) is rotated with the microscope tube it is necessary, when photo graphing opaque crystals, to raise the illuminating lens almost to the level of the stage to secure satisfactory illumination, and the opaque disc upon which the crystals rest should be elliptical instead of circular to allow for distortion due to the inclination of the optic axis. T. J. W.

[*Abstractor's Note.*—An angular separation of about 5 degrees will give correct stereoscopic relief with the majority of stereoscopes upon the market.]

Publications Received.

ANALES DEL CONGRESO NACIONAL DE LA INDUSTRIA MINERA. 1921. Torres Aguirre, Lima, Peru.
A collection of Metallurgical Papers.

CATALOGUE OF APPARATUS. A. Hilger & Co., London.

CARBONISATION OF PEAT IN VERTICAL RETORTS. Fuel Research Board Techn. Paper No. 4. H.M. Stationery Office, Imperial House, W.C. 2. Price 6d. net.

LABORATORY EXERCISES IN APPLIED CHEMISTRY. By W. MOLDENHAUER. Translation by S. L. BRADSHAW, D.Sc. Pp. xii+236. Constable. Price 12s. 6d.

THE EMISSION OF ELECTRICITY FROM HOT BODIES. By O. W. RICHARDSON, F.R.S. Monographs on Physics. Pp. vii+320. Longmans. Price 16s. net.

SYNTHETIC TANNINS. By G. GRASSER. Translated by F. G. A. ENNA. Pp. viii+143. London : Crosby, Lockwood. 1922. Price 12s. net.

KELLY'S DIRECTORY OF THE CHEMICAL INDUSTRIES. 15th Ed. Pp. xxxi+856. London : Kelly's Directories, Ltd. 1921. Price 30s.

THE PREPARATION OF SYNTHETIC ORGANIC CHEMICALS AT ROCHESTER. Illustrated. Eastman Kodak Company, Rochester, N.Y., U.S.A. *Copies free on request.*

Reviews.

RAYS OF POSITIVE ELECTRICITY AND THEIR APPLICATION TO CHEMICAL ANALYSES. By Sir J. J. THOMSON, O.M., F.R.S. Second Edition. Pp. 237. London: Longmans, Green & Co. 1921. Price 16s. net.

This volume summarises the immense amount of work which has been carried out on positive rays, those electrically charged particles which stream through an aperture in the cathode of the high vacuum tube. The subject is discussed with great clearness and in some detail, and the conclusions drawn as to the probable structure of atoms represent the latest authoritative views.

The various applications of electrostatic and electromagnetic fields for sorting out the constituents of the positive rays are described, including Aston's focus method with which he has been able to obtain photographs of what are practically mass spectra. These methods give decisive evidence as to whether an element is simple or consists of chemically identical isotopes of differing atomic weights. It is of the greatest interest to know that chlorine consists of a mixture of isotopes of atomic weights 35, 37, and possibly 38, but the analyst must continue to use 35·46 as its atomic weight for everyday work. Many of the atomic weights can be determined with considerable accuracy, and the method has the advantage that impurities do not interfere.

It is perhaps unfortunate that, with one exception, the plates at the end of the book are without any descriptive matter, one can only trace what they represent from the references in the text, and it would have helped the reader who is not a specialist if these plates had been more liberally lettered.

The work described extends our knowledge of atomic and molecular structure to an extent which was unforeseen until comparatively recently. For instance, it is shown that such radicals as CH, CH_2, & CH_3, can have an independent existence in the discharge tube; and there are indications in this book that, before long, there will be further knowledge as to the nature of linkages in carbon compounds. Rapid as have been the advances in this most fundamental branch of knowledge, there is nothing yet in it which affects the ordinary operations of the analytical chemist.

A. J. BULL.

THE PHYSIOLOGY OF PROTEIN METABOLISM. By G. P. CATHCART, M.D., D.Sc., F.R.S. London: Longmans, Green & Co. 1921. Price 12s 6d. net.

The first edition of this work appeared in 1912 and contained a resumé and discussion of the more important results of research up to that date. The present edition deals, in addition, with the mass of research on Protein Metabolism that has been carried out from 1912 to 1921, and it includes the work done in the United States by Lusk, van Slyke, Folin, Osborne, Mendel, and others.

The problem of protein metabolism is one of the most complex and obscure in physiology because the causes which bring about the changes are practically unknown.

The author is to be congratulated on his laborious studies of the literature of this difficult subject, for his work contains the accurate resumé of an enormous amount of research done by numerous investigators in all parts of the world.

The chapter on digestion and absorption of protein is of especial interest, and shows that inactivation of digestive ferments which occurs in *vitro* experiments does not take place in the living animal, since the amino acids are absorbed as they are formed, and so do not render inactive the digestive ferments.

On the other hand, it is shown that pepsin powder and pancreatin will in *vitro* effect greater changes on caseinogen and polypeptides respectively than the natural gastric and pancreatic juices.

In the chapter on Protein Regeneration the work of Abel, Rowntree, and Turner (1914) is described, whereby the animal's blood could be passed through a dialysing apparatus and then returned to the body. By this means it was definitely shown that amino acids existed in the blood stream, and, further, it was shown by Gyorgy and Zunz (1915) that the amino acid content of the blood of normal dogs was remarkably constant. The part played by the leucocyte is fully discussed, and though the post prandial leucocytosis is an undoubted occurrence, it is held to be not proven that these leucocytes are engaged in the manufacture of new food for the tissues.

The chapter on feeding experiments with abiuret products is deserving of close study. In the chapter on deaminization it is brought out that urea formation from amino acids is not a function confined to the liver, but it is common to all cells.

Chittenden's work on protein requirements is scientifically discussed in the light of recent research, and it is pointed out that, in view of observations made during the great war on the caloric value of the field ration of the United States Army, it must be accepted that the allowance claimed by Chittenden for soldiers is inadequate.

A pertinent criticism of the experiments on protein requirements is that the influence of accessory food factors has not been taken into account. The author admits this, and a special monograph is to be published dealing with this important subject.

To conclude, one must express gratification for the complete and admirable summary given by the author of the large amount of recent research done on protein metabolism, and everyone interested in this subject should not fail to obtain a copy of the book.

It should be in the reference library of every laboratory of Physiology, Pathological Chemistry and Bio-Chemistry. W. H. WILLCOX.

THE VITAMINE MANUAL: A PRESENTATION OF ESSENTIAL DATA ABOUT THE NEW FOOD FACTORS. By WALTER H. EDDY. Pp. vi+121. Baltimore, U.S.A.: Williams & Wilkins Co. 1921. Price $2·50.

Since the almost simultaneous discovery in 1906 of hitherto unsuspected factors in our dietary by Eijkman in Holland and Hopkins in this country opened up the subject of vitamine research an immense number of workers has been

tempted into this fruitful field. So unwieldy has the literature of the subject already become that the student may well lose himself in the maze of contradictory and irrelevant results unless guided in picking out the essential features of the yet unfinished story. For this reason a clear historical outline of the subject, with a critical examination of its present position, would be of great value both to the student and the general public; it is such a want that the author sets out to supply in the present work. The full bibliography is evidence that Dr. Eddy has approached the subject in a conscientious and industrious spirit, whilst the titles of the chapters show that all aspects of the subject have received attention.

Chapter I., on the discovery of vitamines, contains some surprises; the author starts with the work of Funk, dismissing later, in a few cursory sentences, the pioneer work of Hopkins and of Eijkman, merely assigning to these observers the credit "of calling the world's attention to the unknown substances which Funk was to christen later." Throughout this and succeeding chapters Funk is treated as the real discoverer of vitamines; we are told (p. 8) how "the ground was prepared for Funk's harvest," and (p. 9) how he was "the first to announce the discovery of the unknown factor which he christens vitamine"; later (p. 73) we read of "the antineuritic vitamine discovered by Funk," which is throughout referred to as "Funk's vitamine." When however the author gets to grips with Funk's actual work he makes no attempt to support these claims; thus in discussing that worker's gallant attempt to isolate the vitamine from yeast we read (p. 25):—"Funk was forced to admit that his crystalline complex was not the pure substance, as analysis showed that it contained large amounts of nicotinic acid. His product might well be considered as nicotinic acid contaminated with vitamines." Such treatment of Funk's work is unfair to that worker and misleading to the casual reader who may fail to appreciate its contradictory nature. The author would have contributed more both to Funk's reputation and to the value of his own book had he recognised the salient points of the latter's work, and pointed out how, by the combined use of chemical and biological methods, this worker succeeded in fractioning from immense quantities of raw material (rice, polishings, and later yeast) a small fraction of high curative potency, thereby indicating the exceedingly low concentration in which these physiologically active substances are present both in foodstuffs and in the animal tissues where they play so vital a part. In the same chapter the evidence by which McCollum was led to suspect and finally establish the existence of a second vitamine in milk forms interesting reading; in this connection however the author's historical sense seems somewhat at fault. In referring to the now famous experiments of Hopkins (p. 18) he says:—"In the same year F. G. Hopkins in England announced that the addition of 4 per cent. of milk to diets consisting of purified nutrients would convert them into growth producers. . . . This work has recently been repeated by Osborn and Mendel, who fail to find the high potency in milk ascribed to it by Hopkins; but the latter's work, at that time, was accepted without question, and became the impetus to important discoveries." As a matter of fact, on the friendly invitation of Osborn and Mendel, Hopkins

himself repeated his experiments and amply confirmed them and published his results in a paper, which is included in the author's bibliography, and which he has presumably read. The paragraph quoted therefore might well receive qualification.

Chapter IV. "The Methods used in Testing for Vitamines," is useful as regards vitamines A and B both to workers actually engaged in feeding experiments, and also to those who would interpret critically the work of others. The description, however, of the method used in testing for the "C" vitamine is inadequate, and gives no account of how by the method elaborated by Chick and others it has been possible to make accurate comparative experiment on the antiscorbutic potency of various foods, nor of the far-reaching importance of such work.

The chapter on deficiency diseases is perhaps the least satisfactory in the book. Both from a scientific and utilitarian standpoint it is undoubtedly in this field that vitamine research has reaped its richest harvest. The history of scurvy and beri-beri is barely dealt with, and the reader gains from the book but little idea of the previous magnitude of these scourges, nor of the potency of the weapon which a knowledge of vitamines has given us against them. In connection with this section it seems a pity that the author should discuss in the text a paper by E. C. Bulley, in which she registers her opinion that keratomalacia (or xerophthalmici) is not a deficiency disease, whilst he ignores (except in the bibliography) a later paper, published by other workers from the same laboratory, consisting of a detailed study of the disease and explaining the cause of the first writer's erroneous observation.

Chapter V., "The Sources of Vitamines," consists of the tables published in the report of the (British) Medical Research Committee on vitamines, for which acknowledgment is made. As this report was published in July, 1919, it would have been well had the author amplified and corrected these tables in the light of much recent work, instead of copying them verbatim.

Chapter VI. is a useful summary of scattered indications obtained from various workers by means of which we may form conjectures on the chemical nature of vitamines, and may well prove useful to courageous workers embarking on the attempt to isolate any one of them.

On the whole, in spite of somewhat unbalanced judgments, the author has succeeded better in dealing with the chemical than with the physiological aspects of his subject, although it is in the latter sphere that vitamine research has made the more remarkable advances.

The book lacks an index, but contains a very full bibliography.

It should be added that, for the sake of uniformity, the author's spelling of "vitamines" has been retained, although the "e" is now omitted by the chemical societies in this country. M. STEPHENSON.

THE YEAR BOOK OF PHARMACY, 1921. Pp. 484. London: J. & A. Churchill. Price 12s. 6d. nett.

In this work the pharmacist has for many years possessed a valuable Annual Report on the Progress of Pharmacy and Pharmaceutical Chemistry, while chemists

in other branches of the science have only comparatively recently had their needs supplied by similar publications. The work appears this year in its usual form, containing in the first part Abstracts of Scientific papers dealing with Chemistry, Materia Medica, and Pharmacy. The Chemical Abstracts occupy 146 pages, and contain a large number of analytical papers, many of them not abstracted elsewhere. The abstracts, as far as the reviewer has been able to test them, appear to be well and accurately done.

It is curious to note that the *Year Book of Pharmacy* persists in maintaining in some of its abstracts the old symbols "Am" for ammonium and "Cy" for "Cyanogen," while the orthodox chemical notation is employed in others. It would appear advisable that a uniform system should be used throughout. There is certainly as much to be said for the use of "Am" for "Ammonium" as for "Et" for "ethyl," "Ac" for "acetyl," etc., which are used in most chemical abstracts, but "Cy" has no apparent advantages.

The second division of the book consists of the Transactions of the British Pharmaceutical Conference. The Science Section contains fifteen original papers on Analytical Chemistry, most of which have already been abstracted in the ANALYST, and do not call for comment here.

The index is complete, but it would be an advantage if the subjects and authors were in separate divisions.

The *Year Book of Pharmacy* is certainly an indispensable publication to all those regularly engaged in the analysis of drugs or chemicals, and will be found a most valuable source of information to those analysts whose practice only occasionally brings them into contact with these products. NORMAN EVERS.

Institute of Chemistry of Great Britain and Ireland.

PASS LIST.

EXAMINATIONS: JANUARY, 1922.

The following candidates have been successful in the recent Examinations and have been duly elected Associates of the Institute:—*Examination in General Chemistry:* John Harold Crossingham; John Lawrence Hyland; Frederick Charles Randall, B.Sc. (Lond.); Samuel Gordon Stevenson. *Examination in Organic Chemistry:* William Ernest Brazier; Malcolm Cuckney; William Derrick. *Examination in the Chemistry of Foods and Drugs, etc.:* Neville Lushanus Wright, D.I.C.

The following candidates have been successful in the Examination and have been duly elected Fellows of the Institute:—*Examination in Inorganic Chemistry (Section II.) Metallurgy:* Alfred Scholes. *Examination in Agricultural Chemistry:* Charles William Brown Arnold, B.Sc. (Lond.).