

INORGANIC ANALYSIS.

New Method of Estimating Ammonia. A. Ronchèse. (*Journ. Pharm. Chim.*, 1907, **25**, 611-617.)—The method is based upon Delépine's observation that formaldehyde reacts with ammonium chloride to form hexamethylene-tetramine, and if the formaldehyde be in excess the whole of the acid of the ammonium salt is liberated and may be titrated with standard alkali.

Ammonium Salts.—If the solution be neutral it is diluted to about 100 c.c. with water freed from carbon dioxide, treated with a few drops of phenolphthalein solution, and then with a large excess of a neutral solution of formaldehyde (1 : 1), and titrated with $\frac{N}{10}$ sodium hydroxide solution, each c.c. of which corresponds to 0.0017 gram of ammonia in the sample. In the case of an acid solution of an ammonium salt the free acid must be neutralised, before the addition of formaldehyde. If the solution does not contain more than 10 c.c. of $\frac{N}{10}$ ammonia solution, the excess of sodium hydroxide required is practically proportional to the amount of ammonium salt (viz., about 0.1 c.c. for each 3 c.c. of $\frac{N}{10}$ ammonia solution). When the amount of acid is large the solution may be divided into two parts, in one of which the ammonia is estimated without previous neutralisation as described above, whilst in the other the acidity is estimated in presence of an indicator not affected by ammonium salts.

Total Nitrogen.—Kjeldahl's method is employed, and the ammonia in the ammonium sulphate estimated as described.

Ammonia in Urine.—Ten c.c. of the urine are diluted to 100 c.c. with water freed from carbon dioxide, and neutralised with $\frac{N}{10}$ sodium hydroxide, with phenolphthalein as indicator. The liquid is then treated with 20 c.c. of a neutral solution of formaldehyde (1 : 1), the liberated acid titrated, and the correction given above applied.

Estimation of Urea in Urine.—Sallerin's method is recommended. It is based upon the fact that magnesium chloride melts at 112° to 115° C. in its own water of crystallisation, and that the liquid thus obtained boils at 160° C. When urine is heated with this salt and with hydrochloric acid the urea is rapidly decomposed into ammonium chloride. The ammonia in the urine may then be estimated by the new method, and the amount of ready-formed ammonia previously found deducted from the result.

C. A. M.

Estimation of Small Amounts of Antimony by the Marsh-Berzelius Method. C. R. Sanger and J. A. Gibson. (*Journ. Soc. Chem. Ind.*, 1907, **26**, 585-589.)—Having shown by a series of preliminary experiments that practically all the antimony is evolved as hydride if only small amounts are added to the

reduction flask of the apparatus, and that the hydride can be decomposed entirely by heating the capillary tube to a certain temperature, the authors give the details of the method as applied to the estimation of minute quantities of antimony. About 3 grams of pure zinc are placed in the reduction flask, 30 c.c. of dilute hydrochloric acid are added, and a current of hydrogen previously freed from hydrogen sulphide is passed through the flask. This current is obtained from a large generator, and several reduction flasks may be supplied at the same time. When the whole apparatus (flask, mirror-tube, etc.) is full of hydrogen, the antimony solution, containing not more than 0.1 mgm. of antimonious oxide, is introduced through a funnel-tube into the flask, and the capillary portion of the mirror-tube is heated to a temperature of about 500° C. for a length of 3 mm. To attain this a brass tube or collar is slipped over the capillary, so as to protect the glass from direct contact with the flame of the burner. The test should be allowed to run for forty minutes to ensure complete deposition of the antimony. The deposit obtained is then compared with that produced by known quantities of antimony, the standard solution being prepared most conveniently from recrystallised potassium antimony tartrate. As the antimony mirrors are affected by moist air and light, the tubes must be sealed up and kept in the dark.

W. P. S.

The Detection of Traces of Hydrogen Arsenide in the Air. A. Hébert and F. Heim. (*Bull. Soc. Chim.*, 1907 [4], **1**, 573-575.)—Dowzard's method (*Journ. Chem. Soc.*, 1901, **79**, 715) is employed, the air being aspirated through a 15 per cent. solution of cuprous chloride in hydrochloric acid, which absorbs hydrogen sulphide, phosphide, and antimonide, whilst the unabsorbed hydrogen arsenide may be detected by means of mercuric chloride paper. By experiments upon air containing known quantities of hydrogen arsenide, the authors found that it is possible in this way to detect as little as 1 part in 100,000.

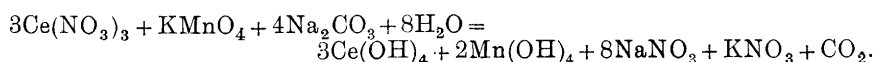
C. A. M.

Separation and Estimation of Bismuth and Mercury by Sodium Phosphate. A. Stähler. (*Chem. Zeit.*, 1907, **31**, 615, 616.)—In the separation of bismuth by precipitation as phosphate in acid solution, certain precautions are necessary to avoid the precipitation of basic chlorides. The improved method is briefly as follows: To the acid mixture of the solutions of bismuth and mercury in a 500 c.c. beaker, 3 c.c. of a 10 per cent. solution of pure orthophosphoric acid are added; the liquid is then diluted with boiling water to about 200 c.c. To this liquid a boiling 10 per cent. solution of trisodium phosphate is added drop by drop until the solution becomes only slightly acid. Since it is important that at no stage the liquid should be neutral, a few drops of rosolic acid are added as an indicator. The precipitate is allowed to subside, and the liquid is decanted off hot through a Gooch crucible containing a previously ignited filter of asbestos moistened with some of the washing liquid. The completeness of the precipitation is tested by adding more sodium phosphate to the filtrate until it becomes nearly neutral, and then a few drops of phosphoric acid. Any precipitate which forms is boiled up and returned to the main precipitate. The precipitate in the beaker is washed by decantation with

a boiling solution of 1 gram of ammonium nitrate and 4 drops of nitric acid in a litre of water. It is finally washed rapidly into the crucible, dried, ignited, and weighed as BiPO_4 . For the precipitation of the mercury the filtrate is treated with an excess of ammonia and ammonium chloride, and a rapid current of sulphuretted hydrogen is passed through the hot solution for not more than five to six minutes. The precipitate is carefully washed by decantation with boiling water, collected in a Gooch crucible and dried at 105°C .

J. F. B.

Volumetric Estimation and Separation of Cerium by Means of Potassium Permanganate. R. J. Meyer and A. Schweitzer. (*Zeits. Anorg. Chem.*, 1907, **54**, 104.)—In the presence of bases potassium permanganate oxidises cerium compounds quantitatively according to the equation—



In the presence of other rare earths, however, a small quantity of their higher oxides is also always formed. For quantitative purposes zinc oxide, or preferably magnesium oxide, is substituted for the sodium carbonate, the reaction being carried out by mixing well ignited magnesium oxide with water, heating to 60° or 70°C ., adding a measured volume of potassium permanganate solution, and then running in the practically neutral cerium solution from a burette until the red colour disappears. In this way the quantity of permanganate consumed by any other rare earths present is reduced to a minimum, and the results are accurate to about 1 per cent. of the cerium present. For purposes of separation this method cannot be used, since the excess of magnesium oxide precipitates the whole of the rare earths. It is preferable to determine the proportion of cerium present as above, and then to modify the procedure according to whether pure cerium dioxide is to be obtained or the whole of the cerium is to be removed from the remaining earths. A practically pure cerium compound is obtained by heating the solution to 60° or 70°C ., and adding the calculated quantity of potassium permanganate in the form of a solution containing 3 molecules of Na_2CO_3 to 1 of KMnO_4 , whilst the whole of the cerium (together with a portion of the other earths) is precipitated by using a solution containing 5 molecules of Na_2CO_3 to 1 of KMnO_4 .

A. G. L.

Volumetric Estimation of Hydrogen in Mineral and Organic Substances. A. P. Lidoff. (*Zeit. anal. Chem.*, 1907, **46**, 357-370.)—The substance is heated with metallic magnesium and the hydrogen evolved is measured. From 0.025 to 0.5 gram of the sample is mixed with about 1 gram of powdered magnesium, and the mixture is introduced into a tube, closed at one end, and having a length of 130 mm. and diameter of 7 to 9 mm. A layer of the powdered metal is placed in the tube over the mixture, so that the tube is filled to a height of 80 mm., and a small spiral of aluminium foil is placed above this layer. The open end of the tube is now connected with a gas-measuring burette, the usual precautions being taken in adjusting the zero, and the layer of aluminium powder is heated to redness, the heating being then extended to the mixture. The volume of hydrogen obtained in the burette is finally

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read off. The results of many estimations are given, showing that the method enables the amount of hydrogen to be estimated with a fair degree of accuracy in such substances as ammonium chloride, ammonium thiocyanate, sodium hydrogen carbonate, paraformaldehyde, starch, tartaric acid, iodoform, etc. A few substances, such as theine, fatty acids, acetamide, and the toluidins, however, yield results which are from 1 to 2 per cent. too low.

W. P. S.

A New Reaction for Iron. O. Lutz. (*Chem. Zeit.*, 1907, **31**, 570.)—Ferric salts in faintly acid solution give a bluish-green coloration with protocatechuic acid, which becomes red in the presence of alkali. Ferrous salts do not give the acid coloration, but in presence of alkali they give the same red coloration as ferric salts. Excess of acid or alkali (hydrate) weakens the coloration considerably, and must be neutralised in order to obtain the full reaction. The coloration in alkaline solution is the more useful in practice; a few drops of a solution of protocatechuic acid are added to the liquid to be tested, and excess of normal sodium carbonate solution is run in. A fairly large excess of sodium carbonate does not interfere with the delicacy of the test. If iron be present the red coloration is obtained, but if precipitates of other metals be formed it may be necessary to filter the solution before the iron coloration can be detected. The limit of sensitiveness is 1 part of iron per 10,000,000. Various salts which interfere with the other colour reactions for iron have no effect on this. Salts of uranium, cerium, and titanium give colorations with protocatechuic acid and sodium carbonate, which have to be taken into account. The ferric-protocatechuic acid compound is a sensitive indicator for acids and alkalis.

J. F. B.

The Estimation of Iron in Presence of Titanium. F. A. Gooch and H. D. Newton. (*Zeits. Anorg. Chem.*, 1907, **54**, 213.)—The authors show that the customary titration of iron with potassium permanganate after reduction with zinc gives excellent results even in the presence of titanium, provided that the cold reduced solution be shaken with cupric oxide, or, preferably, with bismuth oxide, and filtered before titrating. The reduced titanium is reoxidised in this way, whilst ferrous salts remain unaffected.

A. G. L.

Colorimetric Method for the Determination of Lead in Potable Waters. M. R. Moffatt and H. S. Spiro. (*Chem. Zeit.*, 1907, **31**, 639.)—The authors have found that hæmatein (the colouring matter of logwood) yields blue compounds with salts of copper, zinc, and lead. The reaction is exceedingly delicate, and since copper and zinc are of rare occurrence in potable waters, it is proposed to use the reaction for the determination of lead in such waters. For this purpose $\frac{1}{2}$ to 1 c.c. of a freshly-prepared solution of hæmatein (0.5 gram per litre) is added to 100 c.c. of the water to be examined and to similar quantities of pure water containing 1 part and upwards of lead per 1,000,000 parts of solution, the colours produced being compared.

Subjoined are the colours produced by a number of salts with hæmatein: Copper sulphate, blue; potassium antimoniate, cherry-red; potassium dichromate, black-

brown; sodium nitrate, acetate and arseniate, none; alum, bismuth nitrate, and stannous chloride, violet; ferrous sulphate, black; lead acetate and zinc sulphate, blue; sodium sulphate, ammonium chloride, and mercuric nitrate, yellow; potassium ferrocyanide, purple; chrome alum, yellowish-brown; magnesium sulphate, orange; silver nitrate and nickel nitrate, brown.

A. G. L.

The Separation of Magnesium from the Alkalis by the Arsenate Method. E. Browning and W. A. Drushel. (*Zeits. Anorg. Chem.*, 1907, **54**, 141.)—Magnesium is separated from the alkalis by precipitation with a moderate excess of ammonium arsenate. The solution used should measure 100 to 250 c.c., and should be definitely, but not strongly, ammoniacal. The precipitation may be hastened by adding 15 to 20 per cent. of the total volume of alcohol, or by freezing. The precipitate is collected in a weighed asbestos crucible immediately after settling, washed with a little dilute ammonia, dried, and ignited to magnesium pyroarsenate. Arsenic is removed from the filtrate by evaporating it to dryness after the addition of 10 c.c. of hydrochloric acid (specific gravity 1.20), and 10 c.c. of hydrobromic acid (specific gravity 1.30), or 1 to 3 grams of ammonium bromide. The determination of the alkalis is then completed as usual. Satisfactory test results are given. A. G. L.

Action of Iodine on Phosphorus Sesquisulphide and the Detection of the Latter in Ignition Mixtures. L. Wolter. (*Chem. Zeit.*, 1907, **31**, 640.)—On adding to a carbon disulphide solution of phosphorus sesquisulphide a 10 per cent. solution of iodine in carbon disulphide until the dark colour of the latter solution is permanent, then adding 30 to 40 per cent. by volume of benzene or petroleum ether, cooling to 0° C. and stirring, a new substance of the formula $P_4S_3I_2$ is obtained. It separates in silky rhomboid crystals, and melts at 119.5° C. This compound can be kept unchanged in well-stoppered bottles, but gradually decomposes in moist air. Water decomposes it with evolution of hydrogen sulphide, whilst alcohol liberates sulphur. Xylene, toluene, and warm ether dissolve the substance, which is practically insoluble in benzene, petroleum ether, chloroform, and glacial acetic acid. This reaction may be used for the detection of phosphorus sesquisulphide in matches.

A. G. L.

A Delicate Reaction for Titanium. E. Knecht. (*Chem. Zeit.*, 1907, **31**, 639.)—The test consists in the reduction of certain dyes by titanium trichloride. The mixture of silicic and titanous acids obtained in the usual manner is warmed for some time with a few drops of dilute (1 : 1) hydrochloric acid and a little zinc foil, and is then added to an aqueous solution of about 0.5 gram Rochelle salt which is just coloured by indigo. If titanium is present the blue colour will disappear, but will reappear again on shaking the tube. As little as 0.00004 gram of titanium can be detected in this way. Still more delicate is the similar reaction with methylene blue, which can be obtained with 0.00001 gram of titanium. In this case Rochelle salt should not be added.

A. G. L.

A New Method for the Separation of the Yttrium Earths. C. James. (*Journ. Amer. Chem. Soc.*, 1907, **29**, 495.)—The method depends on the different degrees of solubility of the oxalates of the gadolinite earths in ammonium carbonate solution. The oxalates used should contain not more than traces of the cerium earths, and should be freshly precipitated and moist. They are dissolved by stirring and warming in a dilute solution of ammonium hydroxide (1 to 4) which has been saturated with solid ammonium carbonate. The liquid is then heated to boiling, so as to drive off the carbon dioxide gradually, the precipitates obtained being filtered off from time to time. Finally, the liquid is evaporated to dryness.

The precipitates consist at first of carbonates, and later of oxalates, the earths separating in the following order: Cerium group; yttrium, terbium; dysprosium, holmium; erbium; thulium; ytterbium. The author states that the method yields in a very short time "pure" erbium, which he believes to be a complex similar to didymium.

A. G. L.