

## INORGANIC ANALYSIS.

**Rapid Pressure Method for Estimation of Carbon Dioxide in Carbonates.**

**W. H. Chapin.** (*J. Ind. and Eng. Chem.*, 1918, **10**, 527-529.)—The carbonate is allowed to dissolve in dilute hydrochloric acid contained in a flask of known volume to which is attached a manometer. A 600-c.c. distilling flask serves well, the side tube being sealed to a manometer of 5 mm. bore. The neck of the flask is closed with a rubber stopper, pierced with one hole and carrying a short piece of glass tubing terminating in a stopcock. The capacity of the flask from the lower end of the near limb of the manometer to the under side of the stopper is determined once for all. In use, the flask is immersed in a cold-water bath, filled with carbon dioxide, and charged with 10 c.c. of 3N hydrochloric acid saturated with carbon dioxide. The substance to be analysed (0.5 gm.) is weighed out in a copper capsule which is suspended in the neck of the flask by a thread held by the stopcock above the cork, the level of the mercury in the two arms of the manometer is adjusted by opening the cock whilst holding the thread, and the thread is then released with the finger on the open end of the stopcock tube. The cock is closed and the pressure read off after five minutes, the weight of carbon dioxide evolved being calculated from the formula  $\frac{VP \times 273 \times 0.001965}{760 \times (273 \times t)}$ , where V is the volume of the flask less 10 c.c. (the volume of acid used), P the manometer reading in millimetres, and *t* the temperature of the bath in degrees C., or, since  $\frac{V \times 273 \times 0.001965}{760}$  is a constant for the apparatus,

this value,  $K$ , may be calculated once for all, and the weight of carbon dioxide is then given by  $\frac{KP}{273 \times t}$ .

G. C. J.

**Methods for the Commercial Analysis of Ferro-Silicon. E. M. Anger.** (Amer. Electrochem. Soc., April to May, 1918 [Advance copy]; through *J. Soc. Chem. Ind.*, 1918, **37**, 306A.)—Carbon is estimated by burning 0.5 gm. of the finely-ground sample, with addition of 2 grms. of fine mild steel turnings of known carbon content, to facilitate combustion. The solution of the finely ground sample for analysis is effected by covering 0.5 gm. in a platinum dish with 10 c.c. of dilute nitric acid (1:1), and slowly adding hydrofluoric acid, drop by drop, until solution is complete. The solution is evaporated to dryness, and the residue dissolved in nitric acid. Manganese, calcium, magnesium, and sulphur, are estimated in this solution by known methods. Total phosphorus is precipitated by ammonium nitromolybdate; the small residue left undissolved when the solution is prepared as described above must be rendered soluble by fusing with sodium carbonate, as it contains a large proportion of the phosphorus. Phosphorus, which can be liberated as hydrogen phosphide, is estimated by treating the ferro-silicon with 40 per cent. caustic soda solution, absorbing the hydrogen phosphide in bromine, and subsequently precipitating. For the estimation of iron, hydrogen peroxide is used instead of nitric in preparing the solution, and the hydrochloric acid solution is reduced with stannous chloride and titrated with bichromate. When titanium and barium are to be estimated, a small quantity of sulphuric acid must be added in the process of solution, otherwise these elements volatilise as fluorides. For the estimation of silicon, ferro-silicon with up to 25 per cent. silicon can be decomposed by carbonate fusion in a platinum crucible, but with higher proportions of silicon, the platinum is rapidly attacked. Fusion with sodium peroxide in iron crucibles is recommended. An approximate method, accurate to 0.5 per cent., is based on the evolution of silicon as tetrafluoride by the solution process described above, with subsequent ignition of the residue to oxides. A factor should be used to counteract the difference in the weight of aluminium and iron.

**Occurrence of Hydrogen Selenide in Rain-Water and Snow. T. Gassmann.** (*Helvetica Chim. Acta*, 1918, **1**, 52-54.)—The presence of hydrogen selenide in rain-water and snow may be detected by the red precipitate of selenium produced by sulphur dioxide, and by the escaping gas blackening lead acetate paper. The hydrogen selenide in rain water and snow is probably in combination with another constituent.

C. A. M.

**Assay of Molybdenum Ores and Concentrates. H. C. Mabee.** (*Eng. and Min. J.*, 1918, **105**, 836-837; through *J. Soc. Chem. Ind.*, 1918, **37**, 307A.)—From 0.5 to 1 gm. of the sample is treated with 2 to 3 c.c. of fuming nitric acid in a silica or platinum crucible of 50 c.c. capacity, and the mixture evaporated just to dryness. The residue is fused with 30 grms. of potassium bisulphate, the product extracted with hot water and heated till completely dissolved, and the iron precipitated with

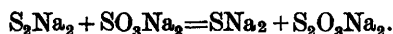
ammonia. The washed precipitate should be dissolved and reprecipitated. Fifty c.c. of sulphuric acid (1 : 1) are added to the filtrate, which is passed through a 24-inch reductor into a 1-litre flask, using suction. The reductor contains 10-mesh zinc previously washed with hot sulphuric acid (1 : 1); 20 c.c. of 15 per cent. ferric alum solution and 20 c.c. of "titrating mixture" are placed in the receiver. After the molybdenum solution has been drawn through the reductor, the latter is washed at least four times with hot sulphuric acid (1 : 1); the solution is titrated warm with permanganate standardised against pure molybdenum trioxide, following the same procedure as in the actual determination.

**Estimation of Sodium and Potassium. S. W. Rhue.** (*J. Ind. and Eng. Chem.*, 1918, 10, 429-431.)—The sample, contained in a porcelain dish, is covered with 25 per cent. sulphuric acid, evaporated to dryness on the steam-bath, and charred completely on the hot plate, and finally incinerated over an open flame. The ash is digested with hot dilute hydrochloric acid, the solution filtered, almost neutralised with ammonia, and enough magnesia mixture is added to precipitate phosphates. After fifteen minutes, 5 to 10 c.c. concentrated ammonia are added and the mixture allowed to stand overnight. The precipitate is filtered off, washed with dilute ammonia, and the filtrate and washings are mixed with 20 c.c. of nitric acid and a little hydrochloric acid, evaporated to dryness on the hot plate, and heated to expel acid. The residue is dissolved, treated with sufficient barium hydroxide to precipitate all the magnesia present, and the precipitate filtered off and washed with hot water. The filtrate and washings are made ammoniacal, boiled, and barium and calcium are precipitated by addition of ammonium carbonate and oxalate. After two hours the liquid is filtered, the precipitate washed with hot water, and 5 c.c. of ammonium sulphate solution (7 to 8 per cent.) added to the filtrate and washings, which are then evaporated to dryness. The residue is dissolved in water, transferred to a small platinum dish, evaporated to dryness, and heated carefully to dull redness. The residue is redissolved in hot water, and the solution is filtered into a tared platinum dish, evaporated to dryness, and the residue of potassium and sodium sulphate is heated to constant weight.

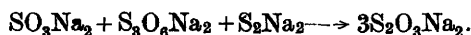
For the estimation of potassium, the ash is prepared and digested as described above, the solution rendered ammoniacal, boiled, and filtered. The filtrate and washings are treated with ammonium oxalate to precipitate calcium, and the calcium oxalate filtered off next day and washed with dilute ammonia. Nitric acid (20 c.c.) and a little hydrochloric acid are added, and the mixture evaporated to dryness and heated to expel acid. The residue is dissolved in hot water and a few drops of hydrochloric acid, and the solution is filtered, treated with chloriplatinic acid, and evaporated almost to dryness. A few c.c. of 80 per cent. alcohol is added, and the precipitate brought on to a filter and washed, first with 80 per cent. alcohol and then with 20 per cent. ammonium chloride solution saturated with potassium platinichloride, until all white or pale orange matter is dissolved. Calcium and magnesium chlorides are much more readily washed out than the corresponding sulphates which have to be removed at this stage when following the A.O.A.C. official method. The precipitate is finally washed once more with 80 per cent. alcohol to remove ammonium

chloride, and is then dissolved in hot water and the solution evaporated in a tared platinum dish and heated to constant weight at 105° C. G. C. J.

**Estimation of Thiosulphuric, Sulphurous, Trithionic, and Sulphuric Acids in Admixture.** O. Billetter and B. Wavre. (*Helvetica Chim. Acta*, 1918, 1, 174-180.)—Sulphurous and thiosulphuric acid may be estimated together iodimetrically, and the sulphurous acid then estimated by a method based on the reaction—



This reaction takes place rapidly at about 100° C., and the end-point is the persistent yellow colour produced by excess of the reagent. The addition of ammonium chloride accelerates the reaction. The sodium bisulphide is prepared by saturating  $\frac{N}{1}$  sodium hydroxide solution with hydrogen sulphide, removing the excess of gas under diminished pressure, adding an equal volume of  $\frac{N}{1}$  sodium hydroxide solution, and dissolving in the hot liquid 16 grms. of sulphur which has been purified by crystallisation from carbon bisulphide. Throughout the preparation air is excluded by a current of inert gas. The solution is standardised by adding 20 c.c. to a solution containing sodium acetate, and a slight excess of acetic acid, boiling off the hydrogen sulphide in a current of carbon dioxide, collecting the sulphur on a filter of tared glass wool, and drying it in an exhausted desiccator. The small amount of thiosulphuric acid in the filtrate is titrated with iodine, and the correction applied to the weight of the sulphur. The volume of the sulphurous acid solution to be titrated ought not to exceed 100 c.c. for 5 c.c. of the reagent, and the liquid should contain at least 5 c.c. of a  $\frac{N}{2}$  solution of ammonium chloride per 100 c.c., and be slightly alkaline (4 c.c. of  $\frac{N}{1}$  sodium carbonate solution per 50 c.c.). During the titration a current of carbon dioxide should be passed over the surface of the liquid. The result of the titration may be controlled by iodimetric estimation of the thiosulphuric acid formed in the reaction. Trithionic acid is not affected by iodine in the cold, but reacts with sodium sulphide to form sodium thiosulphate— $\text{S}_3\text{O}_6\text{Na}_2 + \text{SNa}_2 = 2\text{S}_2\text{O}_3\text{Na}_2$ . This reaction takes place rapidly on heating. For estimating trithionic acid the dilute solution is heated for a few minutes with a slight excess of sodium sulphide or bisulphide (separation of sulphur) nearly to boiling-point, in presence of ammonium chloride, and is then treated with sodium acetate and a slight excess of acetic acid, heated for fifteen minutes in a current of carbon dioxide, and titrated with  $\frac{N}{10}$  iodine solution. In the case of a mixture of sulphite and trithionate simultaneous conversion of the two compounds into thiosulphate is effected by the sodium bisulphide, so that the reactions take place practically as one—



The presence of an excess of trithionate is indicated by the appearance of a turbidity (due to sulphur) after the conversion of the whole of the sulphite. The end-point in the titration of sulphurous acid with bisulphide is not affected by the presence of trithionate. Another method of estimating trithionic acid is to heat the liquid with excess of iodine solution under pressure (after titration of the sulphite and thiosul-

phate with iodine in the cold). This converts both the trithionate and the tetrathionate from the previous titration into sulphate. Or a method may be based on the decomposition of trithionic acid when heated—



For this purpose the solution is acidified with hydrochloric acid, and heated near the boiling-point in a current of carbon dioxide until sulphur dioxide is no longer evolved, after which the sulphur is filtered off, and the sulphuric acid precipitated with barium chloride. Under these conditions 97.5 to 98 per cent. of the trithionic acid is converted into sulphuric acid. In the case of mixtures of the four acids the total sulphur is estimated by oxidation with bromine water and precipitation with barium chloride. The difference between the total sulphur and the amounts of sulphur as thiosulphuric, sulphurous, and trithionic acid corresponds with the sulphuric acid. C. A. M.

**Rapid Estimation of Tungsten.** F. W. Foote and R. S. Ransom, jun. (*Eng. and Min. J.*, 1918, 105, 836; through *J. Soc. Chem. Ind.*, 1918, 37, 307A.)—One grm. of finely powdered ore is mixed with 1.2 grms. of a mixture of calcium carbonate and sodium chloride (1 : 1) in a porcelain crucible, and heated gently at first, then with the full heat of a Bunsen burner. The cold mass is transferred to a dish and digested on a water-bath with 40 c.c. of strong hydrochloric acid; 15 c.c. of nitric acid are added and the liquid concentrated to 15 c.c. after fifteen minutes' digestion. It is diluted with 100 to 125 c.c. of boiling water, allowed to stand two to three hours, filtered, and the precipitate washed three times with 2 per cent. hydrochloric, and twice with 2 per cent. nitric, acid. The residue of tungstic acid and silica is treated as usual.

**Gravimetric and Volumetric Determination of Zinc precipitated as Zinc Mercury Thiocyanate.** G. S. Jamieson. (*J. Amer. Chem. Soc.*, 1918, 40, 1036-1039.)—According to a method described by Lundell and Bee (*J. Soc. Chem. Ind.*, 1914, 33, 967), zinc in alloys is determined as zinc mercury thiocyanate, after removal of the copper by electrolysis, by precipitation with a reagent containing 39 grms. of potassium thiocyanate and 27 grms. of mercuric chloride per litre, 25 c.c. of the reagent being used for 100 c.c. of the zinc solution. The amount of free acid in the zinc solution should not exceed 5 per cent. The presence of cadmium, cobalt, copper, bismuth, manganese, and mercurous compounds interferes with this method, as those metals give insoluble double thiocyanates; nickel in small amounts does not interfere appreciably; when ferric compounds are present in appreciable quantities they should be reduced with sulphur dioxide, otherwise the zinc precipitate will be coloured. Excellent results are obtained by employing ammonium thiocyanate instead of potassium. By the gravimetric method the solution of zinc salt is treated with 20 to 25 c.c. of the reagent and 20 c.c. of water. The solution is vibrated by striking the side of the beaker with a rod to facilitate the separation of the crystals. After standing for about five minutes the solution is briskly stirred with a glass rod, previously moistened with water, for about a minute, and then allowed to stand for at least an hour before filtration. The precipitate is collected in a Gooch crucible and washed

four or five times with a solution containing 10 c.c. of the thiocyanate reagent with 490 c.c. of water. The precipitate is dried at 102° to 108° C. for an hour and weighed; it is anhydrous, having the composition corresponding to  $\text{ZnHg}(\text{SCN})_4$ , and the zinc factor is 0.13115. The results are perfectly accurate.

The volumetric method is based on the titration of the precipitate with potassium iodate solution in the presence of strong hydrochloric acid and an immiscible solvent. The zinc mercury thiocyanate is precipitated as described above, and the precipitate is collected on a washed filter, 7 cms. diameter, with a gentle suction, and washed four or five times with small quantities of the washing solution. The washed precipitate with the filter is placed in an 8-ounce stoppered titration bottle. A thoroughly cooled mixture of 35 c.c. of concentrated hydrochloric acid and 10 c.c. of water, with 7 c.c. of chloroform, is added to the precipitate in the bottle, and the liquid is at once titrated with a solution containing 39.2882 grms. of potassium iodate per litre. At first the iodate solution is run in rapidly while rotating the bottle. When the iodine liberated in the first stage of the reaction has disappeared from the solution, the stopper is inserted and the contents of the bottle are thoroughly shaken for half a minute. Afterwards, the iodate is added slowly and the bottle shaken after each addition until the iodine colour has disappeared from the chloroform solution, which marks the end-point. If more than 50 c.c. of potassium iodate solution are required, 10 to 15 c.c. more of the strong hydrochloric acid are added to prevent the hydrolysis of the iodine monochloride which is formed during the reaction. One c.c. of iodate solution is equivalent to 0.002 gm. of zinc. The results are extremely satisfactory. This method has been applied to the analysis of commercial zinc arsenite. About 0.2 gm. of the sample is dissolved in 3 c.c. of strong hydrochloric acid, 10 c.c. of sulphurous acid solution are added, and the excess of sulphur dioxide is expelled by heating on the water-bath; after cooling, the precipitation and titration are performed as above, the arsenious acid having no ill-effect on the accuracy of the estimation.

J. F. B.