

## INORGANIC ANALYSIS.

**The Estimation of Cadmium as Oxide.** By Philip E. Browning and Louis C. Jones. (*Zeits. Anorg. Chem.*, xiii., 2 and 3, p. 110.)—The authors have repeated Muspratt's methods for the estimation of cadmium as oxide, and show that the inaccuracies which he found, owing to reduction of the oxide, can be avoided, and the precipitation of the element as carbonate and conversion into oxide serves as a reliable method for the determination of cadmium.

The authors operated on quantities of cadmium sulphate corresponding to from 0.1140 to 0.2555 gramme cadmium oxide. They proceeded in the following manner: Weighed quantities of cadmium sulphate were dissolved in hot water, diluted to about 300 c.c., and a 10 per cent. solution of potassium carbonate was slowly added, and the solution shaken constantly, until no further precipitation took place; the solution was then boiled for fifteen minutes, and the precipitated carbonate converted into the crystalline form. The solution was then filtered into a Gooch crucible containing a layer of ignited asbestos, the precipitate, after careful washing, was dried, and heated to redness until constant. The authors show that the estimation yields reliable results, and that the process is much more expeditious than that proposed by Muspratt. The results are, however, liable to be a little too high, owing to the presence of small quantities of potassium carbonate.

H. C. L. B.

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**The Quantitative Estimation of Bismuth.** By W. Muthmann and F. Mawrow. (*Zeits. Anorg. Chem.*, xiii., 2 and 3, p. 209.)—The authors show that bismuth can be accurately estimated, as such, by precipitation with hypophosphorous acid,

\* Franke apparently referred to the original form of the Jodlbauer process (cf. ANALYST, xxi., 164), which the present author objects to on the ground of its being too tedious.—ABS.

and they state that their method in many cases exceeds, in accuracy and speed, those hitherto known. The experiments were carried out with bismuth oxychloride, which was suspended in a little water, and solution effected by the addition of a few drops of hydrochloric acid.

The following procedure is recommended as yielding the best results :

To the somewhat concentrated, but not too strongly acid, solution is added an excess of hypophosphorous acid, and the solution warmed on the water-bath until the supernatant liquid is clear ; the solution should then be heated to the boiling-point, and a further addition of the reagent should cause no further coloration. The metal separates as a reddish-gray spongy mass (which is readily filtered and washed) ; this is collected either upon a weighed filter-paper, or in a Gooch crucible, washed first with boiling-water, and then with absolute alcohol, and dried at 105°.

The filtrate should be tested for bismuth with hydrosulphuric acid, when a slight brown coloration will be obtained if the solution has not been warmed sufficiently long.

The method, it is claimed, serves also for the separation of bismuth from such metals as lime and cadmium, which are not precipitated by hypophosphorous acid.

H. C. L. B.

**The Separation of Vanadium from Arsenic.** C. Field and E. F. Smith. (*Jour. Amer. Chem. Soc.*, 1896, xviii., 1051, 1052).—The method is based on the difference in volatility of the sulphides of vanadium and arsenic, when heated in an atmosphere of hydrochloric acid gas, the latter being completely expelled at a temperature little above 150° C., whilst the brown vanadium sulphide is not altered. In the experiments the results of which are given below both sulphides were in perfectly dry condition, and the temperature was not allowed to exceed 250° C. :

Taken.		Left.
Vanadium Sulphide.	Arsenic Sulphide.	Vanadium Sulphide.
Gramme.	Gramme.	Gramme.
0·1303	0·1302	0·1297
0·1290	0·2242	0·1297
0·0828	0·0582	0·0827
0·1306	0·2028	0·1308
0·1403	0·2409	0·1404

The following course was adopted in the analysis of a specimen of vanadinite : 0·2500 gramme of the air-dried and finely-divided mineral was placed in a porcelain boat, which was gently heated in a combustion-tube in a current of dry hydrochloric-acid gas. This treatment expelled vanadic and arsenic oxides, leaving lead phosphate and chloride. The receiver containing the vanadium and arsenic was made alkaline and digested with ammonium sulphide, and from the solution of the sulpho-salts the sulphides were set free by a dilute acid. After washing and drying, the sulphides were separated in the manner indicated above, then converted into oxides, and determined in the usual way. The sum of the constituents determined as lead oxide, phosphoric oxide, vanadic and arsenic oxides, with some lead chloride, amounted to 0·2501 gramme.

C. A. M.

**The Separation of Manganese from Copper and Zinc, and of Copper from Zinc and Nickel, etc.** P. Jannasch. (*Zeit. f. anorg. Chem.*, xii., 2, 134-142.)—

1. Separation of manganese from zinc.—Dissolve about 0.4 gramme of the substance under examination in 10-15 c.c. of water slightly acidulated with hydrochloric acid. Add 15 c.c. of glacial acetic acid, and pour drop by drop, with constant stirring, into a mixture of 40-50 c.c. concentrated ammonia and 30-40 c.c. hydrogen peroxide (3 per cent.). Cover and heat on a water-bath for fifteen minutes. Filter off the precipitate, wash with concentrated and then with dilute ammonia, and finally with warm water. It is then absolutely free from zinc, which latter may be estimated in the filtrate.

2. Manganese from copper.—Proceed precisely as in 1, using, however, a mixture of 60 c.c. ammonia and 50 to 60 c.c. hydrogen peroxide. Heat for half an hour, filter off and wash several times by filling up the filter with a warm solution (30 per cent.) of ammonium acetate in strong ammonia. Then wash with ammonia alone, and finally with hot water.

The copper is estimated in the filtrate by any of the usual methods, or, if preferred, it may be removed from the solution first either (1) by hydrogen sulphide, or (2) by potassium or ammonium sulphocyanide. In the first case the author advocates the use of sulphuric acid, as above, instead of hydrochloric. After filtering off the copper sulphide evaporate the filtrate to get rid of  $\text{SH}_2$ , and then pour into a mixture of 30 c.c. strong ammonia, and 30 c.c. hydrogen peroxide, and treat as already described. If the copper is precipitated as sulphocyanide, destroy the excess of the precipitate in the filtrate in the usual manner with hydrochloric and nitric acids, and determine the manganese as already described.

The hydrogen peroxide method has yielded excellent results in the author's hands, and its advantages, as compared with methods in common use, are discussed at some length.

C. H. C.

**The Valuation of Borax.** J. G. Heid. (*Zeit. angew. Chem.*, 1896, 679.)—The usual commercial method is to separately determine the various impurities and deduct the sum of these from 100, the difference being taken as the amount of crystallized sodium diborate ( $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ ). Since the amount of various impurities is frequently very great, the analysis often requires a long time, and in consequence the author has devised the following method:

Ten grammes of the borax are dissolved in 250 c.c., and the sodium chloride estimated gravimetrically in an aliquot portion of the solution. A second portion (25 c.c.) is diluted with water in a flask, and boiled with an excess of hydrochloric acid for five minutes. The liquid is then evaporated to dryness on the water-bath, and the sodium chloride in the residue determined. From the result that previously found is deducted, and the difference calculated into the equivalent of sodium diborate.

C. A. M.

**The Use of Boric Acid in the Analysis of Silicates.** P. Jannasch. (*Zeit. f. anorg. Chem.*, xii., 3, 208-218.)—The process consists in fusing the mineral with finely powdered boric acid, and subsequently removing the latter by repeated evapora-

tion with methyl chloride. The pure boric acid, free from alkalis, is prepared by recrystallizing the commercial salt, first from 2 to 3 per cent. hydrochloric acid, and then from water. It is dried, fused, and powdered, as previously described (ANALYST, xx. 51).

The methyl chloride must be freshly prepared, as it seems to lose its efficiency after long keeping. For this purpose the author employs a wash-bottle with ground-in tubes, instead of the usual cork, into which he pours 250 c.c. of pure anhydrous methyl alcohol. A rapid current of hydrochloric acid gas is then passed through the cooled liquid for two or three hours.

The analysis is conducted as follows :

Mix in a crucible of 60-65 c.c. capacity 1 gramme of the powdered silicate with from three to eight times the quantity of boric acid, the proportion depending on the ease with which the substance is decomposed. Heat gently for five to ten minutes, then strongly, destroying any large bubbles that may be formed with a short platinum wire. When the formation of bubbles has almost stopped, cover the crucible, and continue heating, finally using a blowpipe flame. Place the hot crucible on a pipe-clay triangle immersed in cold water, weighting the lid as a further security against loss. Remove the contents, as far as possible, to a large platinum dish, soak in water, add hydrochloric acid, and evaporate to dryness. Now add about 60 c.c. of methyl chloride, wash down the sides of the dish with the same liquid, and evaporate at a temperature of about 75-80°. Repeat with fresh quantities of methyl chloride three or four times. Wash down the *outside* of the dish (which may have a slight incrustation of boric acid) with methyl chloride into a large clock-glass, and evaporate to dryness—no residue should be left.

The complete removal of the boric acid from the contents of the dish may be ascertained by placing a Bunsen burner near the water-bath, and fanning a little of the vapour towards the flame, which will exhibit the characteristic green colour if any boron compound is still being evolved. A clock-glass should be at hand to place over the dish should the vapour catch fire.

After the final evaporation with methyl chloride, heat the dish for an hour to 110° C., then add 5 c.c. of hydrochloric acid, and proceed in the usual manner.

The method previously described, although of almost universal application for the analysis of silicates is not applicable to the analysis of minerals of the Andalusite group. In the analysis of one of them ("cyanite") the author found treatment with calcium fluoride and hydrogen potassium sulphate, etc., quite unavailing; but, after various experiments, succeeded in effecting complete decomposition by the following means: The powdered material was put in a crucible with 10 c.c. of strong ammonia, diluted with water, and strongly acidulated with hydrofluoric acid, evaporated, fused for some time, the excess of ammonium fluoride being driven off. The silico-fluoride thus produced was treated with dilute sulphuric acid and evaporated, and the excess of acid driven off. The residue was then found to entirely dissolve in dilute hydrochloric acid.

The rest of the paper is occupied with the composition of the mineral in question.

C. H. C.

**The Iodometric Determination of Selenious and Selenic Acids.** J. F. Norris and H. Fay. (*Amer. Chem. Journ.*, 1893, xviii., 703-706).—It is claimed that the method here described requires fewer reagents, occupies less time, and gives more accurate results than that of Gooch and Peirce (*Am. J. Sci.*, i. [4] 31), hitherto considered the most suitable volumetric process. It depends on the reaction between sodium thiosulphate and selenious acid in the presence of hydrochloric acid, in which, although the complete reaction is not known, one molecule of selenious acid is exactly equivalent to four molecules of sodium thiosulphate.

*Determination of Selenious Acid.*—The selenious acid used in the test experiments was prepared by evaporating commercial selenium to dryness with concentrated nitric acid, reducing the dioxide thus obtained by sodium sulphite and hydrochloric acid, again oxidizing the selenium with nitric acid and subliming the residue. About two grammes of the selenious acid were dissolved in water and made up to 500 c.c., aliquot portions being taken for each determination.

The definite portion taken was diluted with ice-water and 10 c.c. of hydrochloric acid (1.12 sp. gr.), an excess of decinormal thiosulphate solution added and titrated back with standard iodine solution. The titration was not affected by a large excess of hydrochloric acid when the solution was cold. Results :

SeO <sub>2</sub> taken. gramme.	SeO <sub>2</sub> found. gramme.	SeO <sub>2</sub> taken. gramme.	SeO <sub>2</sub> found. gramme.
0.0829	0.0829	0.1366	0.1367
0.1242	0.1242	0.1656	0.1659
0.1242	0.1242	0.2070	0.2071

*Determination of Selenic Acid.*—The selenic acid was prepared by dissolving about two grammes of selenium dioxide in 200 c.c. of water, and adding a strong solution of potassium permanganate until a pink colour remained after heating for thirty minutes at 60° C. Sulphurous acid was then added until only a small amount of manganese dioxide remained, and the solution filtered and diluted to 500 c.c.

In making a determination 25 c.c. of concentrated hydrochloric acid were added to a definite portion of this solution, which was then diluted to 100 c.c. After being boiled for an hour, care being taken not to allow the volume to go below 75 c.c., the liquid was cooled, diluted with ice-water, and the selenious acid determined by titration. Results :

SeO <sub>3</sub> taken. gramme.	SeO <sub>3</sub> found. gramme.	SeO <sub>3</sub> taken. gramme.	SeO <sub>3</sub> found. gramme.
0.1011	0.1009	0.1598	0.1595
0.1067	0.1067	0.2023	0.2024
0.1067	0.1065	0.2665	0.2662

*Determination of a mixture of Selenious and Selenic Acids.*—Two portions of a solution containing known quantities of selenious and selenic acid were measured off. In one the selenious acid was determined by direct titration ; in the other the total selenium, after reduction of the selenic acid. Some selenium was precipitated on heating the solution during the reduction, but this dissolved when the chlorine was evolved. Results :

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SeO <sub>2</sub> taken. gramme.	SeO <sub>2</sub> found. gramme.	SeO <sub>3</sub> taken. gramme.	SeO <sub>3</sub> found. gramme.
0·0467	0·0467	0·1013	0·1015
0·0467	0·0466	0·1013	0·1016
0·1868	0·1865	0·1012	0·1015

The reagents used in the test experiments were all carefully purified. Resublimed iodine was sublimed from one-third its weight of potassium iodide, and dissolved in potassium iodide free from iodate. The sodium thiosulphate was purified by recrystallization, and the solution standardized with resublimed iodine and pure sodium arsenite.

C. A. M.

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**Alcohol as a Source of Error in Volumetric Analysis.** L. F. Kebler. (*Amer. Jour. Pharm.*, 1896, lxviii., 667-673.)—Referring to Caspari's paper (*ANALYST*, xxi., 293), the author describes experiments which prove the correctness of the conclusions there stated as to the disturbing influence of commercial alcohol in volumetric analysis, but it is further shown that absolutely pure alcohol does not so interfere, except in the case of methyl orange and tropæolin OO. Absolute alcohol was prepared by repeated fractional distillation from commercial alcohol which had been made faintly alkaline with potassium hydrate, and with the purified product thus obtained, the results on titrating alkaloids and alkaloidal residues in alcoholic solution were as accurate as those found in aqueous solution.

C. A. M.

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 APPARATUS.

**A New Baryta Tube.** H. C. Geelmuyden. (*Zeit. anal. Chem.*, 1896, xxxv., 516, 517.)—In estimating the amount of carbon dioxide in the air by Pettenkofer's method of drawing a known volume of the latter through a tube containing standard baryta water, and titrating an aliquot portion of this with acid after the absorption, it may easily happen that the baryta water changes in volume during the experiment, especially when this is long continued. As a remedy for this, the author has constructed a tube on the principle of the Gay-Lussac burette, which during the absorption is placed almost horizontally, with the open ends of the tubes bent upwards. The wide tube is graduated, and the volume of baryta water is read before and after the absorption, the tube being placed in a vertical position during the readings.

C. A. M.