of the conductance of solutions when low voltages are being used and means for the discovery and elimination of this error are explained.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE PREPARATION OF ANTIMONY-FREE ARSENIOUS OXIDE AND THE ESTIMATION OF MINUTE AMOUNTS OF ANTIMONY IN ARSENIOUS OXIDE

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In the preparation of arsenious oxide of a high degree of purity, antimonous oxide is, by far, the most troublesome of the impurities to remove. Chapin[1] seems to be the first to call attention to the importance of this impurity and has given a method for removing it. He points out that it is impossible to accomplish this by the usual methods of purification such as recrystallization and sublimation; indeed, he states that it is entirely possible after recrystallization and sublimation to end with a "purified" arsenious oxide more impure than the original material. On the other hand a number of careful workers have regarded these methods as sufficient. Washburn,[2] in his investigation of the theory and practice of the iodimetric determination of arsenic acid, purified arsenious oxide by recrystallization from hot water and by sublimation. Baxter and Coffin[3] in their work on the revision of the atomic weight of arsenic say, "commercial C. P. arsenious oxide was recrystallized three times from dilute hydrochloric acid solution and after being rinsed with water and centrifugally drained, it was converted into arsenic acid by means of nitric and hydrochloric acid in a porcelain dish," and "arsenious oxide was twice resublimed in a current of dry air and then once recrystallized from dilute hydrochloric acid solution."

In the present investigation Chapin's work was repeated and his method found to be all he claimed for it, but inadequate if the product is to be used in atomic weight determinations or other precise work. The following proposed method is shorter and is believed to effect not only the complete removal of antimony but to a very large extent that of all other impurities as well.

Briefly stated the new method consists in converting arsenious oxide into arsenious chloride which is then repeatedly shaken out in a separatory funnel with concentrated hydrochloric acid to remove antimony. The arsenious chloride is next hydrolyzed with water to give arsenious oxide

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[1] Chapin, *J. Ind. Eng. Chem.*, **10**, 522–524 (1918).

[2] Washburn, THIS JOURNAL, **30**, 31–46 (1908).

[3] Baxter and Coffin, *ibid.*, **31**, 297 (1909).

again, which then may be subjected to the usual methods of purification such as recrystallization and sublimation.

Preparation of Arsenious Chloride.—Arsenious chloride is usually prepared by distilling a hydrochloric acid solution of arsenious oxide in a current of hydrogen chloride gas. This distillation method has been used by a large number of workers for the detection and estimation of arsenic and has been most recently studied by Roark and McDonald,[4] who give it as an effective means of separating arsenious chloride from antimony, lead, copper, zinc, iron and calcium. The present writers find, however, that unless the arsenious chloride is redistilled several times, it still contains traces of antimony.

The apparatus used for the preparation of the arsenious chloride consists of a one-liter pyrex distilling flask connected to an ordinary condenser. The condenser is provided with an adapter reaching nearly to the bottom of a 700-cc. Erlenmeyer flask used as a receiver and kept cool with ice.

In a typical experiment a solution of 150 g. of arsenious oxide in 350 cc. of concentrated hydrochloric acid was distilled in a current of hydrogen chloride gas from a suitable generator.[5] The distillate consists of two layers, oily arsenious chloride and hydrochloric acid. As distillation proceeds the distilling flask is recharged from time to time wth arsenious oxide until the desired amount of arsenious chloride is obtained.

Removal of Antimony from the Arsenious Chloride.—It was discovered that antimonous chloride is much more soluble in concentrated hydrochloric acid than in arsenious chloride and hence can easily be removed from the arsenious chloride by repeatedly shaking with portions of concentrated hydrochloric acid and subsequent separation of the two layers. So great is the difference in the solubility of antimonous chloride in the two layers that the shaking out with only a few portions of acid will remove completely a considerable amount of antimonous chloride. The procedure is as follows.

To the oily arsenious chloride in a separatory funnel is added two-thirds of its volume of concentrated hydrochloric acid and the separatory funnel shaken one minute. (The arsenious chloride layer will be diminished in volume about 10% due to its solubility in the acid.) The lower layer is now carefully drawn off and the shaking out process repeated with a fresh portion of acid until the acid layer shows no antimony by the following test.

Test for Antimony.—In order to test the acid layer for antimony it is

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[4] Roark and McDonald, *J. Ind. Eng. Chem.*, **8**, 327 (1916).

[5] The hydrogen chloride generator used in this work was of the type developed by Sweeney, THIS JOURNAL, **39**, 2186–2188 (1917). However, if preferred, the concentration can be kept up just as effectively by frequent additions of concentrated hydrochloric acid direct to the distilling flask.

transferred to the distilling apparatus and heated only as long as any oily arsenious chloride which it holds in solution distils over. The residue in the distilling flask is then transferred to a beaker and treated, while still hot, with hydrogen sulfide. All of the arsenic remaining in the acid is precipitated as yellow arsenious sulfide, leaving antimony in solution. The precipitate is filtered off using a double filter paper, on account of the action of the strong acid, and the filtrate diluted with three times its volume of water and again saturated with hydrogen sulfide. Under these conditions, antimony, if present, will come down as orange antimonous sulfide. In the detection of small amounts of antimony, however, the solution should be allowed to stand for a day or two after passing in hydrogen sulfide, for sometimes an orange-colored turbidity may later develop into a distinct precipitate.

The advantage of this method lies in the fact that the antimony can be removed from very large amounts of arsenious oxide, thus permitting the detection of less than 0.001%. Furthermore, when the amount of antimony is very small a fairly good quantitative determination can be made by comparing the precipitated sulfide with a series of similarly prepared precipitates of known amounts of antimony. The following is a typical experiment with the method.

By means of a dilute standard solution, 3.7 mg. of antimonous chloride was added to 300 g. of arsenious chloride, free from antimony. This is at the rate of one part of antimony in 150,000 of the chloride or in 160,000 of the oxide. The arsenious chloride was then shaken once with two-thirds of its volume of concentrated hydrochloric acid. The acid was then distilled until no more oily drops of arsenious chloride could be seen passing over.[6] The residual acid in the distilling flask was next treated with hydrogen sulfide as described above and after removing the sulfide of arsenic the solution was diluted and again saturated with hydrogen sulfide. An orange-colored precipitate was obtained slightly less in bulk than that from 3.7 mg. of antimony trichloride precipitated in the same way, that is, by saturating its concentrated hydrochloric acid solution with hydrogen sulfide, diluting and again passing hydrogen sulfide into it.

Arsenious Oxide by Hydrolysis of the Chloride.—Having obtained antimony-free arsenious chloride, the final step of converting it into the oxide is accomplished simply by allowing the chloride to run slowly from a separatory funnel into a large beaker of boiling water with vigorous stirring. On cooling, arsenious oxide separates as a fine white solid and after being filtered and washed free from acid it can be further purified if desired by recrystallization and sublimation.

[6] The usual situation will be the detection of antimony in arsenious oxide in which case, if only a trace of antimony is suspected, 100 g. of the oxide is converted into the chloride by the method described above and the residual acid solution in the distillation flask is then examined for antimony.

Summary

A rapid and simple method for the preparation of antimony-free arsenious oxide has been described, and also an application of this method to the qualitative detection and rough quantitative estimation of minute amounts of antimony in arsenious oxide.

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NOTE

An Inexpensive Pyrex Conductivity Cell.—Because of its small thermal expansion and its chemical resistance, pyrex glass is most suitable for the construction of conductivity cells, hydrogen electrodes and similar apparatus. Unfortunately there is considerable difficulty in making satisfactory seals of platinum to pyrex. The writer recently required a conductivity cell which would be gas tight at five atmospheres' pressure and withstand the action of solutions of sulfur dioxide, so that a pyrex cell seemed advisable if it could be constructed. The makers of pyrex were not able to recommend any suitable method of construction but eventually by making use of the suggestions of Housekeeper[1] a suitable cell was made. As the cell is easily and cheaply made and as the construction may be readily modified for other uses, it is described herewith.

The essential point in the construction is that platinum foil, *if sufficiently thin*, may be fused firmly onto the surface of any glass. The cell used by the writer was in the form of a tube about one centimeter in inside diameter with electrodes about six by twenty millimeters spaced about ten centimeters apart. The platinum foil used was a piece recovered as salvage from a platinum resistance furnace and was in the form of a ribbon 6 mm. wide by 0.7×10^{-3} mm. thick. Somewhat heavier foil would probably be satisfactory but was not tried. A piece of this foil was cut approximately as shown at A and the 1-cm. pyrex tube had a three-millimeter side tube attached, as shown at B. The piece of foil was then put in so that the narrow tail extended into the side tube while the wider portion was bent around the inside of the large tube as shown by the dotted line in B and C. The wide tube was then heated to softening and the foil gently pressed into contact with the softened glass, a heavy piece of platinum wire being used to do the pressing. After this portion of the foil had been attached, the side tube was heated at the junction with the large one until it fell in on the foil. A gentle pinch with the tongs when the glass was soft ensured a tight joint. Enough of the tail projected

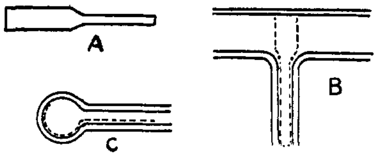

Fig. 1.

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[1] Housekeeper, *J. Am. Inst. Elec. Eng.*, **42**, 954 (1923).