ART. XLIV.—*The Detection and Separation of Arsenic associated with Antimony and Tin;* by F. A. GOOCH and B. HODGE.

[Contributions from the Kent Chemical Laboratory of Yale College—XXIX.]

UPON the well known fact that hot strong hydrochloric acid is capable of dissolving the sulphides of antimony and tin while exerting solvent action to a very slight degree upon arsenious sulphide is based the simplest and most rapid method in common use for the separation of arsenic from antimony and tin. Unfortunately, however, the forcible treatment necessary to bring about the solution of large amounts of antimony is sufficient* to dissolve small quantities of arsenious sulphide, so that for the purposes of general analysis the method is inadequate. Koehler† has shown that only the arsenic is precipitated, and that very completely, when hydrogen sulphide acts upon the solution of arsenious and antimonious salts in hydrochloric acid of 20 per cent strength, but

* Rose-Finkener, Anal. Chem., ii, 423.
† Zeit. für Anal. Chem , xxix, 192.

the adaptability of Koehler's treatment to the detection of arsenic in the ordinary course of analysis is limited by the necessity of so constituting the solution to be tested that hydrogen sulphide shall occasion no deposit of free sulphur to conceal or be mistaken for a precipitation of arsenious sulphide. In the course of analysis the mixed sulphides of arsenic, antimony, and tin, remaining after the removal of the sulphides insoluble in alkaline sulphides and recovered from solution by the action of hydrochloric acid, require for their complete solution the action of an oxidizing agent which must, of course, interfere with the immediate use of Koehler's method. If simple means can be found for the destruction of the excess of the oxidizing agent and the simultaneous reduction of the arsenic and antimony to the lower condition of oxidation, it is plain that the test for arsenic by passing hydrogen sulphide into the solution of antimony and tin in hot hydrochloric acid of half-strength should be sure and easy. In a former paper from this laboratory* a method was described for the quantitative separation of arsenic from antimony, based upon the reduction and volatilization of salts of arsenic by the action of a current of gaseous hydrochloric acid upon the solution containing potassium iodide. It is this reaction—the reduction of arsenic and antimony and the volatilization of the former by the simultaneous action of potassium iodide and hydrochloric acid—which we have now endeavored to apply in simple form to the rapid detection of small amounts of arsenic associated with antimony and tin. We have studied the effect of repeated distillations of small portions of concentrated hydrochloric acid upon mixtures of the salts with potassium iodide. The apparatus which we employ is essentially the distillation apparatus of Mohr, and consists of a 25cm³ flask fitted by means of a rubber stopper to a pipette bent, drawn out at the lower end, and dipped into a test tube which is at the same time supported and cooled in a flask partly filled with water. The pipette tube is wide enough (about 0·7^{cm} in diameter) to prevent the formation of bubbles within it, and the bulb, holding about 20cm³, is sufficiently large to retain any liquid which may be momentarily forced back by the accidental cooling of the flask during the distillation.

In the test experiments recorded below the arsenic was introduced into the flask in the form of arsenic acid dissolved with 3 grm. of potassium iodide in 5cm³ of water, an equal volume of the strongest hydrochloric acid (sp. gr. 1·20) was added, the distillation was carried nearly to dryness, and the distillate was

* Gooch and Danner, this Journal, xlii. 308.

condensed in 10cm³ of a mixture of strong hydrochloric acid and water in equal parts. The iodine evolved during the distillation was bleached by the addition to the distillate of stannous chloride dissolved in hydrochloric acid of half-strength, and hydrogen sulphide was passed to precipitate the arsenic if present. The residue in the flask was treated with 10cm³ of the strongest hydrochloric acid and the process of distillation was repeated, but this time the distillate was condensed in 10cm³ of water in order that the final acidity of the liquid should be that of acid of half-strength, and so, after bleaching by stannous chloride, immediately available for the test for arsenic by hydrogen sulphide. Subsequent treatments of the residue were carried out similarly until arsenic ceased to appear in the distillate.

The results of experiments (1) to (5) show that four successive distillations of 10cm³ portions of the strongest acid are enough to transfer 0·01 grm. of arsenic completely to the distillate, while a single distillation appears to be sufficient to volatilize anything less than 0·003 grm.

Experiments (6) to (9) made similarly with antimony, taken in the form of purified tartar emetic and oxidized by iodine in alkaline solution previous to treatment, either alone or with arsenic, show that antimony is discoverable in the residues when even so little as 0·0001 grm. of that element is originally introduced, though it was very evident that a portion of the antimony may pass to the distillate when much of it is present in the flask. Indeed when large quantities of antimony are treated the appearance of the brownish-red fumes of antimonious iodide in the distilling tube may serve as a very good indication that the concentration should go no further, since the antimonious iodide may, if it reaches the receiver in quantity, impart to the distillate a color which is not discharged, by the stannous chloride used to bleach the iodine and which makes it necessary to look subsequently for a precipitate of arsenious sulphide in a liquid of its own tint. The amount of antimony volatilized seems to be proportioned to the amount present, and, if the distillation is properly conducted, enough antimony remains in the residue to be found if it was originally present in discoverable quantity.

The results of similar work with tin alone, and with tin and arsenic, are recorded in experiments (10) to (15), and the evidence goes to show that, though like antimony it may pass to the distillate under the conditions, enough tin always remains to be found in the residue, if the amount originally taken was discoverable.

	Arsenic taken as H_3O_3AsO. grm.	Antimony taken as H_3O_3SbO. grm.	Tin taken as $SnCl_4$. grm.	Precipitation by H_2S in successive distillates.	Precipitation by H_2S in the residue dissolved in water.
(1)	0·0001	----	----	I. Found. II. None.	None.
(2)	0·0033	----	----	I. Found. II. None.	None.
(3)	0·0050	----	----	I.–III. Found. IV. None.	None.
(4)	0·0100	----	----	I–IV. Found. V. None.	None.
(5)	0·1000	----	----	I–VII. Found. VIII. None.	None.
(6)	----	0·0001	----	I. None.	Distinct color.
(7)	0·0050	0·0001	----	I–IV. Found. V. None.	Distinct color.
(8)	0·0001	0·4	----	I. Found. II. None.	Large.
(9)	0·0100	0·4	----	I–IV. Found. V. None.	Large.
(10)	----	----	0·0001	I. None.	Distinct color.
(11)	0·0100	----	0·0001	I–IV. Found. V. None.	Distinct color.
(12)	0·0001	----	0·0005	I. Found. II. None.	Distinct.
(13)	0·0100	----	0·0005	I–IV. Found. V. None.	Distinct.
(14)	0·0001	----	0·5	I. Found. II. None.	Large.
(15)	0·0100	----	0·5	I–IV. Found. V. None.	Large.

It is plain that a single distillation, which may easily be completed in five minutes, is sufficient to discover the presence of 0·0001 grm. of arsenic associated with so much as 0·4 grm. or 0·5 grm. of antimony or tin.

It is also evident that amounts of arsenic not exceeding 0·003 grm. may be completely removed from the residue by a single distillation. When larger amounts of arsenic are to be removed, so that the tin and antimony may be obtained free from that element, the result may be accomplished by repeating the distillation sufficiently; or, inasmuch as only a little iodine remains after the first distillation, the end may be attained by dissolving the residue in hydrochloric acid of half-strength, bleaching the iodine with exactly the necessary amount of sulphurous acid or sodium thiosulphate (since the use of the stannous chloride is here precluded), and passing hydrogen sulphide.