On standing, all three solutions became turbid, owing to a gradual separation of the zinc sulphide.

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THE DETERMINATION OF ANTIMONY AND ARSENIC IN LEAD-ANTIMONY ALLOYS.

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The separation and determination of antimony and arsenic in alloys with anything like commercial rapidity, and at the same time with a fair degree of accuracy, is by no means a simple matter. The apparent lack of satisfactory published methods led to the development several years ago of the method here described, which, while involving nothing radically new, has proved very serviceable in the author's laboratory.

One great advantage of this method is that tin does not interfere and does not have to be removed, which makes it available for type metal, etc. Iron and copper in small amounts are also without effect, and in fact there seems to be nothing at all likely to be present which interferes. The method is applicable also to many other cases besides lead-antimony alloys—as for instance to the mixed sulphides of antimony and arsenic obtained in many analyses. Some operators object seriously to any method involving the use of hydrogen sulphide, but if the details of manipulation here given are followed there will be no inconvenience whatever from that source.

The procedure is as follows:

The sample in fine filings, 0.5 to 2 grams according to circumstances, is weighed into a 125 cc. Erlenmeyer flask, 60–70 cc. of strong hydrochloric acid added, and two or three drops (not more) of nitric acid (1.4). The flask is then placed on a hot plate where it will be just short of boiling until solution is complete. Frequent agitation considerably hastens the action. It is sometimes necessary to make further additions of nitric acid, but this should be done carefully and an excess avoided. When the metal is all dissolved (10–20 minutes) the flask should be moved where it will boil vigorously for a few minutes until the color changes from reddish yellow to colorless—or, if iron or copper is present, to straw yellow. Now, while still hot, hydrogen sulphide is passed into the solution until it is completely saturated—15 minutes is usually sufficient. If insufficient hydrochloric acid has been used, or the solution has been boiled so long on the plate that much has been lost, antimony sulphide will be precipitated as the solution cools. The hydrogen sulphide treatment is most conveniently handled by fitting the flasks with two-hole stoppers and inlet and outlet tubes, and connecting several in series to the generator. If the outlet from the last flask is led into a bottle of caustic soda solution, no gas whatever comes off free. When saturated, the flasks are transferred to a current of air, still in series and again absorbing the gas from the last flask in caustic soda, and the air passed until all the hydrogen sulphide is removed (1/2 hour is sufficient for two flasks). The hydrogen sulphide precipitates nothing but arsenic as sulphide, but reduces all salts capable of reduction—antimony, tin, copper, iron, etc. The current of air then reoxidizes all of these except the antimony, which remains in the antimonious form.

To the now cold solution a little tartaric acid is added, and water until its bulk is about doubled, when it is filtered, best through a double filter, into a 16 oz. flask. Practically all of the lead chloride must be washed out of the precipitate with hot water, but it is not necessary to add all the washings to the filtrate, as the antimonious chloride is readily washed out by decantation with cold water.

Antimony.—The filtrate is nearly neutralized by adding powdered sodium carbonate in small portions, care being used not to reach the point of precipitation of the lead, or, if this is reached, making it slightly acid again with hydrochloric acid. The neutralization is then completed with sodium bicarbonate and a slight excess added (about one spoonful of powder). The antimony is then determined by titrating with standard iodine solution, using fresh starch solution as indicator. The precipitate of lead carbonate does not affect the titration, and with a little practice the end point can be recognized just as easily as in a clear solution. Too much starch should be avoided, as it makes the end point obscure. A convenient strength for the iodine solution is 1 cc. = 0.005 gram antimony; then with 0.5 gram samples 1 cc. = 1 per cent. antimony.

If arsenic is negligibly low—which, with a little experience, can be pretty well gauged by the appearance of the precipitate—or for any reason is not to be determined, the filtering may be dispensed with. In this case the whole solution, with the arsenious sulphide, if any, and free sulphur in suspension, is merely transferred to a larger flask, neutralized and titrated. The suspended arsenious sulphide and free sulphur are without effect.

Arsenic.—The bulk of the arsenious sulphide and sulphur is washed off the filter back into the same flask in which the precipitation was made, using not over 20 cc. or so of water. A few drops of sodium hydroxide are added (5 drops of 20 per cent. solution is ample), the solution boiled for a few moments and then decanted through the filter into an 8 oz. Erlenmeyer flask. This weak soda readily dissolves the arsenious sulphide, while taking up only a small part of the free sulphur. If the amount of precipitate is at all considerable, it is safer to give a second treatment with soda solution.

The filter is washed with hot water and discarded. To the filtrate is added hydrogen peroxide solution, which should be reasonably fresh, or else its strength known. 20 cc. of 3 per cent. solution is sufficient for arsenic up to several per cent. The hydrogen peroxide oxidizes the arsenic and also all sulphur compounds, giving a colorless solution. This is now boiled down to a small bulk, about 20 cc., the excess of peroxide being decomposed in the process. When cool, potassium iodide solution is added in amount equivalent to about 0.1 gram KI, then 20 cc. of strong hydrochloric acid. After standing five minutes it is cooled and titrated with standard thiosulphate, adding three drops of starch solution only when the color is almost gone. A convenient strength for the thiosulphate solution is 1 cc. = 0.001 gram arsenic, and it should, of course, be frequently standardized. It is well also to run a blank titration, using the same amounts of reagents as in the analysis, to determine whether there is any constant to be deducted from the burette reading, due to impurities in the reagents.

The difficulty with the end point experienced by many in this titration appears to be due to using too large an excess of potassium iodide and too much starch. With the proportions given above, the end point is exceedingly sharp, and the reaction seems to be just as complete as when more potassium iodide is used. The heating due to adding the strong hydrochloric acid is sufficient without any digesting, as is sometimes recommended.

After oxidizing and concentrating, the arsenic is in a form to be readily determined in several ways, although the above method is preferred on account of ease and rapidity. For instance, the arsenic may be precipitated with silver nitrate as silver arsenate, after neutralization with acetic acid, and the combined silver titrated with thiocyanate, as in the well known modified Pearce method. In this case care must be used to wash the sulphide free from lead chloride, and also to have all reagents free from chlorine (most of the hydrogen peroxide solutions on the market contain hydrochloric acid). Or, the arsenic may be determined gravimetrically by precipitation as ammonium magnesium arsenate. In this case it is better to use ammonia instead of sodium hydroxide to dissolve the arsenious sulphide.

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