#### WALKER: QUALITATIVE SEPARATION OF

# XVII.—Qualitative Separation of Arsenic, Antimony, and Tin.

### By JAMES WALKER.

THE following method for the separation of arsenic, antimony, and tin has been tested for more than a year in my laboratory, and has been found to give good results in the hands of moderately careful workers. It differs from the ordinary methods chiefly in this, that the tin is first separated from the arsenic and antimony, instead of being left as a residue, which frequently escapes detection if the tin was originally present in small quantity. As an alternative method, therefore, it may be found of service in many cases.

If the sulphides of arsenic, antimony, and tin are dissolved in caustic soda, and if the solution thus obtained is boiled with sodium peroxide, the sulphides pass ultimately into sodium arsenate, antimonate and stannate. Now stannic acid is a much feebler acid than either arsenic or antimonic acid-so feeble, indeed, that it is incapable of forming in solution, a stable salt with a weak base like ammonia. If, therefore, a solution containing sodium stannate is boiled with excess of ammonium chloride, double decomposition occurs, and the ammonium stannate which is produced decomposes with evolution of ammonia, stannic acid (stannic hydroxide) being at the same time precipitated. The sodium salts of arsenic and antimonic acids are not decomposed by ammonium chloride in this way, so that advantage may be taken of this difference in order to effect a separation of tin from arsenic and antimony. The separation is not quantitative, as a little antimony is usually found in the tin precipitate, but for qualitative purposes it is perfectly satisfactory. No trouble has been experienced from the formation of insoluble sodium metantimonate.

In order that the arsenic group may be in a state suitable for treatment with sodium peroxide, caustic soda (or potash) should be used to effect the separation of the sulphides of the copper from those of the arsenic group. In connection with this, the following points have to be noted. Firstly, stannous sulphide is often very imperfectly attacked by the caustic alkali. This difficulty may be overcome by

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adding a few drops of yellow ammonium sulphide to the caustic alkali used in treating the mixed sulphides. The accumulation of sulphur in the filtrate, which occurs when ammonium sulphide alone is employed in the separation, is thereby avoided, and subsequent operations are in consequence simplified. Secondly, mercuric sulphide readily dissolves in caustic soda when sulphides of the arsenic group are present. This solvent action is caused by excess of caustic soda reacting partially with the sodium thio-salts of the arsenic group to form sodium sulphide, in a solution of which mercuric sulphide is freely soluble. When such a solution, however, is boiled with sodium peroxide, the sodium sulphide is oxidised to sodium sulphate, and the mercuric sulphide is repre-Details of the actual operations are given in the following cipitated. paragraphs.

Separation and Oxidation of the Arsenic Group.—The precipitate of mixed sulphides is diluted with a little water in a porcelain basin, and caustic soda solution is gradually added to the hot liquid until no more precipitate seems to dissolve, any large excess of caustic soda being avoided. Three or four drops of yellow ammonium sulphide solution are then added, and the liquid boiled until it no longer smells of ammonia. The solution is now diluted with warm water, and the copper group precipitate filtered off and washed.

The filtrate contains the arsenic group and, possibly, mercury. After further dilution, it is heated to the boiling point in a porcelain basin, and sodium peroxide gradually added in small quantities to the gently boiling solution until there is a permanent effervescence of oxygen, showing that excess of peroxide is present. If mercury was contained in the alkaline solution, it now appears as a black precipitate of mercuric sulphide, which is filtered off and tested separately. The filtrate then contains only sodium arsenate, antimonate, and stannate.

Separation of Tin from Antimony and Arsenic.—The filtrate is transferred to a beaker and gently boiled after the addition of solid ammonium chloride; this salt must be in considerable excess, about three times the bulk of the sodium peroxide employed being generally sufficient. If tin is present, it separates as a white, gelatinous precipitate. A further amount of ammonium chloride is added to see if the precipitate increases in bulk, and boiling is continued for about five minutes in order that the precipitate may coagulate, after which it is collected. Greatly prolonged boiling is inadvisable, as the liquid then filters rather slowly. The precipitate should be washed with warm water containing in solution a little ammonium chloride.

Confirmation of Tin.—The precipitate is dissolved on the filter in a few drops of warm concentrated hydrochloric acid, a solution of stannic chloride being thereby produced. A portion of the solution

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may then be tested with sulphuretted hydrogen, which gives a yellow precipitate of stannic sulphide. The remainder of the solution should be reduced from the stannic to the stannous state, this operation being best effected by means of iron as recommended by Bloxim. Zinc is so strongly electropositive that it not only reduces the stannic compound to the stannous state, but precipitates metallic Copper, on the other hand, cannot precipitate the metal, being tin. electronegative to tin, but, in consequence, the reduction to the stannous state is slow. Iron is intermediate between these two metals, being close to tin in the electrochemical list, and slightly It therefore easily reduces stannic to stannous tin, but positive to it. does not readily precipitate metallic tin from the acid stannous In effecting the reduction, the stannic solution, strongly solution. acidified with hydrochloric acid, is heated to the boiling point with the iron. At first the solution assumes a vellow colour, owing to the formation of ferric chloride, but this colour disappears in a few moments and the reduction of the stannic compound proceeds. Unless iron filings are known to be pure, it is inadvisable to use them for the reduction. Iron wire acts well, though somewhat slowly. If rapid reduction is required, reduced iron (ferrum redactum) may be employed. With reduced iron, the operation does not take more than a minute; with iron wire, the solution should be allowed to stand for five minutes. After the excess of iron has been removed, by filtration if necessary, one portion of the solution is treated with sulphuretted hydrogen, which gives a brown precipitate of stannous sulphide, and the remainder is tested with mercuric chloride. Ammonium molybdate cannot, in this case, be used to detect the stannous compound, as a blue coloration is sometimes produced even when tin is absent.

Separation of Antimony and Arsenic.-The filtrate from the tin precipitate contains arsenic and antimony in the form of arsenate and antimonate respectively. These may be separated by Bunsen's method by means of sulphuretted hydrogen as follows. The solution is acidified with hydrochloric acid and warmed until oxygen ceases to be evolved. It is then cooled and treated with a rapid current of sulphuretted hydrogen. Antimony, if present, is at once precipitated as an orange or golden-yellow sulphide, which may be filtered off and confirmed in the ordinary way. To the filtrate, which ought to smell feebly of sulphuretted hydrogen, a few drops of sodium thiosulphate solution are added, and the solution is warmed until a precipitate begins to separate. Sulphuretted hydrogen is then passed through the solution. If the precipitate which separates is white, it consists merely of sulphur; if bright yellow, it contains arsenious sulphide, which may be filtered off and confirmed in the ordinary manner.

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Sometimes the yellow precipitate of arsenious sulphide is produced on warming with the sodium thiosulphate, but its quantity is usually increased by subsequent treatment with sulphuretted hydrogen.

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