

the clear mixture becomes turbid, and then a dense, cloudy precipitate forms which separates out rapidly. Allow to stand for 2 hours, filter through a weighed sintered glass or porcelain filtering crucible, wash several times with cold water to remove the excess of pyrogallol (50 mL is usually sufficient), dry at 100–105 °C to steady weight. To confirm that no pyrogallol remains wash again with cold water, dry at 100–105 °C, and weigh; repeat the operation until the weight is constant. Weigh as $\text{Sb}(\text{C}_6\text{H}_5\text{O}_3)$.

It should be pointed out that the titrimetric methods described for the determination of antimony (Chapter 10) are to be preferred to the gravimetric methods as they are simpler, more rapid, and quite as accurate.

11.17 ARSENIC

Arsenic(III) sulphide, As_2S_3 : Discussion. The arsenic must be present as arsenic(III). In this condition [ensured by the addition of, for example, iron(II) sulphate, copper(I) chloride, pyrogallol, or phosphorous(III) acid] arsenic may be separated from other elements by distillation from a hydrochloric acid solution, the temperature of the vapour being held below 108 °C; arsenic trichloride (also germanium chloride, if present) volatilises and is collected in water or in hydrochloric acid.

Procedure. Pass a rapid stream of washed hydrogen sulphide through a solution of the arsenic(III) (Note 1) in 9M hydrochloric acid at 15–20 °C. Allow to stand for an hour or two, and filter through a weighed filtering crucible (sintered glass or porcelain) (Note 2). Wash the precipitate with 8M hydrochloric acid saturated with hydrogen sulphide, then successively with ethanol, carbon disulphide (to remove any free sulphur which may be present), and ethanol. Dry at 105 °C to constant weight, and weigh as As_2S_3 .

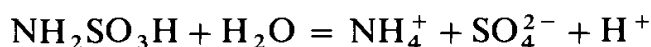
Notes. (1) A suitable solution for practice in this determination is prepared by dissolving about 0.3 g of arsenic(III) oxide, accurately weighed, in 9M hydrochloric acid.

(2) Sometimes a film of the sulphide adheres to the glass vessel in which precipitation was carried out; this can be dissolved in a little ammonia solution and the sulphide re-precipitated with the acid washing liquor.

11.18 BARIUM

Determination of barium as sulphate: Discussion. This method is most widely employed. The effect of various interfering ions (e.g. calcium, strontium, lead, nitrate, etc., which contaminate the precipitate) is dealt with in Section 11.72. The solubility of barium sulphate in cold water is about 2.5 mg L^{-1} ; it is, however, greater in hot water or in dilute hydrochloric or nitric acid, and less in solutions containing a common ion.

The barium sulphate may be precipitated either by the use of sulphuric acid, or from homogeneous solution by the use of sulphamic acid solution which produces sulphate ions on boiling:



Procedure: Precipitation with sulphuric acid. The solution (100 mL) should contain not more than 0.15 g of barium (see Note) and not more than 1 per cent by volume of concentrated hydrochloric acid. Heat to boiling, add a slight excess

of hot 0.5M sulphuric acid slowly and with constant stirring. Digest on the steam bath until the precipitate has settled, filter, wash with hot water containing two drops of sulphuric acid per litre, and then with a little water until the acid is removed. Full experimental details of the filtration, washing, and ignition processes (900–1000 °C) are given in Section 11.72. Weigh as BaSO₄.

Note. A suitable solution for practice may be prepared by dissolving about 0.3 g of accurately weighed barium chloride in 100 mL water and adding 1 mL of concentrated hydrochloric acid.

Procedure: Precipitation from homogeneous solution (sulphamic acid method). The sample solution may contain up to 100 mg of barium, preferably present as the chloride. A solution prepared from about 0.18 g of accurately weighed barium chloride may be used to obtain experience in the determination. Dilute the solution to about 100 mL; add 1.0 g sulphamic acid. Heat the covered beaker on an electric hotplate at 97–98 °C; continue the heating for 30 minutes after the first turbidity appears. Filter through a weighed porcelain filtering crucible and wash with warm distilled water. Ignite to constant weight at 900 °C (preferably in an electric muffle furnace). Weigh as BaSO₄.

11.19 BERYLLIUM

Determination of beryllium by precipitation with ammonia solution and subsequent ignition to beryllium oxide:* **Discussion.** Beryllium may be determined by precipitation with aqueous ammonia solution in the presence of ammonium chloride or nitrate, and subsequently igniting and weighing as the oxide BeO. The method is not entirely satisfactory owing to the gelatinous nature of the precipitate, its tendency to adhere to the sides of the vessel, and the possibility of adsorption effects.

Beryllium is sometimes precipitated together with aluminium hydroxide, which it resembles in many respects. Separation from aluminium (and also from iron) may be effected by means of oxine. An acetic (ethanoic) acid solution containing ammonium acetate is used; the aluminium and iron are precipitated as oxinates, and the beryllium in the filtrate is then precipitated with ammonia solution. Phosphate must be absent in the initial precipitation of beryllium and aluminium hydroxides.

The precipitation by ammonia solution of such elements as Al, Bi, Cd, Cr, Ca, Cu, Fe, Pb, Mn, Ni, and Zn may be prevented by complexation with EDTA: upon boiling the ammoniacal solution, beryllium hydroxide is precipitated quantitatively.

In all the above methods the element is weighed as the oxide, BeO, which is somewhat hygroscopic [compare aluminium(III) oxide]. The ignited residue, contained in a covered crucible, must be cooled in a desiccator containing concentrated sulphuric acid or phosphorus(V) pentoxide, and weighed immediately it has acquired the laboratory temperature.

Procedure. The beryllium solution (200 mL), prepared with nitric acid or hydrochloric acid and containing about 0.1 g of Be, must be almost neutral and contain no other substance precipitable by ammonia solution. Heat to boiling,

* Beryllium and its compounds are toxic and care should be taken to avoid inhalation of dusts or contact with eyes and skin.