

PRACTICAL GRAVIMETRIC ANALYSIS

11.13 INTRODUCTION

The student should, of course, become familiar with the general technique of gravimetric analysis before commencing experimental work. Sections 3.32–3.37 in particular should be carefully studied, along with Sections 3.1 for an introduction to laboratory working and 3.5 for care and use of balances. It is, however, essential to emphasise here the importance of careful working at all stages in a gravimetric determination and of performing each determination in duplicate.

For all gravimetric determinations described in this chapter, the phrase 'Allow to cool in a desiccator' should be interpreted as cooling the crucible, etc., **provided with a well-fitting cover** in a desiccator. The crucible, etc., should be weighed as soon as it has acquired the laboratory temperature (for a detailed discussion, see Section 3.22).

In the succeeding sections an account of the gravimetric determination of cations, arranged in alphabetical order, is followed by a similar arrangement for anions. One selected procedure is given in detail for each cation and anion, the essential features of other procedures being summarised in Sections 11.52 and 11.77 respectively. The determinations listed below are particularly suitable for students seeking to gain experience in the technique of gravimetric analysis.

1. Determination of aluminium as the 8-hydroxyquinolate (Section 11.14).
2. Determination of bismuth as oxyiodide (Section 11.20).
3. Determination of copper as copper(I) thiocyanate (Section 11.26).
4. Determination of lead as chromate (Section 11.29).
5. Determination of nickel as the dimethylglyoximate (Section 11.35).
6. Determination of strontium as strontium hydrogenphosphate (Section 11.42).
7. Determination of zinc as 8-hydroxyquinaldinate (Section 11.50).
8. Determination of chloride as silver chloride (Section 11.57).
9. Determination of fluoride as lead chlorofluoride (Section 11.59).
10. Determination of sulphate as barium sulphate (Section 11.72).

CATIONS

11.14 DETERMINATION OF ALUMINIUM AS THE 8-HYDROXYQUINOLATE, $\text{Al}(\text{C}_8\text{H}_6\text{ON})_3$, WITH PRECIPITATION FROM HOMOGENEOUS SOLUTION

Discussion. Some of the details of this method have already been given in Section 11.11(C). This procedure separates aluminium from beryllium, the alkaline earths, magnesium, and phosphate. For the gravimetric determination a 2 per cent or 5 per cent solution of oxine in 2*M* acetic acid may be used: 1 mL of the latter solution is sufficient to precipitate 3 mg of aluminium. For practice in this determination, use about 0.40 g, accurately weighed, of aluminium ammonium sulphate. Dissolve it in 100 mL of water, heat to 70–80 °C, add the appropriate volume of the oxine reagent, and (if a precipitate has not already formed) slowly introduce 2*M* ammonium acetate solution until a precipitate just appears, heat to boiling, and then add 25 mL of 2*M* ammonium acetate solution dropwise and with constant stirring (to ensure complete precipitation).

If the supernatant liquid is yellow, enough oxine reagent has been added. Allow to cool, and collect the precipitated aluminium 'oxinate' on a weighed sintered glass (porosity No. 4) or porous porcelain filtering crucible, and wash well with cold water. Dry to constant weight at 130–140 °C. Weigh as $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$.

Precipitation may also be effected from homogeneous solution. The experimental conditions must be carefully controlled. The solution containing 25–50 mg of aluminium should also contain 1.25–2.0 mL of concentrated hydrochloric acid in a total volume of 150–200 mL. After addition of excess of the oxine reagent, 5 g of urea is added for each 25 mg of aluminium present, and the solution is heated to boiling. The beaker is covered with a clockglass and heated for 2–3 hours at 95 °C. Precipitation is complete when the supernatant liquid, originally greenish-yellow, acquires an orange–yellow colour. The cold solution is filtered through a sintered-glass filtering crucible (porosity No. 3 or 4), the precipitate washed well with cold water, and dried to constant weight at 130 °C.

Procedure. The solution should contain 25–50 mg of aluminium and 1.0–2.0 mL of concentrated hydrochloric acid in a volume of 150–200 mL. For practice in this determination, weigh out accurately about 0.45 g of aluminium ammonium sulphate, dissolve it in water containing about 1.0 mL of concentrated hydrochloric acid, and dilute to about 200 mL. Add 5–6 mL of oxine reagent (a 10 per cent solution in 20 per cent acetic acid) and 5 g of urea. Cover the beaker with a clockglass and heat on an electric hotplate at 95 °C for 2.5 hours. Precipitation is complete when the supernatant liquid, originally greenish-yellow, acquires a pale orange–yellow colour. The precipitate is compact and filters easily. Allow to cool and collect the precipitate in a sintered-glass filtering crucible (porosity No. 3 or 4), wash with a little hot water and finally with cold water. Dry at 130 °C. Weigh as $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$.

11.15 AMMONIUM

Ammonium may be determined by precipitation with sodium tetraphenylborate as the sparingly soluble ammonium tetraphenylborate $\text{NH}_4[\text{B}(\text{C}_6\text{H}_5)_4]$, using a similar procedure to that described for potassium; it is dried at 100 °C. For further details of the reagent, including interferences, notably potassium, rubidium, and caesium, see Section 11.38.

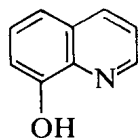
If the ammonium salt is present with other cations and anions, a titrimetric procedure (see Chapter 10) is usually employed.

11.16 ANTIMONY

Antimony pyrogallate, $\text{Sb}(\text{C}_6\text{H}_5\text{O}_3)$. Antimony(III) salts in the presence of tartrate ions may be quantitatively precipitated with a large excess of aqueous pyrogallol as the dense antimony pyrogallate. The method facilitates a simple separation from arsenic; the latter element may be determined in the filtrate from the precipitation of antimony by direct treatment with hydrogen sulphide.

Procedure. The solution should contain antimony(III) (0.1–0.2 g). Add a slight excess over the calculated quantity of potassium sodium tartrate to avoid the formation of basic salts upon dilution. Dissolve approximately five times the theoretical quantity of pure pyrogallol in 100 mL of air-free water, add this all at once to the antimony solution, and dilute to 250 mL. After 30–60 seconds

C. 8-Hydroxyquinoline (oxine) (VI). Oxine (C_9H_7ON) forms sparingly soluble derivatives with metallic ions, which have the composition $M(C_9H_6ON)_2$ if the coordination number of the metal is four (e.g. magnesium, zinc, copper, cadmium, lead, and indium), $M(C_9H_6ON)_3$ if the coordination number is six (e.g. aluminium, iron, bismuth, and gallium), and $M(C_9H_6ON)_4$ if the coordination number is eight (e.g. thorium and zirconium). There are, however, some exceptions, for example $TiO(C_9H_6ON)_2$, $MnO_2(C_9H_6ON)_2$, $WO_2(C_9H_6ON)_2$, and $UO_2(C_9H_6ON)_2$. By proper control of the pH of the solution, by the use of complex-forming reagents and by other methods, numerous separations may be carried out: thus aluminium may be separated from beryllium in an ammonium acetate-acetic acid buffer, and magnesium from the alkaline-earth metals in ammoniacal buffer. The pH values, extracted from the literature, for the quantitative precipitation of metal oxinates are collected in Table 11.3.



(VI)

8-Hydroxyquinoline is an almost colourless, crystalline solid, m.p. $75-76^\circ C$; it is almost insoluble in water. The reagent is prepared for use in either of the following ways.

- Two grams of oxine are dissolved in 100 mL of 2M acetic acid, and ammonia solution is added dropwise until a turbidity begins to form; the solution is clarified by the addition of a little acetic (ethanoic) acid. This solution is stable for long periods, particularly if it is kept in an amber bottle.
- Two grams of oxine are dissolved in 100 mL of methanol or ethanol (this reagent cannot be used for the determination of aluminium) or in acetone. The solution is stable for about ten days if protected from light. It is stated that the alcoholic solution may be employed in cases where precipitation occurs at a high pH, and the acetic acid solution for precipitations at low pH.

Table 11.3 pH range for precipitation of metal oxinates

Metal	pH		Metal	pH	
	Initial precipitation	Complete precipitation		Initial precipitation	Complete precipitation
Aluminium	2.9	4.7- 9.8	Manganese	4.3	5.9- 9.5
Bismuth	3.7	5.2- 9.4	Molybdenum	2.0	3.6- 7.3
Cadmium	4.5	5.5-13.2	Nickel	3.5	4.6-10.0
Calcium	6.8	9.2-12.7	Thorium	3.9	4.4- 8.8
Cobalt	3.6	4.9-11.6	Titanium	3.6	4.8- 8.6
Copper	3.0	> 3.3	Tungsten	3.5	5.0- 5.7
Iron(III)	2.5	4.1-11.2	Uranium	3.7	4.9- 9.3
Lead	4.8	8.4-12.3	Vanadium	1.4	2.7- 6.1
Magnesium	7.0	> 8.7	Zinc	3.3	> 4.4

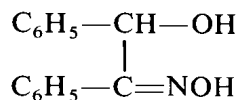
The following general conditions for conducting precipitations with 8-hydroxyquinoline may be given.

1. The reagent is added to the cold solution (or frequently at 50–60 °C) until the yellow or orange–yellow colour of the supernatant liquid indicates that a small but definite excess is present.
2. The precipitate is coagulated by a short period of heating at a temperature not exceeding 70 °C.
3. The precipitate may be filtered through paper or any variety of filtering crucible.
4. The filtrate should possess a yellow or orange colour, indicating the presence of excess of precipitant. If a turbidity appears, a portion should be heated; if the turbidity disappears, it may be assumed to be due to excess of reagent crystallising out, and is harmless. Otherwise, more reagent should be added, and the solution filtered again.
5. Washing of the precipitate may often be effected with hot or cold water (according to the solubility of the metal 'oxinate') and is continued until the filtrates become colourless. The use of ethanol is permissible if it is known to have no effect upon the precipitate.
6. The washed precipitate may be dried at 105–110 °C (usually hydrated 'oxinate') or at 130–140 °C (anhydrous 'oxinate'). In cases where prolonged heating at 130–140 °C is required, slight decomposition may occur. Frequently, ignition to the oxide yields a more suitable form for weighing, but care must be exercised to prevent loss, since many 'oxinates' are appreciably volatile; it is usually best to cover the complex with oxalic acid (1–3 g) and heat gradually. The determination may also be completed titrimetrically by dissolving the precipitate in dilute hydrochloric acid and titrating with a standard solution of potassium bromate as detailed in Section 10.134.

D. Benzoin- α -oxime (cupron) (VII). This compound yields a green precipitate, $\text{CuC}_{14}\text{H}_{11}\text{O}_2\text{N}$, with copper in dilute ammoniacal solution, which may be dried to constant weight at 100 °C. Ions which are precipitated by aqueous ammonia are kept in solution by the addition of tartrate; the reagent is then specific for copper. Copper may thus be separated from cadmium, lead, nickel, cobalt, zinc, aluminium, and small amounts of iron.

From strongly acidic solutions benzoin- α -oxime precipitates molybdate and tungstate ions quantitatively; chromate, vanadate, niobate, tantalate, and palladium(II) are partially precipitated. The molybdate complex is best ignited at 500–525 °C to MoO_3 before weighing; alternatively, the precipitate may be dissolved in ammonia solution and the molybdenum precipitated as lead molybdate, in which form it is conveniently weighed.

Benzoin- α -oxime is a white, crystalline solid, m.p. 152 °C, which is sparingly soluble in water but fairly soluble in ethanol. The reagent is employed as a 2 per cent solution in ethanol.



(VII)

E. Nitron (VIII). The strong organic base 1,4-diphenyl-3-phenylamino-1*H*-