Experiment (11)

Determination of calcium as oxalate

Theory:

- The calcium is precipitated as calcium oxalate $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ by treating a hot hydrochloric acid solution with ammonium oxalate and slowly neutralising with aqueous ammonia solution:

$$\text{Ca}^{++} + \text{C}_2\text{O}_4^{-2} + \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$$

- The ppt. is washed with dilute ammonium oxalate solution and the weighed in one of the following forms:

  (i) As $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ by drying at 100 - 105 °C for 1 - 2 hours. This method is not recommended for accurate work because of the hygroscopic nature of the oxalate and the difficulty of removing the coprecipitate ammonium oxalate at this low temp.

  (ii) As $\text{CaCO}_3$ by heating at 475 - 525 °C in an electric muffle furnace. This is the most satisfactory method since calcium carbonate is non-hygroscopic.

$$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{CO} + \text{H}_2\text{O}$$

  (iii) As $\text{CaO}$ by igniting at 1200°C. This method is widely used but the resulting lime has a comparatively small molecular weight and is hygroscopic, precautions must therefore be taken to prevent absorption of moisture and CO$_2$.

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$$

- The solubility of calcium oxalate is less in neutral solutions containing moderate concentrations of ammonium oxalate owing to the common ion effect, hence a dilute solution of ammonium oxalate is employed as the wash liquid in the gravimetric
determination. Calcium oxalate being the salt of a weak acid, its solubility increases with increasing hydrogen ion concentration of the solution because of the removal of the oxalate ions to form bi-oxalate ions and oxalic acid:

\[ CaC_2O_4 \rightarrow Ca^{++} + C_2O_4^{-2} \]
\[ C_2O_4^{-2} + H^+ \rightarrow HC_2O_4^- \]
\[ HC_2O_4^- + H^+ \rightarrow H_2C_2O_4 \]

Calculation shows that precipitation is quantitative at pH of 4 or higher.

- Precipitation from cold neutral or ammoniacal solution yields a very finely divide ppt which is difficult to filter. Satisfactory results are obtained by adding ammonium oxalate to a hot acidic solution of the calcium salt and finally neutralizing with aqueous ammonia solution. The ppt formed after digesting for about 1 hour, consists of relatively coarse crystals which are readily filtered.

**Procedure:**

1. Weigh out accurately 0.5g of A.R. calcium carbonate (which has been finely powdered and dried at 110-130°C for 1 hour) into a 400 ml beaker.

2. Add 10 ml of water followed by about 15 ml dilute HCl (1:1).

3. Heat the covered mixture until the solid has dissolved and boil gently for several minutes in order to expel CO₂.

4. Rinse down the sides of the beaker and the cover, dilute to 200 ml then add 2 drops of methyl red indicator.

5. Heat the solution to boiling and add very slowly 50ml of a warm 4% ammonium oxalate solution.

6. Add to the resultant hot solution (about 80°C) dilute ammonia solution (1:1) drop wise and with stirring until the mixture is neutral or faintly alkaline (color change from red to yellow).
7- Allow the solution to stand without further heating for at least an hour.
8- After the ppt has settled test the solution for complete precipitation with a few drops of ammonium oxalate solution.

9- Decant the clear supernatant liquid through a Whatman No. 40 filter paper, transfer the ppt to the paper and wash with a cold 0.1-0.2% ammonium oxalate solution until free from chloride.
10- Transfer the paper to a weighed crucible, dry in an oven for half one hour, burn away the paper with the crucible covered and then ignite at 500°C for 30 min., cool and weigh.
11- Calculate the percentage of calcium in the sample.