

Principles and Application of Gravimetric Analysis

Introduction

- **Gravimetric analysis** is one of the oldest and most fundamental techniques in quantitative analytical chemistry, relying on the measurement of mass.
- The method involves isolating the analyte by converting it into a highly pure, stable, weighable compound (a **precipitate**).
- Accurate results depend entirely on the high **purity** of the precipitate and the successful conversion of all the analytes into the weighable form.
- A deep understanding of **solubility product** (K_{sp}) and the factors that influence solubility are essential for controlling the precipitation process to achieve quantitative recovery.
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Learning Objectives

By the end of this module, you will be able to:

- Apply the concepts of **solubility products** (K_{sp}) and factors affecting solubility (e.g., common ion effect, pH, temperature) to control the formation and purity of precipitates in gravimetric analysis.
- Solve **problems** applying the gravimetric analysis principles, including calculating the mass of the analyte, percent composition, and required precipitating agent.

Key Concepts and Definitions

Term	Definition
Gravimetric Analysis	A quantitative method where the amount of analyte is determined by accurately measuring the mass of a pure, solid compound containing the analyte.
Precipitate	The insoluble solid compound formed during the analysis that contains the analyte.
Solubility	The equilibrium constant for the dissolution of a sparingly soluble ionic compound; determines maximum ion concentration.
Solubility Product (K_{sp})	The reduction in solubility of a salt when a soluble compound containing one of the same ions is added to the solution.
Common Ion Effect	The process of heating the precipitate in the solution from which it was formed to yield a purer, more filterable product.
Gravimetric Factor (GF)	The ratio of the molar mass of the analyte to the molar mass of the weighable precipitate, used for stoichiometric conversion.

Detailed Discussion

Principles of Gravimetric Analysis

Gravimetric analysis follows four main steps: precipitation, filtration, washing/digestion, and weighing.

- **Precipitation:** The analyte is converted into a sparingly soluble compound by adding a precipitating agent. This step is governed by the K_{sp} equilibrium.
- **Digestion:** The precipitate is allowed to stand (often while heated) in the presence of the mother liquor. This process dissolves and re-precipitates smaller, less perfect crystals, leading to the formation of larger, purer crystals that are easier to filter (**Ostwald ripening**).
- **Filtration and Washing:** The solid precipitate is separated from the liquid solution (**mother liquor**) and washed to remove impurities.
- **Drying/Ignition and Weighing:** The precipitate is heated to remove solvent and volatile impurities, converting it into a stable, weighable form. The final mass is measured using an analytical balance.

Factors Affecting Solubility and Purity

Controlling solubility and purity is the heart of successful gravimetric analysis.

- **Solubility Product (K_{sp}):** The smaller the K_{sp} value, the lower the solubility and the more quantitative the precipitation will be.

$$K_{sp} = [Cation]^x [Anion]^y$$

- **pH Control:** For precipitates whose anion is a weak base (e.g., hydroxide or oxalate), solubility is highly dependent on pH. Decreasing the pH (adding acid) increases the solubility by removing the anion via protonation.
- **Impurities (Coprecipitation):** The main challenge is contamination of the precipitate by soluble compounds. This error, known as **coprecipitation**, occurs when soluble materials are physically trapped (**occlusion** or **inclusion**) or chemically adsorbed (**surface adsorption**) onto the growing crystal lattice. Methods like digestion and reprecipitation are used to minimize coprecipitation errors.

Solving Gravimetric Problems

Gravimetric calculations rely on converting the measured mass of the final product back to the initial mass of the analyte using the **Gravimetric Factor (GF)**.

- **Gravimetric Factor (GF):** The stoichiometric ratio of the analyte's molar mass to the precipitate's molar mass.

$$GF = \frac{\text{Molar Mass of Analyte}}{\text{Molar Mass of Precipitate}} \times \frac{\text{Moles Mass of Analyte}}{\text{Moles Mass of Precipitate}}$$

- **Calculate Mass of Analyte:** Multiply the measured mass of the precipitate by the GF.

$$\text{Mass of Analyte} = \text{Mass of Precipitate} \times GF$$

- **Determine Percent Composition:** Use the calculated mass of the analyte and the initial mass of the sample.

$$\% \text{ Analyte} = \frac{\text{Mass of Analyte}}{\text{Mass of Sample}} \times 100$$

Example: To analyze Fe in an ore, it is precipitated as $\text{Fe}(\text{OH})_3$ and ignited to Fe_2O_3 (the weighable form). The GF is calculated to convert the mass of Fe_2O_3 back to the mass of Fe.

$$GF = \frac{2 \times \text{Molar Mass Fe}}{\text{Molar Mass Fe}_2\text{O}_3}$$

References:

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