

Principles and Application of Analytical Separations

Introduction

- **Analytical separations** are fundamental steps in nearly all chemical analyses, as samples usually consist of complex mixtures.
- The goal of separation is to isolate the analyte of interest from the **matrix** (the rest of the sample components) that could interfere with the final measurement.
- Separation techniques rely on differences in the **physical or chemical properties** of the components, such as solubility, volatility, charge, or ability to form a complex.
- The effectiveness of a separation is determined by its **efficiency** (speed of separation) and its **selectivity** (ability to separate the desired component from others).

Learning Objectives

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

- Recognize the **general principles** of common laboratory separation methods, including:
 - **Solvent extraction**
 - **Ion-exchange**
 - **Complex formation**
 - **Precipitation**
 - **Electrodeposition**
 - **Solid phase extraction (SPE)**
- Solve problems concerning the **principles of separation methods**, particularly those involving equilibrium and distribution ratios

Key Concepts and Definitions

Term	Definition
Separation	The process of isolating one or more components of a sample from its complex matrix.
Distribution (<i>D</i>)	The ratio of the total concentration of a solute in one phase (e.g., organic) to its total concentration in another phase (e.g., aqueous).
Extraction Efficiency (%<i>E</i>)	The percentage of the analyte that is successfully transferred from one phase to another.
Chelating Agent	A ligand that forms two or more bonds to a single metal ion, typically used in complex formation for separation.
Ion Exchanger	A solid, insoluble resin containing acidic or basic functional groups used to exchange ions with a solution.
Eluent/Eluate	The mobile phase solvent used to carry components through a stationary phase/The solution collected after passing through the stationary phase.

Detailed Discussion

General Principles of Separation

All separation techniques involve partitioning the analyte between two immiscible or physically distinct phases:

- **Mobile Phase:** A fluid (liquid or gas) that moves through the system.
- **Stationary Phase:** A solid or immobilized liquid that remains fixed.

The efficiency of a separation is quantified by the **Distribution Ratio (*D*)**:

$$D = \frac{\text{Total concentration of solute in Phase 1}}{\text{Total concentration of solute in Phase 2}}$$

The higher the value of D , the more effectively the solute moves into Phase 2. The goal is to maximize the D for the analyte and minimize the D for the interfering matrix components.

Specific Separation Techniques

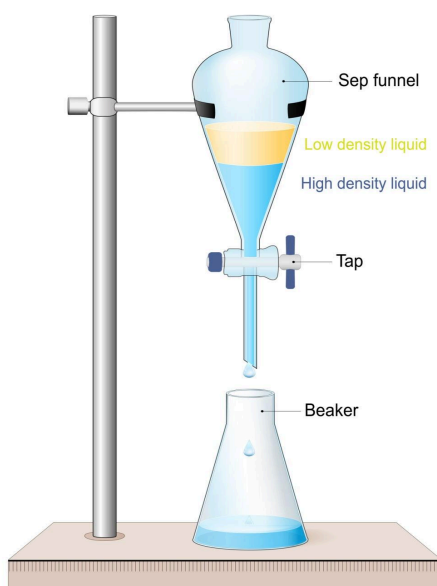
1. Solvent Extraction (Liquid-Liquid Extraction)

- **Principle:** Separation based on the differential solubility of a solute between two immiscible liquids (e.g., water and an organic solvent).
- **Application:** Commonly used to extract non-polar organic compounds or metal ions (after complexing them with an organic ligand) from an aqueous sample.
- **Problem Solving:** The Extraction Efficiency ($\%E$) for a single extraction can be calculated using the distribution ratio (D) and the volumes of the two phases (V_1 and V_2):

$$\%E = \frac{DV_2}{DV_2 + V_1} \times 100$$

Multiple extractions using smaller volumes of the solvent are far more effective than a single extraction with a large volume.

Separatory funnel



2. Precipitation

- **Principle:** Separation based on the difference in the **solubility product** (K_{sp}) of compounds. By adding a precipitating agent, an analyte can be converted into an insoluble solid, leaving soluble interferents behind.
- **Application:** Used in **gravimetric analysis** and for bulk separation. Techniques like controlling the pH or adding a **masking agent** (complex formation) can selectively precipitate one ion while keeping others in solution.

3. Complex Formation

- **Principle:** Selective separation by reversibly binding the analyte to a chelating agent to form a highly stable, charged or neutral complex.
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- **Application:** Often used in conjunction with solvent extraction (e.g., to make a metal ion soluble in the organic phase) or to mask an interfering metal ion, preventing it from reacting in a subsequent analysis step.

4. Ion-Exchange

- **Principle:** Separation based on the **reversible exchange** of ions between a liquid phase and a solid **ion-exchange resin**. The resin is an insoluble polymer containing fixed charged groups (e.g., SO_3^- for cation exchange).
- **Mechanism:** Ions in the solution compete for the binding sites on the resin. Separation is achieved by eluting the ions sequentially using a mobile phase (eluent) of varying ionic strength or pH.
- **Application:** Used for water softening (removing Ca^{2+} and Mg^{2+}), and separating mixtures of metal ions or amino acids.

5. Electrodeposition

- **Principle:** Separation based on differences in the reduction potentials of metal ions. By controlling the voltage applied across two electrodes, a metal ion can be selectively reduced and deposited as a solid metal layer on a working electrode.
- **Application:** Used for the quantitative analysis of certain metals and for purifying solutions by removing trace metals.

6. Solid Phase Extraction (SPE)

- **Principle:** Separation based on partitioning the analyte between a liquid sample (mobile phase) and a solid packing material (stationary phase) held within a cartridge or disc.
- **Mechanism:** Components are selectively retained on the solid phase based on polarity (**reversed-phase** for non-polar analytes) or charge (**ion-exchange** for charged analytes), and then eluted with a stronger solvent.
- **Application:** A very common technique for sample cleanup, pre-concentration of trace analytes, and matrix removal prior to instrumental analysis.

References:

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