22–1 Solvent Extraction

Extraction is the transfer of a solute from one phase to another. Common reasons to carry out an extraction in analytical chemistry are to isolate or concentrate the desired analyte or to separate it from species that would interfere in the analysis. The most common case is the extraction of an aqueous solution with an organic solvent. Diethyl ether, toluene, and hexane are common solvents that are *immiscible* with and less dense than water. They form a separate phase that floats on top of the aqueous phase. Chloroform, dichloromethane, and carbon tetrachloride are common solvents that are denser than water.[*] In the two-phase mixture, one phase is predominantly water and the other phase is predominantly organic.

Suppose that solute S is partitioned between phases 1 and 2, as depicted in Figure 22-1. The **partition coefficient**, K, is the equilibrium constant for the reaction

$$\text{S (in phase 1)} \rightleftharpoons \text{S (in phase 2)}$$

Partition coefficient:

$$K = \frac{\mathcal{A}_{S_2}}{\mathcal{A}_{S_1}} \approx \frac{[S]_2}{[S]_1} \tag{22-1}$$

where $\mathcal{A}_{S_1}$ refers to the activity of solute in phase 1. Lacking knowledge of the activity coefficients, we will write the partition coefficient in terms of concentrations.

Suppose that solute S in V_1 mL of solvent 1 (water) is extracted with V_2 mL of solvent 2 (toluene). Let n be the moles of S in the system and let q be the fraction of S remaining in phase 1 at equilibrium. The molarity in phase 1 is therefore qn/V_1. The fraction of total solute transferred to phase 2 is $(1 - q)$, and the molarity in phase 2 is $(1 - q)n/V_2$. Therefore,

$$K = \frac{[S]_2}{[S]_1} = \frac{(1 - q)n/V_2}{qn/V_1}$$

from which we can solve for q:

$$\frac{\text{Fraction remaining in phase 1}}{\text{after 1 extraction}} = q = \frac{V_1}{V_1 + KV_2} \tag{22-2}$$

Equation 22-2 says that the fraction of solute remaining in the water (phase 1) depends on the partition coefficient and the volumes. If the phases are separated and fresh toluene (solvent 2) is added, the fraction of solute remaining in the water at equilibrium will be

$$\frac{\text{Fraction remaining in phase 1}}{\text{after 2 extractions}} = q \cdot q = \left(\frac{V_1}{V_1 + KV_2}\right)^2$$

After n extractions, each with volume V_2, the fraction remaining in the water is

$$\frac{\text{Fraction remaining in phase 1}}{\text{after } n \text{ extractions}} = q^n = \left(\frac{V_1}{V_1 + KV_2}\right)^n \tag{22-3}$$

EXAMPLE Extraction Efficiency

Solute A has a partition coefficient of 3 between toluene and water, with three times as much in the toluene phase. Suppose that 100 mL of a 0.010 M aqueous solution of A are extracted with toluene. What fraction of A remains in the aqueous phase (a) if one extraction with 500 mL is performed or (b) if five extractions with 100 mL are performed?

Solution (a) With water as phase 1 and toluene as phase 2, Equation 22-2 says that, after a 500-mL extraction, the fraction remaining in the aqueous phase is

$$q = \frac{100}{100 + (3)(500)} = 0.062 \approx 6\%$$

[*] Whenever a choice exists between $CHCl_3$ and CCl_4, the less toxic $CHCl_3$ should be chosen. Hexane and toluene are greatly preferred over benzene, which is a carcinogen.

22-2 What is Chromatography?

Chromatography operates on the same principle as extraction, but one phase is held in place while the other moves past it.[8,9] Figure 22-5 shows a solution containing solutes A and B placed on top of a column packed with solid particles and filled with solvent. When the outlet is opened, solutes A and B flow down into the column. Fresh solvent is then applied to the top of the column and the mixture is washed down the column by continuous solvent flow. If solute A is more strongly adsorbed than solute B on the solid particles, then solute A spends a smaller fraction of the time free in solution. Solute A moves down the column more slowly than solute B and emerges at the bottom after solute B. We have just separated a mixture into its components by *chromatography*.

The **mobile phase** (the solvent moving through the column) in chromatography is either a liquid or a gas. The **stationary phase** (the one that stays in place inside the column) is most commonly a viscous liquid chemically bonded to the inside of a capillary tube or onto the surface of solid particles packed in the column. Alternatively, as in Figure 22-5, the solid particles themselves may be the stationary phase. In any case, the partitioning of solutes between mobile and stationary phases gives rise to separation.

Fluid entering the column is called **eluent.** Fluid emerging from the end of the column is called **eluate:**

eluent in → COLUMN → eluate out

The process of passing liquid or gas through a chromatography column is called **elution.**

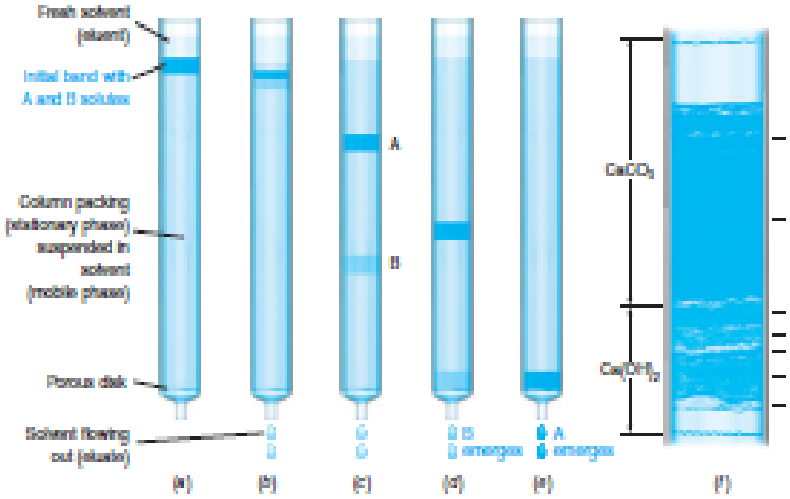


FIGURE 22-5 The idea behind chromatography: solute A, with a greater affinity than solute B for the stationary phase, remains on the column longer. Panel *f* is a reconstruction of the separation of pigments from red paprika skin from the work of L. Zechmeister in the 1930s. Bands marked by horizontal lines are different pigments. The lower stationary phase is $Ca(OH)_2$ and the upper stationary phase is $CaCO_3$. [Panel *f* from L. S. Ettre, "The Rebirth of Chromatography 75 Years Ago," *LCGC* **2007**, *25*, 640.]

Columns are either **packed** or **open tubular**. A packed column is filled with particles of stationary phase, as in Figure 22-5. An open tubular column is a narrow, hollow capillary with stationary phase coated on the inside walls.

Types of Chromatography

Chromatography is divided into categories on the basis of the mechanism of interaction of the solute with the stationary phase, as shown in Figure 22-6.

Adsorption chromatography. A solid stationary phase and a liquid or gaseous mobile phase are used. Solute is adsorbed on the surface of the solid particles. The more strongly a solute is adsorbed, the slower it travels through the column.

This form of chromatography was invented by Tswett in 1903.

Partition chromatography. A liquid stationary phase is bonded to a solid surface, which is typically the inside of the silica (SiO_2) chromatography column in gas chromatography. Solute equilibrates between the stationary liquid and the mobile phase, which is a flowing gas in gas chromatography.

For their pioneering work on liquid-liquid partition chromatography in 1941, A. J. P. Martin and R. L. M. Synge received a Nobel Prize in 1952.

Ion-exchange chromatography. Anions such as $—SO_3^-$ or cations such as $—N(CH_3)_3^+$ are covalently attached to the stationary solid phase, usually a *resin*. Solute ions of the opposite charge are attracted to the stationary phase. The mobile phase is a liquid.

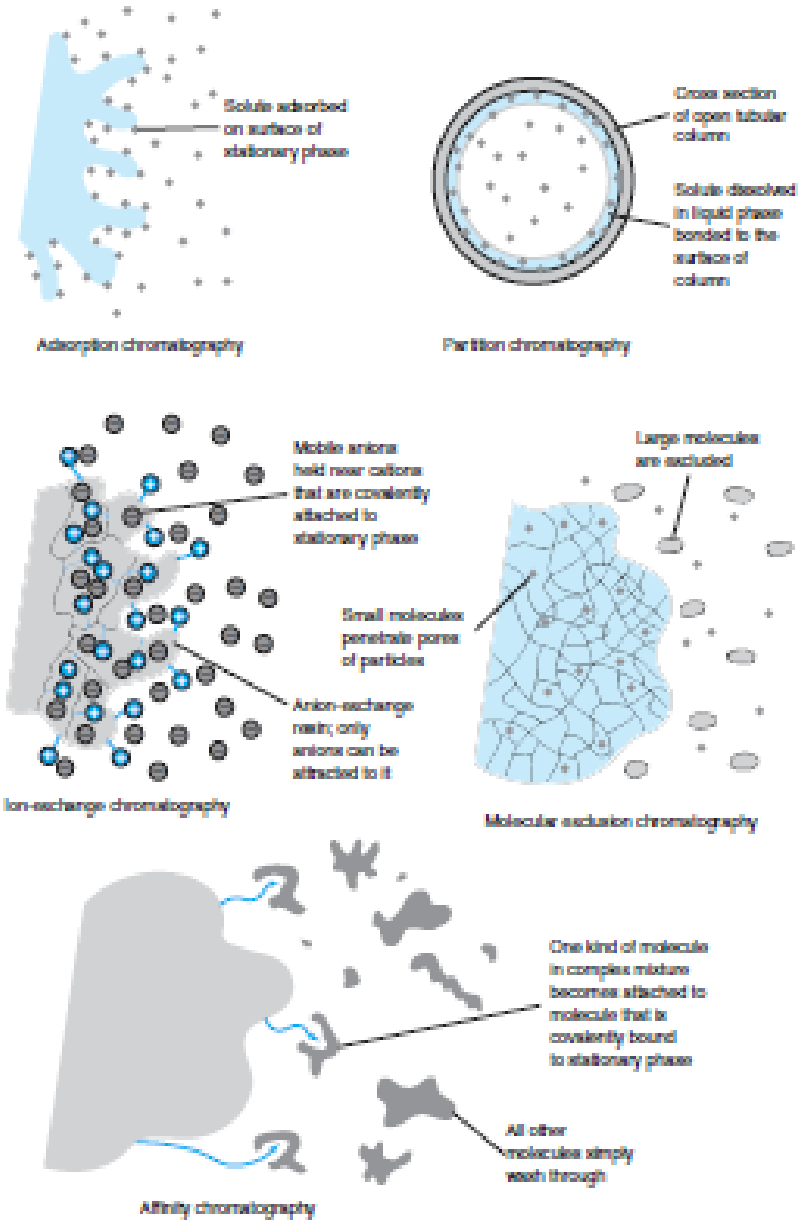
B. A. Adams and E. L. Holmes developed the first synthetic ion-exchange resins in 1935. *Resins* are relatively hard, amorphous organic solids. *Gels* are relatively soft.

Molecular exclusion chromatography. Also called *size exclusion*, **gel filtration**, or **gel permeation** chromatography, this technique separates molecules by size, with the larger solutes passing through most quickly. In the ideal case of molecular exclusion, there is no attractive interaction between the stationary phase and the solute. Rather, the liquid or gaseous mobile phase passes through a porous gel. The pores are small enough to exclude large solute molecules but not small ones. Large molecules stream past without entering the pores. Small molecules take longer to pass through the column because they enter the gel and therefore must flow through a larger volume before leaving the column.

Large molecules pass through the column faster than small molecules.

Affinity chromatography. This most selective kind of chromatography employs specific interactions between one kind of solute molecule and a second molecule that is covalently attached (immobilized) to the stationary phase. For example, the immobilized molecule might be an antibody to a particular protein. When a mixture containing a thousand proteins is passed through the column, only the one protein that reacts with the antibody binds to the column. After all other solutes have been washed from the column, the desired protein is dislodged by changing the pH or ionic strength.

FIGURE 22-6 Major types of chromatography.



22-3 A Plumber's View of Chromatography

The speed of the mobile phase passing through a chromatography column is expressed either as a volume flow rate or as a linear flow rate. Consider a liquid chromatography experiment in which the column has an inner diameter of 0.60 cm (radius = r = 0.30 cm) and the mobile phase occupies 20% of the column volume. Each centimeter of column length has a volume of $\pi r^2 \times \text{length} = \pi(0.30\text{ cm})^2(1\text{ cm}) = 0.283$ mL, of which 20% (= 0.056 5 mL) is mobile phase (solvent). The **volume flow rate**, such as 0.30 mL/min, tells how many milliliters of solvent per minute travel through the column. The **linear flow rate** tells how many centimeters are traveled in 1 min by the solvent. Because 1 cm of column length contains 0.056 5 mL of mobile phase, 0.30 mL would occupy (0.30 mL)/(0.056 5 mL/cm) = 5.3 cm of column length. The linear flow rate corresponding to 0.30 mL/min is 5.3 cm/min.

Volume flow rate = volume of solvent per unit time traveling through column.

Linear flow rate = distance per unit time traveled by solvent.

The Chromatogram

Solutes eluted from a chromatography column are observed with detectors described in later chapters. A **chromatogram** is a graph showing the detector response as a function of elution