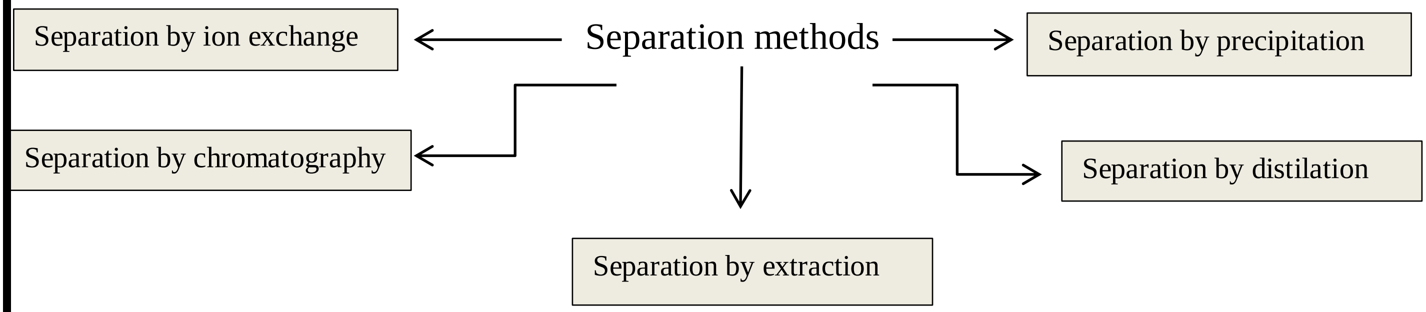
2018-2019

Analytical Separation Methods

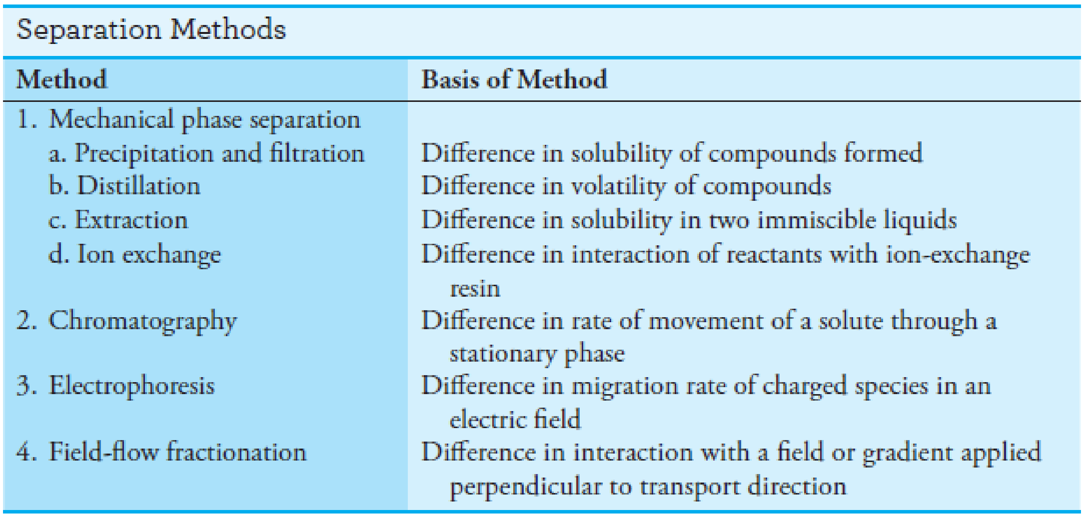
Dr. Mohammed Zaboon Thani

Analytical Separation Methods .

Separations are extremely important in synthesis, in industrial chemistry, in the biomedical sciences, and in chemical analysis. Many techniques for separating and concentrating the species of interest have thus been devised. Such techniques are aimed at exploiting differences in physico-chemical properties between the various components of a mixture. Volatility, solubility, charge, molecular size, shape and polarity are the most useful in this respect. A change of phase, as occurs during distillation, or the formation of a new phase, as in precipitation, can provide a simple means of isolating a desired component. Usually, however, more complex separation procedures are required for multi-component samples. Most depend on the selective transfer of materials between two immiscible phases. Most depend on the selective transfer of materials between two immiscible phases. The most widely used techniques and the phase systems associated with them are summarized in the following scheme .



All separation techniques involve one or more chemical equilibria, consequently the degree of separation achieved can vary greatly according to experimental conditions.



Separation Methods

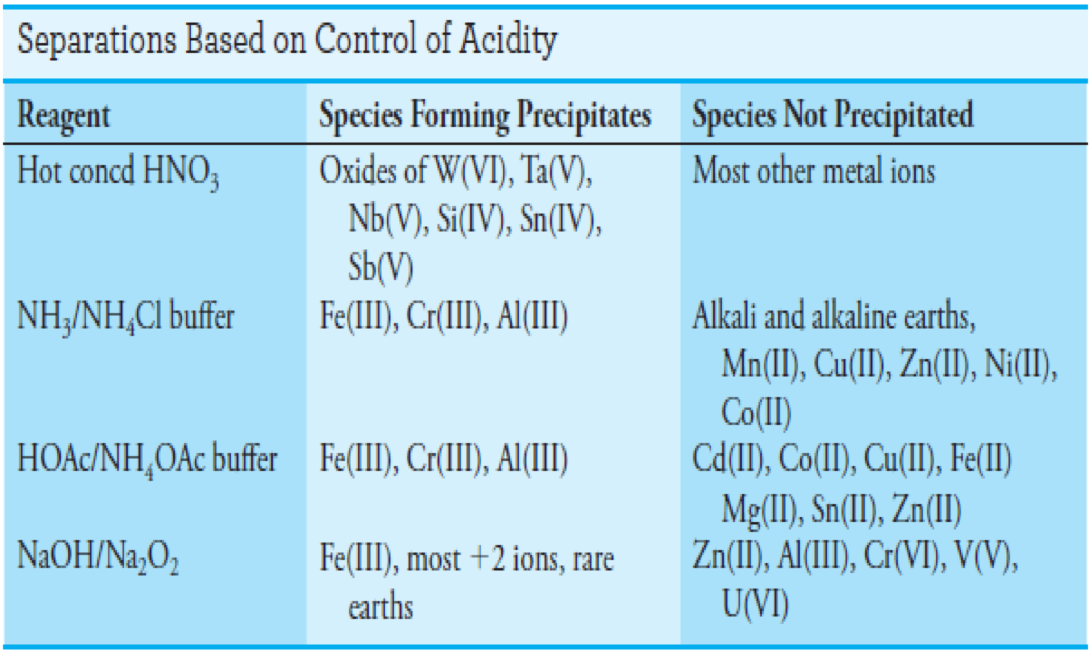
Method	Basis of Method
1. Mechanical phase separation	
a. Precipitation and filtration	Difference in solubility of compounds formed
b. Distillation	Difference in volatility of compounds
c. Extraction	Difference in solubility in two immiscible liquids
d. Ion exchange	Difference in interaction of reactants with ion-exchange resin
2. Chromatography	Difference in rate of movement of a solute through a stationary phase
3. Electrophoresis	Difference in migration rate of charged species in an electric field
4. Field-flow fractionation	Difference in interaction with a field or gradient applied perpendicular to transport direction

1. ***Separation by precipitation***.

Separations by precipitation require large solubility differences between the analyte and potential interferents. The theoretical feasibility of this type of separation can be determined by solubility calculations. When precipitates form as colloidal suspensions, coagulation may be difficult and slow, particularly when the isolation of a small quantity of a solid phase is attempted. Many precipitating agents have been used for quantitative inorganic separations.

1.1: **Separations Based on Control of Acidity.**

There are enormous differences among the solubilities of the hydroxides, hydrous oxides, and acids of various elements. Moreover, the concentration of hydrogen or hydroxide ions in a solution can be varied or can be easily controlled by the use of buffers. As a result, many separations based on pH control are in theory possible . In practice, these separations can be grouped in three categories: (1) those made in relatively concentrated solutions of strong acids,(2) those made in buffered solutions at intermediate pH values, and (3) those made in concentrated solutions of sodium or potassium hydroxide. lists common separations that can be achieved by control of acidity are show in the following table .

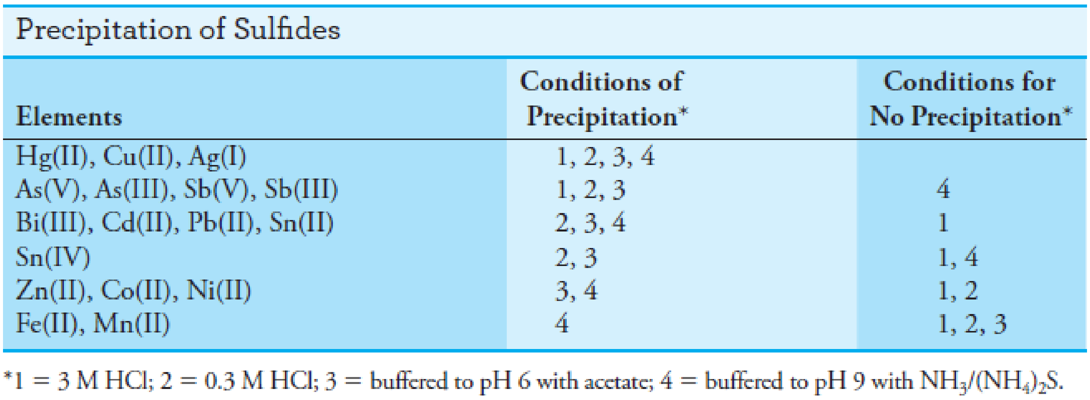


Separations Based on Control of Acidity

Reagent	Species Forming Precipitates	Species Not Precipitated
Hot concd HNO_3	Oxides of W(VI), Ta(V), Nb(V), Si(IV), Sn(IV), Sb(V)	Most other metal ions
NH_3/NH_4Cl buffer	Fe(III), Cr(III), Al(III)	Alkali and alkaline earths, Mn(II), Cu(II), Zn(II), Ni(II), Co(II)
$HOAc/NH_4OAc$ buffer	Fe(III), Cr(III), Al(III)	Cd(II), Co(II), Cu(II), Fe(II) Mg(II), Sn(II), Zn(II)
$NaOH/Na_2O_2$	Fe(III), most +2 ions, rare earths	Zn(II), Al(III), Cr(VI), V(V), U(VI)

1.2. **Sulfide Separations**.

With the exception of the alkali metals and alkaline-earth metals, most cations form sparingly soluble sulfides whose solubilities differ greatly from one another. Because it is relatively easy to control the sulfide ion concentration of an aqueous solution of H_2S by adjustment of pH, separations based on the formation of sulfides have found extensive use . The following table shows some common separations that can be accomplished with hydrogen sulfide through control of pH.



Precipitation of Sulfides

Elements	Conditions of Precipitation*	Conditions for No Precipitation*
Hg(II), Cu(II), Ag(I)	1, 2, 3, 4	
As(V), As(III), Sb(V), Sb(III)	1, 2, 3	4
Bi(III), Cd(II), Pb(II), Sn(II)	2, 3, 4	1
Sn(IV)	2, 3	1, 4
Zn(II), Co(II), Ni(II)	3, 4	1, 2
Fe(II), Mn(II)	4	1, 2, 3

*1 = 3 M HCl; 2 = 0.3 M HCl; 3 = buffered to pH 6 with acetate; 4 = buffered to pH 9 with $NH_3/(NH_4)_2S$.

1.3. **Separations by Other Inorganic Precipitants**.

No other inorganic ions are as generally useful for separations as hydroxide and sulfide ions. Phosphate, carbonate, and oxalate ions are often used as precipitants for cations, but they are not selective. Because of this drawback, separations are usually performed prior to precipitation. Chloride and sulfate are useful because of their highly selective behavior. Chloride can separate silver from most other metals, and sulfate can isolate a group of metals that includes lead, barium, and strontium.

1.4. **Separations by Organic Precipitants.**

The organic precipitants, such as dimethylglyoxime, are useful because of their remarkable selectivity in forming precipitates with only a few ions. Other reagents, such as 8-hydroxyquinoline, yield slightly soluble compounds with many different cations . The selectivity of this sort of reagent is due to the wide range of solubility among its reaction products and also to the fact that the precipitating reagent is usually an anion that is the conjugate base of a weak acid. Thus, separations based on pH control can be realized just as with hydrogen sulfide.

1.5. **Separation of Species Present in Trace Amounts by Precipitation**.

A problem often encountered in trace analysis is that of isolating from the major components of the sample the species of interest, which may be present in microgram quantities. Although such a separation is sometimes based on a precipitation, the techniques required differ from those used when the analyte is present in large amounts. Several problems can accompany the quantitative separation of a trace element by precipitation even when solubility losses are not important. Supersaturation often delays formation of the precipitate, and coagulation of small amounts of a colloidally dispersed substance is often difficult. In addition, it is common to lose an appreciable fraction of the solid during transfer and filtration. To minimize these difficulties, a quantity of some other ion that also forms a precipitate with the reagent is often added to the solution. The precipitate from the added ion is called a **collector** and carries the desired minor species out of solution. For example, in isolating manganese as the sparingly soluble manganese dioxide, a small amount of iron(III) is frequently added to the analyte solution before the introduction of ammonia as the precipitating reagent. The basic iron(III) oxide brings down even the smallest traces of the manganese dioxide. Other examples include basic aluminum oxide as a collector of trace amounts of titanium and copper sulfide for collection of traces of zinc and lead. Many other collectors are described by Sandell and Onishi. A collector may entrain a trace constituent as a result of similarities in their solubilities. Other collectors function by coprecipitation in which the minor component is adsorbed on or incorporated into the collector precipitate as the result of mixedcrystal formation. We must be sure that the collector does not interfere with the method selected for determining the trace component.

1.6. **Separation by Electrolytic Precipitation.**

Electrolytic precipitation is a highly useful method for accomplishing separations.In this process, the more easily reduced species, either the wanted or the unwanted component of the sample, is isolated as a separate phase. The method becomes particularly effective when the potential of the working electrode is controlled at a predetermined level . The mercury cathode has found wide application in the removal of many metal ions prior to the analysis of the residual solution. In general, metals more easily reduced than zinc are conveniently deposited in the mercury, leaving such ions as aluminum, beryllium, the alkaline earths, and the alkali metals in solution. The potential required to decrease the concentration of a metal ion to any desired level can be calculated from voltammetric data. Stripping methods use an electrode position step for separation followed by voltammetry for completion of the analysis.

1.7. **Salt-Induced Precipitation of Proteins**.

A common way to separate proteins is by adding a high concentration of salt. This procedure is termed **salting out** the protein. The solubility of protein molecules shows a complex dependence on pH, temperature, ionic strength, the nature of the protein, and the concentration of the salt used. At low salt concentrations, solubility is usually increased with increasing salt concentration. This **salting in effect** is explained by the Debye- Hückel theory. The counter ions of the salt surround the protein, and the screening results in decreasing the electrostatic attraction of protein molecules for each other. This decrease, in turn, leads to increasing solubility with increasing ionic strength. At high concentrations of salt, however, the repulsive effect of like charges is reduced as are the forces leading to solvation of the protein. When these forces are reduced enough, the protein precipitates and salting out is observed. Ammonium sulfate is an inexpensive salt and is widely used because of its effectiveness and high inherent solubility.

2. **Separation of Species by Distillation.**

Distillation is widely used to separate volatile analytes from nonvolatile interferents.Distillation is based on differences in the boiling points of the materials in a mixture. A common example is the separation of nitrogen analytes from many other species by converting the nitrogen to ammonia, which is then distilled from basic solution. Other examples include separating carbon as carbon dioxide and sulfur as sulfur dioxide. Distillation is widely used in organic chemistry to separate components in mixtures for purification purposes. There are many types of distillation. **Vacuum distillation** is used for compounds that have very high boiling points. Lowering the pressure to the vapor pressure of the compound of interest causes boiling and is often more effective for high boilers than raising the temperature. **Molecular distillation** occurs at very low pressure (,0.01 torr) such that the lowest possible temperature is used with the least damage to the distillate. **Pervaporation** is a method for separating mixtures by partial volatilization through a nonporous membrane. **Flash evaporation** is a process in which a liquid is heated and then sent through a reduced pressure chamber. The reduction in pressure causes partial vaporization of the liquid.

3. **Separation by Extraction**.

The extent to which solutes, both inorganic and organic, distribute themselves between two immiscible liquids differs enormously, and these differences have been used for decades to separate chemical species.

3.1. **Principles.**

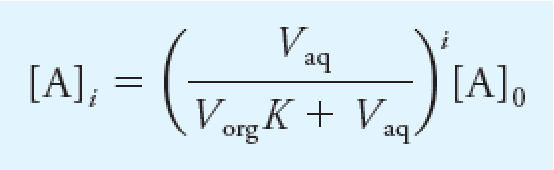
The partition of a solute between two immiscible phases is an equilibrium process that is governed by the distribution law. If the solute species A is allowed to distribute itself between water and an organic phase, the resulting equilibrium may be written as

$$A_{aq} \rightleftharpoons A_{org}$$

where the subscripts refer to the aqueous and the organic phases, respectively. Ideally, the ratio of activities for A in the two phases will be constant and independent of the total quantity of A so that, at any given temperature,

$$K = \frac{(a_A)_{org}}{(a_A)_{aq}} \approx \frac{[A]_{org}}{[A]_{aq}}$$

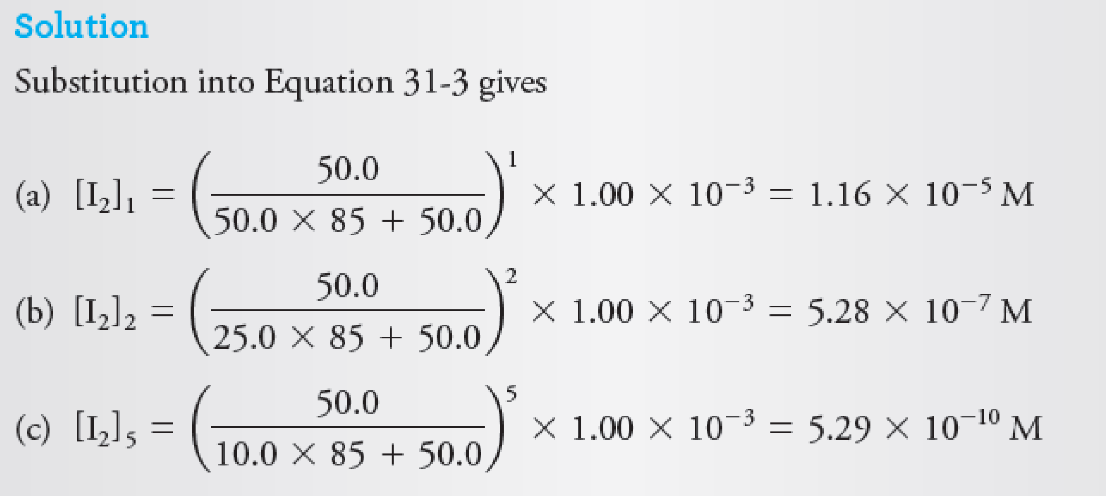
where $(aA)_{org}$ and $(aA)_{aq}$ are the activities of A in each of the phases and the bracketed terms are molar concentrations of A. The equilibrium constant K is known as the distribution constant. Generally, the numerical value for K approximates the ratio of the solubility of A in each solvent. Distribution constants are useful because they permit us to calculate the concentration of an analyte remaining in a solution after a certain number of extractions.The concentration of A remaining in an aqueous solution after i extractions with an organic solvent ($[A]_i$) is given by the equation



$$[A]_i = \left(\frac{V_{aq}}{V_{org}K + V_{aq}}\right)^i [A]_0$$

where $[A]_i$ is the concentration of A remaining in the aqueous solution after extracting V_{aq} mL of the solution with an original concentration of $[A]_0$ with i portions of the organic solvent, each with a volume of V_{org}.

EX1: The distribution constant for iodine between an organic solvent and H_2O is 85. Find the concentration of I_2 remaining in the aqueous layer after extraction of 50.0 mL of 1.00×10^{-3} M I_2 with the following quantities of the organic solvent: (a) 50.0 mL; (b) two 25.0-mL portions; (c) five 10.0-mL portions.



Solution

Substitution into Equation 31-3 gives

$$\text{(a)}\quad [I_2]_1 = \left(\frac{50.0}{50.0 \times 85 + 50.0}\right)^1 \times 1.00 \times 10^{-3} = 1.16 \times 10^{-5}\ \text{M}$$

$$\text{(b)}\quad [I_2]_2 = \left(\frac{50.0}{25.0 \times 85 + 50.0}\right)^2 \times 1.00 \times 10^{-3} = 5.28 \times 10^{-7}\ \text{M}$$

$$\text{(c)}\quad [I_2]_5 = \left(\frac{50.0}{10.0 \times 85 + 50.0}\right)^5 \times 1.00 \times 10^{-3} = 5.29 \times 10^{-10}\ \text{M}$$

3.2. **Extracting Inorganic Species**.

An extraction is often more attractive than a precipitation method for separating inorganic species. The processes of equilibration and separation of phases in a separatory funnel are less tedious and time consuming than conventional precipitation, filtration, and washing.

3.2.1. *Separating Metal Ions as Chelates.*

Many organic chelating agents are weak acids that react with metal ions to give uncharged complexes that are highly soluble in organic solvents such as ethers, hydrocarbons, ketones, and chlorinated species (including chloroform and carbon tetrachloride). Most uncharged metal chelates, on the other hand, are nearly insoluble in water. Similarly, the chelating agents themselves are often quite soluble in organic solvents but of limited solubility in water .The following figure shows the equilibria that develop when an aqueous solution of a divalent cation, such as zinc(II), is extracted with an organic solution containing a large excess of 8-hydroxyquinoline. Four equilibria are shown. In the first, 8-hydroxyquinoline, HQ, is distributed between the organic and aqueous layers. The second is the acid dissociation of the HQ to give H^+ and Q^- ions in the aqueous layer. The third equilibrium is the complex-formation reaction giving MQ_2. Fourth is distribution of the chelate between the two solvents. If it were not for the fourth equilibrium, MQ_2would precipitate out of the aqueous solution.

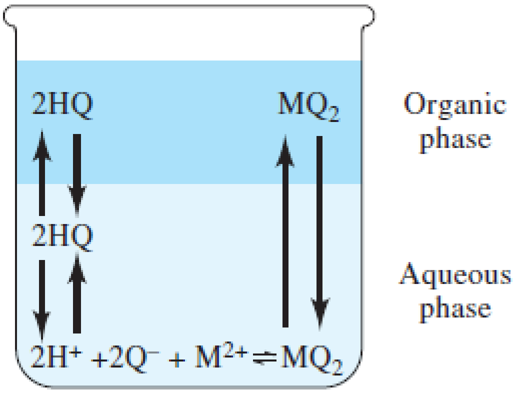


Fig: Equilibria in the extraction of an aqueous cation M^{+2} into an immiscible organic solvent containing 8-hydroxyquinoline.

The overall equilibrium is the sum of these four reactions or

$$2HQ(org) + M^{2+}(aq) \rightleftharpoons MQ_2(org) + 2H^+(aq)$$

The equilibrium constant for this reaction is

$$K' = \frac{[MQ_2]_{org}[H^+]^2_{aq}}{[HQ]^2_{org}[M^{2+}]_{aq}}$$

Usually, HQ is present in the organic layer in large excess with respect to M^{+2} in the aqueous phase so that [HQ]org remains essentially constant during the extraction. The equilibrium-constant expression can then be simplified to

$$K'[\mathrm{HQ}]^2_{\mathrm{org}} = K = \frac{[\mathrm{MQ_2}]_{\mathrm{org}}[\mathrm{H}^+]^2_{\mathrm{aq}}}{[\mathrm{M}^{2+}]_{\mathrm{aq}}}$$

or

$$\frac{[\mathrm{MQ_2}]_{\mathrm{org}}}{[\mathrm{M}^{2+}]_{\mathrm{aq}}} = \frac{K}{[\mathrm{H}^+]^2_{\mathrm{aq}}}$$

Thus, we see that the ratio of concentration of the metal species in the two layers is inversely proportional to the square of the hydrogen ion concentration of the aqueous layer . Equilibrium constants *K* vary widely from metal ion to metal ion, and these differences often make it possible to selectively extract one cation from another by buffering the aqueous solution at a level where one is extracted nearly completely and the second remains largely in the aqueous phase.

3.2.2. *Extracting Metal Chlorides and Nitrates* .

A number of inorganic species can be separated by extraction with suitable solvents. For example, a single ether extraction of a 6 M hydrochloric acid solution will cause better than 50% of several ions to be transferred to the organic phase, including iron(III), antimony(V), titanium(III), gold(III), molybdenum(VI), and tin(IV). Other ions, such as aluminum(III) and the divalent cations of cobalt, lead, manganese, and nickel, are not extracted.

what are several limitations of liquid-liquid extractions?

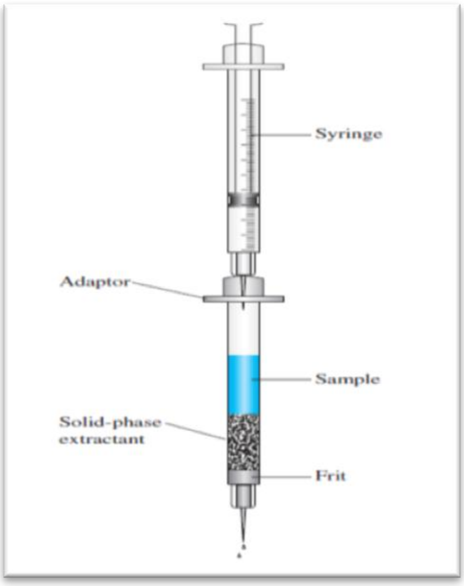
1. The solvents that can be used must be immisicible with water and must not form emulsions.

2. Liquid-liquid extractions use relatively large volumes of solvent, which can cause a problem with waste disposal.

3. most extractions are performed manually, which makes them somewhat slow and tedious.

3.3. **Solid-phase extraction**.

Solid-phase extraction techniques use membranes or small disposable syringe-barrel columns or cartridges . A hydrophobic organic compound is coated or chemically bonded to powdered silica to form the solid extracting phase. The compounds can be nonpolar, moderately polar, or polar. For example, an octadecyl (C18) bonded silica (ODS) is a common packing. The functional groups bonded to the packing attract hydrophobic compounds in the sample by van der Waals interactions and extract them from the aqueous solution. A typical cartridge system for solid-phase extractions is shown in the following figure. The sample is placed in the cartridge and pressure is applied by the syringe or from an air or nitrogen line. Alternatively, a vacuum can be used to pull the sample through the extractant. Organic molecules are then extracted from the sample and concentrated in the solid phase. They can later be displaced from the solid phase by a solvent such as methanol. By extracting the desired components from a large volume of water and then flushing them out with a small volume of solvent, the components can be concentrated. Preconcentration methods are often necessary for trace analytical methods. In some solid-phase extraction procedures, impurities are extracted into the solid phase while compounds of interest pass through unretained.



Solid-phase extraction performed in a small cartridge. The sample is placed in the cartridge and pressure is applied via a syringe plunger. Alternatively, a vacuum can be used to pull the sample through the extracting agent.

Questions and Problems.

1. What is a collector ion and how is it used?

2. What does the term salting out a protein mean? What is the salting in effect?

3. Name three methods based on mechanical phase separation ?

4. Define : a- distribution constant , b- Vacuum distillation , c- Molecular distillation

5. The distribution constant for X between *n*-hexane and water is 8.9. Calculate the concentration of X remaining in the aqueous phase after 50.0 mL of 0.200 M X is treated by extraction with the following quantities of *n*-hexane:

(a) one 40.0-mL portion. (b) two 20.0-mL portions. (c) four 10.0-mL portions. (d) eight 5.00-mL portions.

6. The distribution coefficient for Z between *n*-hexane and water is 5.85. Calculate the percent of Z remaining in 25.0 mL of water that was originally 0.0550 M in Z after extraction with the following volumes of *n*-hexane:

(a) one 25.0-mL portion. (b) two 12.5-mL portions. (c) five 5.00-mL portions. (d) ten 2.50-mL portions.

7. What volume of *n*-hexane is required to decrease the concentration of X in Problem 5 to 1.00 3 1024 M if 25.0 mL of 0.0500 M X is extracted with

(a) 25.0-mL portions? (b) 10.0-mL portions? (c) 2.0-mL portions?

8. What volume of *n*-hexane is required to decrease the concentration of Z in Problem 31-12 to 1.00 3 1025 M if 40.0 mL of 0.0200 M Z is extracted with

(a) 50.0-mL portions of *n*-hexane? (b) 25.0-mL portions? (c) 10.0-mL portions?

9. What is the minimum distribution coefficient that permits removal of 99% of a solute from 50.0 mL of water with

(a) two 25.0-mL extractions with toluene?

(b) five 10.0-mL extractions with toluene?

10. If 30.0 mL of water that is 0.0500 M in Q is to be extracted with four 10.0-mL portions of an immiscible organic solvent, what is the minimum distribution coefficient that allows transfer of all but the following percentages of the solute to the organic layer:

*(a) 1.00×10^{-4}

(b) 1.00×10^{-3}

(c) 1.00×10^{-2}