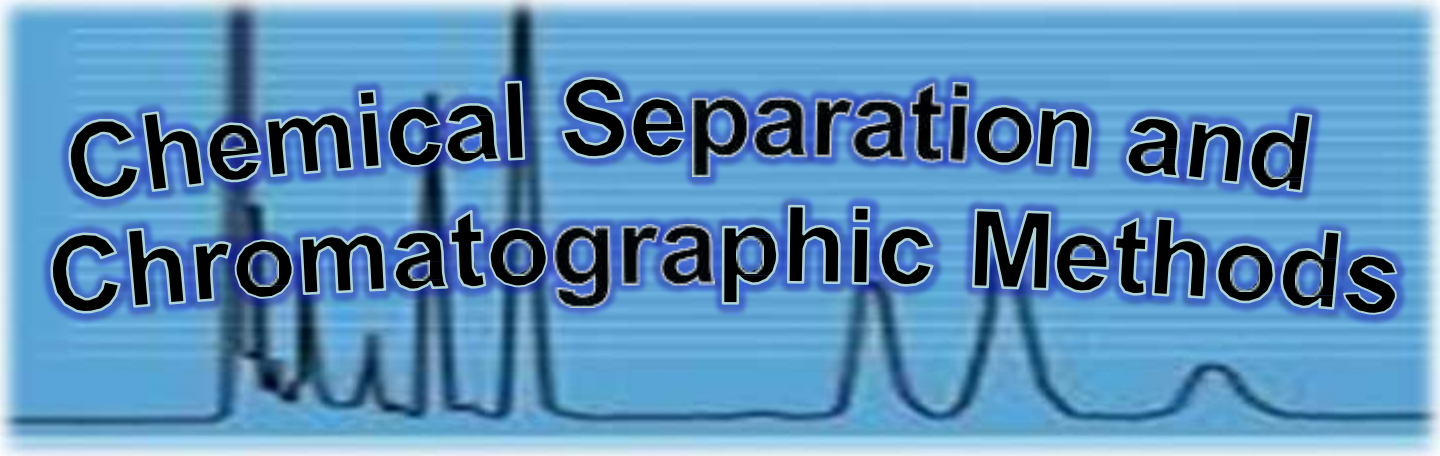


Extraction Methods

Definition

Extraction is a separation process by which a solute is transferred from one phase to a new phase.

Extraction process consisting of a separation of a substance from a matrix use **two immiscible phases** to separate a solute from one phase into the other.

The distribution of a solute between two phases is an **equilibrium condition** described by **partition theory**.

Example:
Boiling tea leaves in water extracts the tannins, theobromine, and caffeine out of the leaves and into the water.

Extraction:
the separation process.

Extract:
is a substance made by extraction.
tannins, theobromine, and caffeine in this example.

Exractant:
material used for extraction the extract.
Water in this example.

Partition Theory

When a phase containing a solute, ***S***, is brought into contact with a second phase, the solute partitions itself between the two phases.

$$S_{\text{phase 1}} \rightleftharpoons S_{\text{phase 2}}$$

The equilibrium constant for this reaction

$$K_{\text{D}} = \frac{[S_{\text{phase 2}}]}{[S_{\text{phase 1}}]}$$

is called the **distribution constant**, or **partition coefficient.** If K_D is sufficiently large, then the solute will move from phase **1** to phase **2**. The solute will remain in phase **1**, however, if the partition coefficient is sufficiently small. If a phase containing two solutes is brought into contact with a second phase, and K_D is favorable for only one of the solutes, then a separation of the solutes may be possible.

The physical states of the two phases are identified when describing the separation process. For example, when the sample is in a liquid phase and the second phase is a solid, the separation involves liquid–solid partitioning.

In a simple extraction the sample is extracted one or more times with portions of the second phase.

Simple extractions are particularly useful for separations in which only one component has a favorable distribution ratio.

Several important separation techniques are based on simple extractions, including liquid–liquid, liquid–solid, solid–liquid, and gas–solid extractions.

The most important and used extraction techniques are:

- Liquid-liquid extraction

- **Solid phase extraction**

Other techniques include

- Super critical fluid extraction
- Subcritical water extraction
- Ultrasonic extraction
- Heat reflux extraction
- Microwave-assisted extraction
- Instant controlled pressure drop
- Thin layer extraction
- Pressurized liquid extraction

Liquid-Liquid Extraction

Liquid–liquid extraction is a method to separate compounds based on their relative solubilities in two different **immiscible liquids**, usually water and an organic solvent (aqueous phase and organic phase).

It is an extraction of a substance from one liquid into another liquid phase.

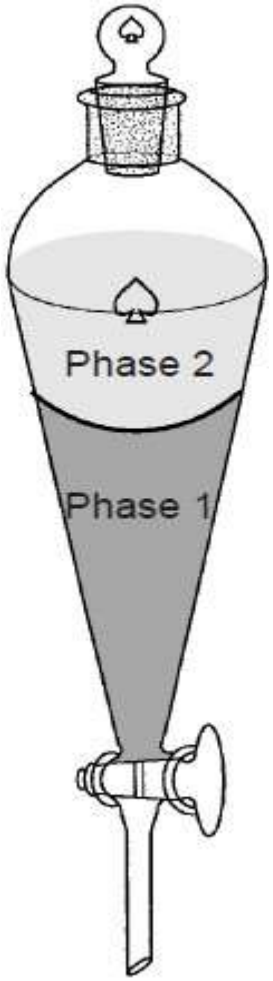
Liquid–liquid extraction is usually performed using a **separatory funnel**.

Separatory Funnel

Liquid–liquid extractions are usually accomplished with a separatory funnel.

The two liquids are placed in the separatory funnel and shaken to increase the surface area between the phases. When the extraction is complete, the liquids are allowed to separate, with the denser phase settling to the bottom of the separatory funnel.

Liquid–liquid extractions also may be carried out in the sample container by adding the extracting solvent when the sample is collected. Pesticides in water, for example, may be preserved for longer periods by extracting into a small volume of hexane added to the sample in the field.



In a simple liquid–liquid extraction the solute is partitioned between two immiscible phases. In most cases one of the phases is **aqueous**, and the other phase is an **organic** solvent such as diethyl ether or chloroform.

Because the phases are immiscible, they form **two layers**, with the denser phase on the bottom. The solute is initially present in one phase, but after extraction it is present in both phases. The efficiency of a liquid–liquid extraction is determined by the equilibrium constant for the solute's partitioning between the two phases.

Extraction efficiency is also influenced by any secondary reactions involving the solute. Examples of secondary reactions include acid–base and complexation equilibria.

Partition Coefficients and Distribution Ratios

The partitioning of a solute between two phases is described by a partition coefficient. If the solute is initially in an aqueous phase and is extracted into an organic phase

$$S_{aq} \rightleftharpoons S_{org}$$

the partition coefficient is

$$K_D = \frac{[S_{org}]}{[S_{aq}]}$$

A large value for K_D indicates that the extraction of the solute into the organic phase is favorable.

In evaluating the efficiency of an extraction, however, we must consider the solute's total concentration in each phase. We define the **distribution ratio, *D*,** to be the ratio of the total concentration of solute in one phase relative to a second phase, all forms of the solute are considered in defining the distribution ratio

$$D = \frac{[S_{org}]_{tot}}{[S_{aq}]_{tot}}$$

When the solute exists in only one form in each phase, then the partition coefficient and the distribution ratio are identical. If, however, the solute exists in more than one form in either phase, then K_D and ***D*** usually have different values. For example, if the solute exists in two forms in the aqueous phase, **A** and **B**, only one of which, **A**, partitions itself between the two phases, then

$$D = \frac{[S_{org}]_A}{[S_{aq}]_A + [S_{aq}]_B} \leq K_D = \frac{[S_{org}]_A}{[S_{aq}]_A}$$

This distinction between K_D and ***D*** is important. The partition coefficient is an equilibrium constant and has a fixed value for the solute's partitioning between the two phases. The value of the distribution ratio, however, changes with solution conditions if the relative amounts of forms **A** and **B** change. If we know the equilibrium reactions taking place within each phase and between the phases, we can derive an algebraic relationship between K_D and ***D***.

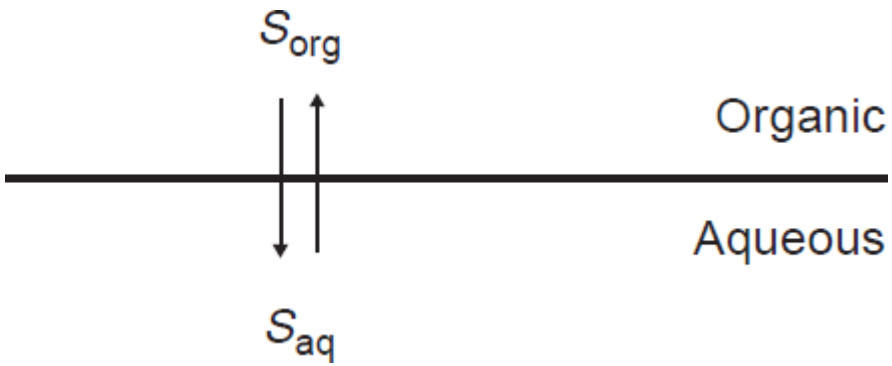
Liquid-Liquid Extraction with No Secondary Reactions

In the simplest form of liquid–liquid extraction, the only reaction affecting extraction efficiency, is the partitioning of the solute between the two phases. In this case the distribution ratio and the partition coefficient are equal.

$$D = \frac{[S_{org}]_{tot}}{[S_{aq}]_{tot}} = \frac{[S_{org}]}{[S_{aq}]} \quad \text{..... (1)}$$

Conservation of mass requires that the moles of solute initially present in one phase equal the combined moles of solute in the aqueous and organic phases after the extraction; thus

$$(\text{Moles aq})_0 = (\text{moles aq})_1 + (\text{moles org})_1 \quad \text{..... (2)}$$



Scheme for a simple liquid–liquid extraction without any secondary reactions.

the resulting equations for the distribution of the solute between the two phases are independent of which phase originally contains the solute.

where the subscript indicates the extraction number. The concentration of ***S*** in the aqueous phase after the extraction is

$$[S_{aq}] = \frac{(\text{moles aq})_1}{V_{aq}} \quad \text{..... (3)}$$

whereas the solute's concentration in the organic phase is

$$[S_{org}] = \frac{(\text{moles org})_1}{V_{org}} \quad \text{..... (4)}$$

where $\boldsymbol{V_{aq}}$ and $\boldsymbol{V_{org}}$ are the volumes of the aqueous and organic phases. Solving equation (2) for $(\text{moles org})_1$ and substituting into equation (4) leave us with

$$[S_{org}] = \frac{(\text{moles aq})_0 - (\text{moles aq})_1}{V_{org}} \quad \text{..... (5)}$$

Substituting equations (3) and (4) into equation (1), we obtain

$$D = \frac{[(\text{moles aq})_0 - (\text{moles aq})_1] / V_{org}}{(\text{moles aq})_1 / V_{aq}} = \frac{(\text{moles aq})_0 V_{aq} - (\text{moles aq})_1 V_{aq}}{(\text{moles aq})_1 V_{org}} \quad \text{..... (6)}$$

Rearranging and solving for the fraction of solute remaining in the aqueous phase after one extraction, $\boldsymbol{(q_{aq})_1}$, gives

$$(q_{aq})_1 = \frac{(\text{moles aq})_1}{(\text{moles aq})_0} = \frac{V_{aq}}{DV_{org} + V_{aq}} \quad \text{..... (7)}$$

The fraction present in the organic phase after one extraction, $\boldsymbol{(q_{org})_1}$, is

$$(q_{org})_1 = \frac{(\text{moles org})_1}{(\text{moles org})_0} = 1 - (q_{aq})_1 = \frac{DV_{org}}{DV_{org} + V_{aq}} \quad \text{..... (8)}$$

equations (7) and (8) are used to calculate the efficiency of a simple liquid–liquid extraction.

Example 1:

A solute, ***S***, has a K_D between water and chloroform of 5.00. A 50.00-mL sample of a 0.050 M aqueous solution of the solute is extracted with 15.00 mL of chloroform. (a) What is the extraction efficiency for this separation? (b) What is the solute's final concentration in each phase? (c) What volume of chloroform is needed to extract 99.9% of the solute?

Solution:

For a simple liquid–liquid extraction, the distribution ratio, ***D***, and the partition coefficient, K_D, are identical.

(**a**) The fraction of solute remaining in the aqueous phase after the extraction is given by equation (7)

$$(q_{aq})_1 = \frac{50.00\ \text{mL}}{(5.00)(15.00\ \text{mL}) + 50.00\ \text{mL}} = 0.400$$

The fraction of solute present in the organic phase is, therefore, 0.600.

Extraction efficiency is the percentage of solute successfully transferred from its initial phase to the extracting phase. The extraction efficiency is, therefore, 60.0%.

(**b**) The moles of solute present in the aqueous phase before the extraction is

$$(\text{Moles aq})_0 = [S_{aq}]_0 \times V_{aq} = \frac{0.050\ \text{mol}}{\text{L}} \times 0.05000\ \text{L} = 0.0025\ \text{mol}$$

Since 40.0% of the solute remains in the aqueous phase, and 60.0% has been extracted into the organic phase, the moles of solute in the two phases after extraction are

$$(\text{Moles aq})_1 = (\text{moles aq})_0 \times (q_{aq})_1 = 0.0025\ \text{mol} \times (0.400) = 0.0010\ \text{mol}$$

$$(\text{Moles org})_1 = (\text{moles aq})_0 - (\text{moles aq})_1 = 0.0025\ \text{mol} - 0.0010\ \text{mol} = 0.0015\ \text{mol}$$

The solute's concentration in each phase is

$$[S_{aq}]_1 = \frac{(\text{moles aq})_1}{V_{aq}} = \frac{0.0010\ \text{mol}}{0.05000\ \text{L}} = 0.020\ \text{M}$$

$$[S_{org}]_1 = \frac{(\text{moles org})_1}{V_{org}} = \frac{0.0015\ \text{mol}}{0.01500\ \text{L}} = 0.10\ \text{M}$$

(**c**) To extract 99.9% of the solute $\mathbf{(q_{aq})_1}$ must be 0.001. Solving equation (7) for V_{org}, and making appropriate substitutions for $\mathbf{(q_{aq})_1}$ and $\boldsymbol{V_{aq}}$ gives

$$V_{org} = \frac{V_{aq} - (q_{aq})_1 V_{aq}}{(q_{aq})_1 D} = \frac{50.00\ \text{mL} - (0.001)(50.00\ \text{mL})}{(0.001)(5.00)} = 9990\ \text{mL}$$

Clearly, a single extraction is not reasonable under these conditions.

In the above Example, a single extraction results in an extraction efficiency of only 60%. If a second extraction is carried out, the fraction of solute remaining in the aqueous phase, $(q_{aq})_2$, is given by

$$(q_{aq})_2 = \frac{(\text{moles aq})_2}{(\text{moles aq})_1} = \frac{V_{aq}}{DV_{org} + V_{aq}}$$

If the volumes of the aqueous and organic layers are the same for both extractions, then the cumulative fraction of solute remaining in the aqueous layer after two extractions, $(Q_{aq})_2$, is

$$(Q_{aq})_2 = \frac{(\text{moles aq})_2}{(\text{moles aq})_0} = (q_{aq})_1 (q_{aq})_2 = \left(\frac{V_{aq}}{DV_{org} + V_{aq}} \right)^2$$

In general, for a series of ***n*** identical extractions, the fraction of analyte remaining in the aqueous phase after the last extraction is

$$(Q_{aq})_n = \left(\frac{V_{aq}}{DV_{org} + V_{aq}} \right)^n \quad \text{.....} \quad \textbf{(9)}$$

Example 2:

For the extraction described in Example 1, determine (a) the extraction efficiency for two extractions and for three extractions; and (b) the number of extractions required to ensure that 99.9% of the solute is extracted.

Solution:

(**a**) The fraction of solute remaining in the aqueous phase after two and three extractions is

$$(Q_{aq})_2 = \left(\frac{50.00\ \text{mL}}{(5.00)(15.00\ \text{mL}) + 50.00\ \text{mL}}\right)^2 = 0.160$$

$$(Q_{aq})_3 = \left(\frac{50.00\ \text{mL}}{(5.00)(15.00\ \text{mL}) + 50.00\ \text{mL}}\right)^3 = 0.064$$

Thus, the extraction efficiencies are 84.0% with two extractions and 93.6% with three extractions.

(**b**) To determine the minimum number of extractions for an efficiency of 99.9%, we set $\mathbf{(Q_{aq})_n}$ to 0.001 and solve for ***n*** in equation 9:

$$0.001 = \left(\frac{50.00\ \text{mL}}{(5.00)(15.00\ \text{mL}) + 50.00\ \text{mL}}\right)^n = (0.400)^n$$

Taking the log of both sides

$$\log(0.001) = n\log(0.400)$$

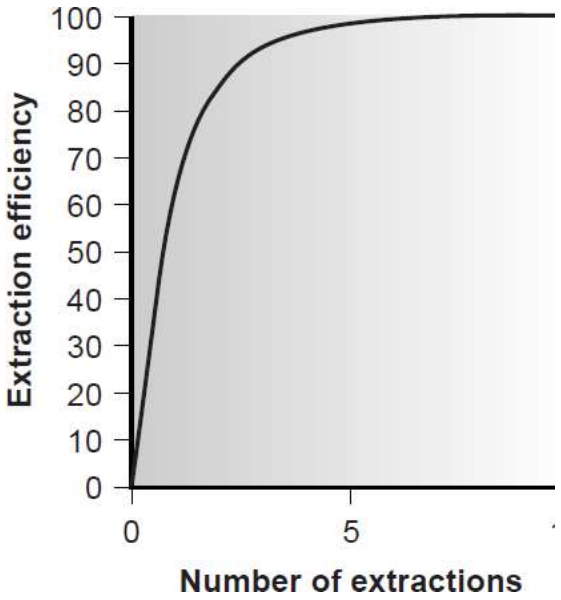
and solving for ***n*** gives

$$n = 7.54$$

Thus, a minimum of eight extractions is necessary.

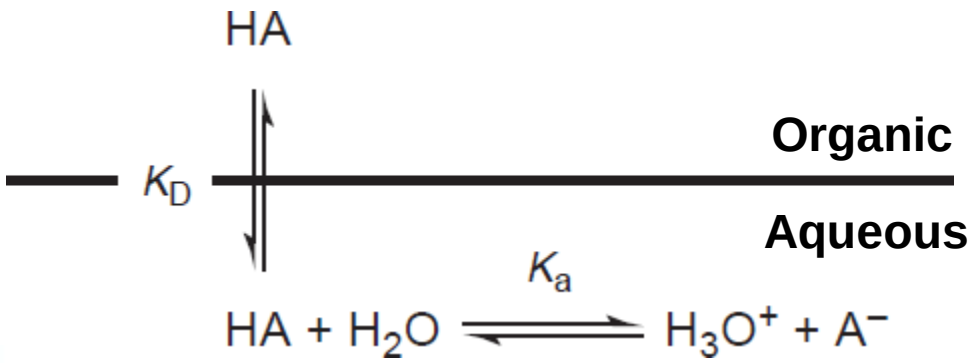
An important observation from **Examples 1 and 2** is that an extraction efficiency of 99.9% can be obtained with less solvent when using multiple extractions.

Obtaining this extraction efficiency with one extraction requires 9990 mL of the organic solvent. Eight extractions using separate 15 mL portions of the organic solvent, however, requires only 120 mL. Although extraction efficiency increases dramatically with the first few multiple extractions, the effect quickly diminishes as the number of extractions is increased. In most cases there is little gain in extraction efficiency after five or six extractions. In **Example 2** five extractions are needed to reach an extraction efficiency of 99%, and an additional three extractions are required to obtain the extra 0.9% increase in extraction efficiency.



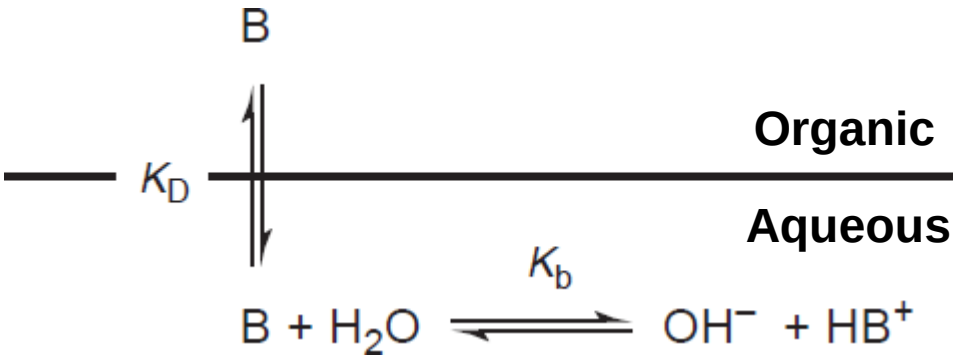
Plot of extraction efficiency versus number of extractions for the liquid–liquid extraction.

Liquid-Liquid Extractions Involving Acid-Base Equilibria



$$D = \frac{K_D[H_3O^+_{aq}]}{[H_3O^+_{aq}] + K_a}$$

Scheme for the liquid–liquid extraction of a molecular weak acid.

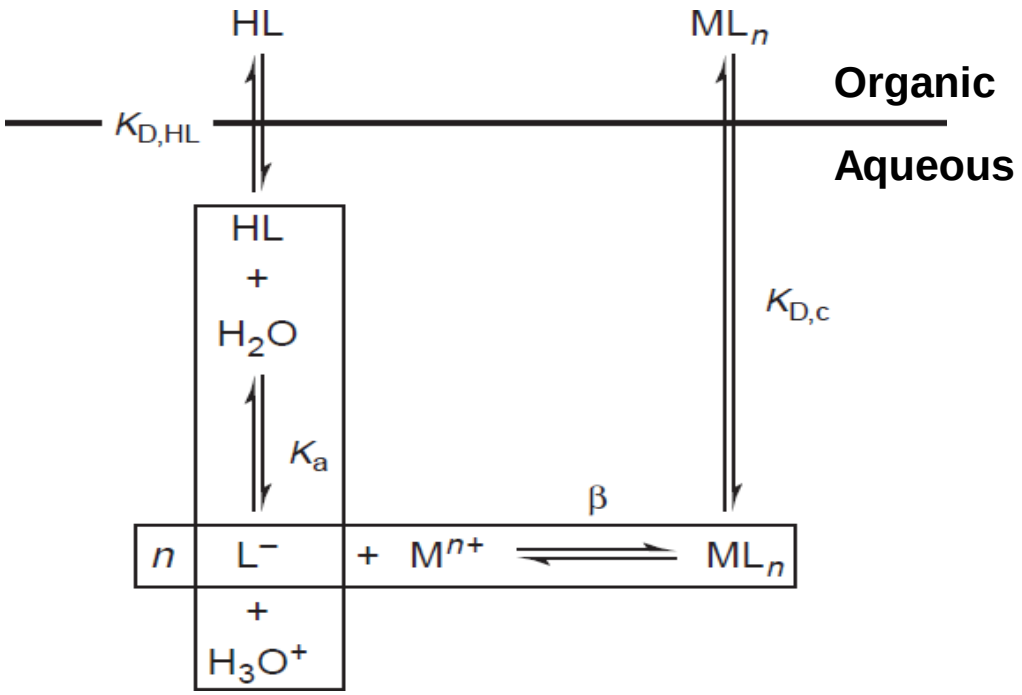


$$D = \frac{K_D K_a}{K_a + [H_3O^+_{aq}]}$$

Scheme for the liquid–liquid extraction of a molecular weak base.

Liquid-Liquid Extractions Involving Metal Chelators

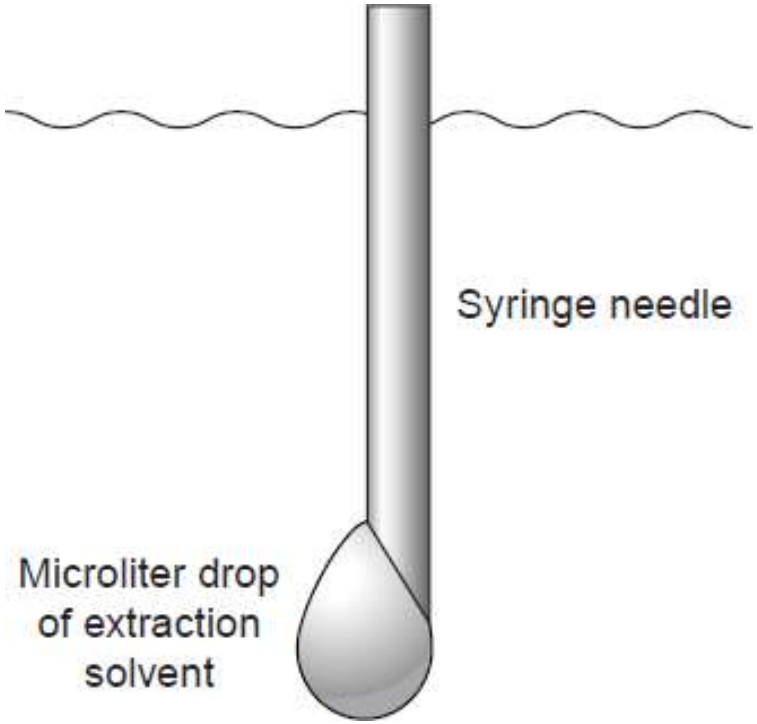
$$D = \frac{\beta K_{D,c} K_a^n C_L^n}{K_{D,L}^n [H_3O_{aq}^+]^n + \beta K_a^n C_L^n}$$



Scheme for the liquid–liquid extraction of a metal ion by a metal chelator.

Liquid-Liquid Microextractions

Liquid–liquid microextractions, in which the extracting phase is a 1-µL drop suspended from a microsyringe also have been described.



Schematic of a liquid–liquid microextraction showing syringe needle with attached 1-µL droplet.

The problem of low instrumental detection limit

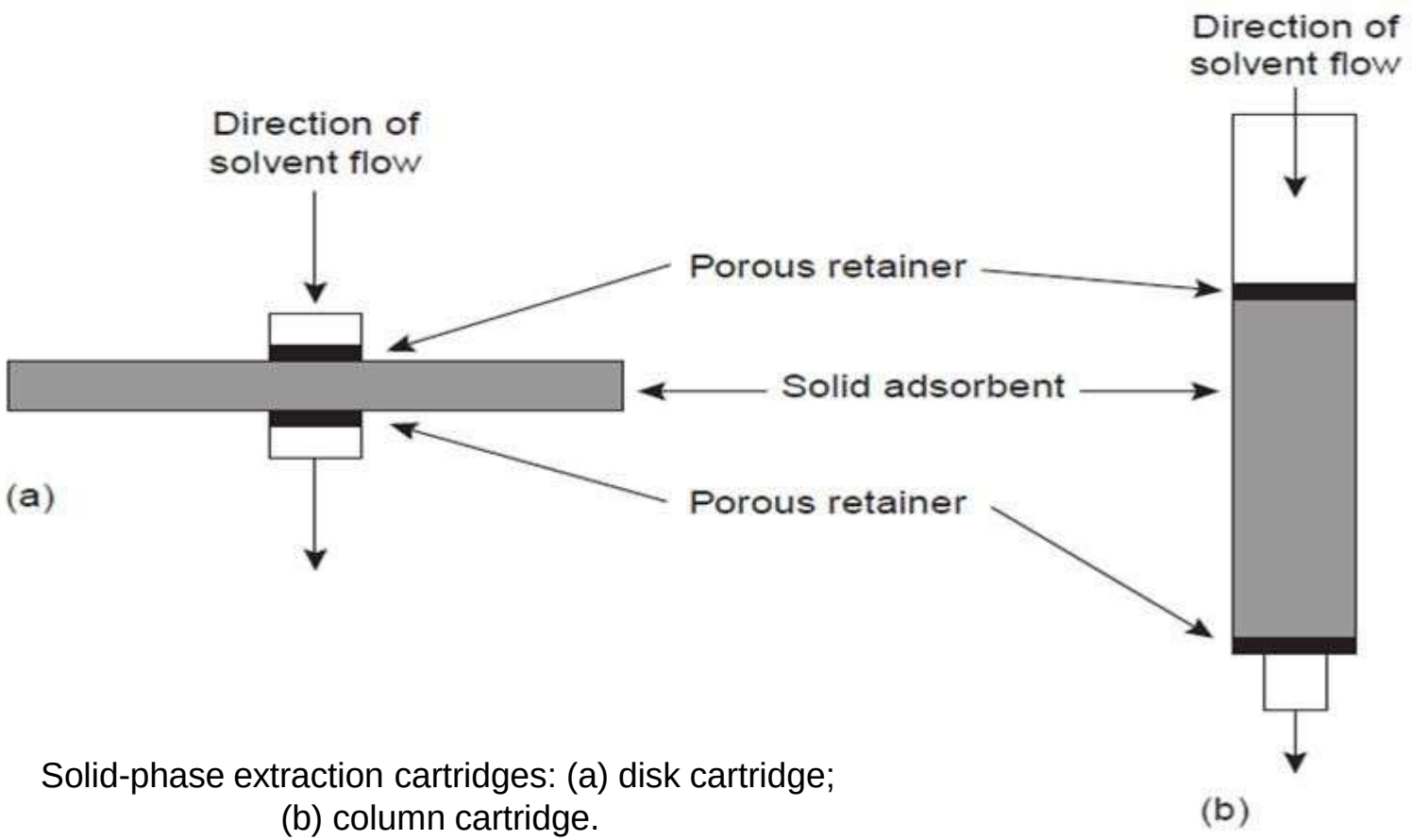
The residual concentrations of many pollutants (e.g., pesticides), usually at very low levels, (there are usually maximum acceptable limits for presence of these pollutants in the environmental samples such as water). Therefore, it is difficult to be detected by usual analytical instruments (e.g., HPLC) due to the inherent limited sensitivity of these instruments. On the other hand, sample matrices are complex and they cannot be directly injected into the analytical system.

Consequently, a sample pretreatment step is indispensable to achieve reliable results based on the comprehensive consideration of these factors. Through the sample treatment step, an effective enrichment or preconcentration step of the target analytes can be attained and the sample matrix can be eliminated.

Solid Phase Extraction (SPE) is one of the most popular techniques used mainly to remove interferences and for preconcentration of analytes prior to analysis.

Solid-Phase Extraction

The sample is passed through a cartridge containing solid particulates that serve as the adsorbent material. For liquid samples the solid adsorbent is isolated in either a **disk cartridge** or a **column**.



Solid-phase extraction cartridges: (a) disk cartridge; (b) column cartridge.

Solid phase extraction is a sample preparation method that use mainly to concentrate (preconcentration) and purify the analytes prior to its analysis. SPE is one of the most common technique for environmental water sample pretreatment because of its advantages.

- High recovery.
- Short extraction time.
- High enrichment factor.
- Low cost.
- Low consumption of organic solvents.
- A wide range of solid phase materials is available.
- No problem with the miscibility of solvent.
- Easily and simplicity to be automated and operated.
- Compatibility with chromatographic analysis.

For many analyses, solid–phase extractions are replacing liquid–liquid extractions due to their advantages.

The three major purposes for SPE are:

1. Sample concentration (Enrichment): frequently, the component of interest is present in levels too low for detection. Sample preparation can concentrate (make preconcetration) the component to adequate levels for measurement (to reach the sensitivity of the analytical instrument).

2. Elimination of contaminations: the presence of interfering matrix elements can mask the analysis of the component of interest. Sample preparation can remove excess contaminations to yield clean, informative chromatograms.

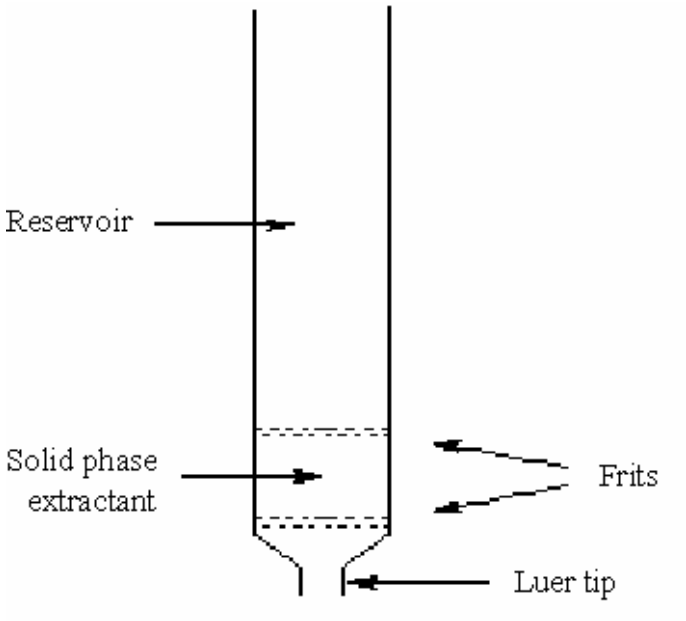
3. Dissolution (sample preparation): for most analyses, the sample must be properly dissolved in a solvent for subsequent analysis.

The history of SPE dates back at least to the early 1970s, when columns packed with Rohm and Hass **XAD** resin particles were used to concentrate very low concentrations of organic pollutants from water samples (Thurman and Mills, 1998), (Burnham *et al.*, 1972).

However, activated carbon had been used for several years prior to 1970 to accumulate organic solutes prior to analysis.

Amberlite (XAD resin) is the tradename of a range of ion-exchange resins **(ion-exchange polymer).** AMBERLITE™ XAD™ polymeric adsorbents are very porous spherical polymers based on highly crosslinked, macroreticular polystyrene, aliphatic, or phenol-formaldehyde condensate polymers.

The stationary phase is retained in a glass or plastic column above a frit or glass wool plugs. The column might have a frit on top of the stationary phase and might also have a stopcock to control the flow of solvent through the column. Usually, SPE cartridges are discarded after use.



A solid-phase extraction column (cartridge).

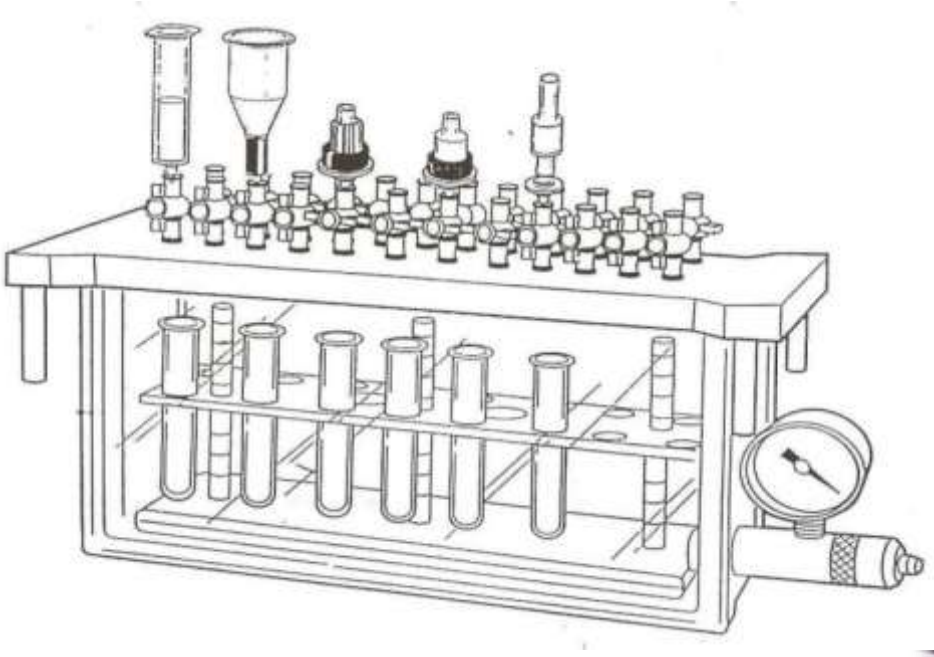
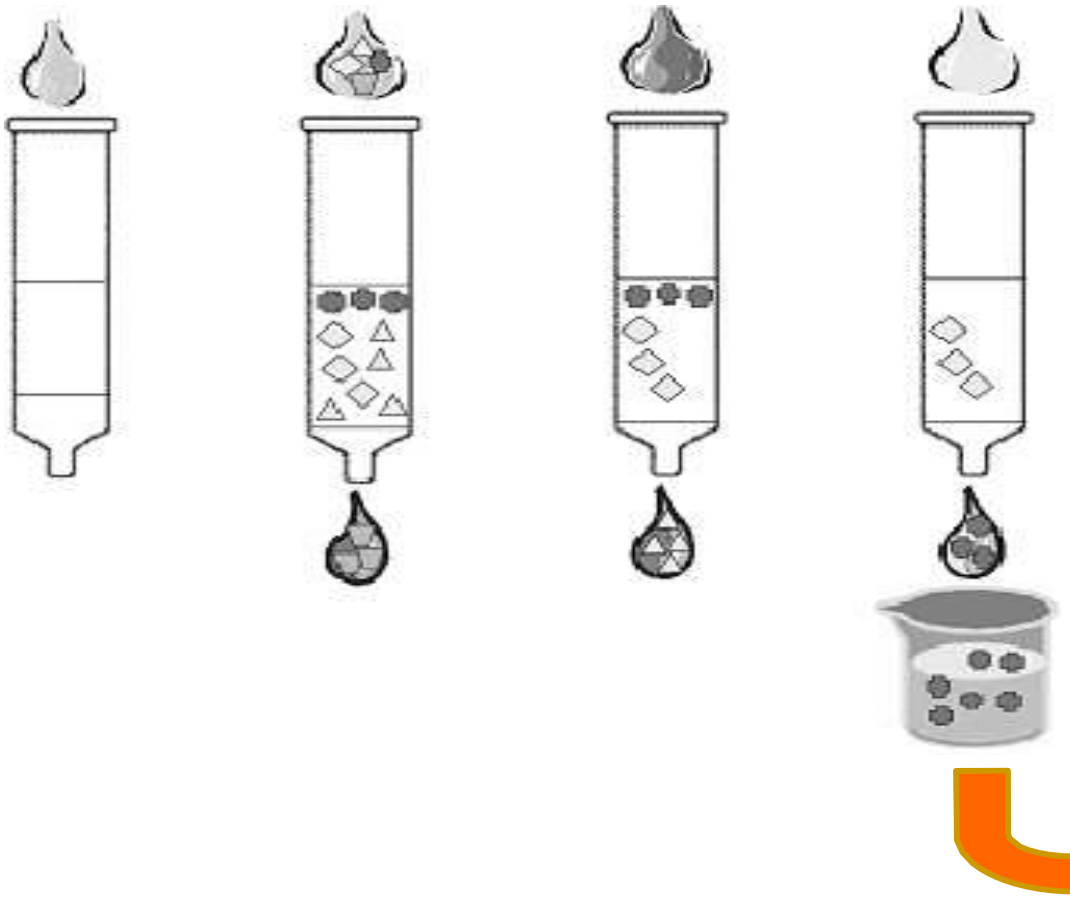


Illustration of a solid-phase extraction set-up.

A collection tube is placed beneath the SPE cartridge (inside the vacuum manifold) to collect the liquid that passes through the column.

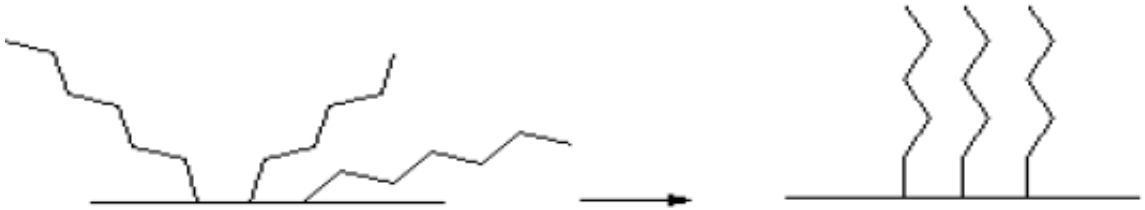
General Solid Phase Extraction Procedure



The general procedure is to load a solution onto the SPE phase, wash away undesired components, and then wash off the desired analytes with another solvent into a collection tube.

Conditioning

Before sample loading, sorbent bed must be prepared and made compatible with the liquid solution. Without pretreatment, the solvent flows in small channels through the solid phase without making the necessary close contact, which lead to inefficient extraction of the analyte and cause problems with sample flow through the disk or cartridge and can ultimately result in low recoveries of analytes. The necessary pretreatment involves the use of a mediating solvent that will promote better surface contact between the phases. Therefore, this step is used to rinse and activate the SPE sorbent with organic solvents or a mixture of organic solvents and reagent water. If the sorbent bed is allowed to dry out, it must be re-solvated prior to use.



Schematic representation of the effect of solvation on a chemically-bonded stationary phase. Activation of stationary phase with the appropriate solvent

Loading

Preparation of sample, followed by extraction of sample by passing the sample through the solid sorbent. It should be noted that the sorbent bed should not be allowed to go dry at any point during the SPE process. The presence of air in the column prevents efficient interfacial contact between the liquid and solid phases.

Washing

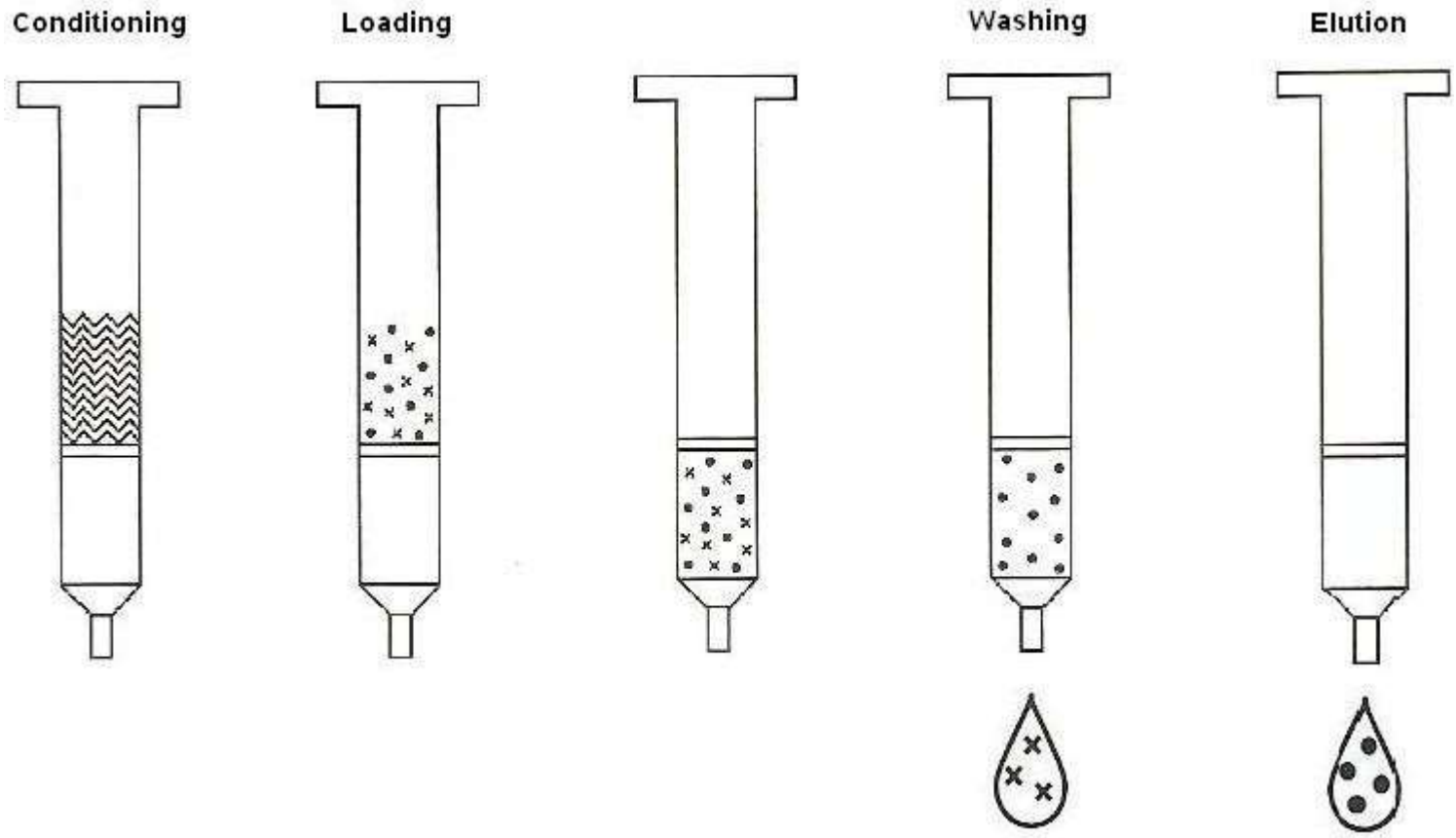
A carefully chosen wash liquid affords the opportunity to remove possible contaminants in the sample, and to move co-adsorbed matrix materials from the cartridge (SPE column) which may interfere with the analysis.

Elution

In the elution step the adsorbed analytes (desired compounds) are eluted from solid sorbent with organic solvents or a mixture of solvents and collected for analysis. The eluting liquid should be chosen carefully, in order to elute the analytes completely from the solid phase using as small an eluent volume as possible. The eluting solvent must be compatible with the analytical measurement step used.

One additional step may be necessary to complete the analytical process, namely evaporation then reconstitution. This step may lead to more enrichment for some analytes.

A schematic of the four stages of SPE



e.g., 1000 mL sample loading volume
Eluted with10 mL solvent
Theoretical enrichment (preconcentration) factor = 1000/10 = 100

The choice of adsorbents is the most important factor to achieve high enrichment efficiency and full recovery of analytes.

The SPE is offered in a wide variety of chemistries and configurations. The range of chemistries covered includes reversed-phase, normal phase, ion-exchange and other sorbents for special applications. Each design offers specific functional benefits:

Normal Phase SPE

Consist of a stationary phase that is more polar than the solvent or sample matrix that is applied to the SPE sorbent. These sorbents include **Silica**, **Amino**, **Cyano**, **Diol** and **Alumina**.

Reversed Phase SPE

Reversed-phase sorbents are packing materials that are more hydrophobic than the sample. And are commonly used in SPE when aqueous samples are involved. These sorbents include **C18** the most commonly used reversed phase. in addition to, **C8**, **C2**, **Cyclohexyl** and **phenyl** bonded phases.

Ion Exchange SPE

Ion exchange phases are more dependent on pH, ionic strength, and counter-ion strength than on solvent strength. These phases depend on ionic interactions as the primary retention mechanism. These sorbents include **anion exchangers** (**AX**) and **cation exchangers** (**CX**).

The nature of the sample and the compounds to be isolated will determine the proper sorbent type. Aqueous or polar organic matrices generally require reversed phases, while nonpolar matrices require a normal phase, The matrix can often be modified by adding an appropriate solvent to increase or decrease its polarity.

The analyst also determines whether the compound of interest is to be retained for later elution, or whether the goal is to retain the interfering compounds, For example, a nonpolar analyte (e.g. pesticides, drug) in a polar sample matrix (e.g. water, urine) would indicate that a reversed phase would be the appropriate sorbent to choose.

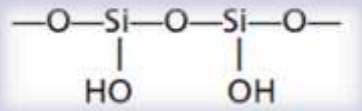
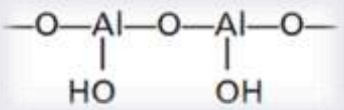
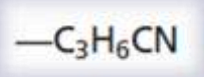
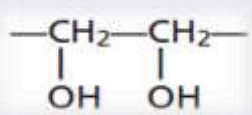
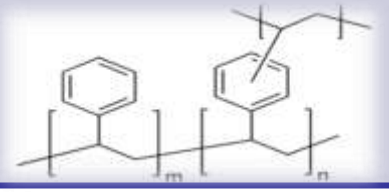
Summary of the different types and guidelines for SPE

Separation guidelines for SPE

Mode	Normal phase	Reversed phase	Ion exchange phase
Sorbent polarity	High	Low	High
Typical solvent polarity range	Low to medium	High to medium	High
Typical sample loading solvent	Hexane, toluene, dichloromethane	Water, buffers	Water, buffers
Typical elution solvents	Ethyl acetate, acetone, acetonitrile	Water, methanol, acetonitrile	Buffers, salt solutions
Sample elution components order	Least polar sample components first	Most polar sample components first	Sample components most weakly ionized first
Solvent change required to elute retained compounds	Increase solvent polarity	Decrease solvent polarity	Increase ionic strength or increase pH (AX) or decrease pH (CX)

The choice of adsorbent is determined by the properties of the species being retained and the matrix in which it is found.

Selected adsorbents for solid-phase extraction of liquid samples

Adsorbent	Surface Structure	Properties and Uses
silica		retains low-to-moderate polarity species from organic matrices, fat-soluble vitamins, steroids.
alumina		retains hydrophilic species from organic matrices.
cyanopropyl		retains wide variety of species from aqueous and organic matrices, pesticides, hydrophobic peptides.
diol		retains wide variety of species from aqueous and organic matrices, proteins, peptides, fungicides.
octadecyl (C-18)		retains hydrophobic species from aqueous matrices, caffeine, sedatives, polyaromatic hydrocarbons, carbohydrates, pesticides.
octyl (C-8)		similar to C-18.
Styrene divinylbenzene		wide variety of organic species from aqueous matrices, polyaromatic hydrocarbons.

SPE process can be referred to as "catch and release".

The type of SPE cartridge (sorbent) and elution solvent that are used depends on the molecules structure and the sample matrix (specially, on the polarity of the compound). So, the first consideration in determining the most appropriate SPE methodology are the structure and polarity of the analytes of interest.

To make effective solid phase extraction we select chemicals that maximize analyte retention for adsorption and minimize analyte retention for elution.

Solid-Phase Microextraction (SPME)

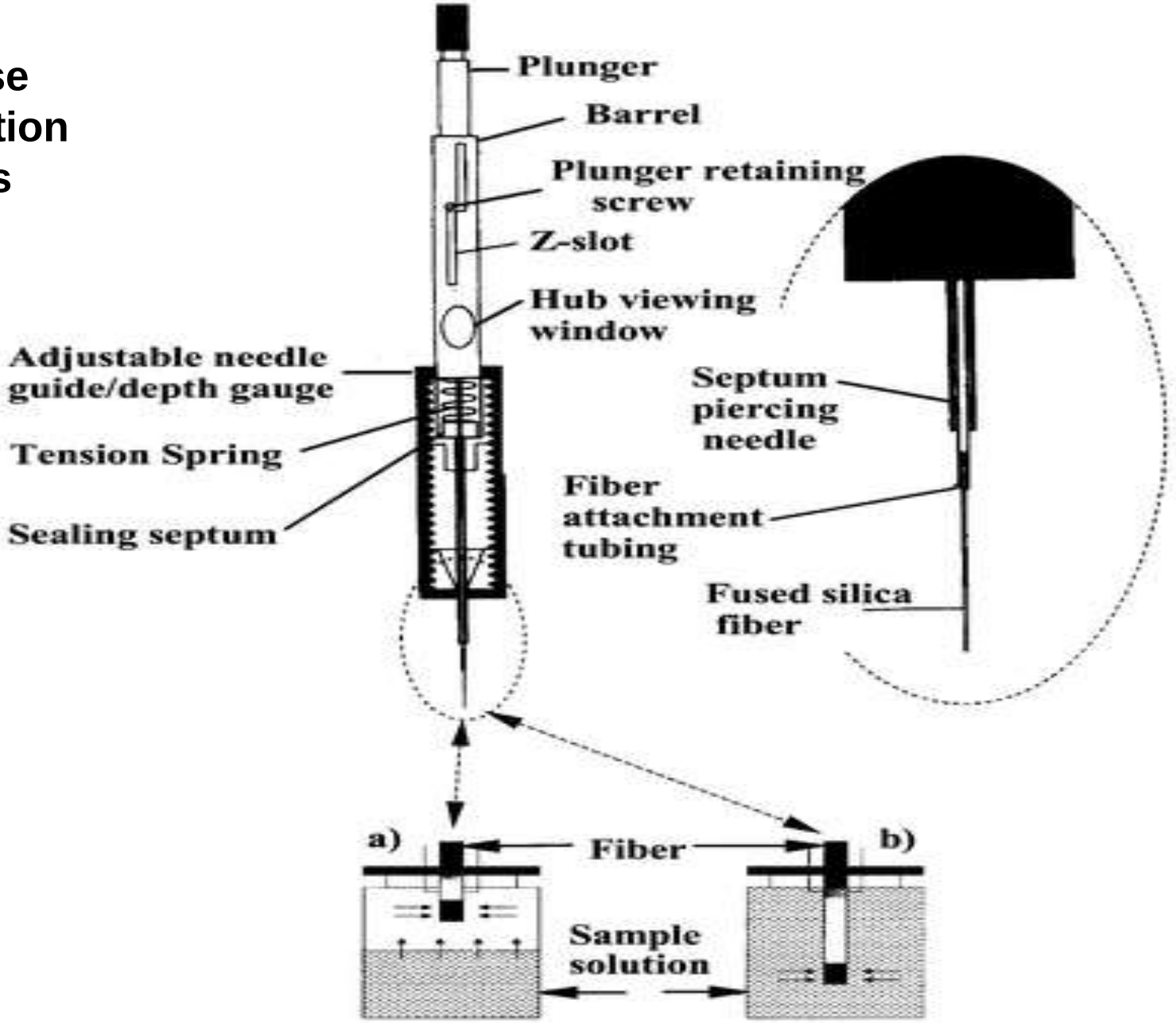
A technique that uses a short, thin, silica fused rod which is coated with absorbent polymer (fiber) for extraction of compounds.

Principle: Equilibrium partitioning of compounds between the fiber and liquid sample.

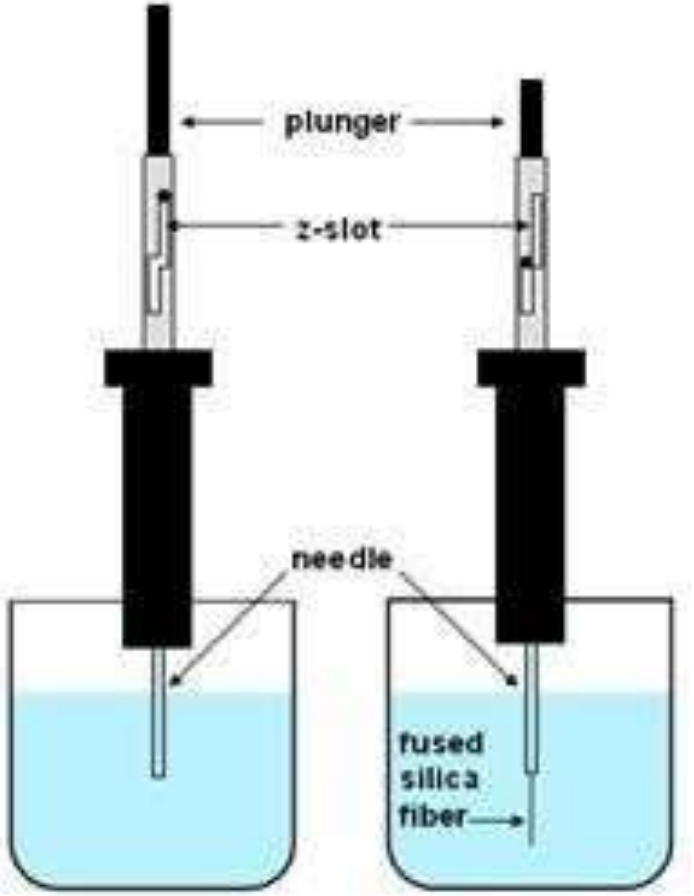
It is fast, sensitive, inexpensive, portable and solvent-free (no solvents used).

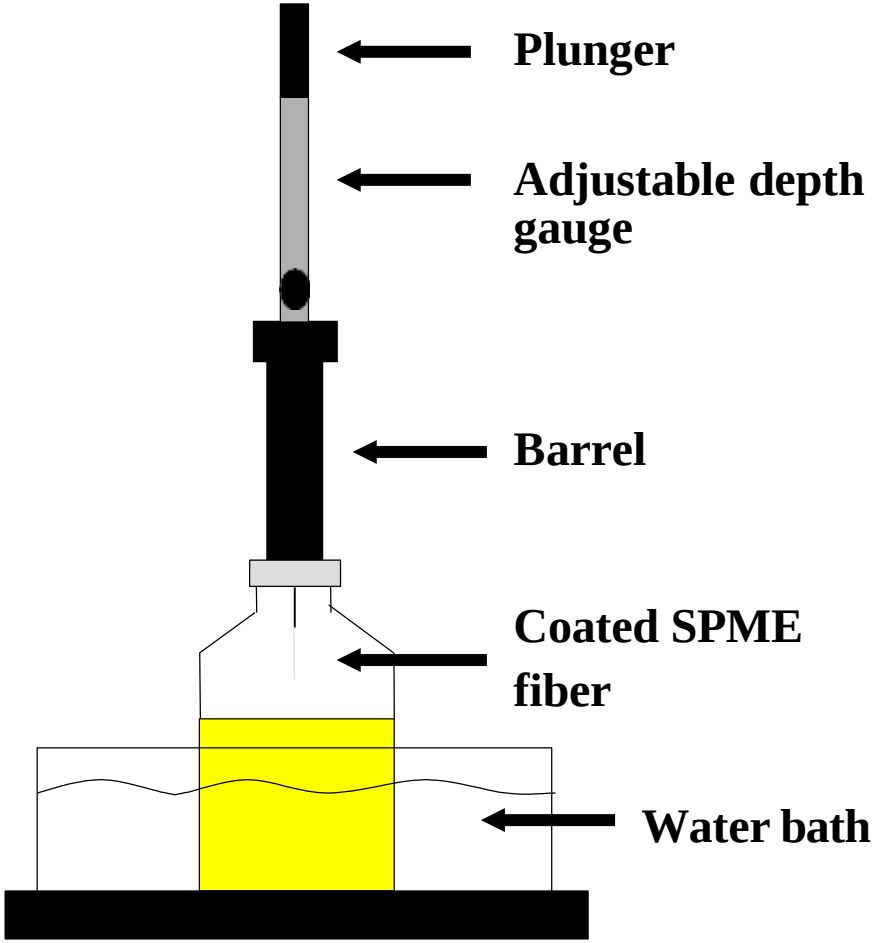
SPME was introduced by Belardi and Pawliszyn in 1989.

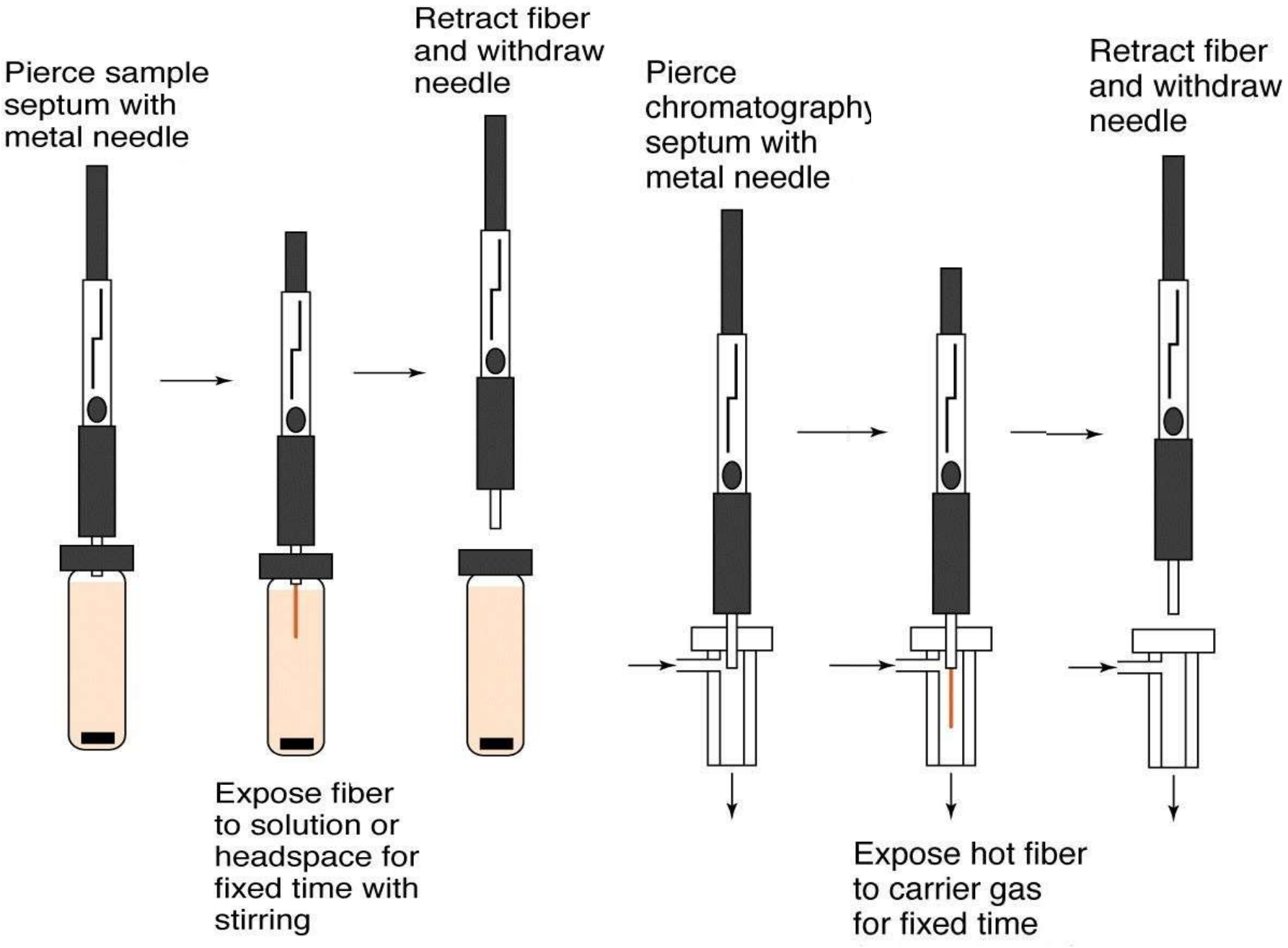
Solid phase microextraction apparatus



For both solutions and as head space (either for **LC** or **GC**).






Pierce sample septum with metal needle
Expose fiber to solution or headspace for fixed time with stirring
Retract fiber and withdraw needle
Pierce chromatography septum with metal needle
Expose hot fiber to carrier gas for fixed time
Retract fiber and withdraw needle

In one approach, a fused silica fiber is placed inside a syringe needle.

The fiber, which is coated with a thin organic film, such as poly(dimethyl siloxane), is lowered into the sample by depressing a plunger and exposed to the sample for a predetermined time.

The fiber is then withdrawn into the needle and transferred to (a gas chromatograph) for analysis.

Gas-Solid Extractions

In gas-solid extractions the sample is passed through a container packed with a solid adsorbent. One example of the application of gas-solid extraction is in the analysis of organic compounds for carbon and hydrogen.

The sample is combusted in a flowing stream of O_2, and the gaseous combustion products are passed through a series of solid-phase adsorbents that remove the CO_2 and H_2O.

Continuous Extractions

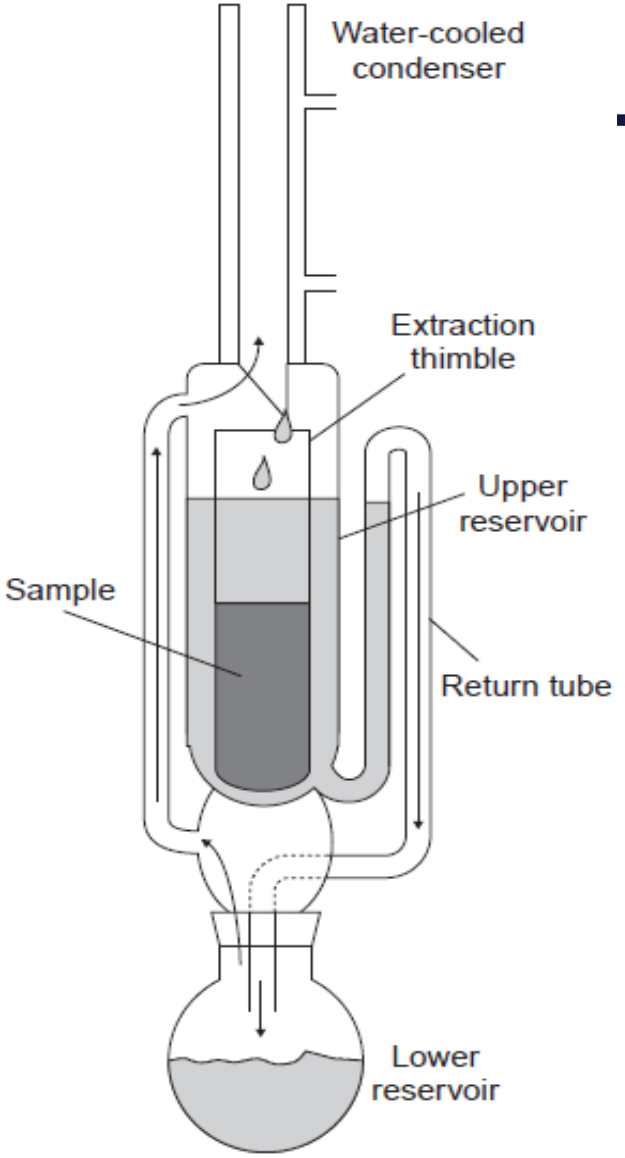
$$S_{\text{phase 1}} \rightleftharpoons S_{\text{phase 2}} \qquad K_D = \frac{[S_{\text{phase 2}}]}{[S_{\text{phase 1}}]}$$

If **partition coefficient K_D** is sufficiently large, then the solute will move from phase 1 to phase 2. The solute will remain in phase 1, however, if the partition coefficient is sufficiently small.

An extraction is still feasible even when the component of interest has an unfavorable partition coefficient, provided that all other components in the sample have significantly smaller partition coefficients. Because the partition coefficient is unfavorable, a simple extraction will not be quantitative. Instead, the extraction is accomplished by continuously passing the extracting phase through the sample until a quantitative extraction is achieved.

Soxhlet Extraction

Many continuous extractions involving solid samples are carried out with a **Soxhlet extractor**. The extracting solvent is placed in the lower reservoir and heated to its boiling point. Solvent in the vapor phase moves upward through the tube on the left side of the apparatus to the condenser where it condenses back to the liquid state. The solvent then passes through the sample, which is held in a porous cellulose filter thimble, collecting in the upper reservoir. When the volume of solvent in the upper reservoir reaches the upper bend of the return tube, the solvent and any extracted components are siphoned back to the lower reservoir. Over time, the concentration of the extracted component in the lower reservoir increases.



Schematic diagram of a Soxhlet extractor.

Soxhlet extractions have been replaced in some applications by **microwave assisted extractions**. The process is the same as that of the microwave digestion.

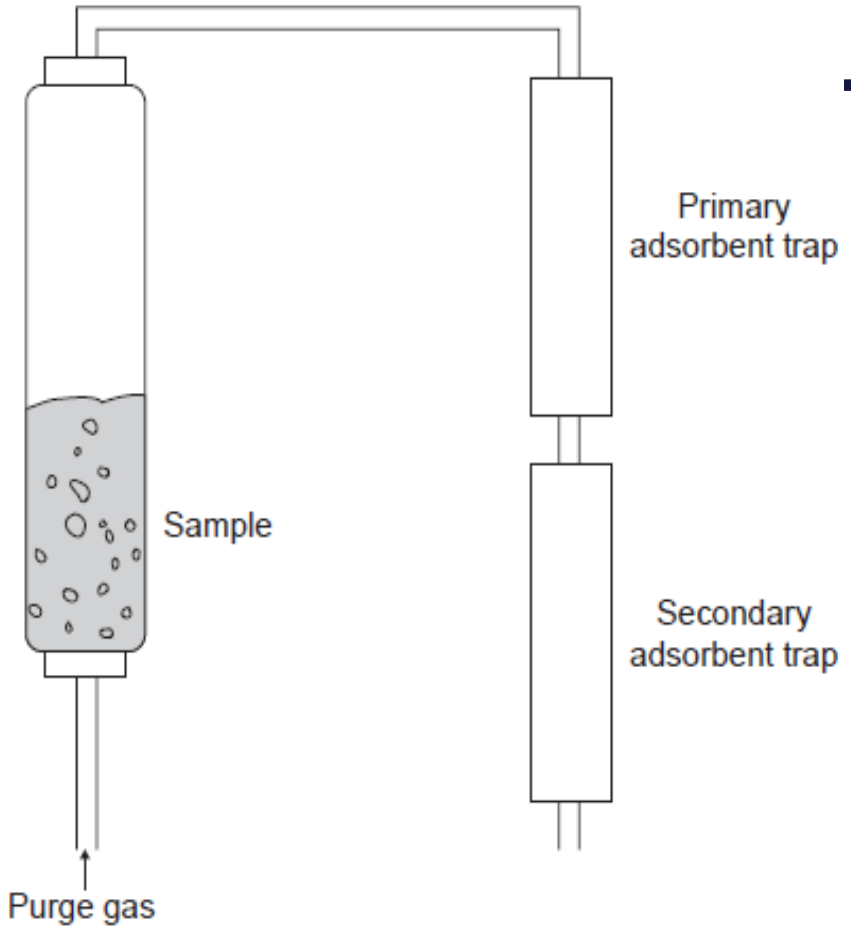
The sample is placed in a sealed digestion vessel along with the liquid extraction phase, and a microwave oven is used to heat the extraction mixture. Using a sealed digestion vessel allows the extraction to take place at a higher temperature and pressure, thereby reducing the amount of time needed for a quantitative extraction.

In a Soxhlet extraction the temperature is limited by the solvent's boiling point at atmospheric pressure. For example, when acetone is the solvent, a Soxhlet extraction is limited to 56 °C (acetone boiling point). With a microwave assisted extraction, however, a temperature of over 150 °C can be obtained when using acetone as the solvent.

Purge and Trap

Purge and trap is a technique for separating volatile analytes from liquid samples in which the analytes are subsequently trapped on a solid adsorbent. Volatile organic compounds (VOCs) can be quantitatively removed from liquid samples by a **liquid–gas extraction**.

As shown in the Figure, the VOCs are removed by passing an inert purging gas, such as **He**, through the sample. The **He** removes the VOCs, which are then carried by the **He** to a tube where they are collected on a solid adsorbent. When the extraction is complete, the VOCs can then be removed from the trap for analysis by rapidly heating the tube while flushing with **He**. Recoveries for analytes using a purge and trap may not be reproducible, requiring the use of internal standards for quantitative work.



Schematic diagram of a purge-and-trap system. Analyte is collected in the primary adsorption trap. The secondary adsorption trap is monitored for evidence of breakthrough.

Continuous extractions also can be accomplished with **supercritical fluids.** When a substance is heated above its critical temperature and pressure, it forms a supercritical fluid whose properties are between those of a gas and a liquid. Supercritical fluids are better solvents than gases, making them a better reagent for extractions.

In addition, the **viscosity** of a supercritical fluid is significantly less than that of a liquid solvent, allowing it to pass more readily through particulate samples.

One example of a supercritical extraction is the determination of total petroleum hydrocarbons (TPHs) in soils, sediments, and sludges with supercritical **CO_2**. Approximately 3 g of sample is placed in a 10-mL stainless steel cartridge, and supercritical CO_2, at a pressure of 340 atm and a temperature of 80 °C, is passed through the cartridge for 30 min at flow rate of 1–2 mL/min. The petroleum hydrocarbons are collected by passing the effluent from the cartridge through 3 mL of tetrachloroethylene at room temperature. At this temperature the CO_2 reverts to the gas phase and is released to the atmosphere.

Supercritical fluid
A state of matter where a substance is held at a temperature and pressure that exceeds its critical temperature and pressure.

Extraction Versus Chromatography

In an extraction, the sample is initially present in one phase, and the component of interest is extracted into a second phase. Separations can also be accomplished by continuously passing one sample free phase, called the mobile phase, over a second sample free phase that remains fixed or stationary.

In the chromatographic separation techniques, the sample is injected or placed into the mobile phase. As the sample's components move with the mobile phase, they partition themselves between the mobile and stationary phases. Those components having the largest partition coefficients are more likely to move into the stationary phase, taking longer to pass through the system.

The difference between HPLC and SPE arises in that liquid chromatography separates the compounds in a continuously flowing system of mobile phase; Whereas SPE retains the solutes onto the solid phase while the rest of the sample passes through, followed by elution of the analyte with appropriate solvent.

The SPE is a simple on/off type of liquid chromatography that does not involve fractionation of the retained analytes.


Thank You!