Solvent Extraction

A significant method based on relative solubility of an analyte in two immiscible liquids

Used to

- remove interference
- concentrate species prior analysis
- produce measurable form of a species

Basic theory is applicable to chromatography.

Solvent extraction theory

For a solute, Z, in equilibrium exists between two immiscible solvents.

$$Z_{aq} \leftrightharpoons Z_{org}$$

$$\Delta G = \Delta G^{O} + RT\,ln\,a_{Z_{org}} - RT\,ln\,a_{Z_{aq}}$$

$$\Delta G = \Delta G^{O} + RT\,ln\frac{a_{Z_{org}}}{a_{Z_{aq}}}$$

where a = activity
G = free energy

One of the solvents is usually water and that's what we'll focus on - as the phase we extract 'from.'

Partition coefficient

Since $\Delta G = 0$ at equilibrium, activity ratio is:

$$\frac{a_{Z_{org}}}{a_{Z_{aq}}} = e^{\frac{-\Delta G^{O}}{RT}}$$

It's also called the thermodynamic partition coefficient:

$$K_P = \frac{a_{Z_{org}}}{a_{Z_{aq}}}$$

Assumes a constant temperature.

Partition coefficient

Rather than use activity, we typically use concentration, giving:

$$K_P = \frac{[Z]_{org}}{[Z]_{aq}} = \frac{[Z]_1}{[Z]_2}$$

So, add the assumption of ideal solution behavior at low concentrations.

Distribution ratio

Due to potential for competing equilibria, we define an alternate form of the partition coefficient:

Distribution ratio

$$D_C = \frac{[Z_{total}]_{org}}{[Z_{total}]_{aq}} = \frac{[Z_{total}]_1}{[Z_{total}]_2}$$

Total Z represents the total of all equilibrium forms of species Z.

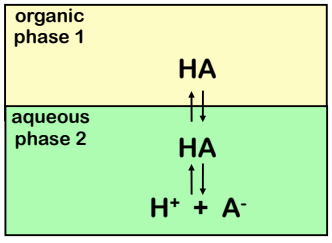
This ratio is based on specific solution conditions such as pH.

Example: pH dependence of D_c

When dealing with aqueous species, the solute may exist in equilibrium with several other forms.

Example

- a weak acid



Example: pH dependence of D_c

Where $K_P = \frac{[HA]_1}{[HA]_2}$ and $K_a = \frac{[H^+]_2[A^-]_2}{[HA]_2}$

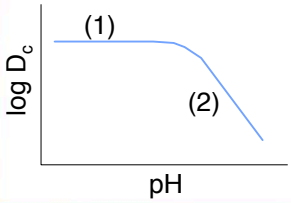
$$D_C = \frac{[HA]_1}{[HA]_2 + [A^-]_2} = \frac{[HA]_1}{\frac{[HA]_1}{K_P} + \frac{K_a[HA]_1}{K_P[H^+]_2}}$$

$$= \frac{K_P[H^+]_2}{[H^+]_2 + K_a}$$

Example: pH dependence of D_c

In the case of a weak acid, D_c is highly dependent on solution pH.

$$D_C = \frac{K_P[H^+]_2}{[H^+]_2 + K_a}$$



A plot of log D_c vs log pH shows two regions.

1 - $[H^+] >> K_a$, $D_c \simeq K_P$

2 - D_c is pH dependent

pH and D_c

So, when dealing with weak acids and bases, pH must be held constant - typically by adding either H_3PO_4 or NaOH.

Goal is to convert species to undissociated (extractable form).

pH is not the only concern. Formation of complexes can also result in multiple forms of Z.

Solute partitioning

D_c can be defined based on total equilibrium concentrations as:

$$D_C = \frac{C_1}{C_2}$$

where:

1 is the phase being extracted into

2 is the phase being extracted from

All solution conditions are assumed constant unless otherwise noted. Total solute amounts are based on solution volume.

Solute partitioning

The initial moles of solute is C_0V_2 so at equilibrium: $n_{solute1} = C_1V_1$

$$n_{solute2} = C_2V_2$$

In terms of fractional amounts:

$$p = \text{fraction in 1} = \frac{C_1V_1}{C_1V_1 + C_2V_2}$$

$$q = \text{fraction in 2} = \frac{C_2V_2}{C_1V_1 + C_2V_2}$$

Solute partitioning

If we define the volume ratio (V_R) as

$$V_R = \frac{V_1}{V_2}$$

then $q = \frac{1}{D_CV_R + 1}$ $\quad p = \frac{D_CV_R}{D_CV_R + 1}$

Single extractions

To help keep things straight, let's define some conditions for a single extraction or contact unit.

Most often, we are interested in extracting from an aqueous into an organic phase.

organic phase

density > or < 1.00 g/ml - call phase 1

aqueous phase

density ~ 1.00 g/ml - call phase 2

Single Extractions

If the aqueous phase is what we are extracting from, then:

V - volumes, all must be in same units

C - total concentrations

C_1 - organic concentration

C_2 - aqueous concentration

C_0 - initial concentration

Solute extraction

We can determine the percent extracted as:

$$\%E = 100\ p$$

Example

For a solute, X, determine [X] and total amounts in each phase if:

V_1 = 100.0 ml

V_2 = 100.0 ml

D_c = 3.0

$[X]_0$ = 1.00 x 10^{-2} M (in aqueous phase)

Solute extraction

Since $V_1 = V_2$, $V_R = 1$,

$$p = \frac{D_C V_R}{D_C V_R + 1} = \frac{3.0}{3.0 + 1} = \frac{3}{4}$$

$$q = \frac{1}{D_C V_R + 1} = \frac{1}{3.0 + 1} = \frac{1}{4}$$

$$\%E = 100\,p = 75\%$$

Solute extraction

Determining amounts

We started with 1.00 x 10^{-2} M in 100.0 ml of the aqueous phase so:

n_T = 0.100 L x 1.00x10^{-2}

= 1.00 x 10^{-3} mol

n_1 = 7.5 x 10^{-4} mol M_1 = 7.5 x 10^{-3}

n_2 = 2.5 x 10^{-4} mol M_2 = 2.5 x 10^{-3}

Deviations from ideal behavior

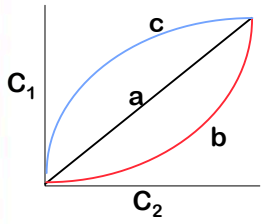
Solutions can vary from ideal behavior either from the start or during an extraction.

Possible causes include:

- dissolution of one phase into the other
- solute saturation of a phase
- reaction of solute with a phase
- alteration of conditions like pH during an extraction.

Deviations from ideal behavior

You can end up with three types of behavior - partition isotherms.



a - ideal behavior.

b - solute association, dimerization, ect.

c - solute approaching saturation.

Deviations from ideal behavior

You must also remember that we assumed that activity and concentration were proportional.

Attempt to avoid problems by:

- Working at low concentrations
- Maintaining factors like pH as constants

We do our best to stay as close to ideal conditions as possible.

Multiple extractions

It is not always possible to quantitative remove the solute using a single extraction.

Your options typically are to:

Increase the volume of the extracting solvent - not usually a good idea.

Use multiple extractions.

Multiple extractions

For n extractions, the amount of solute in each phase can be determined by:

organic phase $pq^{n-1}C_OV_2$

aqueous phase $q^nC_OV_2$

Solute concentrations can be found by:

organic $\frac{pq^{n-1}C_OV_2}{V_1} = \frac{pq^{n-1}C_O}{V_R}$

aqueous $\frac{q^nC_OV_2}{V_2} = q^nC_O$

Multiple extractions

Total amounts extracted are the sum of all extractions so:

$$(p + pq + pq^2 \ldots + pq^{n-1})\, C_0V_2 = (1-q^n)C_0V_2$$

or

$$1 - q^n = E$$

$$\%E = 100\,(1-q^n)$$

Multiple extractions

In our earlier example, 75% of a solute was removed with one extraction. We can determine how much would be removed from 10 sequential extractions.

$n = 10$

$q = 0.25$

$E = 1 - 0.25^{10} = 1 - 9.6 \times 10^{-7}$

$\%E = 99.9999\%$

Countercurrent extractions

A precursor to chromatography.

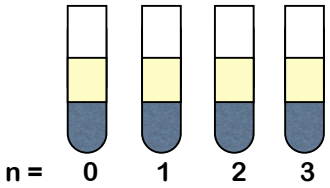
Multiple extractions can effectively remove a single species or a group of related species at the same time.

What do you do if the goal is to separate two or more species with similar D_c values?

Even if the D_c values for two species differ by 1000, you still can't get better than 97% purity.

Countercurrent extractions

We can conduct a sequence of extractions to effect quantitative separation of multiple solutes - countercurrent extraction



We transfer the extracting phase to the next tube and add fresh phase to the first.

Countercurrent extractions

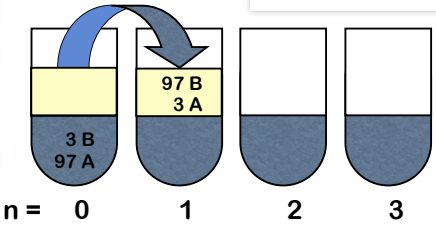
Assume

- Equimolar amounts of solutes A and B.
- Equal volumes of both phases
- A single extraction with an organic phase removes 3% of A and 97% of B.
- After each extraction, you transfer the organic phase to the next tube and add fresh organic phase to the original one.

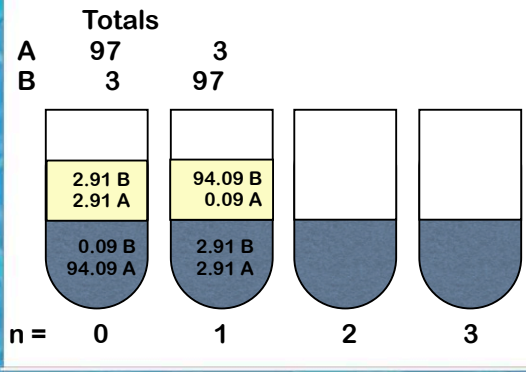
First extraction

Totals
A 100
B 100

Next, the organic phase is transferred to the second tube. A new equilibrium is established.

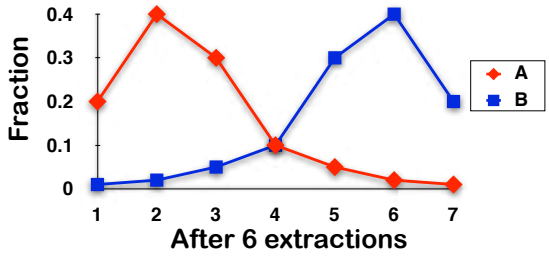


Second extraction



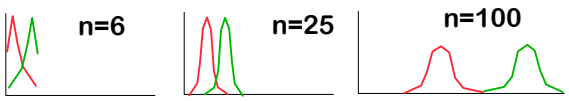
Movement of solutes

Materials with larger D_c values tend to move along with the organic (mobile) phase more rapidly.



Peak shape

As the number of tubes are increased, the distribution of solutes appears more Gaussian. Ultimately, you can resolve them.



The peaks also become broader and shorter - they are distributed over a larger range of tubes.

Continuous extraction

In some cases, it is difficult to efficiently remove a solute unless a large number of extractions are conducted.

An alternate approach is a continuous extraction.

With an appropriate setup, an efficient extraction can be conducted with a minimum of extracting solvent.

Continuous extraction

Advantages

- Only uses a small amount of solvent
- Can remove a high percent of a solute
- Can work unattended for long periods

Setup

Dependent on relative density of liquids or if solids are to be extracted.

Continuous extraction

Continuous extraction

Setup when the extracting solvent is less dense.

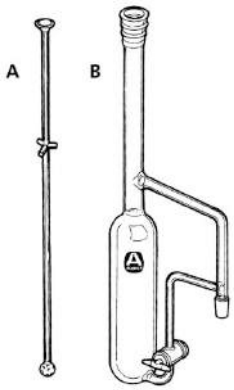
Continuous extraction

For these systems to work

Density difference must be high

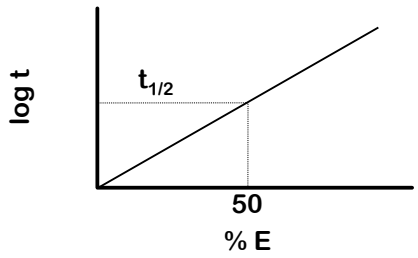
Solute being collected must be less volatile than the extracting solvent

Solute being collected must be thermally stable under conditions used.



Continuous extraction

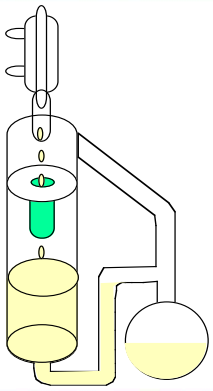
Extraction times follow first order kinetics and are ranked based on half-life.



Continuous extraction

Continuous extraction can also be applied to solids.

Major limitation is a loss in efficiency during extraction due to channels developing in the solid



Soxhlet extraction

An alternate approach to extracting solids.

Repeated soaking of the solid prevents formation of channels

Rapid return of cool fluid can represent a hazard. Solvent should not be flammable.

Solid Phase Extraction

- SPE involves separation of components from a liquid on to a solid medium.
- Mechanism is identical to what will be outlined in LC unit.
- While factors such as pH and ionic strength play a role, the nature of the sorbent is often the most important factor.
- Becoming more popular as a method for removing and concentrating trace organic materials from aqueous media.

Solid Phase Sorbents

Common phases

- C_8 and C_{18} bound phases on silica (most popular).
- Unmodified silica
- Polymeric resins -- polystyrene/divinyl benzene copolymers
- Fluorosil (activated magnesium silicate)
- Alumina
- Charcoal

The silica and bound phase are similar to HPLC phases. The particle size is typically larger than HPLC phases - 40 - 60 μm in diameter.

SPE

The basic idea is to collect (extract) the materials (isolates) of interest on a sorbent and then elute them using a second solvent. This can be set up to:

1. Remove water.
2. Remove interfering species
3. Concentrate the isolates.

The most common format used is the 'Syringe-barrel' cartridge approach.

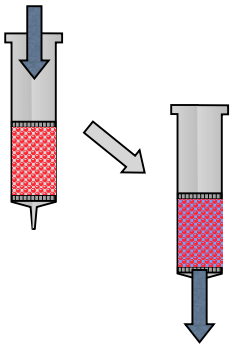
Syringe-barrel cartridges.

- The SPE is carried out using a small packed bed of sorbent (25 - 500 mg).
- The sorbent is contained in a polypropylene syringe barrel and is retained using fritted disks.
- Sorbent typically only fills about half of the barrel so it can accommodate several milliliters of sample solution.
- A distinct four step procedure is then followed to prepare the sample

Syringe-barrel cartridges.

Sorbent conditioning.

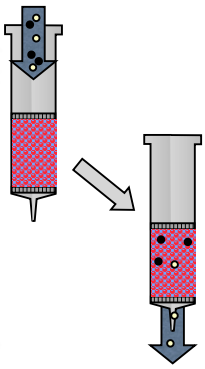
- The cartridge is flushed with sample solvent to remove impurities and wet the sorbent.
- This step also improves the reproducibility of the method.



Syringe-barrel cartridges.

Sampling Loading

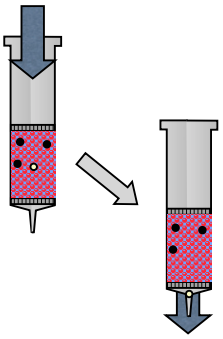
- Sample is then passed through the resin.
- The goal is to retain either the analytes of interest or matrix components.
- The former is used to concentrate analytes.
- The latter is used to remove interferences.



Syringe-barrel cartridges.

Rinsing

Clean solvent is used to remove any remaining 'non-retained' species

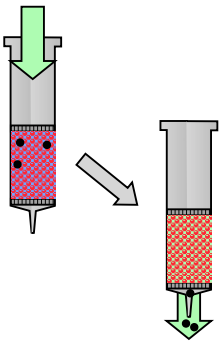


Syringe-barrel cartridges.

Elution

The final step.

The analytes are recovered.



Other approaches

- Thin porous glass fibers.
- Thin coated glass fibers.
- PTFE disks (teflon) in which sorbent particles are embedded.
- Disposable plastic pipette tip fitted with sorbent beds.

The basic process is the same as with the syringe-barrel method.

Coated glass fibers are also being evaluated for solid phase microextraction

Solid phase microextraction

- A fiber (~1 cm) is attached to a modified microsyringe.
- It is then used to extract trace components from a liquid or gas sample.
- The fiber is retracted into the needle of the syringe.
- The needle is then injected into a gas or liquid chromatograph.
- The fiber is then exposed and the sample components desorbed.

Solid phase microextraction