Sample Preparation: Basics and Physical Methods
(Skoog, nothing)

(Harris, Chapt. 23 & 28)
(641-646 & 817-839)

Other References

- **Sample Preparation in Chromatography** by S.C. Moldoveanu and V. David, Elsevier, 2002
Sample Preparation

- Reasons for pre-treatment
  - Improve method sensitivity
    - Concentrate analyte
    - Change chemical nature of analyte to get greater detector response
  - Remove interfering substances (isolation)
  - Solvent (or phase) transfer for compatibility with analytical method

Physical Pretreatment

- Concentration
  - Phase change
    - Freeze concentration, freeze drying, vacuum distillation, atmospheric pressure distillation
  - Membrane processes
    - Reverse osmosis (RO), ultrafiltration (UF), dialysis
- Isolation
  - Gas transfer / gas stripping
    - Purge & trap (P&T), closed loop stripping (CLSA), headspace analysis
  - Solvent Extraction (SE)
    - Liquid-liquid extraction (LLE), soxhlet extraction, sonication extraction, supercritical fluid (SFE)
  - Solid-phase Extraction (SPE) or adsorption
    - Ion exchange resins, hydrophobic resins, activated carbon, polar adsorbents, micro methods (SPME)
Physical Pretreatment (cont.)

- Change in Solvent/Phase
  - Solid to liquid
    - Many of the same techniques as solvent extraction
  - Liquid to liquid
    - Solvent exchange: again similar to earlier solvent extraction

Chemical Pretreatments

- Derivatization
  - Alkylation
  - Silylation
  - Detector-specific derivatives
- Digestion
- Complexation
- Reduction
Liquid/liquid extraction

- Transfer from one liquid to another
  - Solvents:
    - Water
    - Organics: diethyl ether, pentane, methyl tertiary butyl ether, ethyl acetate
  - Rely on equilibrium partitioning

\[ S_{(aq)} \overset{K}{\leftrightarrow} S_{(sol)} \]

Liquid/Liquid Extraction

- Partition Coefficients
  - Relative solubility of an analyte in an organic solvent to its solubility in water
    \[ K_D = \frac{C_s}{C_w} \]
  - Or more generally, the relative solubilities in two different and immiscible solvents
    \[ K = \frac{[S_1]}{[S_2]} \]
LLE calculations

- Fractional extraction efficiency
  - The mass of analyte in the organic solvent divided by the total analyte mass

\[
f_e = \frac{m_s}{m_s + m_w}
\]

\[
f_e = \frac{C_s V_s}{C_s V_s + C_w V_w}
\]

LLE Calculations (cont.)

- Divide numerator and denominator by \(C_s V_s\)

\[
f_e = \frac{1}{1 + \left(\frac{C_w}{C_s}\right)\left(\frac{V_w}{V_s}\right)}
\]

- And substituting for the partition coefficient

\[
f_e = \frac{1}{1 + \left(\frac{1}{K_D}\right)\left(\frac{V_w}{V_s}\right)}
\]
Example

- Chloroform has a pentane:water partition coefficient of 50 at 20°C. What is the fractional extraction efficiency for a system consisting of 1 liter of aqueous solution and
  - a. 50 mL pentane?
  - b. 25 mL pentane, followed by phase separation, then a second 25 mL volume of pentane?

\[
f_e = \frac{1}{1 + \left( \frac{1}{50} \right) \left( \frac{1000}{50} \right)} = 0.714
\]

\[
f_e = \frac{1}{1 + \left( \frac{1}{50} \right) \left( \frac{1000}{25} \right)} = 0.555
\]

Example (cont.)

- however, for the second extraction, the concentration is reduced to 1-\(f_e\) of the original, so that the overall, two-step serial extraction efficiency, \(f_{2e}\), is:

\[
f_{2e} = f_e + (1 - f_e)f_e
\]

\[
f_{2e} = 0.555 + (1 - 0.555)0.555 = 0.802
\]

- Or 80.2%
LLE Calculations (cont.)

- Writing a mass balance on the analyte before and after extraction
  \[ C_{wi}V_w = V_wC_w + V_sC_s \]
- Allows us to calculate the concentration factor achieved by extraction
  \[ \frac{C_s}{C_{wi}} = \frac{1}{1 + \frac{V_s}{V_wK_D}} \]

And if \( K_D \) is large:
  \[ \frac{C_s}{C_{wi}} \approx \frac{V_w}{V_s} \]

Effect of speciation

- Distribution Coefficients
  \[ D = \frac{\text{total concentration in phase 2}}{\text{total concentration in phase 1}} \]
  - Which for a basic analyte partitioning between water and an organic solvent becomes
    \[ K_a = \frac{[B]}{[BH^+]} \]
  - And since:
    \[ K_a = \frac{\text{H}^+ [B]}{[BH^+]} \]
  - Then:
    \[ D = \frac{K \cdot K_a}{K_a + [H^+]} = K\alpha_l \]
Complexation Methods

- Importance of Speciation
- Ligands

Complexation methods (cont.)

- Extraction of metal ions by dithizone into carbon tetrachloride.
Other issues in LLE

- Salting out
  - Increases $K_D$
  - Produces more stable interface, fewer emulsions
- Addition of colored reagent
  - Improve visual identification of interface
    - e.g., CuSO$_4$

- To next lecture