# CEE 772:
# Instrumental Methods in Environmental Analysis

Lecture #10

**Sample Preparation**: Basics and Physical Methods

(Skoog, nothing)

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

# Other References

- <u>Solid Phase Extraction: Principles and Practice</u>, by E.M. Thurman and M.S. Mills, Wiley, 1998
- <u>Extraction Methods for Environmental Analysis</u>, by J.R. Dean, Wiley, 1998
- <u>Sample Preparation in Chromatography</u> by S.C. Moldoveanu and V. David, Elsevier, 2002
- <u>Sample Preparation for Trace Elemental Analysis</u>, by Z. Mester & R.L. Sturgeon, Elsevier, 2003
- <u>Handbook of Derivatives for Chromatography</u>, by K. Blau & J. Halket, 2nd Edition, Wiley, 1993
- <u>Handbook of Analytical Derivatization Reactions</u>, by D.R. Knapp, Wiley, 1979

# 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

o Concentration
  o Phase change
    o Freeze concentration, freeze drying, vacuum distillation, atmospheric pressure distillation
  o Membrane processes
    o Reverse osmosis (RO), ultrafiltration (UF), dialysis
o Isolation
  o Gas transfer/ gas stripping
    o Purge & trap (P&T), closed loop stripping (CLSA), headspace analysis
  o Solvent Extraction (SE)
    o Liquid-liquid extraction (LLE), soxhlet extraction, sonication extraction, supercritical fluid (SFE)
  o Solid-phase Extraction (SPE) or adsorption
    o 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

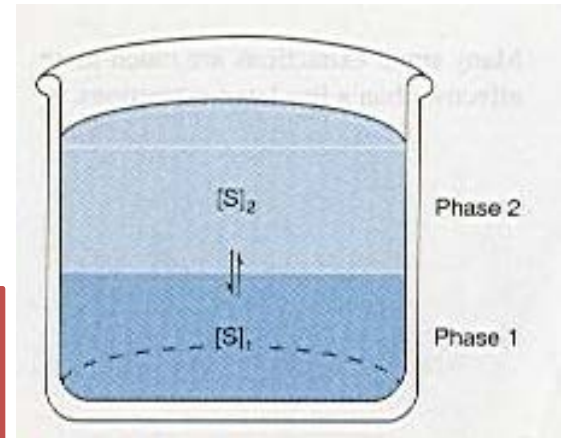$$S_{(aq)} \xleftarrow{\quad K \quad} S_{(sol)}$$
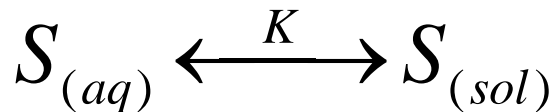
# Liquid/Liquid Extraction

- 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

$$K = \frac{[S]_2}{[S]_1}$$

# 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.)

o Divide numerator and denominator by $C_s V_s$

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

o And substituting for the partition coefficient

$$f_e = \frac{1}{1 + \left( \dfrac{1}{K_D} \right)\left( \dfrac{V_w}{V_s} \right)}$$

# 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?

$$f_e = \frac{1}{1 + \left(\dfrac{1}{50}\right)\left(\dfrac{1000}{50}\right)} = 0.714$$

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

# 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:

$$f_{2e} = f_e + \left(1 - f_e\right)f_e$$

$$f_{2e} = 0.555 + \left(1 - 0.555\right)0.555 = 0.802$$

- Or 80.2%

# LLE Calculations (cont.)

❑ Writing a mass balance on the analyte before and after extraction

$$C_{wi}V_w = V_w C_w + V_s C_s$$

❑ Allows us to calculate the concentration factor achieved by extraction

$$\frac{C_s}{C_{wi}} = \frac{1}{\dfrac{1}{K_D} + \dfrac{V_s}{V_w}}$$

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

$$D = \frac{[B]_2}{[B]_1 + [BH^+]_1}$$
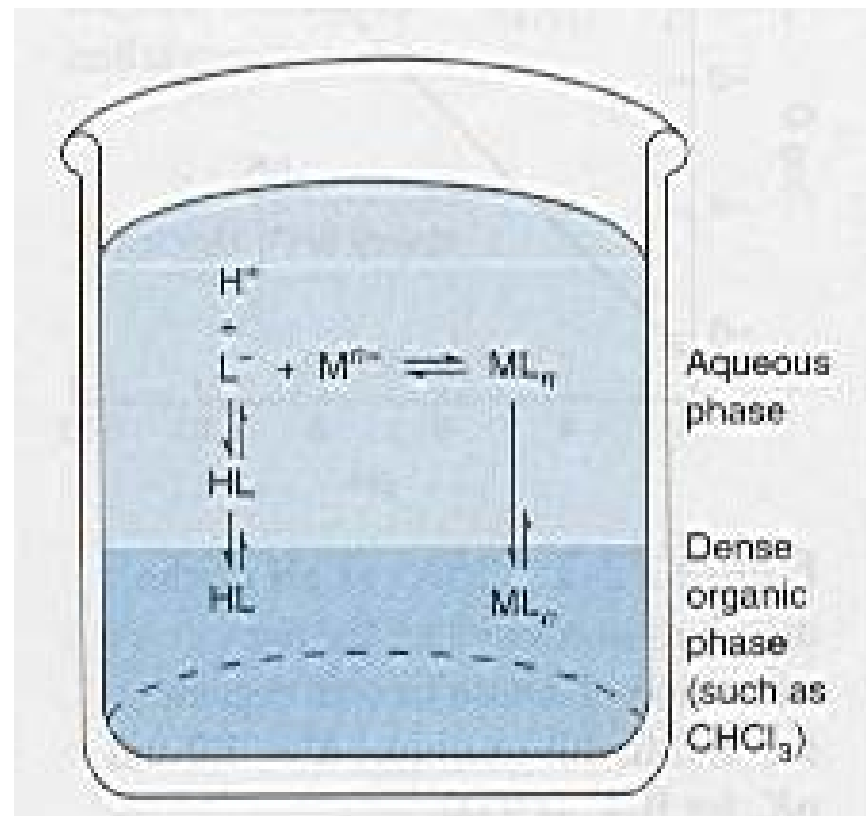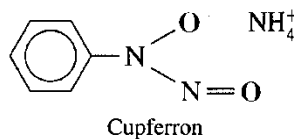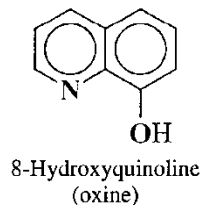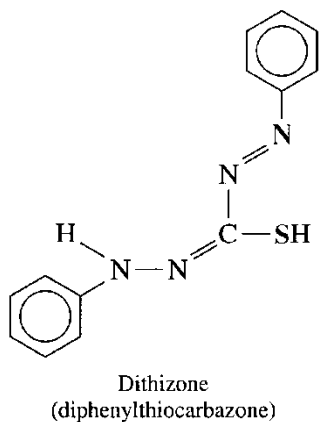
- And since:

$$K_a = \frac{[H^+][B]}{[BH^+]}$$

- Then:

$$D = \frac{K \bullet K_a}{K_a + [H^+]} = K\alpha_1$$
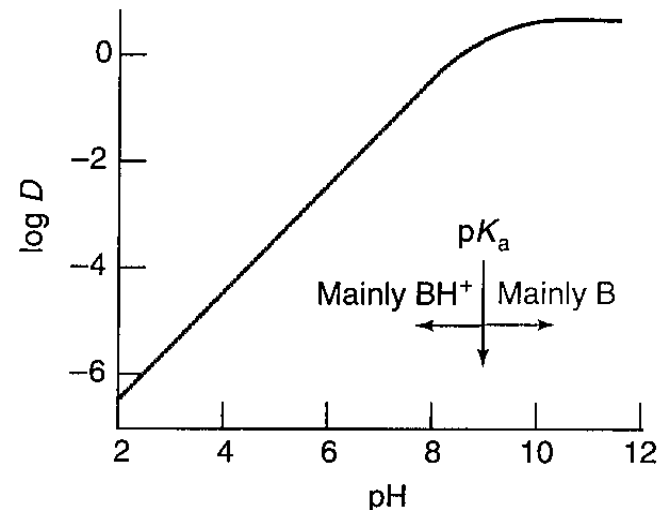
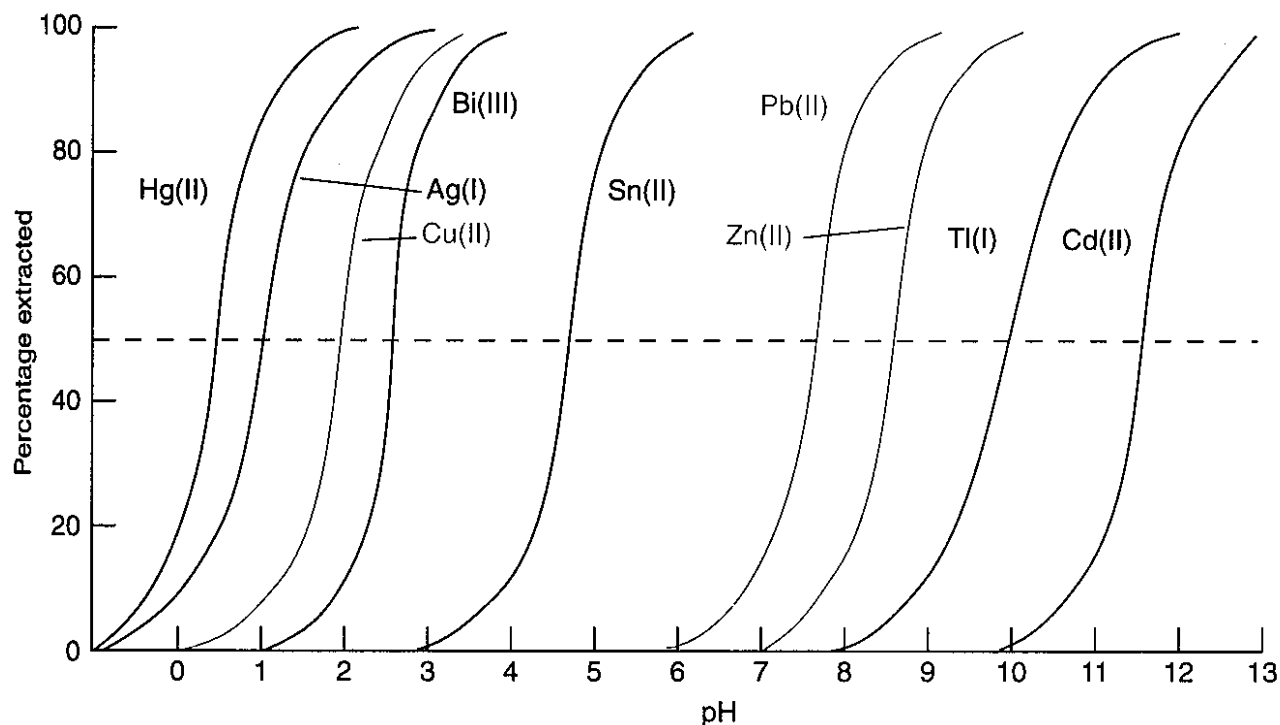# Complexation Methods

- Importance of Speciation
- Ligands



Dithizone
(diphenylthiocarbazone)

8-Hydroxyquinoline
(oxine)

Cupferron

# 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](#)