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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)

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Other References

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

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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

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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)

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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

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Chemical Pretreatments

➢Derivatization
- ➢Alkylation
- ➢Silylation
- ➢Detector-specific derivatives

➢Digestion

➢Complexation

➢Reduction

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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
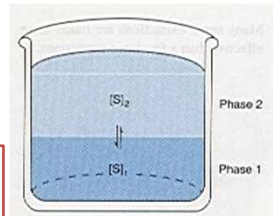
$$S_{(aq)} \xleftrightarrow{\ K\ } S_{(sol)}$$
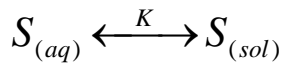
Liquid/Liquid Extraction

- 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

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

[S]$_2$ Phase 2

[S]$_1$ Phase 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?

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

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

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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%

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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

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

And if K_D is large:

$$\frac{C_s}{C_{wi}} \approx \frac{V_w}{V_s}$$

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Effect of speciation

▪ Distribution Coefficients

$$D = \frac{\text{total concentration in phase 2}}{\text{total concentration in phase 1}}$$

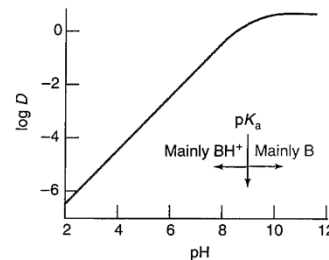 ▪ Which for a basic analyte partitioning between water and an organic solvent becomes

$$D = \frac{[B]_2}{[B]_1 + [BH^+]_1}$$

  ▪ And since:

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

  ▪ Then:

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

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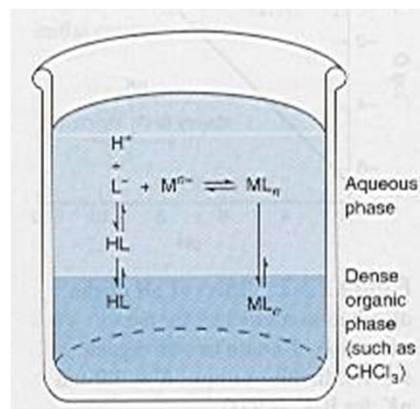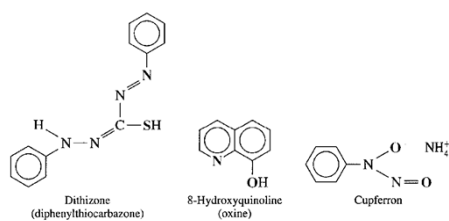
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Complexation Methods

- Importance of Speciation
- Ligands
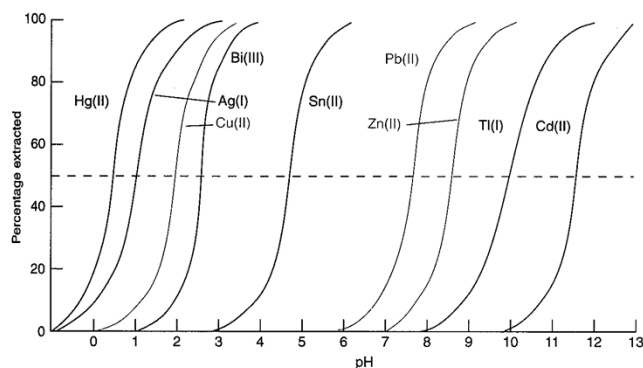

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Complexation methods (cont.)

- Extraction of metal ions by dithizone into carbon tetrachloride.

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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., $CuSO_4$

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- To next lecture

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