

Syllabus

- Course Topics

- “Core” Topics
 - Simple Extractions
 - Separation by Ion - Exchange
 - Chromatography (emphasizing instrument based methods)
- Selected “Specialized” Topics
 - Student Presentations and Discussions
 - I will give some “example” special topics:
 - GC x GC

Syllabus

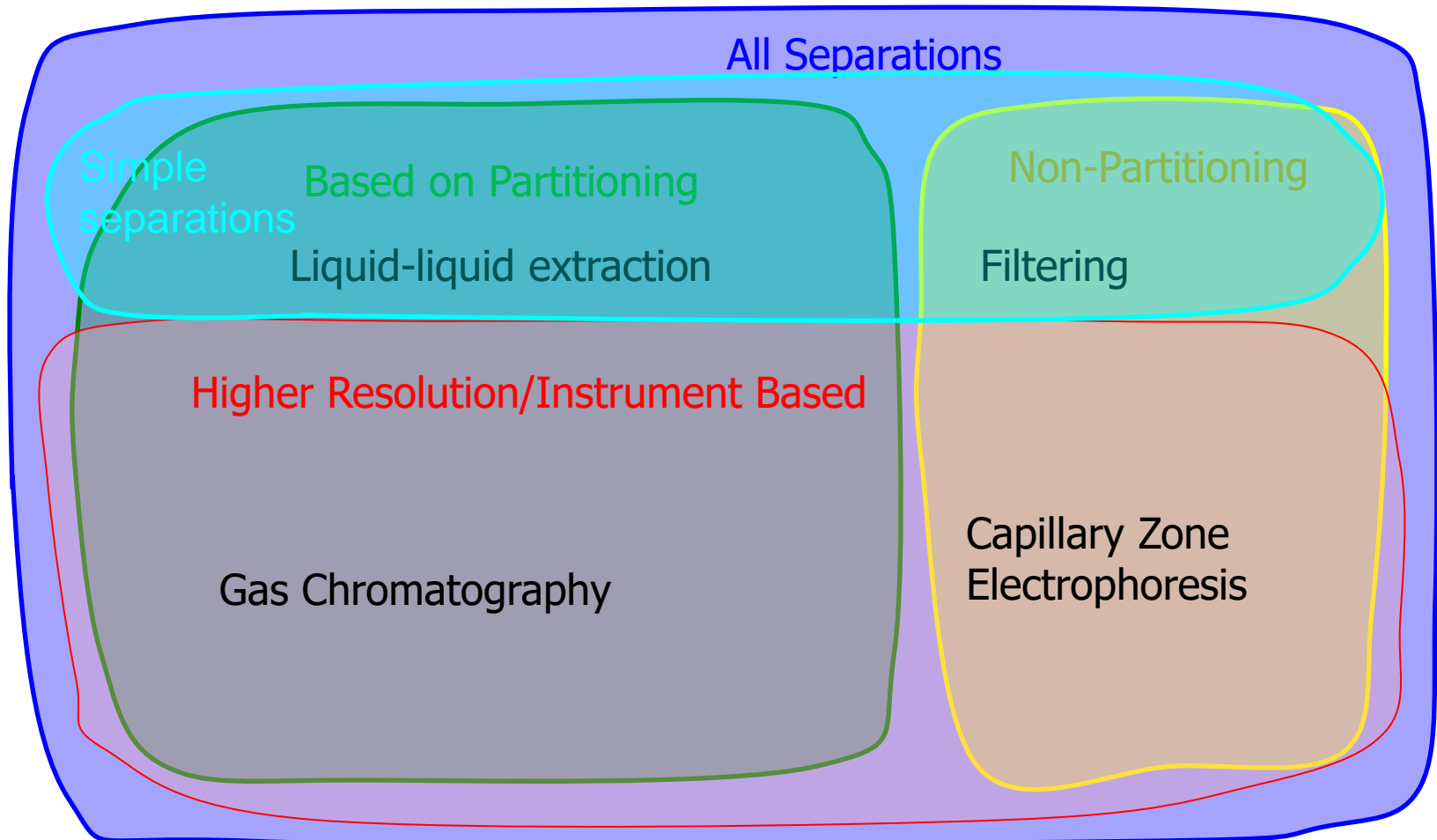
- Notes on Grading

- 40 Minute Exams
 - Previously had 5 quizzes, but switching this semester due to only 14 meetings
 - Used to fit with breakdown of topics and because of 1 long lecture
- Final Exam
 - Fairly standard exam
 - About 35% will come from student presentations

Separation Purposes

- Isolation/Purification/Removal of Compound(s)
- Qualitative Analysis
- Quantitative Analysis

Separations Diagram



classification of separation methods

- A general classification of separation methods is attempted. The two criteria were phase transformations and interfacial transfers. All separation methods of homogenous mixtures were divided into five groups: (i) methods that are based on the formation of new phases by substances to be separated; (ii) methods that are based on differences in the interphase distribution processes, chromatographic methods being singled out as a separate group; (iii) membrane methods that are based on induced transfers of substances from one phase into another one across a third phase, which separates the two; (iv) separation methods within a single phase that are based on velocity and direction differences in spatial displacement of particles of substances to be separated within one fluid phase under the action of various fields; and (v) combined methods working combining previously listed methods.

Simple Separations - aim

- Main purpose is to remove analyte(s) from interferants
- A common purpose is to concentrate analyte(s)
- For complicated samples with numerous analytes, simple separation can be used as coarse separation step
- Often integrated with sample collection (e.g. filtration of air to collect aerosol particles) or sample modification (derivatization)
- Typically insufficient for isolating analytes but needed for reduction of interferants
- common main strategies:
 - “isolation/trapping” of analytes (usually 2 step)
 - “removal” of contaminants (often single step)
 - Primary and secondary separations

Simple Separations

- Examples of Strategies

1. You want to measure combustion exhaust gases by GC. There are around 15 gases of interest that are present at moderately high concentrations. Water also is present at high concentration and interferes.
2. You are interested in measuring phenols present in sea-water at very low concentrations by HPLC. Interference by other organics is not a major issue.
3. You are interested in analyzing oligosaccharides present in glycoproteins by HPLC. There are close to 100 compounds of interest present in the sample.

Simple Separations

- Almost all separations require more than one discrete phase
- The most common separations involve partitioning between two phases
 $X(\text{phase 1}) \leftrightarrow X(\text{phase 2})$
- Some types of non-partitioning separations (mostly involving physical separations):
 - Filtration (removal of solids from gases or liquids)
 - Centrifugation (removal of solids from liquids)
 - Membrane based separations (separation based on molecule size or charge)

Simple Separations

- An effective simple separation requires effective phase transfer plus significant differences in process between analyte and contaminants (good selectivity)
- Sample preparation steps often require as much or more analyst time as instrument based analysis (i.e. are labor-intensive)
- Preferred processes are: simpler, require less equipment, faster, effective with volumes desired, can be automated
- For concentrating samples, it is important that the method can handle large sample volumes, but result in small “processed” volumes

Types of Simple Separations

| Phases | Examples |
|-----------------------------|---|
| Gas - Liquid | Distillation (l to g), denuders (g to l), bubblers (g to l), condensation (g to l) |
| Liquid - Liquid | Liquid – Liquid Extraction (to be covered in detail) |
| Gas - Solid | Adsorption tubes (g to s), sublimation (s to g), freeze-drying (s to g), filtration |
| Liquid - Solid | Dissolution (s to l), Soxhlet extraction (s to l), precipitation (l to s), filtration |
| Supercritical Fluid - Solid | Supercritical Fluid Extraction (s to sfc) |

Solid to Liquid

- Solid-liquid separation is a necessary step in obtaining the desired product from a precipitation or crystallization reaction
 - Centrifugation is the way to achieve the required solid-liquid separation
 - There are two types of centrifugation
 - Sedimenting
 - Filtering
 - Most popular in chemical and pharmaceutical applications and the main focus of this selection process
- Crystallization. A way to separate components based on one component having lower solubility in a particular solvent or with particular counter ions
- Precipitation of ions
- Use of polar/non-polar liquids for compounds of variable polarity
- Phase separation by filtration or centrifugation most common

Extractions – Liquid to Solid

- Trapping applications (such as solid phase extraction – discussed later)
- Precipitation/Filtration (or centrifugation)
 - A way to separate components based on one component having lower solubility in a particular solvent or with particular counter ions
 - Precipitation of ions
 - Use of polar/non-polar liquids for compounds of variable polarity
 - Phase separation by filtration or centrifugation most common

Extractions – Liquid to Solid

- Precipitations
 - Removal of ionic compounds/highly polar compounds. Through addition of less polar organic solvent (e.g. ethanol) to water
 - Removal of less polar compounds from organic solvent by adding more polar solvent (e.g. addition of ethanol to CH_2Cl_2 or water to ethanol)

Extractions – Liquid to Solid

- Precipitations
 - Of Ions
 - Can select counter ion that will selectively precipitate one ion but not the other ion (ion to be precipitated should have lower K_{sp} , although will also depend on stoichiometry)
 - Can use K_{sp} values to calculate how successful the separation will be

Extractions – Liquid to Solid

- Precipitation Example:

Separation of Sr^{2+} from Ca^{2+} :

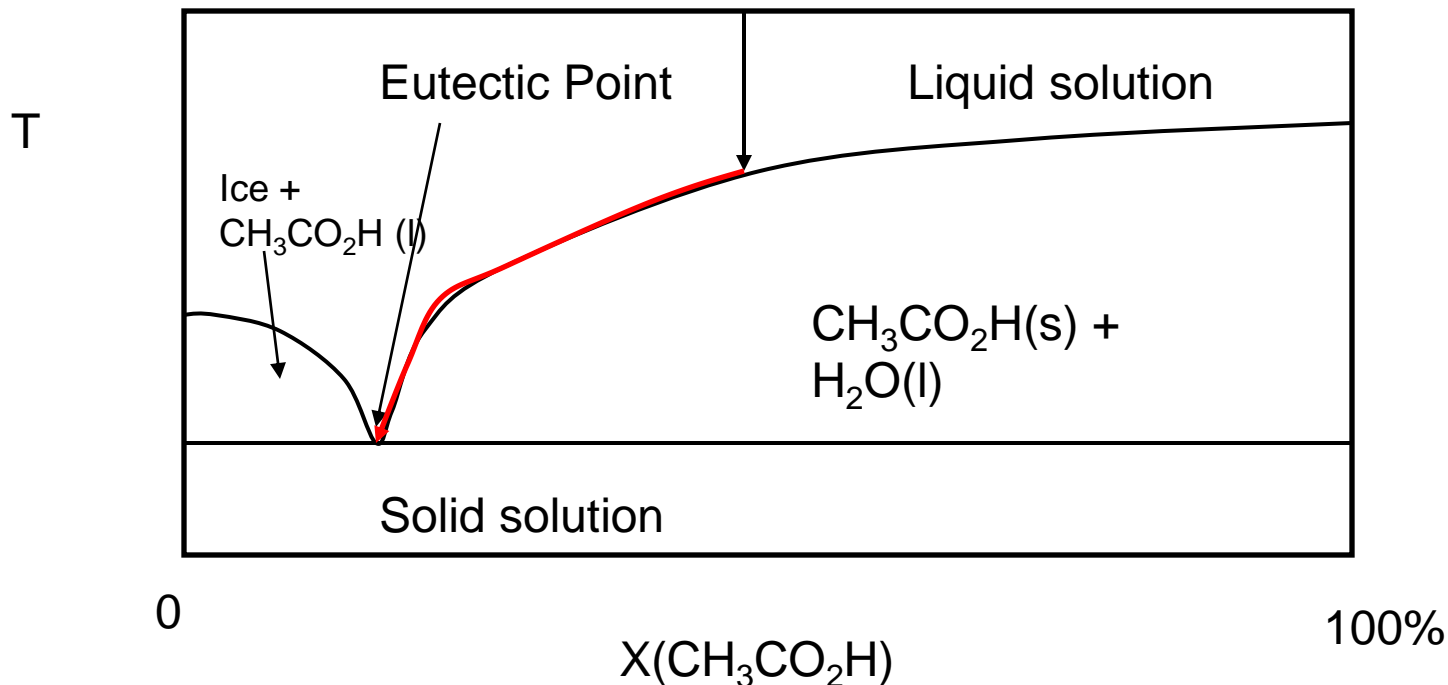
An examination of K_{sp} shows smaller K_{sp} for SrSO_4 vs. CaSO_4 (3.2×10^{-7} vs 2.4×10^{-5})

If a mixture contains 1.0×10^{-2} M Sr^{2+} and Ca^{2+} , how much SO_4^{2-} can be added before Sr^{2+} starts to precipitate?, before Ca^{2+} starts to precipitate? What % of Sr can be isolated?

Extractions – Liquid to Solid

- Temperature in precipitation processes
 - Example: Acetic Acid and Water

Liquid “path” for cooling 50% acetic acid in water



Next Time

- Will cover liquid – liquid extractions from a quantitative perspective in more detail