Chromatographic Theory

• References:
  – Skoog, Principles of Instrumental Analysis
    • 1985 (3rd ed): parts of Chapter 25
    • 1991 (4th ed): parts of Chapter 25
    • 1998 (5th ed): parts of Chapter 26
Chromatography basics

- The basis for gas chromatography is the distribution of a sample between 2 phases, namely a stationary phase and a gas phase
- Gas Chromatography
  - A technique for separating volatile substances by partitioning between the vapor phase and a dissolved or solid phase
    - Gas-Liquid Chromatography — Stationary phase is a liquid.
    - Gas-Solid Chromatography — Stationary phase is a solid.

Components of a Chromatographic System

- Source of Carrier Flow (mobile phase)
  - Cylinder of carrier gas or solvent bottles
- Injection port (sample inlet)
- Column with stationary phase
- Detector(s)
- Signal Transducers & Data Analyzers
  - Recorders, integrators
  - Computers for library matching
- Controllers
  - Temperature controls for injectors, columns and detector
  - Flow controllers and pressure regulators
A Gas Chromatograph

[Diagram showing the components of a gas chromatograph: Carrier Gas, Injector, Detector, Three Heated Zones, Column Oven, and Data System.]

[Image of a gas chromatograph equipment setup in a laboratory.]
The Column

- Gas Chromatograph
- Stationary Phase
- Fused Silica Open Tubular Column
- Mobile Phase
- Column Wall
- Flow

Injector → Flow of Mobile Phase → Detector

T=0
Most Interaction with Stationary Phase

T=10'

T=20'
Least
**LLE & Chromatography**

**Solvent Extraction:**

Organic phase  \( A_{\text{org}} \)  →  \( A_{\text{aq}} \)

Aqueous phase  \( A_{\text{aq}} \)  →  \( A_{\text{org}} \)

\[ K = \frac{[A]_{\text{org}}}{[A]_{\text{aq}}} \]

**Chromatography:**

Mobile phase  \( A_{m} \)  →  \( A_{s} \)

Stationary phase  \( A_{s} \)  →  \( A_{m} \)

\[ K = \frac{C_{s}}{C_{m}} \]

**Symbols:**
- \( A = \) Analyte
- \( C = \) Concentration of analyte
- \( m = \) mobile phase
- \( s = \) stationary phase
Two Measures of Retention

1. Relative retention:

\[ \alpha = \frac{t_{2}'}{t_{1}'} = \frac{291 \text{ s}}{209 \text{ s}} = 1.39 \]

2. Capacity factor:

\[ k_1' = \frac{t_r - t_m}{t_m} = \frac{209 - 42}{42} = 3.98 \]

Linear Partitioning

- This equilibrium is governed by linear partitioning, where the ratio of the concentration of a solute in the stationary phase \( C_s \) to the concentration in the mobile phase \( C_m \) is a constant, known as the stationary phase partition coefficient, \( K_S \)

\[ K_S = \frac{C_s}{C_m} \]
Retention Time

- The average rate at which a solute migrates along a column, $v$-bar, is directly proportional to the fraction of time that it spends in the mobile phase. This is dependent on the partition coefficient.

\[
\bar{v} = u \cdot \left( \frac{\text{# moles of solute in mobile phase}}{\text{total # of moles of solute}} \right)
\]

\[
\bar{v} = u \cdot \left( \frac{C_m V_m}{C_m V_m + C_s V_s} \right)
\]

- And now we define, a capacity factor
  - Which is equal to the mass of analyte in the stationary phase to that in the mobile phase

\[
\bar{v} = u \left( \frac{1}{1 + \frac{c_s}{c_m} \left( \frac{V_s}{V_m} \right)} \right)
\]

\[
k' \equiv K_S \left( \frac{V_s}{V_m} \right)
\]
where $t_m$ is the residence time of the mobile phase in the column.

$$v = u \left( \frac{1}{1 + k'} \right)$$

$$t_R \equiv \frac{L}{v} \quad t_m \equiv \frac{L}{u}$$

$$\frac{L}{t_R} = L \left( \frac{1}{1 + k'} \right)$$

$$k' = \frac{t_R - t_m}{t_m}$$

$$t_R = \frac{L}{u} (k' + 1)$$

Detector signal

$\text{Time}$
Example I

- Sequential countercurrent extractions

Example II

- Separation of Maleic acid from fumaric acid using ether and 0.5 F HCl
  - A. 10 transfers
  - B. 25 transfers
  - C. 40 transfers

From: Potts, 1987, pg.601
• Gaussian Concentration Profile

Theoretical Plate model

• The plate model supposes that the chromatographic column contains a large number of separate layers, called theoretical plates. Separate equilibrations of the sample between the stationary and mobile phase occur in these "plates". The analyte moves down the column by transfer of equilibrated mobile phase from one plate to the next.

• It is important to remember that the plates do not really exist; they are a figment of the imagination that helps us understand the processes at work in the column. They also serve as a way of measuring column efficiency, either by stating the number of theoretical plates in a column, \( N \) (the more plates the better), or by stating the plate height; the Height Equivalent to a Theoretical Plate (the smaller the better).
• If the length of the column is $L$, then the HETP is

$$HETP = \frac{L}{N}$$

• The number of theoretical plates that a real column possesses can be found by examining a chromatographic peak after elution;

$$N = \frac{5.55 \left( \frac{t_R}{w_{1/2}} \right)^2}{w_{1/2}^2}$$

• where $w_{1/2}$ is the peak width at half-height.

• To next lecture