9 – Chromatography.

General Topics

1] Explain the three major components of the van Deemter equation. Sketch a clearly labeled diagram describing each effect. What is the salient point of the van Deemter equation? Which of the three effects is greatest in analytical GC, and which in LC? Explain why. [1]

2] The plate height in chromatography is best described as ____________________ [2]

3] Do Harris Chapter 22 problem 28 part a and b (8th ed.) [3]

4] Be able to define the following terms: [4]

- A] Partition coefficient
- B] Resolution
- C] Retention Time

5] The plate height in chromatography is best expressed by ______________. [5]

a) band broadening / column length
b) mobile phase flow rate / column length
c) stationary phase volume / column length
d) (band broadening)^2 / column length
e) (mobile phase flow rate)$^{1/2}$ / column length

6] Resolution in chromatographic separations is expected to increase in the following manner: [6]

a) $Rs \propto$ column length
b) $Rs \propto$ mobile phase flow rate
c) $Rs \propto$ [1 / mobile phase flow rate]
d) $Rs \propto$ [column length]^2
e) $Rs \propto$ [column length]$^{1/2}$

Gas Chromatography

7] The major contribution to the band broadening in gas chromatography is ______ [7]

8] Choose the true statements. In gas chromatography, capillary columns provide better resolution than packed columns because: [8]

A. they have decreased plate heights.
B. they don't have band broadening due to the multipath process.

(a) A only.

(b) B only.
(c) Both A and B.
(d) Neither A nor B.

9] A GC-FID analysis was conducted on a soil sample containing pollutant X. The following separations were conducted: [9]

		tr(minutes)	peak area
Injection 1	21.1 ppm Toluene Internal Standard	10.11	36,242
	33.4 ppm X	14.82	45,997
Injection 2	21.1 ppm Toluene Internal Standard	10.05	38,774
	unknown concentration X	14.77	39,115

What is the concentration of X in the sample?

10] In gas chromatography, what is the main advantage of a FID over a TCD? [10]

Liquid Chromatography (HPLC)

11] The elution order for the following solutes in a liquid chromatography system consisting of a toluene mobile phase and a silica stationary phase would be [11]

(a) benzene, tetrahydrofuran (C_4H_8O), methanol
(b) methanol, benzene, tetrahydrofuran (C_4H_8O)
(c) tetrahydrofuran (C_4H_8O), methanol, benzene
(d) methanol, tetrahydrofuran (C_4H_8O), benzene
(e) benzene, methanol, tetrahydrofuran (C_4H_8O)

12] The major contribution to band broadening in liquid chromatography is_______ [12]

Answers

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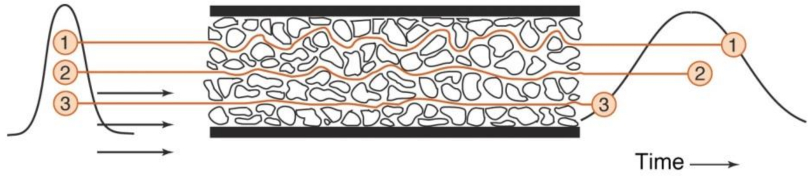
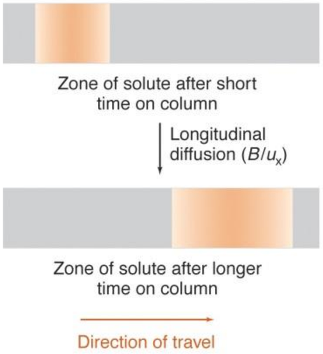
[1] The van Deemter equation ($H = A + B/u + Cu$) describes three major contributions to band broadening in chromatography.

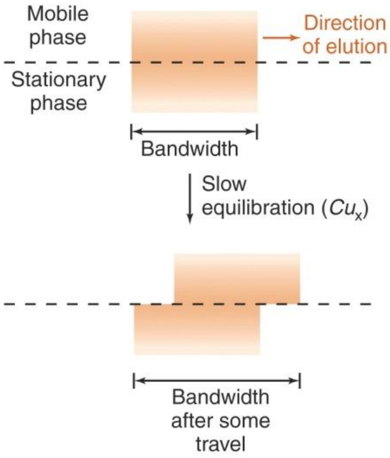
A – multiple paths may be evident in some column designs. This can be viewed as paths taken by the solute particles as they elute through the separation column. The figure taken from Harris is a useful graphic:



B/u – longitudinal diffusion is caused by diffusional forces, i.e. the drive for solutes to leave a more concentrated plane to a less concentrated plane. The longer the time the solute spends in the column the more evident the band broadening from this effect, thus B/u effects are inversely proportional to mobile phase flow rate. This Harris Figure illustrates this phenomenon:

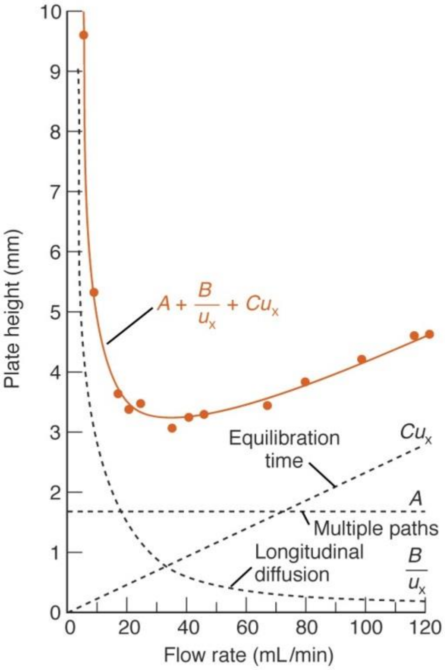


Cu – limited mass transfer kinetics causes band broadening. If equilibrium between the solute in the mobile and the stationary phases is not reached instantaneously solute particles in the latter will lag behind the former. Figure 23-17 demonstrates this feature:



This effect is directly proportional to mobile phase flow rate, i.e. the faster the flow rate the more likely solute particles in the stationary phase are likely to lag behind the ones in the mobile phase.

Overall all three effects can be summed up in the following plot (Figure 23-15):



This plot indicates that there is a optimal flow rate that will provide minimal band broadening. In the graph above that would be about 30 ml/min. In GC we would expect that longitudinal diffusion (B/u) would be of most concern as diffusion in the gas phase is significant. Faster mobile phase flow rates would be most helpful in minimizing H. In HPLC or LC the mass transfer term is the most important as diffusion in the condensed phases at lower temperatures than GC limit mass transport between the mobile and stationary phases.

[2] Variance per unit length or σ^2/L, where σ is the std. deviation of the broadened peak.

[3] a) column 1 (sharper peaks) b) column 2 (broader peaks)

[4] Go over the lecture notes and read Harris.

[5] (Band broadening)^2/ column length.

[6] Rs $\propto$ [column length]$^{1/2}$

[7] longitudinal diffusion

[8] c

[9] 39,115*(36,242/38,774)*(33.4ppm/45,997) = 26.5 ppm

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[10] It is more sensitive to most organic compounds.

[11] a

[12] a