Chem 230, Fall, 2014
Homework Set # 3
Do by Oct. 28

Short Answer Questions

1. List two advantages of temperature programming in GC.

2. What van Deemter term is nearly zero with OT GC columns?

3. Why would it normally not make sense to use a 0.53 mm diameter column with a thin film thickness (e.g. 0.25 μm) in GC?

4. List three important criteria for detector performance.

5. A polar compound is analyzed on an OV-1 column and a carbowax column using GC. If the column dimensions and flow rates are the same, on which column will the retention time be greater?

6. What type of GC detector could be used if comprehensive detection of hydrocarbons in the sample is desired?

7. For what type of samples would you want to use a fixed loop injector in GC?

8. It is desired to analyze for small to moderate sized (C2 to C10) linear alcohols in water. Water cannot be directly injected into the GC. What other methods could be used to inject the alcohols? How could this method bias the sample?

9. Imagine that you have a sample containing various low molecular weight chlorinated hydrocarbons at concentrations in the percent range. What type of column (packed or capillary) would you use? Now imagine that the concentrations were in the parts per billion ranges. What type of column would you use (specify the phase)?

10. When the results from a sample obtained using GCxGC are plotted (in 3D), most of the peaks are found to lie close to a diagonal through the 1^{st} and 2^{nd} dimension retention times of the plot. Is GCxGC effective for this sample? Why or why not?

11. List two pieces of additional equipment needed for GCxGC.

12. List four different subtypes of liquid-based chromatography based on separation mechanism.

13. What change in packing material geometry (but not column dimensions) in HPLC leads to greater resolution without an increase in back pressure?

14. List one advantage to using polymeric packing material in place of silica in HPLC.

15. List a non-bonded packing material that can be used for reversed phase HPLC separations.

16. A chemist was performing a silica based normal phase HPLC separation. Her 12% 2-propanol in hexane eluent was running low, so she re-preparing her eluent. Then, she found k values shifted by about 10%. Explain the change.

17. A biochemist analyzing triglycerides by normal phase HPLC wants to perform a gradient using the eluents hexane and methylene chloride. The % of which solvent should increase in the gradient run?

18. To what pH value range should the mobile phase be adjusted for a reversed phase (silica-based C18) HPLC separation of benzoic acid?

19. What is a problem in the separation of amines (weak bases) with pK_a values greater than 8 by reversed phase (silica-based C18) HPLC? Is this also a problem for the separation of anilines (aromatic amines with pK_a values of around 4)?

20. What is one advantage of using monolithic columns in HPLC?

21. What is one disadvantage to using polymeric packing material in HPLC?

22. List two factors besides solvent polarity that may be important in choosing solvents for the mobile phase in HPLC.

23. What aspect of the stationary phase is normally changed to affect retention in SEC?

24. List two ways to decrease retention in anion exchange chromatography.

25. What affects analyte sensitivity with a refractive index detector for HPLC?

26. Is use of lower wavelengths (e.g. 205 nm) better for simple samples or complex samples if the goal is to quantitate individual compounds using UV detection with HPLC?

27. A chemists shifts from analytical bore HPLC (4.6 mm diameter) to microbore (say 1 mm diameter):

a) Why may it be necessary to reduce the cell volume in a UV detector?

b) What effect will this have on analyte sensitivity (just the change in cell volume – assuming all cell dimensions are reduced)

b) Is it normally necessary to inject less sample with microbore HPLC?

Longer Problems – to be turned in

1. One μL of isooctane (density = 0.69 g/mL) is injected into a GC (whole sample on column). If isooctane is quickly volatilized in the GC under the conditions of 180°C and 1.8 atm,

a) What is the volume of the isooctane gas? The ideal gas law (PV = nRT) will be needed to calculate the density of isooctane gas.

b) If the flow inside the column is 2 mL/min, what is the minimum width in seconds that the peak could possibly have (assuming no broadening).

c) What reduces this as a problem in split injection, and what is required to keep this from becoming a problem in splitless injection?

2. A gas bubble meter is used to determine the flow rate for a 0.32 mm (open tubular), 30 m column. If the column effluent takes 136 s for a bubble to travel 10.0 mL in the meter, calculate:

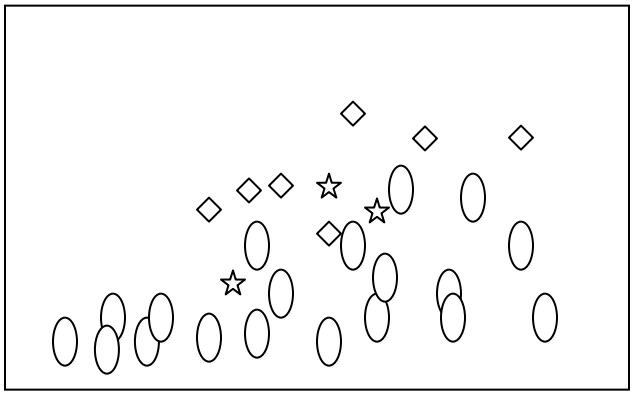
a) the flow rate at the bubble meter (mL/min)

b) the linear velocity (m/s)

c) the time expected for unretained solute to elute

For this question, you can ignore changes in temperature and pressure as the gas flows through the column.

3. It is desired to characterize the aromatic and oxygenated compounds in gasoline. Because of the complexity of gasoline, GC x GC is used with a non-polar 1st column,a polar 2nd column, and flame ionization detection. Looking at the 2D chromatogram (below),



2nd Column Ret. Time

1st column Ret. Time

Note: **aromatic compounds** shown by diamonds (◇), **oxygenated compounds** shown by stars (☆) and **other compounds** shown by ovals (◯). (10 points)

a) Did the GC x GC provided added resolution for the desired compounds over an expected 1D run? Explain.

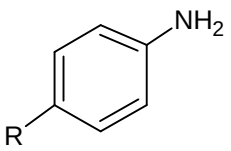
b) Based on the chromatogram, rate the three types of compounds based on "average" polarity (least to most polar).

4. It is desired to determine wax composition by GC. A DB-5 (non-polar) 0.32 mm diameter x 0.5 μm film thickness x 30 m column is being used. The wax molecules consist of esters made from medium chain (6 to 12 carbon) alcohols attached to long chain (12 to 18 carbon) fatty acids (with no, one or two double bonds). Initial runs show that the column must be at the maximum of 325°C for 45 minutes to elute all compounds. Separation of each wax molecule is good except if the only difference is in the number of double bonds.
a) List two changes in the column (dimensions or stationary phase) that would allow faster elution of the wax molecules.
b) What change might improve separation of wax molecules with the same number of carbons but different number of double bonds?

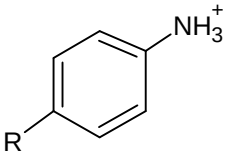
5. A scientist is using a 4.6 x 150 mm, 5 μm particle size C18 HPLC column to carry out a separation. The isocratic separation occurs at a flow rate of 1.0 mL/min (50% methanol, 50% water) with a back pressure of 160 bar, takes 18 min., and gives a resolution of 1.8 for the two least well resolved peaks (with k values of 2.7 and 2.8). The unretained time is 1.5 min. He wants to speed up the separation by buying a similar column with 3 μm particles.
a) If the maximum pressure of the HPLC is 300 bar, what length (to the nearest 25 mm) should he purchase so that he can still run at 1.0 mL/min?
b) Estimate how long it will take to perform the separation at the length found in a) assuming the % methanol stays the same and K_C and β remain the same (β will probably increase some).
c) Estimate how long it will take to perform the separation at the length found in a) with % methanol optimized so that resolution remains the same. Hint: indicate how you expect N to be changed, then adjust k so that resolution remains the same, and assume the same % change occurs to the k value for the last eluting peak.

6. It is desired to analyze a series of anilines (see structure below) using HPLC with a silica-based reversed phase column. If the conjugate acids of anilines (anilinium ions) have pK_a values ranging from 4 to 5, indicate to what pH the eluent should be buffered for:
a) retention of anilines
b) retention of ion pairs (with the addition of the strong acid, hexanesulfonic acid to the eluent)
Explain your answer.

aniline



anilinium ion



7. The table below shows the retention times and peak widths for 3 compounds separated with reversed phase HPLC using an eluent of 45% acetonitrile, 55% pH 5 aqueous acetate buffer and a C18 column:

Compound	Retention time (min.)	Peak Width at base (min.)	pK_a
Unretained Peak	1.60	-	-
2,4-dichlorophenol	5.68	0.25	7.80
2-Methylphenol	5.97	0.26	10.09
3-EthylPhenol	6.72	0.30	10.05

a) Using the same column and same two eluent constituents (acetonitrile and pH 5 buffer), how can the resolution between 2,4-dichlorophenol and 2-methylphenol be improved (assuming α remains constant with % acetonitrile)?

b) Suggest a different pH to improve the above separation of 2,4-dichlorophenol and 2-methylphenol by increasing the separation factor (α). Discuss how you would expect elution to change.