

Complete these problems on separate paper and staple it to this sheet when you are finished. Please initial each sheet as well. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT.

**Warm-up (3 points each)**

1. In \_\_\_\_\_, species are separated based on their ability to move in and out of the pores in the stationary phase packing material.
2. An \_\_\_\_\_, is the detector of choice for GC separations of halogenated compounds.
3. A \_\_\_\_\_, is attached to the inlet end of an HPLC column to extend its useful life.
4. In a CE experiment, \_\_\_\_\_, results in the general movement of all species toward the cathode.

**You must complete problem 5.**

5. Much of the development in LC recently has been focused on methods to decrease particle size from the 5  $\mu\text{m}$  diameter particles that had become the industry standard to particles of 2  $\mu\text{m}$  or smaller. Why has there been such a focus on decreasing particle size? Be sure to reference the van Deemter equation in your discussion. What challenges accompany the implementation of LC columns with smaller particles? (15 points)

**Complete 5 of the following. Be concise in your answers and show work for problems involving calculations. Clearly indicate which problems are not to be graded. (15 pts ea)**

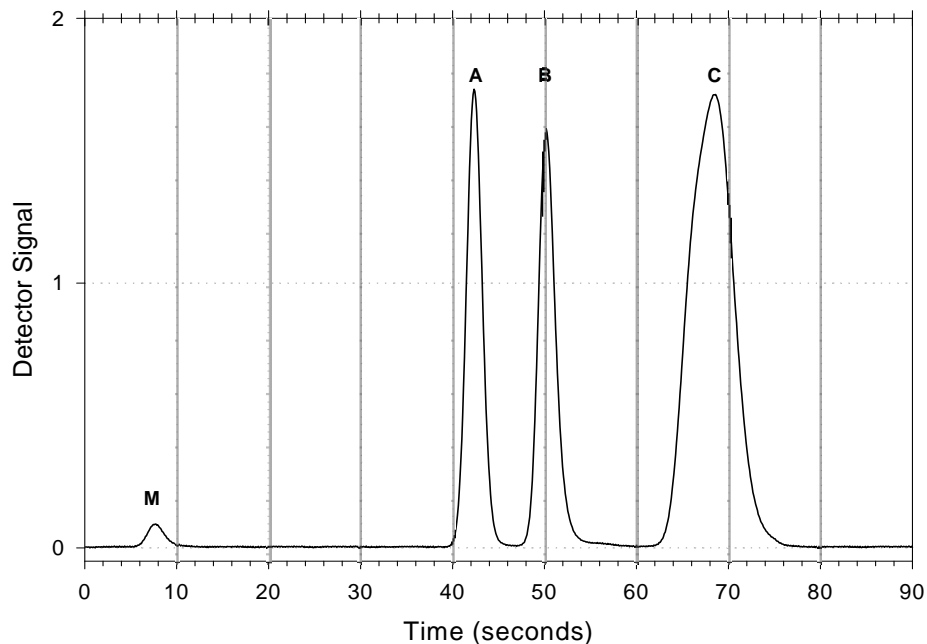
6. For years, mating LC and MS had posed a significant challenge. Why was this the case? Describe two approaches for interfacing LC with mass spec.
7. Compare the operation of a UV absorbance detector with **one** of the following detectors in LC: fluorescence, refractive index, electrochemical, ELSD. Include a diagram of the components and discuss the benefits and limitations of each detector, paying particular attention to selectivity and sensitivity.
8. Compare and contrast the role of the mobile phase in GC with that in LC. Include a description of the important properties of the mobile phase in each separation and its impact on the quality of a separation.
9. One method for evaluating the efficiency of a separation is to calculate the number of theoretical plates (N) for the separation, with larger numbers of theoretical plates generally leading to better separations. Given that  $N = H/L$ , where H is the "size" of the theoretical plate and L is the length of the column, we can increase N by decreasing H or increasing L. Given this relationship, why don't we simply use very long columns to perform separations? In an HPLC experiment, how might you work to decrease H in order to increase N?
10. You intend to perform a separation of a mixture of the five components below using capillary electrophoresis with pressure injection and absorbance detection at 200 nm at the cathode end of the capillary. The table below describes the properties of each of the components under the conditions of the separation. Sketch an electropherogram you would expect for two experiments:
  - (1) capillary zone electrophoresis in a fused silica capillary **and**
  - (2) capillary zone electrophoresis in a capillary whose surface has been reacted with trimethylchlorosilane.

*Identify each peak in your electropherograms and describe why you chose to draw them as you did.*

species	concentration (ppm)	molar mass (g/mol)	molar absorptivity @ 200 nm ( $M^{-1}cm^{-2}$ )	charge
A	50.0	101.3	1000	+1
B	100.0	100.9	500	-1
C	50.0	100.2	2000	+2
D	100.0	99.9	1000	0
E	50.0	100.5	1000	-2

11. Why is a thermal conductivity detector a much more universal GC detector than a flame ionization detector? If the TCD is so much more universal, why use an FID at all?

12. Answer the following questions related to the gas chromatogram below. Experimental conditions: Packed column (4 mm diameter x 2 m long), Carbowax stationary phase, 40 mL/min helium carrier gas flow rate, FID detector, column temperature = 100°C, injector temperature = 150°C, detector temperature = 150°C. Peak M corresponds to an unretained compound.



- Calculate the selectivity factor and resolution for peaks A and B.
- Calculate the number of theoretical plates for peak B.
- Based on the size of the peaks, what can you say about the relative concentrations of components A and B?
- It appears that peak C is the result of co-elution of two compounds. How would you change experimental conditions to resolve these two peaks? What effect are these changes likely to have on the separation of components A and B?

### Possibly Useful Information

$A = \log(P_0/P) = \epsilon bc$	$\pi = 3.14159$
$k'_A = K_A \frac{V_S}{V_M} = \frac{t_R - t_M}{t_M}$	$\alpha = \frac{K_B}{K_A} = \frac{k'_B}{k'_A}$
$N = L/H$	$H = \frac{\sigma^2}{L} = L \left( \frac{W}{4t_R} \right)^2$
$N = \left( \frac{4t_R}{W} \right)^2 \approx \left( \frac{2.35t_R}{W_{1/2}} \right)^2$	$H = A + \frac{B}{u} + Cu = A + \frac{B}{u} + (C_s + C_m)\mu$
$R_s = \frac{\Delta Z}{W_A/2 + W_B/2} = \frac{2\Delta Z}{W_A + W_B}$	$R_s = \frac{\sqrt{N}}{4} \left( \frac{\alpha - 1}{\alpha} \right) \left( \frac{k'_B}{1 + k'_B} \right)$
$v = (\mu_e + \mu_{e0})E = (\mu_e + \mu_{e0})V/L$	$N = \frac{(\mu_e + \mu_{e0})V}{2D}$

### PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	INERT GASES	
1 H 1.00797															1 H 1.00797	2 He 4.0026	
3 Li 6.939	4 Be 9.0122										5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183	
11 Na 22.9898	12 Mg 24.312										13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948	
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

#### \* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
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#### † Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)
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