

CHEM 133 Exam 3  
May 12, 2015  
Solutions

Equations and constants that you may find useful:

$0^{\circ}\text{C} = 273 \text{ K}$ ; Planck's constant  $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$

Boltzman Constant =  $k = 1.38 \times 10^{-23} \text{ J/K}$

Pascal's triangle:

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      1
     1 1
    1 2 1
   1 3 3 1
  1 4 6 4 1
 1 5 10 10 5 1
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SHORT ANSWER SECTION: (Each question worth 4 points)

1. What main spectrometer component is needed in atomic absorption spectrometers but not in atomic emission spectrometers? Component = **lamp** (+1 for flame or graphite tube)
2. NMR is a relatively insensitive technique. Signal averaging by repeated radio frequency pulsing can be used to improve the signal to noise ratio. What needs to be considered in determining the pulsing rate?  
a) the **spin-lattice relaxation time**      b) splitting coupling constants  
c) the ppm of the absorption              d) all of the above
3.  $^{14}\text{N}$  is an  $I = 1$  nucleus. How many spin states does it have?  $2I + 1 = 3$   
a) 1    b) 2    c) **3**    d) 4
4. List a mass spectrometric ionization method that can be applied to solid samples. Method = MALDI or DESI (could have ICP with digestion) (give name or acronym)
5. What generally occurs to ions in between two mass spectrometers in MS-MS?  
a) removal of excess ion energy              b) addition of an extra ion  
c) isotope exchange                              d) **collision with reagent gas to induce fragmentation**
6. List one type of mass analyzer (component of a mass spectrometer). magnetic sector, double focusing, quadrupole, ion trap, linear ion trap, time of flight, orbitrap, or Fourier transform ion cyclotron resonance
7. Triglycerides in fats and oils can be analyzed by HPLC using reversed phase columns. However, they typically are only a little more polar than the stationary phase but much less polar than solvents commonly used in reversed phase HPLC (e.g. acetonitrile and water). What is a potential problem in their analysis?  
a) very small retention factors  
b) **excessively long retention times**  
c) interference from other compounds that elute early  
d) the need for a solvent more polar than water to elute compounds

SECTION II. PROBLEM SECTION. Show work – use the back side if needed

1. In flame atomic absorption spectroscopy a number of processes can decrease the atomization efficiency. (8 pts)

a) Give an example of one process that decreases atomization efficiency

- 1) Formation of low volatile salts (e.g. phosphates)
- 2) Ionization
- 3) Oxide or hydroxide formation
- 4) Viscous solution giving poor atomization efficiency

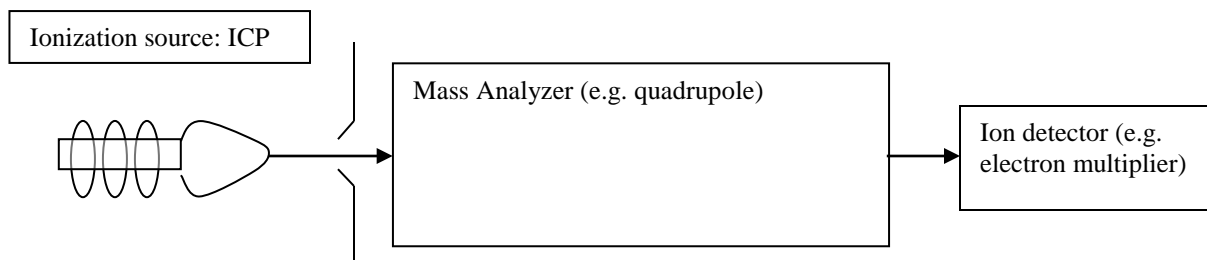
b) Give a method to reduce the effect of this process

- 1) Use metal that binds more strongly to low volatility anion (e.g.  $\text{Ca}^{2+}$ ); use hotter flame
- 2) Use metal that ionizes more readily (e.g.  $\text{Cs}^+$ )
- 3) Use fuel rich flame

Also, standard addition could be used to reduce effects of any of these

bonus) List a second example and method to reduce its effect (3 pts)  
see above

2. Give a block diagram for an ICP-MS instrument showing the ionization source, the way to separate ions, and the way to detection ions (6 pts)



3. In a 4.70 Tesla field, the magnetogyric ratios ( $\gamma$ ) for  $^{31}\text{P}$  is  $1.08 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$ .

Equations and constants you might need:  $\nu$  (frequency) =  $(\gamma/2\pi)H$  ( $H$  = magnetic field strength)

a) At what frequency (in MHz) does  $^{31}\text{P}$  absorb light? (5 pts)

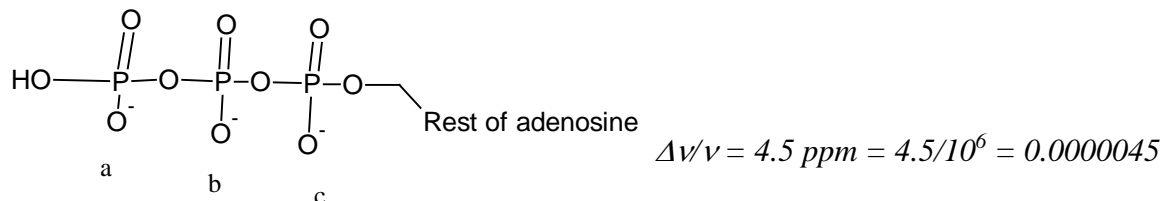
$$\nu(\text{frequency}) = (\gamma/2\pi)H = (1.08 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}/2\pi)(4.70 \text{ T}) = 8.08 \times 10^7 \text{ Hz} = \mathbf{80.8 \text{ MHz}}$$

b) Calculate the ratio of  $^{31}\text{P}$  in the excited state to  $^{31}\text{P}$  in the ground state at 298 K to 6 significant figures.  $g^* = g_o$ . (8 pts)

$$N^*/N_o = (g^*/g_o)e^{-E/kT} \text{ and } E = h\nu = (6.626 \times 10^{-34} \text{ Js})(8.08 \times 10^7 \text{ s}^{-1}) = 5.36 \times 10^{-26} \text{ J}$$

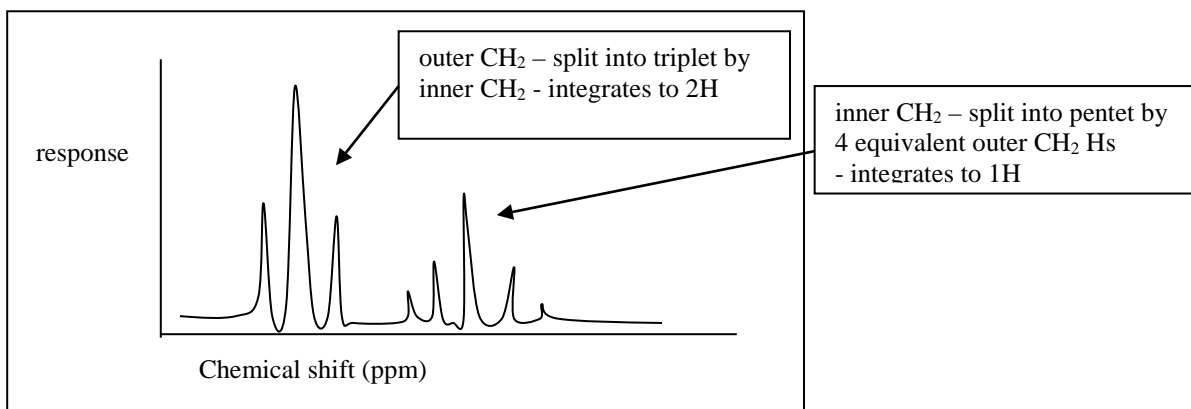
$$N^*/N_o = e^{-5.36 \times 10^{-26} \text{ J}/[(1.38 \times 10^{-23})(298\text{K})]} = \mathbf{0.999987}$$

c) If the peaks from two closest (spectrally) phosphorous atoms in ATP (see structure below) are located 4.5 ppm apart, what is their difference in Hz? (5 ppm)



$$\Delta\nu = (0.0000045)(8.08 \times 10^7 \text{ Hz}) = \mathbf{364 \text{ Hz}}$$

4. Sketch what the  $^1\text{H}$  NMR spectrum of  $\text{Cl}(\text{CH}_2)_3\text{Cl}$  looks like. You don't need to give values for the ppm scale, but make sure to give 1) the number of types of proton peaks, 2) the position of the peaks relative to other peaks and to tetramethylsilane (TMS, the standard with  $\delta = 0$  ppm), 3) the relative intensity of the peaks, and 4) the splitting pattern for each peak (e.g. label as doublet, triplet, etc. or "complex" if a multiplet of multiplets. You may want to explain your answers. (12 pts)



Notes: 1) all of the outer  $\text{CH}_2$  groups are equivalent, so there are just two sets of equivalent Hs. 2) The outer  $\text{CH}_2$  groups are down field because they are more deshielded due to proximity to the Cl atoms. 3) the relative intensity is a ratio of the number of Hs (2 to 4 or 1 to 2) 4) The splitting is  $n + 1$  from  $n$  equivalent neighboring peaks (or can use Pascal's triangle).

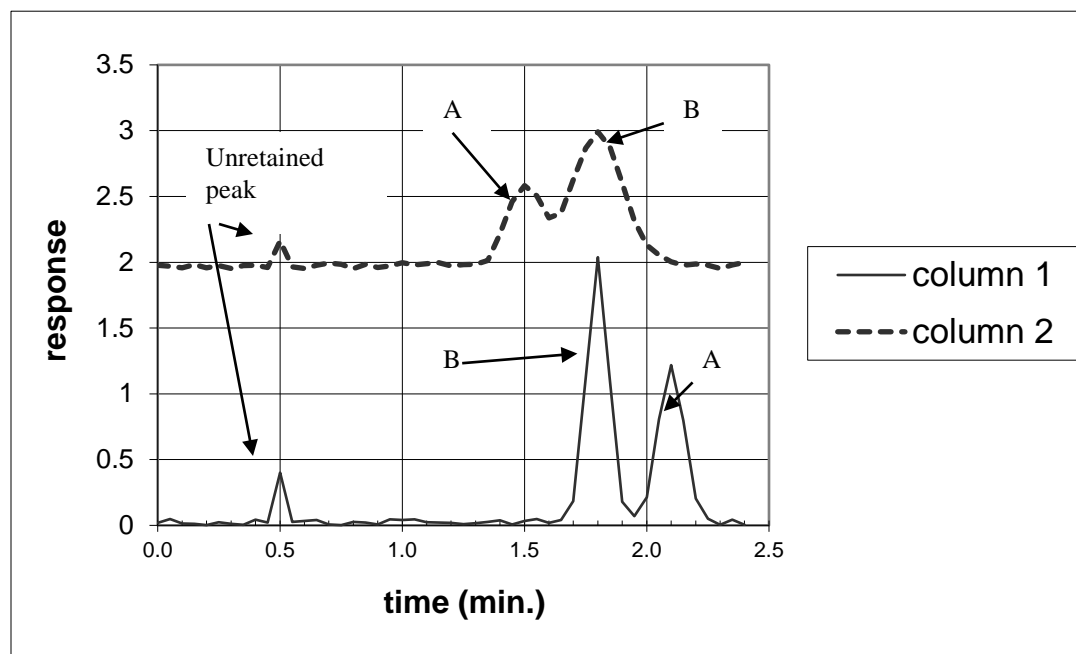
5. A halogenated hydrocarbon is analyzed by mass spectrometry with a parent ion observed with a mass to charge ratio of 238. Fragments indicate that it has at least one Br atom and one Cl atom. Given the ratio of  $M + 2/M$ ,  $M + 4/M$  and  $M + 6/M$  (below), **determine the number of Br and Cl atoms** assuming no other isotopes contribute significantly to these peaks. There is no observable peak at the  $M + 8/M$  location. The relative abundances of these isotopes are  $^{37}\text{Cl}/^{35}\text{Cl} = 32/100$  and  $^{81}\text{Br}/^{79}\text{Br} = 97/100$ . Show your work. (12 pts)

Observed ratios	$M + 2/M$	$M + 4/M$	$M + 6/M$
	160.2/100	72.1/100	9.9/100

Because  $M+2$  to  $M+6$  peaks are observed, we can assume there are 3 halogens. Since there must be one of each, this leads to 2 Brs and 1 Cl or 2 Cls and 1 Br. We can calculate the ratios from this. First 2 Brs and 1 Cl:  $M+2/M = 2(97) + 32 = 226/100$  vs. for 2 Cls and 1 Br:

$M+2/M = 2(32) + 97 = 161$ . For 2 Brs,  $M+4/M = 97^2/100 + 2(32)(97)/100 = 156$  and  $M+6/M = (97)^2 32/100^2 = 30$ . For 2 Cls,  $M+4/M = 2(97)(32)/100 + 32^2/100 = 72$  and  $M+6/M = (32)^2(97)/100^2 = 9.9$  Clearly, 2Cl and 1 Br matches better.

6. Using the HPLC chromatograms for separating components A and B provided below and the fact that the separation occurring on column 1 (lower chromatogram) was a reversed phase separation, answer the following questions: (16 pts)



Determine:

a) Which compound is more polar: A or B? Explain your answer.

*The early eluting compound on the reversed-phase column (column 1) is polar (sticks less to a non-polar stationary phase). This is **compound B***

b) Is the separation occurring on column 2 most-likely reversed-phase or normal phase? You can assume that the main factor affecting separation for both columns is polarity. Explain your answer.

***Normal phase.** This is because the elution order of the two compounds is reversed from the reversed-phase column.*

c) The retention factor ( $k$ ) for A for the separation on column 1.

$$k = (2.1 - 0.5)/0.5 = 3.2$$

d) Whether one would want to increase the percent hexane or 2-propanol for the column 2 separation if it is desired to retain both components to increase separation.

*Assuming that column 2 is normal phase, we want to increase the weak solvent to increase retention. The hexane is the weak solvent (opposite in polarity as the polar stationary phase). **The percent hexane needs to be increased.***