Chem 310 First Hour Exam Answers

Feb. 17, 2004

Write your answers on the blank pages provided. Number each page in sequence and write your name at the top of each page. Answer all of the questions.

Some possibly useful equations:

$S = mC + S_{bl}$	$LOD = 3s_{bl}/m$	$LOQ = 10s_{bl}/m$	$(\sin \theta_1)/(\sin \theta_2) = n_2/n_1$
$R_{12} = [(n_2 - n_1)/(n_2 + n_1)]^2$	$\lambda = 2dn/m$	$\lambda = (d/m)(\sin i + \sin r)$	
$R = mN$	$A = \epsilon bC$	$S/N = k\sqrt{N}$	

Calculations: There are 5 points per answer. Two points will be awarded for correctly setting up the problem. SHOW ALL OF YOUR WORK! Two points will be deducted if I cannot see how you got your final answer. Underline or circle your final answers. Include the correct units or lose a point per answer.

1. An IR spectrum has a signal-to-noise of 25 after 25 scans are ensemble-averaged. How many scans would need to be ensemble-averaged to achieve a signal-to-noise of 100?
$(S/N)/\sqrt{N} = 25/\sqrt{25} = 100/\sqrt{N}$; $\sqrt{N} = 100/(25/5) = 20$; $N =$ ***400 scans***

2. A Beer s law plot was obtained using the following data. Absorbance was measured using a 0.10 cm cuvet.

C	A
2.0×10^{-3} M	0.269
5.0×10^{-3} M	0.587

(a) What is the sensitivity of this method? Note: the blank absorbance is NOT zero.
Slope = sensitivity = $(0.587 - 0.269)/(5.0\times10^{-3} - 2.0\times10^{-3}) = 0.318/(3.0\times10^{-3}\ M) =$ ***$106\ M^{-1}$***

(b) Calculate the limit of quantification (LOQ) if the standard deviation of the blank is 0.010.
$LOQ = 10(0.010)/(106\ M^{-1}) =$ ***9.4×10^{-4} M***

3. If a solution has a 10.0% transmittance, what is the % transmittance of a solution with exactly ½ the concentration of the first solution?
$A = -\log(0.100) = 1.000$. New $A = (½)(1.000) = 0.500$. $T = 10^{-0.500} = 0.316$ or ***31.6%***

4. A KBr salt plate has an index of refraction of 2.4 in the infrared.

(a) Calculate the fraction of light reflected at a single air/KBr interface.
$R_{12} = [(2.4 - 1.0)/(2.4 + 1.0)]^2 =$ ***0.170***

(b) Calculate the %T of light passing through both air/KBr interfaces.

$T_{12} = 1 - 0.170 = 0.830$; $T_{total} = (0.830)^2 = 0.690$ *or* ***69.0%***

5. A cuvet was filled with 3.0 mL of a solution containing quinine and the fluorescent signal measured. Without moving the cuvet, 1.0 mL of a 2.0 ppb standard solution of quinine was added, the total solution mixed, and the fluorescent signal measured again. Calculate the original concentration of quinine if the first signal was 555 counts and the second signal was 1250 counts.

This is a standard addition problem.

$S = mC$; $555 = mC$

$1250 = m(C(3.0/4.0) + (2.0\ \text{ppb})(1.0/4.0))$

$1250 = 555(0.75) + m(0.50\ \text{ppb})$; $m = (1250 - 416.25)/0.50 = 1667.5/\text{ppb}$

$555 = (1667.5/\text{ppb})C$; $C =$ ***0.33 ppb***

Short answer: Provide a word, phrase, sketch, or a few sentences. 5 points per question.

6. What are the two assumptions that you used to do the calculation in Question 5?

The signal was linear with concentration, and the blank signal was zero.

7. Define Limit of Detection (LOD) using a sentence (NOT an equation).

The LOD is the lowest concentration at which you are 95% confident that the analyte is present in the sample.

8. Name two continuum sources that are useful in the UV spectral region.

The D_2 arc and the Xe (or Hg/Xe) high pressure arc sources.

9. In which spectral domain is light with a wavenumber of 40,000 cm^{-1}?

$\lambda = 1/\lambda^* = (1/40000\ cm^{-1})(10^7\ nm/cm) = 250\ nm$; *UV domain*

10. Why must cutoff filters be used with grating monochromators?

Cutoff filters are used to block higher order wavelengths and to allow only first order wavelengths to be transmitted.

11. Sketch a double-beam UV-VIS spectrometer and label the parts. Show the light path through the instrument. Include internal details of the monochromator (all 5 components).

The sketch should show a continuum source, a grating monochromator, a chopper, a sample cuvet and a reference cuvet, and a detector. The monochromator should show an entrance slit, a collimator, a grating, a focusor and an exit slit. Light travels from the source through the *monochromator. The chopper alternately sends the light through the sample and reference cuvet. The two beams are combined and sent to a single detector.*

12. A grating monochromator has a blaze wavelength of 600 nm. Over what range of wavelengths will the throughput be high for this monochromator?
The throughput is high for the following wavelength range: $2/3\lambda_B < \lambda < 2\lambda_B$. *The wavelength range is 400 nm - 1200 nm.*

13. List 5 techniques for reducing matrix effects. Definitions of the techniques are not needed.
    - *(a) Matrix substitution*
    - *(b) Separation*
    - *(c) Pre-concentration.*
    - *(d) Derivatization.*
    - *(e) Masking.*

14. Why are vacuum phototubes and photomultipliers blind to IR light?
IR photons do not have sufficient energy to knock an electron out of the photocathode into vacuum.

Discussion: <u>Give as much detail as possible</u>. I am expecting a minimum of a half-page. Write in complete sentences and organized paragraphs. Up to 5 points will be deducted for poorly written answers.
(20 points)

15. What assumptions must be true for Beer s Law to be valid? What are the factors (both general and instrumental) that cause deviations from linearity in a Beer's Law plot? Your answer to the second question should refer to an assumption where appropriate. Provide sketches showing the type of deviations in the Beer s Law plots. Indicate whether the deviation is positive or negative at higher concentrations of analyte.
The three assumptions are: (a) constant analyte absorbance over the bandpass of the transmitted beam, (b) the analyte molecules do not interact with each other, and (c) the concentration is uniform across the sample.

The general factor is chemical equilibrium. The analyte exists in a chemical equilibrium of two or more forms which shifts with changing concentration. The second assumption is invalid. Deviations from Beer s Law can be positive or negative for the general factors. The sketch is a plot of Absorbance vs concentration. As the conc. increases, the plot curves up (positive *deviation) or down (negative deviation) Examples include dimerization, acid-base, and complexation equilibria. The instrumental factors include non-constant absorbance over the instrumental bandpass (first assumption), and stray light. Non-constant absorbance can be caused by the bandpass of the spectrometer being large with respect to the bandwidth of the absorption peak, or the absorbance being measured at a wavelength where the absorbance changes rapidly with wavelength. Both factors lead to excess light reaching the detector, causing negative deviations of Beer s Law plots at higher concentrations (show a sketch).*