Chem 210 First Hour Exam Answers

Feb. 8, 2001

Calculations: SHOW ALL OF YOUR WORK! 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. (4) A solution of 2.0×10^{-2} M copper sulfate is placed in a 0.50 cm cell and its transmittance measured at 620 nm. Calculate the molar absorptivity of copper sulfate if %T = 45.8%.

$A = -\log(T) = -\log(0.458) = 0.339 = \epsilon bC = \epsilon(0.50\ \text{cm})(0.020\ \text{M});\ \ \epsilon = 33.9\ \text{M}^{-1}\text{cm}^{-1}$

2. (6) (a) A diffraction grating with 1200 blazes/mm is used in a 0.25 meter monochromator with 0.50 mm slits. Calculate the bandpass $\Delta\lambda$ for the 1st-order wavelength.

$d = 1/(1200\ \text{blazes/mm}) = 8.33 \times 10^{-4}\ \text{mm}(10^6\ \text{nm/mm}) = 833\ \text{nm}$
A.D. $= m/d = 1/(833\ \text{nm}) = 1.2 \times 10^{-3}$ radians/nm
$D = (\text{A.D.})(\text{f.l.}) = (1.2 \times 10^{-3}\ \text{radians/nm})(250\ \text{mm}) = 0.30\ \text{mm/nm}$
$\Delta\lambda = (W)(D^{-1}) = (0.50\ \text{mm})/(0.30\ \text{mm/nm}) = 1.7\ \text{nm}$

(4) (b) If the grating width is 50 mm, what is the maximum theoretical resolution of the monochromator?

$R = mN = (1)(1200\ \text{blazes/mm})(50\ \text{mm}) = 60{,}000$

3. (4) A bandpass filter has a dielectric layer with a thickness of 400. nm and a dielectric constant of 1.45. Calculate the 2nd order wavelength transmitted by the filter.

$\lambda = 2dn/m = (2)(400\ \text{nm})(1.45)/(2) = 580\ \text{nm}$

4. (6) An atomic emission spectrometer is used to detect ytterbium (I always wanted to include this element on a test) in mineral samples. The sensitivity of the method is 3.6 ppb^{-1}. The blank signal is 0.040 and its standard deviation is 0.012. Calculate (a) LOD and (b) LOQ.

(a) $\text{LOD} = 3s_{bl}/m = (3)(0.012)/(3.6\ \text{ppb}^{-1}) = 0.010\ \text{ppb}$

(b) $\text{LOQ} = 10s_{bl}/m = (10)(0.012)/(3.6\ \text{ppb}^{-1}) = 0.033\ \text{ppb}$

5. Ten replicate measurements of praseodymium yield an average of 26 ppb and a standard deviation
(4) of 2.6 ppb. Calculate (a) the S/N and (b) the number of replicate measurements needed to increase the S/N to 25.

(a) $S/N = \langle x \rangle /s = (26 \text{ ppb})/(2.6 \text{ ppb}) = 10.$

(b) $S/N = k\sqrt{N}$; $\sqrt{N}/(S/N) = (10)^{0.5}/(10.) = (N)^{0.5}/(25)$; $N = (25/10)^2(10) = 62.5 \rightarrow 63$

6. Fluoride in drinking water is determined by ion chromatography. The signal from a drinking
(6) water sample is 0.38. 10.0 mLs of drinking water is mixed with 10.0 mLs of 2.0 ppm fluoride. The signal for this mixture is 0.57. Calculate the fluoride concentration in drinking water.

$S = mC$; $0.38 = mC$

$0.57 = m\{C(10.0/20.0) + (2.0 \text{ ppm})(10.0/20.0)\}$

$C = 1.0 \text{ ppm}$

Short answer: Provide a word, phrase, formula, or short sentence.

7. A wavelength of 4.0 μm lies in the **IR** domain.
(4)

8. What type of noise is reduced by cooling the detector of an optical spectrometer?
(4) Johnson noise

9. The f# of a concave mirror is the ratio of the **focal length** divided by the **diameter**.
(4)

10. A continuum source useful for the UV, VIS and near IR domains is the **high pressure arc lamp**.
(4)

11. Why are vacuum phototubes and PMTs blind to IR wavelengths?
(4) The energy of IR photons is insufficient to overcome the work function of electrons in the photocathode of these detectors. No electrons ejected into vacuum results in no current.

12. What are the advantages of the multichannel design for UV/VIS spectrometers?
(6) There are 2 advantages. First, the multiplex advantage - all wavelengths are detected simultaneously, leading to very rapid acquisition of a spectrum. Second, there are no moving parts, leading to excellent precision in wavelengths.

13. In question 6, what assumption(s) was made in order to do the calculation?

(4) That the signal was linear with respect to concentration, and that the blank signal was zero (or the data was blank-corrected).

14. Define chromatic aberration.

(4) The change in focal length of a lens with wavelength due to the change in the index of refraction with wavelength (optical dispersion). The focal length becomes shorter as the wavelength decreases.

Discussion: Give as much detail as possible. Each question is worth 16 points.

15. What are calibration curves? What is standard addition? Discuss how calibration curves are used to define the sensitivity and dynamic range of a method. What are matrix effects? If matrix effects are severe, which method is better - calibration curve or standard addition?

Calibration curves are plots of signal vs concentration for a series of standards (including blanks)(a sketch would be nice). The plots usually exhibit a linear response over a concentration range known as the dynamic range. The plots tend to be curved at concentrations outside the dynamic range. A linear regression fit of the data in the dynamic range yields a slope, which is defined as the sensitivity. Thus, the data fit the equation: $S = mC + S_{bl}$. With this equation in hand, signals for samples can be converted to concentrations. Alternately, signals for two standards that bracket the signal of a sample can be used to calculate (via linear interpolation) the concentration of the sample.

Standard addition is a two-step method. The signal is measured using just the sample. Then the sample is "spiked"; its concentration is changed by a known amount by adding a known volume of a standard (known concentration) to a known volume of the sample. The signal is measured for the mixture. Two equations are set up in two unknowns, taking care to account for dilution:

$$S_1 = mC_s$$

$$S_2 = m(C_s(V_sV_{total}) + C_{standard}(V_{standard}/V_{total}))$$

Solving these equations yields the sample concentration C_s.

Matrix effects are cases where the matrix containing the sample interferes with the measurement. Examples include light scattering and highly colored samples, or interferences (atoms, ions, or molecules that generate a signal in the instrumental method). When matrix effects are severe, the standard addition method is best.

16. Sketch a Czerny-Turner monochromator with a planar grating and label the 5 main parts. Discuss how the wavelength of the monochromator is scanned. How is stray light reduced? How is a grating matched to a spectral range? Why must cutoff filters be used with grating monochromators?

The sketch should show the entrance slit, the collimator, the grating, the focuser and the exit slit. Light from the entrance slit is collimated, diffracted by the grating, and brought to a focus along the focal plane as a rainbow - spread of wavelengths. The exit slit selects the wavelengths transmitted out of the monochromator. Rotating the grating moves the wavelengths along the focal plane and scans the wavelengths.

Stray light is reduced by including internal baffles to restrict light to certain paths, avoiding dust (sealed optics), and painting all internal surface flat black to kill reflections. For the lowest levels of stray light (such as in Raman spectroscopy), a double or triple monochromator is used. The exit slit of one monochromator becomes the entrance slit of the next monochromator. These systems are expensive.

The grating is matched to the spectral range two ways. First, the "d" spacing of the grating is roughly the same distance as the wavelenght being diffracted. Second, the grating is blazed at a wavelength (λ_B) near the middle of the desired wavelength range. High throughput is achieved for wavelengths ranging from 2/3 λ_B to 2 λ_B.

Diffraction grating monochromators transmit light of the selected 1st order wavelength, and light of higher orders (λ/m, where m = 1, 2, 3, 4,...). Cutoff filters are used to block the higher order wavelengths. As the wavelengths are scanned, the cutoff filters must be periodically changed to avoid blocking the 1st order wavelength.