Chemistry 4440 Second Test
Thursday, October 20, 2011

1. (***15 points***) If I want to decrease the detection limit of a spectrometric experiment I can increase the light intensity of the source lamp. In fluorescence spectrometry this does indeed decrease detection limits; however, in UV/vis, in general, this does not. In both cases why? Think carefully about the sources of these two experiments' signals.

2. (***20 points***) Compare and contrast FTIR and dispersive IR spectrometers. Include significant 5 similarities and 5 significant difference.

Differences	Similarities

(***10 points***) Leaving instrumental costs and robots out of your answer, provide three reasons would you purchase an ICP instead of an AAS for your lab?

(***20 points***) A postmortem forensic analysis for a lead metabolite in blood, $Pb(CO_3)_2$, involves a fluorescence assay carried out in the following manner:

A 5.00 mL blood sample was drawn and mixed with 3.50 mL of an anticoagulant/buffer solution. The blood solids were spun down and the supernatant decanted (assume insignificant volume change for this step). The supernatant was diluted to a volume of 10 mL with another buffer and cleaned by solid phase extraction (SPE), that is, by passing all 10 mL through an extraction filter to remove common, soluble blood contaminants that might interfere with the next analytical step; again assume no volume change. A 25.00 μL aliquot of that solution was diluted to 25.00 mL with lead-free water. When 2.00 mL of that final solution were exposed to 205 nm light in a fluorometer they fluoresced at 405 nm. A LLS calibration with acidified $Pb_3(PO_4)_2$ standards of **ppm** concentrations (fluorescence units versus $[Pb_3(PO_4)_2]$) produced a blank-corrected fit whose line was $y = 0.004 + 10.12x$. If the final diluted solution above produced a fluorescence signal of 0.097 fluorescence units and a blank blood sample handled the same way—but containing no lead—produced a signal of 0.015, what was the concentration of $PbCO_3$ metabolite in the victim's blood in **ppb**? Note that the metabolite is $Pb(CO_3)_2$, and the standards were $Pb_3(PO_4)_2$.

(15 points) We have studied three different light ranges in our waltz through analytical spectroscopy, the UV, visible, and IR light regions. In general the sorts of energy transitions involved include movements among **rotational**, **electronic**, and **vibrational** energy states (in no particular order) for molecules examined by these techniques, and can encompass absorption, **fluorescence** and **phosphorescent** processes. Using only a correctly labeled Jablonski diagram, draw a single absorption event that can yield examples of each of the five bolded terms above. Make sure that all energy states and transitions are correctly labeled. For instance, assume a laser excites a sample of identical molecules all to the same excited state. What happens next. Any written explanation of your Jablonski diagram beyond the labels use will be disregarded. Use the back of this sheet for your diagram.

(***20 points***) Match the **best answer** given the following:

1. resonance fluorescence _____

2. units of molar absorptivity _____

3. A > 2.5 _____

4. releasing agent _____

5. protective agent _____

6. assumption that sample density is 1 _____

7. assumption that you need sample density to determine ppm analyte _____

8. ionization suppressor _____

9. double beam spectrophotometer_____

10. interferogram _____

A. preferentially react with interferants in AAS

B. form stable but volatile species w/analyte

C. good if sample is concentrated with analyte

D. $A_{254} = -1.39$

E. cigarettes still cause cancer

F. same energy as photons absorbed

G. same energy as ground state

H. inductively coupled plasma

I. uranium is a great one

J. M cm^{-1}

K. amount of absorbance

L. less than 0.32 % of light passes though sample

M. more than 100% of the light passes through the sample

N. LSD

O. examples: our UV/vis & AAS spectrometers

P. examples: our ICP and UV/vis spectrometers

Q. examples: our UV/vis and fluorescence spectrometers

R. blank absorbance added to sample absorbance

S. contains all monochromator wavelengths simultaneously.

T. alkali metal salts do this well

U. good if sample is very dilute

V. corrects for light emission by AAS flame

X. contains samples emissions simulteneously

Y. $M^{-1}cm^{-1}$

Z. contains data from all wavelengths simultaneously

Formulae that <u>may</u> be useful:

$$\Delta f = \frac{1}{3t_r}$$

$$c_x = \frac{(S_1 c_s V_s)}{[(S_2 - S_1) V_x]}$$

Beer's Law: $A = \varepsilon bc$

$$v = \sqrt{4kTR\Delta f}$$

$$\text{Frequency} = \frac{1}{\text{Conversion rate}}$$

Equation for a line: y = mx + b

$E = h\nu$

mass electron 9.11×10^{-28} grams

$$C_x = \frac{S_1 c_s V_s}{(S2 - S1)V_x}$$

$h = 6.626 \times 10^{-34}$ Js

$$i_{rms} = \sqrt{2Ie\Delta f}$$

$$s = \sqrt{\frac{\sum x_i^2 - (\sum x_i)^2 / N}{N - 1}}$$

speed of light = 3.00×10^8 m/s

$$\gamma = \frac{m}{S_s}$$

$c = \lambda\nu$

$$A = \log \frac{P_0}{P}$$

$A = -\log T$

$$E = \frac{1}{2} mv^2$$

$1J = kg \cdot m^2 \, sec^{-2}$

photons rest mass = 0