Analytical Chemistry Cumulative Exam Jan. 18, 2018

Don't Panic

Units! (15%)

1. What are the standard S.I. units for the following "base" variables:
a) Mass **b)** Length **c)** Time **d)** Temperature

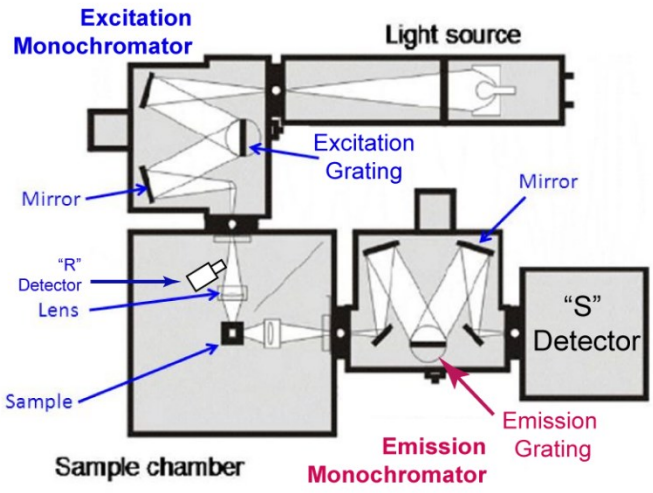
2. More complex variables are referred to as "derived" units. What are the base units for:
a) Force **b)** Pressure **c)** Volume **d)** Energy **e)** Frequency
Hint: Don't answer with Newtons, Atmospheres, Liters, Joules, and Hertz (especially not Atmospheres or Liters)!

3. Given your answers to the above, tell me:
a) What are the base units of Liters? **b)** What are the base units of molarity? **c)** Is molarity expressed in standard S.I. units? (hint: this is yes or no question)

Fluorescence! (50%)

4. Analytical methods are used to detect the presence of analytes. Which method can ultimately detect the smaller amount of analyte: absorption or fluorescence, and why do you answer as you do?

As shown here, a fluorimeter has a light source, monochromator (usually composed of a single grating), sample, and a detection system composed of another monochromator and photodetector. Some of the questions below are based on this design.



5. Most fluorimenters measure the intensity of emission at a singular wavelength using a photodetector. The instrument creates an emission spectrum by making such measurements, point by point, until the intensity over full spectral range has been collected. If the excitation lamp "flickers" while doing so, the fluorescence intensity measurement at that point will be affected. As a result, all fluorimeters have two photodetectors- one that measures the intensity of fluorescence from the sample (the "S" signal), and another that measures the excitation light intensity (the "R" signal).
Now, if your measuring the emission spectrum of a dye, you don't want to plot just the "S" signal because the spectrum will be corrupted by lamp flickering. Rather, what would you plot instead? Hint: It's a function of "R" and "S", such as "R" – "S" for example (note, the answer is not "R" – "S").

6. Some expensive fluorimenters use a double monochromator system for the excitation. In such an instrument, the "white" excitation lamp light goes through one monochromator, and the resulting output goes through another monochromator before exciting the sample. As this is very expensive, why would anyone do this?

7. Most fluorimeters have a silicon photodetector. However, there are other types of detectors that employ other semiconductors such as InGaAs, HgCdTe, or PbS. Why would there be more than one type of photodetector available?

8. Most photodetectors respond with a greater efficiency to higher energy (blue) light vs. lower energy (red) light. As a result, fluorescence spectra produced by the unprocessed output of a photodetector will appear "misshapen"; for example, the red side of the emission spectrum will be less intense than it should be, while the blue side is conversely too intense.
Do you know how (or can you propose a method) to fix this? Hint: you do not have to make any physical adjustments to the instrument or detector.

9. While we are on detectors- what is an integrating sphere, or what does an integrating sphere do?

10. What is Photoluminescence Excitation Spectroscopy?

Fluorescence Resonant Energy Transfer! (20%)

Fluorescence Resonant Energy Transfer (FRET) is a physical phenomenon where the energy of an excited chromophore ("the donor") is transferred to a nearby chromophore ("the acceptor"). The emission of the donor must overlap the absorption of the acceptor, and the dye pair usually has to be within ~5 nm proximity to each other. This phenomenon is similar to what would happen if you walked up to a radio transmission tower holding a metal rod. FYI don't do that.

11. Name one potential (or actual) analytical use of FRET.

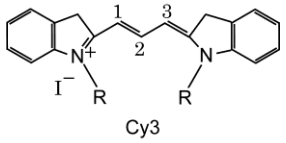
12. The overlap of the donor emission and acceptor absorption is given by the "overlap integral":

$$J = \int f_{norm}(\lambda) \cdot \varepsilon(\lambda) \cdot \lambda^4 \cdot \partial\lambda$$

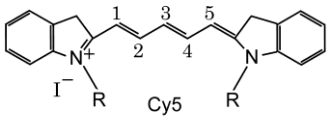
where $\varepsilon(\lambda)$ is the molar absorptivity of the acceptor in $M^{-1}cm^{-1}$, and $f_{norm}(\lambda)$ is the normalized donor emission which has units of cm^{-1}. The units of J should be cm^6, (centimeters to the sixth power); however, this won't be true if you evaluate J using $\varepsilon(\lambda)$ in $M^{-1}cm^{-1}$. What's wrong?

Fluorescent Dyes! (5%)

13. Here are two cyanine dyes: Cy3 and Cy5



Cy3



Cy5

Which one emits at lower energy than the other and why? Please answer using the structure of the dye.

Safety! (10%)

14. What is an SOP?

15. Do you need to worry about laser safety if you are using a FTIR? Why or why not?

16. Let's say that you work with a large machine that uses a lot of electrical power. Is there any danger of electrical shock if the instrument is unplugged? Why or why not?
Note: I didn't say switched off but still plugged in. I said the *plug is disconnected from the wall socket*.

17. Under what circumstances do you ***not*** need to wear safety glasses in a lab?

18. Which acid is more dangerous: HCl or HF, and why?

Useful Data

Gas Constants	Atmospheric Pressures
8.314 J / K / mol	101325 Pascals
0.0821 atm L / K / mol	1.0 atm
62.36 mmHg L / K / mol	760 mmHg
62.36 Torr L / K / mol	760 Torr
1.206 psi L / K / mol	14.696 psi
0.0831bar L / K / mol	1.01325 bar

Plank's constant (h) = 6.62606896×10^{-34} J·s
h/2π (ħ) = $1.054571628\times10^{-34}$ J·s
electron mass = 9.10938188×10^{-31} kg
proton mass = 1.67262158×10^{-27} kg
neutron mass = 1.67492729×10^{-27} kg
photon mass = 0.00000 kg
photon momentum = h/λ
photon energy = $h\nu = h\cdot c/\lambda$
frequency of light (ν) = c/λ
Speed of light (c) = 2.99792×10^{8} m/s

Semiconductor	**Bandgap (eV)**
Si	1.1
InGaAs	0.7
HgCdTe	0.5
PbS	0.37