Please answer all questions in a blue exam booklet, and make sure the question number is clearly indicated. Good Luck!!

1. Please indicate whether the following statements are True (T) or False (F) (note: the entire statement must be true for the statement to be true!) (24 pts) .

    a) In a Michelson interferometer, when the retardation ( ) is equal to zero, this means that the minimum intensity of radiation from the source will strike the IR detector.

    b) The purpose of the laser beam within a Michelson interferometer is to determine the exact timing for sampling the signals from the IR detector, and this also provides a measure of the speed of the moving mirror.

    c) A tungsten lamp is an excellent source of radiation in the far IR region of the spectrum.

    d) In flame atomic absorption spectroscopy, a refractory compound is one that decreases the intensity of light striking the detector (appears as positive error in absorbance) owing to a significant change in the refractive index of the flame due to the presence of this species.

    e) The use of a more intense excitation source for molecular fluorescence will always lead to an increase in the fluorescence quantum yield of the molecule being excited, and hence better detection limits.

    f) Graphite furnace atomic absorption instruments will generally yield lower detection limits for a given element than corresponding flame instruments because the atomization efficiency of the sample is much greater.

    g) Use of a tunable laser source for UV-Vis spectrophotometry is always preferred, owing the improvements in detection limits that normally results in spectroscopy from using a more intense source.

    h) Electron impact and field desorption are both good examples of hard ionization methods used in mass spectrometry.

    i) Very high vacuums (very low pressures) are required in most mass spectrometry instruments to prevent contaminating the instruments with ambient species, and to also prevent collisions of the ions with high levels of atmospheric molecules, which would degrade the ability to separate these ionic species in the gas phase.

    j) The lower detection limits observed for elemental analysis by ICP vs. flames and other atomization sources (for nearly all elements) is mostly the result of the inert argon atmosphere, due to the large amount of argon gas used to create the plasma.

k) A hypsochromic shift in the λ_{max} of a species when recording a UV-Vis absorption spectrum means that the λ_{max} shifted to a higher wavelength or lower energy.

l) The purpose of a nebulizer in atomic spectroscopy is to create very small dried salt particles the analyte ion before the sample enters the flame or plasma region where actual atomization occurs.

2. Please indicate the correct answer to the following multiple choice questions (make sure you write correct letter answer next to question number in your blue exam book) (21 points)

2.1 A mixture of A and B was partially separated on an HPLC column, resulting in overlap of their chromagraphic peaks. The absorbance of the effluent was monitored at 310 nm ($\varepsilon_A = 1800$, $\varepsilon_B = 1600$) and 330 nm ($\varepsilon_A = 2100$, $\varepsilon_B = 3200$); ε is the molar absorptivity in $L \cdot mol^{-1} \cdot cm^{-1}$. The absorbance at the maximum of the first chromatographic peak at 310 nm was 0.020 and at 330 nm was 0.030. What is the major component of the first eluting peak and what percentage of the total absorbance at 310 nm is due to this component?

(A) A, 60%

(B) B, 60%

(C) A, 40%

(D) B, 40%

2.2 Using the following table of prominent absorption wavelengths and molar absorptivities for napthalene and

Compound	Absorption wavelength, nm	Molar absorptivity
napthalene	221	130000
	286	9300
	312	290
	375	0
anthracene	221	15000
	312	1200
	375	9000

anthracene, suggest a wavelength at which anthracene can be determined in the presence of an unknown amount of napthalene and calculate the minimum detectable concentration (MDC) of anthracene (in M) at its optimum wavelength. Assume a cell path length of 1.00 cm and the MDC yields a %T of 97.0.

Molar Mass	
anthracene	166 $g \cdot mol^{-1}$

(A) 221 nm, 6.7×10^{-6} (B) 286 nm, 1.4×10^{-6}
(C) 375 nm, 1.8×10^{-4} (D) 375 nm, 1.5×10^{-6}

2.3 In the atomic absorption spectrometric measurement of sodium, an analyst records a signal of 0.110 absorbance units for a 1 ppm solution of sodium, while the same solution containing also 20 ppm potassium gives a reading of 0.125. A 20 ppm solution of potassium exhibited a blank reading of zero. Explain the results.

(A) A potassium–sodium intermetallic compound is formed in the flame, and it absorbs the radiation from the sodium and source.

(B) The presence of the potassium suppresses ionization of the sodium atoms in the flame.

(C) The added potassium causes the flame to cool down due to the energy required to atomize it.

(D) The potassium particles cause scattering of the light.

2.4 An important advantage of a double–beam spectrophotometer over a single–beam spectrophotometer is that it permits

(A) compensation for source power fluctuations.

(B) narrower slits to be used; therefore, greater spectral purity.

(C) rapid response detection systems to be used.

(D) use of a greater range of wavelengths.

2.5 The intensity of the molecular fluorescence of a compound is related to all of these parameters except

(A) the power of the excitation radiation.

(B) the fluorescence quantum efficiency of the fluorescing molecule.

(C) the molar mass of the compound.

(D) the absorptivity of the compound.

The path that excitation radiation travels in a UV–visible spectrophotometer is

(A) light source → sample → monochromator → photomultiplier tube

(B) light source → photomultiplier tube → sample → monochromator

(C) light source → monochromator → sample → photomultiplier tube

(D) light source → sample → photomultiplier tube → monochromator

Which of the following is *not* a required assumption in the use of Beer's Law for absorption spectrometry?

(A) The radiation must be monochromatic.

(B) Only one absorber can be present.

(C) The incident radiation must be in the ultraviolet or visible region.

(D) All of the above are *not* required.

3. Sketch the basic instrument components in their proper orientations of a conventional spectrofluorimeter (assume diffraction grating based). Briefly explain the purpose of each component and further explain why it would be possible that a interference filter-based fluorometer could actually yield lower detection limits for quantitating a given fluorescence molecule than the spectrofluorometer instrument that you have drawn. (15 points)

4. Lithium can be used as an antidepressant drug (usually in the form of lithium carbonate). If lithium was determined by flame emission spectroscopy using a resonant line at 671 nm, estimate the % change in intensity of the emission signal that would possibly result (for a given concentration of lithium ions) if the flame temperature was changed from 2200 to 2300 °C. Would such a change be positive or negative, and would you expect the detection limits to be lower or higher at the more elevated temperature. Explain! (hint: you need to do some calculations using the appropriate equation). (15)

5. Sketch a photomultiplier tube arrangement (top down view) and explain how it can be used to detect very low intensities of electromagnetic radiation in the UV and Visible ranges of the spectrum. Why is this detector not used modern FT-IR instruments that operate in the mid-IR region? Explain! (10)

6. Magnesium was determined by flame atomic absorption using an appropriate hollow cathode lamp and setting the monochromator to 285.2 nm. When a blank solution (w/o) magnesium was introduced into the flame, the current detected at the photomultiplier was 125 μA. In the presence of a given diluted serum sample containing Mg, the current was 75 μA (diluted with 0.12 M NaCl). A standard solution of 20 μM Mg in a solution containing physiological levels of NaCl (0.12 M) yielded a photocurrent of 80 μA when aspirated into the flame. What was the concentration of Mg in the sample based on these current measurements (assume zero curent if a shutter was placed in front of the hollow cathode lamp to block light from the source from striking the detector). Given that the standard used to calibrate the instrument did not contain organic species (i.e., the 20 μM Mg standard), and that Mg was being detected using radiation in the UV region of the spectrum, do you believe that this measurement has a significant source of error? If so, is the error positive or negative and why? Also, what type of AA instrument would enable you to correct for this error? (15)

7. Briefly define the following terms (1-2 sentences!) (5 pt each):

   a) continuum source
   b) multiplex advantage
   c) incoherent source of radiation