Exam #2

Name ______________________________

Instructions: This exam is worth 100 points. Question 2 allows a choice as to which parts are answered. Only answer the number of parts requested.
1. (32 points) Circle the correct answer for each of the following:

a. Furnace atomizers in atomic spectroscopy

(1) are less widely used than flame atomizers due to their reactive atmosphere.
(2) require larger sample volumes than flame atomizers. [Red Circle]
(3) offer better limits of detection than flame atomizers due to increased atomization efficiency.
(4) None of the above.

b. Fluorescence emission signals

(1) increase with quantum yield.
(2) increase with molar absorptivity.
(3) increase with sample pathlength
(4) All of the above.

c. \( n \)-Hexane \((\text{CH}_3\text{(CH}_2)_4\text{CH}_3)\) exhibits no absorptions in the UV-visible region because

(1) it readily undergoes photodecomposition.
(2) its electron excitation energies are outside of the UV-visible range. [Red Circle]
(3) it undergoes rapid vibrational and rotational relaxation, thereby preventing the absorption from being observed.
(4) it contains no lone-pair electrons.

d. Arc emission

(1) is particularly suited to quantitative analysis of metal atoms.
(2) uses a graphite furnace to achieve the atomization of the sample.
(3) cannot be used with solid samples. [Red Circle]
(4) is particularly suited to samples containing metal mixtures due to the simultaneous excitation of each mixture component.

e. Flame atomizers

(1) often employ nitrous oxide as a fuel gas.
(2) require sample sizes on the order of microliters.
(3) vary in temperature according to the fuel and oxidant used. [Red Circle]
(4) have the disadvantage of long analysis times relative to furnace atomizers.

f. Infrared spectroscopy

(1) is based on electronic transitions involving atoms forming s bonds.
(2) features absorptivities that are typically larger than those found in visible spectroscopy.
(3) provides a useful "fingerprint" of the sample molecule due to the presence of many absorptions between 600 and 700 nm. [Red Circle]
(4) None of the above.
g. In fluorescence spectroscopy, an instrument geometry of $90^\circ$ is used between the source and detector

1. to minimize the heating of the detector by the high intensity source beam.
2. to minimize the size of the spectrometer enclosure.
3. to allow source photons to be separated from photons being emitted by the sample.
4. to allow longer sample pathlengths to be used.

h. The problem of broadband molecular absorption can be minimized in flame atomic absorption spectroscopy

1. by using a lower atomizer temperature.
2. by using a broadband light source and measuring the interfering absorbance.
3. by using a smaller sample volume, thereby reducing the magnitude of the interfering absorbance.
4. by using a burner with a longer slot, thereby increasing the optical pathlength.

2. (56 points) Answer seven of the following:

a. What is a bond dipole? What is the significance of bond dipoles in spectroscopy?

b. Why does increasing source intensity improve the limit of detection of a fluorescence measurement but typically does not similarly improve an absorption measurement?

c. Differentiate between the terms "excitation spectrum" and "emission spectrum" in fluorescence spectroscopy.

d. Sketch a hollow cathode lamp and describe how it operates. Where is this lamp used?

e. Define the term, "atomization".
f. Name two advantages and two disadvantages of infrared spectroscopy relative to UV-visible spectroscopy for making quantitative measurements.

g. Why are multichannel detectors appropriate for atomic emission measurements?

h. Name one advantage afforded by each of these methods: atomic emission, flame atomic absorption, furnace atomic absorption.

3. (12 points) You have an unknown solid sample containing Mg (MW=24.312, λ_max=285.2 nm) and Cu (MW=63.54, λ_max=324.7 nm). You weigh out 1.3399 g of this material, dissolve it in acid and dilute to 1000.0 mL in a volumetric flask. This is your stock solution.

Experiment 1: A 1.000 mL aliquot of the stock solution is diluted to 50.0 mL and the resulting solution is aspirated into an air-acetylene flame. The absorbance is measured at 285.2 nm as 0.117.

Experiment 2: A 1.000 mL aliquot of the stock solution is mixed with 1.000 mL of a mixture solution that is 75.2 mg/L Mg and 44.7 mg/L Cu. The resulting solution is diluted to 50.00 mL and its absorbance is measured as 0.924.

What is the weight percent of Mg in the original solid sample?

Let C = Mg concentration in the original 1000 mL solution and K = the unknown product of absorptivity and path length. Assume that in atomic absorption, the Cu and Mg do not have overlapping spectral lines (i.e., Cu does not interfere).

Expt 1: 0.117 = K((0.001 L * C mg/L) / (0.05 L))

Expt 2: 0.924 = K((0.001 L * C mg/L + 0.001 L * 75.2 mg/L) / (0.05 L))

Divide the two equations to remove the K term. The 0.05 L terms also cancel:

0.117 / 0.924 = (0.001 L * C mg/L) / (0.001 L * C mg/L + 0.0752 mg)

Solving for C --> C = 10.9 mg/L

Work backward to original sample: 10.9 mg/L * 1 L = 10.9 mg --> 10.9 mg / 1339.9 mg * 100 = 0.813%