CHEM 322 **Name**____________________________________
Exam 3 **Fall 2014**

Complete these problems below and those on page 2 on separate paper and staple it to these sheets when you are finished. Please initial each sheet as well. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT.

Warm-up (3 points per blank)

1. The sensitivity of a PMT can be attributed to a cascade of increasing numbers of electrons

   down a series of _________________________________.

2. In FTIR, resolution is dependent on the _____________________________________; the difference in optical path down the two arms of the interferometer.

3. Experimentally determined linewidths for atomic transitions are typically much larger than the uncertainty principle would predict. The two primary reasons for the increased linewidth

   are ______________________________ and ______________________________

You must complete problem 4.

4. You have been given the task of establishing the detection limits for the determination of several elements using atomic spectroscopy. The data below are the detection limits in ppb that were determined for Flame AAS, Flame AES, GFAAS and ICP-AES for two elements. Your colleague is somewhat confused by the different behavior of each element. Clearly explain the trends in the data, including why the trends for the two elements are different. (15 points)

Element	Flame AAS	GFAAS	Flame AES	ICP AES
K	1	0.004	0.01	30
Ag	0.9	0.001	2	0.2

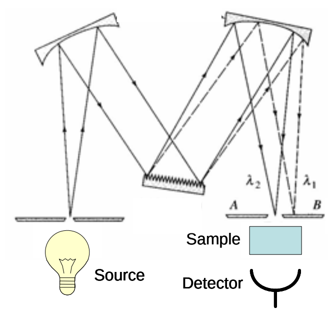
Complete 5 of the following. Be concise in your answers and show work for problems involving calculations. Clearly indicate which problems are not to be graded. (15 pts ea)

5. In the development of Beer's law, *at least* two assumptions must be made. Identify two assumptions that must be valid for a system to follow Beer's law and describe the impact on a quantitative measurement should these assumptions fail.

6. Why are atomic emission methods with an ICP source better suited for multi-element analysis than flame absorption methods? Include block diagrams of ICP-AES and Flame AAS instruments.

7. What role does the interferometer play in an FTIR instrument? How does it accomplish this role? How does the incorporation of an interferometer lead to the two primary advantages for doing Fourier transform spectroscopy?

8. There is currently a great deal of interest in decreasing the size of traditional bench-top instruments, resulting in small, portable analytical devices. This is true for optical instruments as well, leading to the development of devices like the Ocean Optics spectrometers we use in several courses. Historically, the resolution for these small instruments is poorer than that for traditional bench-top devices. Discuss possible reasons for this observation. For convenience, you may want to consider "large" and "small" versions of the design at the right.



9. Describe how continuum-source background correction works in atomic absorption spectrometry.

10. Sketch and label a block diagram for a fluorescence spectrometer. Why are high intensity sources like xenon arc lamps and lasers typically used in fluorescence experiments where deuterium lamps and tungsten lamps are adequate for most UV-VIS absorbance experiments?

11. You have been instructed to build a UV-Vis instrument using a linear CCD array detector that has 1024 pixels aligned on a 2.00 cm chip.
    a. If you want the first order diffraction of light from 200-800 nm to completely fill the array, how many grooves per millimeter should his grating have? Assume the focal length of the monochromator is 0.20 m.
    b. If you were building a scanning spectrometer using the grating from part a, what slit width would be required to produce the same effective bandwidth as in the CCD instrument? Could the two emission lines of hydrogen (656.28 and 656.10 nm) be resolved using under these conditions?

Possibly Useful Information

$\eta_1 \sin\theta_1 = \eta_2 \sin\theta_2$	$R = \dfrac{\lambda}{\Delta\lambda} = nN$
$\Delta\lambda_{eff} = wD^{-1}$	$n\lambda = d(\sin i + \sin r)$
$D = \dfrac{dy}{d\lambda} = F\dfrac{dr}{d\lambda}$	$\dfrac{dr}{d\lambda} = \dfrac{n}{d\cos r}$
$T = P/P_0$	$D^{-1} = 1/D$
$A = -\log T = \log(P_0/P) = \varepsilon bc$	$E = \dfrac{hc}{\lambda}$
$\Delta\bar{\nu} = \bar{\nu}_1 - \bar{\nu}_2 = \dfrac{1}{\delta}$	$\dfrac{N}{N_0} = \dfrac{g}{g_0} e^{-E/kT}$
$E = \dfrac{hc}{\lambda} = h\nu$	$c = 3.00 \times 10^{8}\ ms^{-1}$ Planck's Constant = 6.63×10^{-34} Js
$k = 1.38 \times 10^{-23}\ JK^{-1}$	AAS = Atomic absorption spectrophotometry AES = Atomic emission spectrophotometry ICP = Inductively coupled plasma

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIII		IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	‡89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

‡ Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)