

Complete these problems as instructed below. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT.

Bonus: (4 points) What experimental challenges are each of the following designed to address?

- a. Calibration with an internal standard.
- b. Calibration using standard additions.

Warm-up (2 points each).

1. _____ causes an apparent change in frequency of a photon due to the motion of the emitter either toward or away from the receiver.
2. A _____ provides an obstructed path for nebulized sample as it moves toward the flame or plasma.
3. In a _____, the energy absorbed from a photon results in the movement of an electron from an electron donor to an electron acceptor.
4. In FTIR, resolution is dependent on the _____; the difference in optical path down the two arms of the interferometer.

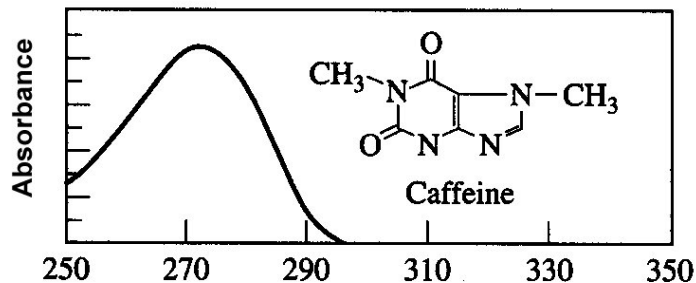
Follow the instructions for the following. Be clear and concise. (15 points each)

Complete problem 5.

5. Why do absorbance spectra from atomic species tend to exhibit narrower bands than for molecular species? Why do spectra from gas phase molecular analytes tend to have narrower features than spectra for the same compound in the condensed phase?

Complete either problem 6 or problem 7 below.

6. Describe the effect of the following on a calibration curve for the spectrophotometric determination of caffeine ($\lambda_{\text{max}} = 273 \text{ nm}$) using a Beer's law-based method. The spectrum of caffeine is given below.



- The solvent is contaminated by an unknown compound that also absorbs at 273 nm.
 - The bandwidth of the instrument is 5 nm and the monochromator is miscalibrated so that the bandwidth is centered at 285 nm instead of 273 nm.
7. 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.

Complete two of problems 8, 9, and 10 below.

8. Why are detection limits for most elements lowest for electrothermal AAS and highest for flame AES, with ICPAES in the middle?
9. Why are atomic emission methods with an ICP source better suited for multielement analysis than flame absorption methods?
10. Why is flame emission in a relatively cool flame actually preferred for the measurement of sodium when compared to that of a hot flame or plasma, even though the hotter source will give a higher excited state population?

Complete either problem 11 or problem 12 below.

11. Clearly describe why photomultiplier tube detectors are typically not suited for use in infrared spectroscopy. Identify the basis of operation for one of the IR detectors we discussed.
12. 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?

Possibly Useful Information

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

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VII B	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 isotopes.

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
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† 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)
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