

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?

- Calibration with an internal standard. **Run-to-run variability**
- Calibration using standard additions. **Matrix effects (physical/chemical interference)**

**Warm-up (2 points each).**

- Doppler broadening (or effect)** \_\_\_\_\_ causes an apparent change in frequency of a photon due to the motion of the emitter either toward or away from the receiver.
- A **spray chamber** \_\_\_\_\_ provides an obstructed path for nebulized sample as it moves toward the flame or plasma.
- In a **charge transfer complex** \_\_\_\_\_, the energy absorbed from a photon results in the movement of an electron from an electron donor to an electron acceptor.
- In FTIR, resolution is dependent on the **retardation** \_\_\_\_\_; 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.**

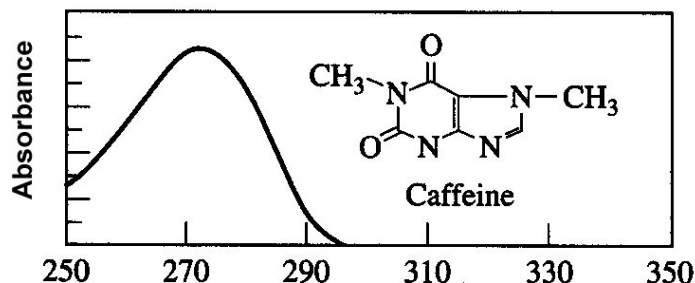
- Why do absorbance spectra from atomic species tend to exhibit narrower bands than for molecular species? Why do spectra from gas phase molecular analytes tend to have narrower features than spectra for the same compound in the condensed phase?

**Key points:**

- Molecular bands are complicated by the addition of rotational and vibrational transitions on top of electronic energy levels. This increases the number and range of energy of the molecular transition in comparison to atomic spectra, which are not complicated by rotations and vibrations.
- In the condensed phase, collisions with neighboring species (other analytes or solvent) result in small energy transfers and a "smearing out" of energy levels within the analyte. This is called collisional broadening. In the gas phase, the likelihood of a collision is less, resulting in narrower features.

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.



- a. The solvent is contaminated by an unknown compound that also absorbs at 273 nm. Since all of your solutions will be prepared using the solvent, the unknown contaminant will be present in all solutions at constant concentration. The result of this will be a calibration curve that has nonzero intercept. The slope of the curve should be the same as you would expect if the contaminant was not present. (Unless the total concentration of contaminant and caffeine causes excessive absorbance, in which case, nonlinearity could result.) Since the contaminant is present in all solutions, appropriate use of a blank and standards should still produce a linear relationship. If the amount of this contaminated solvent is different in the sample compared to standards, the experimentally determined concentration will be unreliable.
- b. 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. In the region surrounding 285 nm, the molar absorptivity of caffeine is changing fairly dramatically. The result will be an absorbance that does not depend linearly on concentration, with the most serious deviation occurring at high absorbance (concentration). At high concentration, the measured absorbance will be smaller than you would predict for a constant average molar absorptivity.
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.
- Beer's law assumes that:
- (1) Incident light is *monochromatic*, or at least the bandwidth of the incident light is much narrower than the absorption band that is to be excited. Under these conditions, the molar absorptivity is essentially independent of wavelength. As the bandwidth increases, molar absorptivity becomes strongly dependent on wavelength. This variation becomes even more pronounced as concentration (and absorbance) increases, causing Beer's Law plots to bend toward the concentration axes as the apparent molar absorptivity decreases.
  - (2) The system is not saturated in light so that a photon moving through the sample has some probability of being absorbed.
  - (3) Absorbers behave independent of one another; otherwise the apparent molar absorptivity of the solution will vary with concentration.
  - (4) Any equilibria present are static to that the composition of the solution does not change during the course of the measurement.

**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?

Electrothermal methods, like GFAAS, lead to lower detection limits primarily because of the efficiency with which the sample is used. In GFAAS, the entire sample is atomized and exposed to the measurement stage. In flame and plasma methods, the bulk of the sample is directed to waste and only a small fraction is actually exposed to the measurement stage.

Plasma emission methods tend to produce lower detection limits than flame methods because the increased temperature of the plasma leads to more efficient atomization and an increased population of the excited state. An increase number of excited state atoms leads to greater emission signals and ultimately lower detection limits.

9. Why are atomic emission methods with an ICP source better suited for multielement analysis than flame absorption methods?

In AAS, an external light source, such as a hollow cathode lamp, must be used to excite the atom of interest. Given that HC lamps provide narrow bandwidth excitation, and given that the absorption spectra for elements vary, multielement analysis by AA requires multiple excitation sources. In Plasma AES, the energy of the plasma is sufficient to excite the atoms in the sample, so the requirement for a separate excitation source is removed.

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?

In this case, the concern is with the ionization of Na to Na<sup>+</sup>. At higher temperature, the easily ionized sodium atoms will be converted to ions, decreasing the number of sodium atoms in the gas phase, therefore decreasing the number of excited state atoms and the atomic emission.

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.

PMT detectors work by taking advantage of the photoelectric effect, in which, the energy of a photon is transferred to a photoemissive material, resulting in the ejection of an electron. IR photons typically are not energetic enough to cause the ejection of a photoelectron, therefore, typical PMT's are not useful in the IR. Other detectors, such as photoconductive or pyroelectric detectors are better suited for IR.

In photoconductive detectors, absorption of infrared radiation results in the promotion of electrons from the valence band to the conduction band in a semiconductor. This change in conductivity is related directly to the intensity of IR light striking the detector. Pyroelectric detectors contain materials whose electric polarization is temperature dependent. When IR light strikes the material, a potential is generated which can be monitored.

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?

The role of the interferometer is to encode spectral information from the frequency domain to a domain that is easier to record experimentally. Your discussion should include a description of an interferometer and its operation. By recording how the light throughput through the interferometer changes as a function of moving mirror position (and ultimately difference in path length), the frequency-dependent signal ( $I$  as  $f(\text{frequency})$ ) is encoded into the distance domain ( $I$  as  $f(\text{retardation})$ ). This dependence can then be decoded using a mathematical transform (like the FT). Since all wavelengths of light are being encoded simultaneously, the detector signal is larger, giving the throughput advantage. Because data for all wavelengths is recorded simultaneously and rapidly, the possibility for signal averaging exists, hence the multiplex advantage.

### Possibly Useful Information

$\Delta \bar{\nu} = \bar{\nu}_1 - \bar{\nu}_2 = \frac{1}{\delta}$	$\frac{N}{N_0} = \frac{g}{g_0} e^{-E/kT}$
$A = \log(P_0/P) = \epsilon bc$	$T = P/P_0$
$E = \frac{hc}{\lambda} = hv$	$c = 3.00 \times 10^8 \text{ ms}^{-1}$ 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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