

Due by 5:00 PM Friday, December 11
NO LATE PAPERS ACCEPTED!

Complete these problems on separate paper and staple it to these sheets when you are finished. Please put your name or initials on each sheet as well. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT.

Instructions

- This is **NOT** an open-book, open-note take exam. You MAY NOT consult any human or nonhuman resource besides Dr. Lamp as you complete the exam. This exam **MUST** be completed **INDIVIDUALLY** and in your own words. Group work or plagiarism will result in a zero for the exam.
- You will be allowed to ask Dr. Lamp a maximum of two (2) questions regarding the exam. Additional questions may be asked at a 3-point penalty per question. If you are working on the exam in the evening, you may try to reach Dr. Lamp on his cell phone at 660-341-0067 before 10:00 PM.
- Before opening the exam, prepare for it like you would for a traditional, in-class exam. Review concepts and examples from the text, as well as those discussed in class. This preparation will help to maximize your effort on the exam and allow you to complete it more efficiently.

Time Restriction

You may spend no more than two (2) hours working on this exam. This must be in one continuous block of time. You are on your honor to adhere to this restriction and record the time spent in the chart below.

Date	Time Began	Time Finished	Total Time
Total Time Spent on the Exam			

Pledge

I pledge on my honor that I have completed the exam in accordance with the above instructions and that I have not provided or received unethical assistance. I realize that failure to comply with these instructions will result in a score of zero on the exam.

Signature

Date

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

Warm-up (2 points each)

1. An echelle polychromator is an instrument that uses the combination of a coarsely ruled grating and a prism to achieve wavelength resolution by dispersing light in two dimensions.
2. An inductively coupled plasma is produced by interaction of ionized argon gas with an induced radio-frequency magnetic field.

Complete seven of the following, be concise. Clearly indicate which problem is not to be graded. (14 points each)

3. Briefly compare and contrast 2 of the following 3 items:
 - a. linear dispersion versus angular dispersion Both terms are related to how light is spread out in space. Linear dispersion is the spread of wavelengths across a plane (typically the focal plane), while angular dispersion takes the point of view of the source and quantifies how light is spread out as a function of geometric angles. Linear dispersion depends on focal length, but angular dispersion does not.
 - b. deuterium arc lamp versus tungsten lamp A deuterium lamps utilize electrical excitation of D_2 gas in a gas-filled tube, followed by dissociation of D_2 accompanied by emission of light to produce a continuum of radiation. Tungsten lamps utilize a heated filament to serve as a blackbody emission source, also producing a continuum. D_2 lamps are typically used as UV sources while tungsten lamps are used primarily in the visible.
 - c. stray light versus scattered light Stray light is light from any light source (not necessarily the instrument source) that reaches the detector, but doesn't follow the prescribed optical path in the instrument. Scattered light is light from the source that is lost by interaction with matter of some sort (particulate, scratches in mirrors/lenses, etc.). Scattered light typically does not reach the detector, but has not been lost through absorbance.
4. Compare and contrast the operation of a PMT versus a PDA as a detector in a spectroscopic measurement, as well as any benefits or challenges associated with each device. Feel free to use well-labeled sketches to clarify your discussion.

A PMT utilizes the photoelectric effect to eject an electron at a photoemissive cathode when a photon strikes the surface. This ejected electron is accelerated toward a dynode where it collides with the dynode surface, causing the ejection of many secondary electrons. This process repeats down a series of dynodes until the large number of electrons produced in this cascade are collected and converted into a current. The key benefit of the PMT is the large gain due to the fact that a single photon can produce many ($>10^6$) electrons. In order to collect a spectrum, the monochromator must physically scan its output across the PMT.

A PDA is a semiconductor device that consists of several individual detectors (pixels) arranged in a two (or three) dimensional array. When light of appropriate energy strikes a pixel, an electron-hole pair is created in the semiconductor. With the appropriate bias voltage, this electron-hole pair produces a current. The magnitude of the current is directly

related to the number of photons striking the pixel. While the PDA does not afford the high gain of a PMT (it is a “unity gain” device), it offers the benefit of being able to collect spectra rapidly by dispersing light across the pixels in the array.

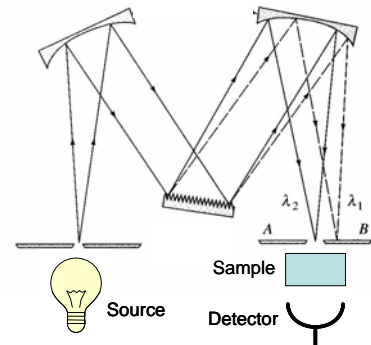
5. Suggest reasons why spectrophotometric precision is poorer:
- when the absorbance is near zero,

When absorbance is small, the signal at the detector is large and differs only very slightly when the sample (P) and blank (P_0) is in the beampath. Therefore, we are relying on determining a small difference between large signals, which poses a challenge.

- when the absorbance is greater than three.

Since $A = \log(P_0/P)$, when the absorbance is 3, P is approximately $0.001P_0$ and the precision relies on the ability to measure a very weak signal when the sample is in the beampath.

6. 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. Typically, 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.



Resolution of a grating-based instrument depends on the ability of the instrument to disperse light across the focal plane of the instrument. This dispersion is a result of the angular dispersion of the grating, the focal length of the monochromator and the width of the entrance and exit slits. As the size of the instrument decreases, the focal length goes down, decreasing the linear dispersion of the monochromator. So, to maintain high resolution, either the “quality” of the grating must be improved in order to produce greater angular and linear dispersion (which is costly), or the width of the slits must be decreased (which leads to low throughput and decreasing signal at the detector).

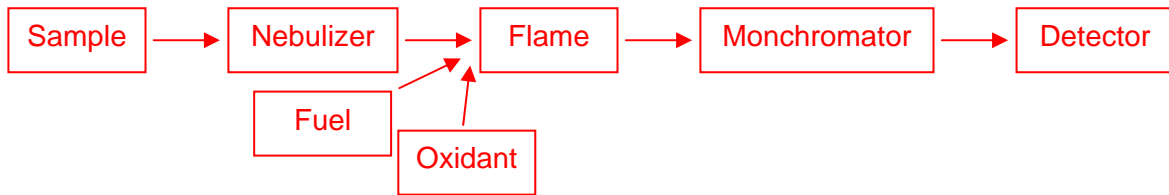
7. Beer's law is theoretically valid only if monochromatic radiation is used. In practice, it is impossible to deliver truly "monochromatic" radiation. What components of the spectrophotometer determine how monochromatic the incident beam is? What will the impact be for a quantitative measurement if the beam is too polychromatic?

The combination of angular dispersion of the grating, the focal length of the monochromator, and the width of the monochromator slits determines the range of wavelengths that are transmitted to the sample. Your discussion should describe why this is so.

Beer's law assumes that 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

8. Draw and label a diagram of an instrument used for flame atomic emission spectroscopy of solution-phase samples. How would a ICP-AES instrument differ?



In ICP AES, an ICP torch and argon gas supply would replace the lamp, fuel, and oxidant.

NOTE: Since this is an emission experiment, no external light source is needed.

9. Why does the identity of flame components and fuel to oxidant ratio play a major role in detectability and sensitivity for atomic spectroscopy?

The combination of flame temperature and residence time often determines the efficiency of gas-phase atom formation in atomic spec. If an analyte is not exposed to enough energy (as a result of a cool flame or short residence time) volatilization and atomization may be incomplete. If the energy is too great (hot flame/excessive residence time), excessive ionization or excitation may occur. In an atomic emission experiment, energy must also be sufficient to excite the analyte without ionization.

10. Describe the operation of a pneumatic nebulizer and graphite furnace atomizer as sample introduction methods for AAS. Specifically note the benefits and challenges of each sample introduction technique.

The differences between the two atomization processes are in the mechanics of the atomization. In a nebulizer, a mechanical means is used to break the stream of sample solution into a stream of fine droplets (aerosol). A portion of this aerosol is carried into the flame or plasma, where thermal energy is used to drive off the remaining solvent and vaporize the sample. In a graphite furnace, the entire sample is deposited into the furnace, and a temperature program is used to gradually dry, ash, volatilize, and atomize the sample.

11. 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

GFAAS provides the lowest DL for both elements, primarily due to efficient use of the sample. Since silver is not easily oxidized or ionized, higher energy sources will provide the

most efficient atomization (and excitation). Therefore ICP AES provides the next lowest DL, followed by Flame AAS. Flame AES is last because of the fairly low energy in the flame, providing less effective excitation. Potassium is much more readily ionized, so as T goes up, ionization increases as well. Flame AES strikes a happy medium, providing efficient atomization, while also exciting sodium atoms. Flame AAS suffers from higher background considerations, while ICP suffers from excessive ionization.

Possibly Useful Information

$\eta_1 \sin \theta_1 = \eta_2 \sin \theta_2$	$R = \frac{\lambda}{\Delta \lambda} = nN$
Planck's Constant = 6.63×10^{-34} Js	$c = 3.00 \times 10^8$ ms ⁻¹
$\Delta \lambda_{\text{eff}} = wD^{-1}$	$n\lambda = d(\sin i + \sin r)$
$D = \frac{dy}{d\lambda} = F \frac{dr}{d\lambda}$	$\frac{dr}{d\lambda} = \frac{n}{d \cos r}$
$T = P/P_0$	$D^{-1} = 1/D$
$A = -\log T = \log(P_0/P) = \epsilon bc$	$E = \frac{hc}{\lambda}$

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	INERT GASES			
1 H 1.00797														2 He 4.0026					
3 Li 6.939	4 Be 9.0122													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 (258)	102 No (258)	103 Lr (257)
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