

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.

Bonus: (6 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. The _____ is a quantitative measure of how a grating spreads incident wavelengths along the focal plane of the monochromator.
2. In _____ molecules are promoted to metastable virtual states before relaxing to lower energy levels.
3. A series of cascades between either continuous or discrete _____ in an electron multiplier results in improved sensitivity over a Faraday cup detector.
4. The _____ uses a series of electrodes to "hold" charge in a potential well so that it can accumulate and increase the sensitivity of the detector.

Complete five of the following. Be clear and concise. Clearly indicate which problems are not to be graded. (10 points each)

5. Sketch an energy-level diagram for a generic molecule and identify transitions in the molecule that either result from the interaction of the molecule with electromagnetic radiation, or result in the emission of electromagnetic radiation. Also identify the region of the spectrum (UV, Visible, IR, etc.) that typically corresponds to each transition.

6. 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. Why do neither of these devices find much utility in the infrared? Feel free to use well-labeled sketches to clarify your discussion.

7. Deuterium (D_2), is a fairly simple molecule with only one bond. Given this simplicity, how can a deuterium lamp serve as a continuum source in the UV?

8. Often, the resolution of a mass spectrometric measurement is not limited by the mass analyzer, but is limited by another component of the instrument instead. Identify this component and describe how its function limits resolving power for most mass analyzers.

9. A major challenge in mass spectrometry of large molecules is the production of gas-phase ions. Describe an ionization approach for large molecules such as proteins and polymers. Include a brief discussion of the advantages and disadvantages of the approach.

10. In simplest terms, most types of mass analyzers operate by adjusting experimental conditions to allow ions of only a small range on m/z to have a “stable” path from the inlet to the outlet of the mass analyzer. Briefly describe how *either* a quadrupole mass filter *or* a dual sector mass analyzer accomplishes this. Include in your description how a mass spectrum is “scanned” in each device.

11. Consider the analysis of a relatively small organic molecule like epinephrine ($C_9H_{13}NO_3$, molar mass 183.20 g/mol). Assuming you use the same mass analyzer and detector, how would mass spectra of epinephrine from electron impact, chemical ionization and ICP sources differ? What aspects of the sources lead to these differences?

Possibly Useful Information

$\lambda = \frac{RT}{\sqrt{2\pi d^2 N_A P}} \approx \frac{5 \text{ cm}}{\text{mtorr}}$	$\frac{m}{z} = \frac{B^2 r^2 e}{2V} = F_c$
$F_M = Bzev = \frac{mv^2}{r} = F_c$	$\frac{N}{N_0} = \frac{g}{g_0} e^{-E/kT}$
$A = \log(P_0/P) = \epsilon bc$	$T = P/P_0$
$E = \frac{hc}{\lambda} = hv$	$c = 3.00 \times 10^8 \text{ ms}^{-1}$
$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$	$\eta_1 \sin \theta_1 = \eta_2 \sin \theta_2$
$\text{Planck's Constant} = 6.63 \times 10^{-34} \text{ Js}$	$n\lambda = d(\sin i + \sin r)$
$\Delta\lambda = wD^{-1}$	$R = \frac{\lambda}{\Delta\lambda} = nN$
$D = \frac{dy}{d\lambda} = F \frac{dr}{d\lambda}$	$\frac{dr}{d\lambda} = \frac{n}{d \cos r}$
$D^{-1} = \frac{d\lambda}{dy} = \frac{d}{nF}$	<p style="text-align: center;">Nothing useful in this cell...sorry!</p>