Complete the following as instructed. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT.

Warm-up (3 points each)
1. A cascade of electrons between a series of _____ dynodes _____ in an electron multiplier or PMT results in the high sensitivity of the device.

2. A Fourier transform must be applied to deconvolute the mass spectrum from data obtained from an

    __ ion cyclotron resonance ___ mass analyzer.

3. The __linear dispersion_____ is a quantitative measure of how a grating spreads incident wavelengths along the focal plane of the monochromator.

4. The __mean free path_____ is a measure of the average distance a particle can move before colliding with another particle.

Complete four (4) of the following. Be concise in your answers and show work for problems involving calculations. Clearly indicate which problem is not to be graded. (15 points each)

5. Mass spectra from electron impact (EI) sources are typically much more complicated than those from chemical ionization (CI), explain why this is the case. Why do typical MS instruments designed for organic mass spectrometry often have both EI and CI capabilities?

    EI sources are hard ionization sources, with ions formed after collision with high energy electrons, producing excited state ions that are typically susceptible to extensive fragmentation. As a result, the molecular ion peak (M^+) is typically very small or nonexistent in a mass spectrum collected using an EI source.

    CI sources are soft ionization sources, with ions produced by collisions with lower energy reagent gas ions, that tend to produce spectra with much less fragmentation. As a result of reactions with the ionizing gas in the source, the molecular ion peak, which is typically strong, occurs at $(M+1)^+$ or $(M-1)^+$.

    The combination of EI and CI capabilities is fairly trivial in terms of hardware and provide the opportunity to get both molecular ion and fragmentation information.

6. The overall resolving power of a mass spectrometer is the result of limitations from all components of the MS. Describe how each of the following serves to limit resolution in a MS experiment.
   a. The ionization source (such as an ICP source)
   Most mass analyzers separation ions on the basis of their kinetic energy, velocity, or momentum. Each of these parameters depends on the extraction of a packet of ions from the ionization source that has a very narrow spread in the parameter being filtered. Depending on the design of the source and extraction ion optics, ions of a single m/z may exit the source with a spread in kinetic energy (or velocity or momentum). The larger the spread, the less effective the mass separation will be.

   b. The mass analyzer (such as a quadropole)
   In their filtering mechanism, most mass analyzers utilize controlled electric or magnetic fields to manipulate ions. Therefore, the ability to precisely control these fields plays a major role in differentiating ions of similar mass to charge.

   c. The detector (such as an electron multiplier)
   Since the role of the detector is to basically count ions, it has very little impact on the resolution of the MS experiment. I suppose in a TOF experiment, the response time of the detector would be very important, so that ions with slightly different flight times could be resolved.

7. Electrospray ionization (ESI), matrix-assisted laser desorption ionization (MALDI) and atmospheric pressure chemical ionization (APCI) are relatively new approaches to ionizing large molecules. Compare how ions are formed in each process and discuss the similarities and differences in the spectra observed from the sources.
   The two main big molecule ionization sources we discussed were MALDI and Electrospray ionization.
   MALDI: The analyte is dispersed in a MALDI matrix (a molecule that readily sublimes when it absorbs energetic photons) and deposited onto a target. The target is irradiated with a laser pulse, resulting in absorption and sublimation of the matrix (including the analyte) and ionization. The result is the formation of intact molecular ions, most are singly charged. Benefits: Soft ionization source. Good for molar mass determination. Challenges: Pulsed source, need mass analyzer that can handle pulsed introduction. Need appropriate matrix.
   Electrospray: The sample solution flows through a needle which is subject to a large electric field. As solution leaves the needle, it obtains a charge. Electrostatic repulsion causes the charged stream to break into smaller charged droplet, which continue to "explode" until solvent is essentially evaporated and ionized analyte remains. This is a more energetic ionization source, capable of producing multiply charged ions and fragments. Benefits: Continuous source. No additional sample handling steps. Challenges: May lead to complex spectra. Need to remove some sample to produce lower pressure for mass analyzer.
   APCI:

8. Currently, two of the most popular mass analyzers are the quadrupole mass filter and the time of flight mass analyzer. These two devices have very different principles of operation. Clearly describe how each device serves to separate ions and the key benefits and limitations of each device.

Quad: As they move through the mass filter, ions are subject to both AC and DC potentials. Depending on their size, ions may be influenced differently by the RF and DC components. For example, heavy ions are least influenced by the RF component, while light ions are most influenced by the RF. The balance between DC and RF determines whether an ion will have a stable path. Spectra can be scanned by systematically adjusting either the RF or DC voltages. Benefits: Small, able to handle higher pressures, able to scan spectra rapidly. Challenges: relatively low resolving power.
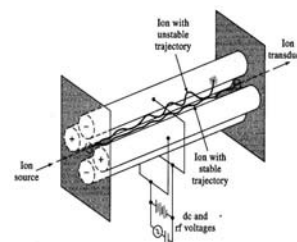
Figure 11-4 A quadrupole mass spectrometer.

TOF: The TOF mass analyzer relies on the fact that ions that have different mass but the same kinetic energy will be moving at different velocities (KE $=mv^2/2$). Therefore, ions are formed in a pulse and the time that takes the ions to move through the field free region of the flight tube is measured. Once calibrated, these times can be used to determine the mass to charge of individual ions. Benefits: potential for high resolution and very fast analysis. Challenges: depending on the length of the drift tube, vacuum requirements might be demanding. Need to coordinate ionization and detection timing.
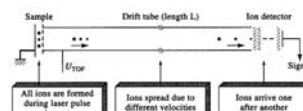
Figure 11-8 Principle of a time-of-flight mass spectrometer. A bunch of ions

9. The mating of mass spectrometry and separations techniques has been and continues to be an area of great interest. Why is this so? Select <u>one separation technique</u> and clearly describe how mass spectrometry has been incorporated as a detection scheme for the separation. Draw a diagram of the instrument and describe in detail how the separation and mass analysis components are interfaced and how ions are formed.

Mating separations and MS allows the analyst to work with more complex samples while obtaining both quantitative and identification information on components of the sample. The key challenge in interfacing separations and MS is the very different conditions at which each instrument operates. For example, in traditional HPLC, eluent exits the column at mL/min flow rates, resulting in a large amount of material exiting the LC in a short time. If all of this material were introduced into the MS, it would be impossible to maintain the high vacuum conditions required to provide a large mean free path for the ions produced in the MS. Therefore, a significant effort has been made optimizing the interface. Since it can tolerate larger pressures, quadropole mass analyzers have been the most popular for interfacing with separation techniques.

GC: For capillary column GC, the low mass flow of gas allows the end of the capillary to be inserted directly into the ionization source of the MS. For packed column GC, a jet separator is typically used to preferentially allow analyte to pass into the source, discarding much of the carrier gas.
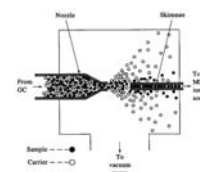
Figure 27-14 Schematic of a jet separator. (Courtesy of DuPont Inst Wilmington, DE.)

LC: The advent of split sample introduction as well as capillary columns, combined with the higher working pressure of quadropole or ion trap MS has been instrumental in combining LC and MS.
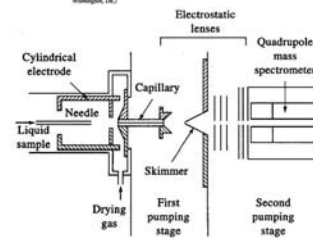
CE: The most common interface for CE is electrospray. Since the volume of material leaving the separation capillary is smaller (nL) than that for LC (mL), the challenge of decreasing pressure between the separation and mass spectrometer is somewhat diminished. Similar approaches are used for LC and CE (sampler and skimmer, etc…)

Figure 20-8 Apparatus for electrospray ionization. (From J. B. Fenn et al., Science, 1989, 246, 65.)

Spectroscopy. Complete two (2) of the following. Be concise in your answers and show work for problems involving calculations. Clearly indicate the problem not to be graded. (15 points each)

10. 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.
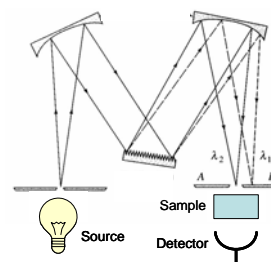
Resolution of a grating-based instrument depends on the ability of the instrument to disperse light across the focal plane of the instrument. This dispersion is a result of the angular dispersion of the grating, the focal length of the monochromator and the width of the entrance and exit slits. As the 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 decreases (which leads to low throughput and decreasing signal at the detector).

11. <u>Select two of the pairs</u> of terms below and briefly compare and contrast the terms within each pair.
    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
    c. photomultiplier tube versus photodiode arrayA 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. A PDA is a semiconductor device that 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. 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 offers the benefit of being able to collect spectra rapidly by dispersing light across the pixels in the array.

12. Can a grating monochromator with the characteristics shown below completely separate the sodium lines at 589.0 and 589.6 nm?

Focal length	0.50 m
Groove density	1640 lines/mm
Order **n** (at 589 nm)	1
Diffraction angle	10.0°
Incident angle	52.5°
Slit width	0.10 mm

We need an effective bandwidth ($\Delta\lambda$) of 0.6 nm/2 or 0.3 nm. Will this optical arrangement produce such an effective bandwidth?

Since $D = F\dfrac{dr}{d\lambda} = \dfrac{Fn}{d\cos r}$ and $\Delta\lambda = wD^{-1}$, then $\Delta\lambda = \dfrac{wd\cos r}{Fn}$.

We know w, r, F, and n, but we need a value for d.

$$d = \frac{1\text{ mm}}{1640\text{ lines}} \times \frac{10^6\text{ nm}}{\text{mm}} = 609.76\text{ nm}$$

Therefore,

$$\Delta\lambda = \frac{(0.1\text{ mm})(609.76\text{ nm})(\cos 10^\circ)}{(500\text{ mm})(1)} = 0.12\text{ nm}$$

Since this value is much less than 0.3 nm, we should be able to resolve the two sodium lines.

Possibly Useful Information

$$E = \dfrac{hc}{\lambda} = h\nu$$	$c = 3.00 \times 10^8 \text{ ms}^{-1}$
$$\lambda = \dfrac{RT}{\sqrt{2}\pi d^2 N_A P} \approx \dfrac{5\,cm}{mtorr}$$	$$F_M = Bzev = \dfrac{mv^2}{r} = F_c$$
$$\dfrac{m}{z} = \dfrac{B^2 r^2 e}{2V} = F_c$$	$U_{dc} + V_{ac}\cos\omega t$
$\eta_1\sin\theta_1 = \eta_2\sin\theta_2$	$$R = \dfrac{\lambda}{\Delta\lambda} = nN$$
Planck's Constant = 6.63 x 10-34 Js	$c = 3.00 \times 108 \text{ ms}^{-1}$
$\Delta\lambda_{eff} = wD^{-1}$	$n\lambda = d(\sin i + \sin r)$
$$D = \dfrac{dy}{d\lambda} = F\dfrac{dr}{d\lambda}$$	$$\dfrac{dr}{d\lambda} = \dfrac{n}{d\cos r}$$
$T = P/P_0$	$D^{-1} = 1/D$
$A = -\log T = \log(P_0/P) = \varepsilon bc$	$$E = \dfrac{hc}{\lambda}$$

PERIODIC CHART OF THE ELEMENTS

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.