

**Due by 4:00 PM Monday, April 12**  
**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 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 one (1) question regarding the exam. Additional questions may be asked at a 3-point penalty per question. If you are working on the exam on the weekend or 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 forty-five (45) minutes 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.

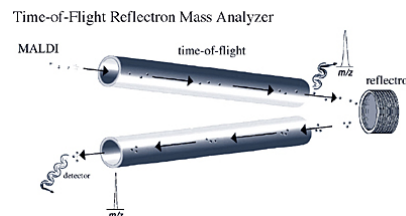
\_\_\_\_\_  
Signature

\_\_\_\_\_  
Date

Complete these problems in the space provided. If you run out of space, continue on the back of the page and direct me where to find the rest of your work. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT. 14 points each.

- Describe the principles of operation and advantages and disadvantages of **one** of the following. Feel free to use clearly labeled drawings in your description.
  - Time of flight mass spectrometer with a reflectron.

**TOF:** The time of flight mass spectrometer separates ions on the basis of velocity by monitoring the time it takes for them to drift through a field-free flight tube. In order for the mass separation to be accurate, ions must be introduced into the flight tube in a small pulse and ions of the same  $m/z$  must have the same kinetic energy to that they have the same velocity. In practice, ions are produced with a small spread in KE leading to a small spread in velocity. The reflectron serves to minimize the impact of this spread in velocities on the resolution of the measurement. It does so by presenting an increasing electric field in such a way that slower moving ions penetrate less deeply into the reflectron and faster moving ions penetrate more deeply before being redirected toward the detector. As a result of this slight difference in flight distance, the packet of ions ends up being more focused once it reaches the detector.



- Ion cyclotron resonance mass spectrometer.

**ICR:** The ion trap is placed in a large magnetic field. Under the influence of this field, ions precess in the trap at their cyclotron frequencies. The application of an RF pulse to the trap causes short-lived deviations of ion paths. These deviations produce a current at the receiver. The magnitude and frequency response of this current depends on the  $m/z$  of the ions present.  $MS^n$  is possible with ICR by adding collision gas and observing the impact on the resulting spectrum. The primary challenge of ICR is that good data processing hardware must be available to rapidly collect and process the data using a Fourier Transform.

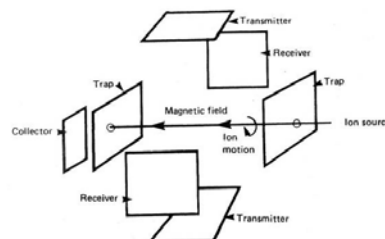


Figure 9.25 "Exploded" view of an ICR ion trap. The ICR has been the used in FTMS, both alone and in newer "hybrid" FTMS instruments.

2. As a newly hired mass spectrometry expert, you have been assigned the task of designing solutions to the MS problems below. For **two** of the issues, use a block diagram to identify the ionization source(s), mass analyzer, and detector you would select to accomplish each task. Provide justification for your choices.

- a. The determination of trace levels of arsenic in municipal drinking water.

This analysis requires good sensitivity for quantitation, moderate mass resolution at a fairly low absolute mass, and the ability to analyze metal ions.

Ionization	Analysis	Detection	Comments
ICP	Quadrupole	Electron Multiplier	Quad is well suited for metal ion work, ICP is most common ionization source

- b. The accurate determination of the molar mass of a protein from the stuff growing in Dr. McCormick's iced tea glass.

This analysis requires the introduction of a nonvolatile sample, and the ability to perform analysis of high-mass components with adequate resolution.

Ionization	Analysis	Detection	Comments
MALDI to help get volatile ions with minimal fragmentation	TOF	Electron Multiplier	TOF provides for a higher mass range than quad or mag. sector

- c. Both molar mass and structural information of a suspected pheromone of the eastern grey squirrel. (note: this pheromone is a small organic compound)

This analysis would benefit from the ability to determine the parent ion mass with high resolution, as well as fragmentation to determine molecular mass. Sensitivity is not a big issue.

Ionization	Analysis	Detection	Comments
Chemical Ionization for molecular ion determination, Electron Impact to promote fragmentation	Double Focussing MS for best resolution (quad also acceptable). Many options here.	Electron Multiplier or Faraday Cup	Switchable ionization allows both hard and soft ionization sources.

3. You have been instructed to build a UV-Vis instrument using a linear CCD array detector that has 1024 pixels aligned on a 2.00 cm chip.
- a. If you want the first order diffraction of light from 200-800 nm to completely fill the array, how many grooves per millimeter should his grating have? Assume the focal length of the monochromator is 0.20 m.

In order for the wavelengths to span a 2.00 cm CCD, the reciprocal linear dispersion must be:

$$D^{-1} = (800-200)\text{nm}/2.00 \text{ cm} = 300 \text{ nm/cm}$$

Based on the relationship  $D^{-1} = d/nF$ , you can calculate the spacing between lines:

$$d = nFD^{-1} = (1)(20 \text{ cm})(300 \text{ nm/cm}) = 6000 \text{ nm/line}$$

This translates to a number of rulings per millimeter of:

$$\frac{1 \text{ line}}{6000 \text{ nm}} \times \frac{1 \text{ nm}}{10^{-6} \text{ mm}} = \frac{167 \text{ lines}}{\text{mm}}$$

- b. If you were building a scanning spectrometer using the grating from part a, what slit width would be required to produce the same bandwidth as in the CCD instrument? Could the two emission lines of sodium (589.0 and 589.6 nm) be resolved using under these conditions?

In using the CCD, each pixel in the array will sample  $(600 \text{ nm}/1024 \text{ pixels}) = 0.586 \text{ nm}$  of the spectrum. To build a scanning spectrometer, this value would define the bandwidth of the instrument ( $\Delta\lambda_{\text{eff}}$ ).

$$w = \frac{\Delta\lambda_{\text{eff}}}{D^{-1}} = \frac{0.586 \text{ nm}}{300 \text{ nm/cm}} = 0.00195 \text{ cm} = 19.5 \mu\text{m}$$

In order to resolve the two lines, we need a  $\Delta\lambda$  of 0.6 nm. Since the effective bandwidth of the instrument is 0.59 nm, we might just be able to resolve the lines, although not particularly well.

### Possibly Useful Information

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