

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

Warm-up

1. A reflectron can be used to narrow the spread of velocities for ions in a TOF mass analyzer. (2 points)
2. Digital filtering using Fourier transforms can help to remove the contributions of specific frequencies to time-dependent signals. (2 points)
3. The rectifier in a power supply converts the incoming AC voltage to an oscillating voltage of either all positive or all negative sign. (2 points)
4. One can reduce flicker noise by increasing the frequency at which the signal is sampled. (2 points)
5. For a mass spectrophotometric analysis, the following calibration curve was obtained:

$$\text{Detector Signal} = (0.467 \text{ mA/ppm}) \times \text{concentration} + 0.024 \text{ mA}$$

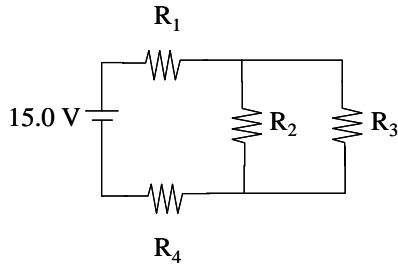
If five blank readings gave 0.022, 0.027, 0.021, 0.025, 0.022 mA, what is the detection limit for this measurement? (10 points)

The detection limit is the concentration that corresponds to a signal that is equal to the blank plus three times the standard deviation of the blank. For this data, $S_{\text{blank}} = 0.00251 \text{ mA}$ and the average blank signal is 0.023_4 mA . That means that the signal at the detection limit is $0.023_4 + 3(0.00251) = 0.0309 \text{ mA}$. To convert this to concentration units, rearrange the calibration curve.

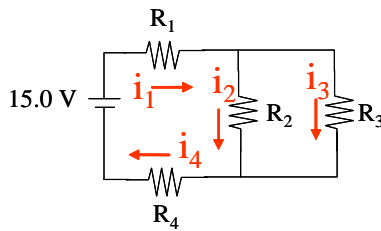
$$c = (0.0309 - 0.024) \text{ mA} / (0.467 \text{ mA/ppm}) = 0.0148 \text{ ppm} = \mathbf{0.015 \text{ ppm}}$$

Electronics: Complete *TWO* of the problems 6-8. Clearly indicate which problem is not to be graded. Show all work for calculations. (12 pts each)

6. Consider the following circuit. If the current through R_1 is $9.24 \mu\text{A}$ and the current through R_2 is $3.69 \mu\text{A}$, what is the value of R_3 ? What is the power that is dissipated by R_1 ? What is the potential difference across R_4 ?



$$\begin{aligned} R_1 &= 200 \text{ k}\Omega \\ R_2 &= 400 \text{ k}\Omega \\ R_3 &= ? \\ R_4 &= 1 \text{ M}\Omega \end{aligned}$$



$$i_1 = i_4 = i_2 + i_3 = 9.24 \mu\text{A}$$

$$P_1 = i_1^2 R_1 = (9.24 \times 10^{-6} \text{ A})^2 (200 \times 10^3 \Omega) = 17.1 \mu\text{W}$$

$$V_4 = i_4 R_4 = 9.24 \mu\text{A} (1 \text{ M}\Omega) = 9.24 \text{ V}$$

$$i_3 = i_4 - i_2 = (9.24 - 3.69) \mu\text{A} = 5.55 \mu\text{A}$$

Since the same potential is applied across R_2 and R_3 , the following must be true:

$$i_2 R_2 = i_3 R_3$$

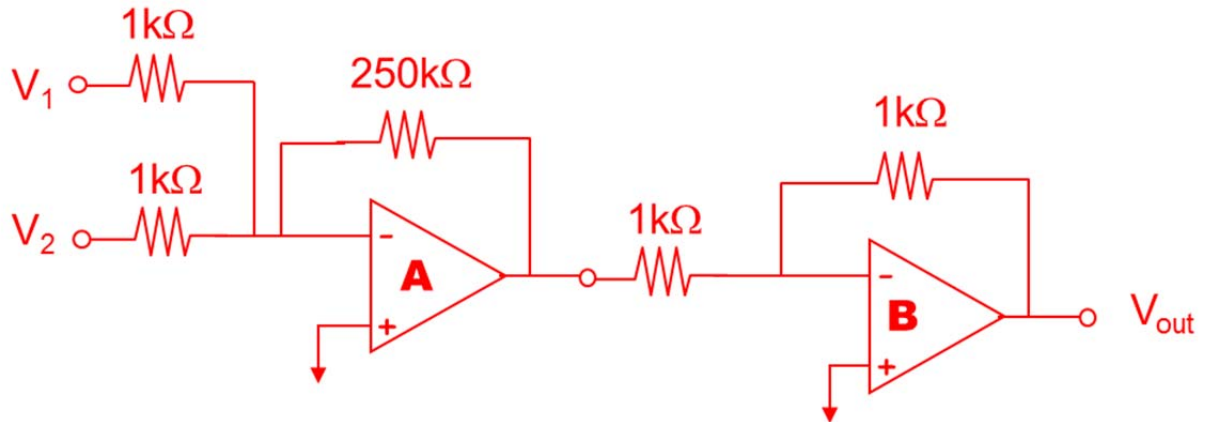
or

$$R_3 = i_2 R_2 / i_3 = (3.69 \mu\text{A} \times 400 \text{ k}\Omega) / (5.55 \mu\text{A}) = 266 \text{ k}\Omega$$

7. Design a circuit for calculating the average value of two input voltages multiplied by 500. Verify the output of your circuit with a calculation.

Ultimately, the math that must be done is $v_o = 500 \times (v_1 + v_2)/2 = 250(v_1 + v_2)$

Here's one circuit that will do the trick:



You should have derived the output for your circuit as well. For this circuit:

Consider the output of opamp A as V_A .

$$[(V_1 - V_-)/1 \text{ k}\Omega] + [(V_2 - V_-)/1 \text{ k}\Omega] = (V_- - V_A)/250 \text{ k}\Omega$$

Since $V_- = V_+ = 0$ in this case, the above simplifies to:

$$-V_A = 250(V_1 + V_2)$$

Now looking at the output of opamp B (V_{out}):

$$(V_A - V_-)/1 \text{ k}\Omega = (V_- - V_{out})/1 \text{ k}\Omega$$

Since $V_- = V_+ = 0$ in this case, the above simplifies to:

$$-V_A = V_{out}$$

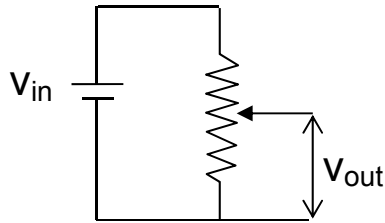
or

$$V_{out} = 250(V_1 + V_2)$$

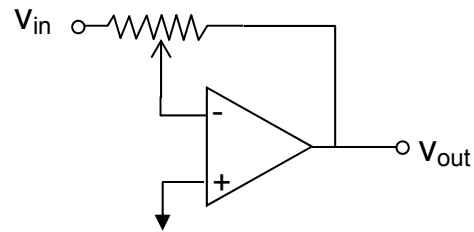
Which is the math we were after.

8. Consider the two circuits below. Both circuits produce similar output. How is v_{out} related to v_{in} for each circuit? What are the benefits of using circuit B compared to circuit A?

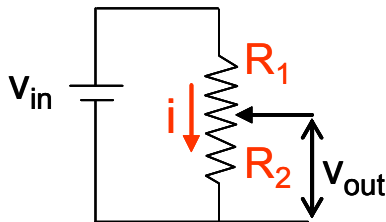
Circuit A



Circuit B



Both circuits employ a potentiometer, or variable resistor. The resistance on opposite sides of the wiper can vary, but always sums to the total resistance of the potentiometer, therefore, we can split the resistance into two components, R_1 and R_2



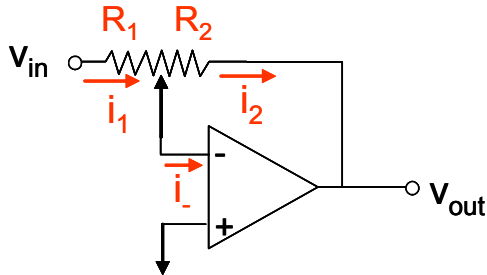
Since there is only one path from V_{in} to ground, the current through the first resistance must be the same as the current through the second ($i_1 = i_2 = i$) so:

$$i = v_{in}/(R_1+R_2) = v_{out}/R_2$$

OR

$$v_{out} = v_{in}R_2/(R_1+R_2)$$

$$i_1 = i_2 + i, \text{ but } i = 0, \text{ so;}$$



$$\frac{v_{in} - v_-}{R_1} = \frac{v_- - v_o}{R_2}$$

$$\text{But, } v_- = v_+ = 0$$

$$\frac{v_{in}}{R_1} = \frac{-v_o}{R_2}$$

$$\frac{R_2 v_{in}}{R_1} = -v_{out}$$

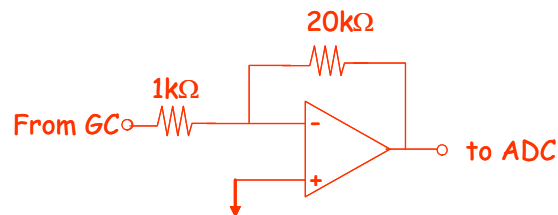
Since the current path through the circuit is through the op-amp, the op-amp circuit will be able to supply some current to the load (because of low output impedance) without loading the voltage source V_1 (because of high input impedance). The resistor-only circuit cannot supply current without loading the source. Also, the multiplier for the op-amp circuit can be larger or smaller than one, depending on the size of R_1 and R_2 , allowing for amplification and attenuation of v_{in} , while the resistor only circuit can only attenuate v_{in} , because $R_2/(R_1+R_2)$ is always less than one.

A/D Conversion, Signals and Noise: Complete TWO of the problems 9-11. Clearly indicate which problem is not to be graded. Show all work for calculations. (12 pts each)

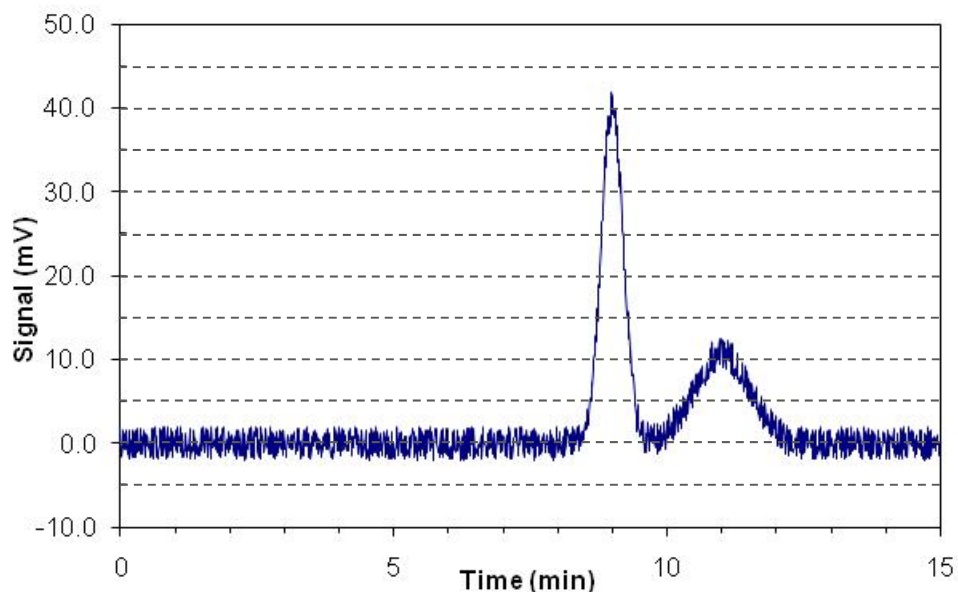
9. White noise corresponds to extraneous signals whose intensity does not depend on frequency. Two of the types of noise we've discussed can be classified as white noise. Name and briefly describe the physical phenomena that give rise to these two types of noise. How do we minimize their contribution to a measured signal?

Shot noise and thermal noise are both independent of frequency. Shot noise is a result of quantized motion of e^- across boundaries in semiconductors and is proportional to the size of the signal. Thermal noise is due to random thermal motion of electrons in conductors (resistors) and is related to temperature and resistance. Decreasing the bandwidth of the measurement can minimize contributions from both sources. Decreasing the magnitude of the signal being measured can also diminish shot noise. Lowering the temperature of the measurement can decrease thermal noise.

10. You have been assigned the task of interfacing a liquid chromatograph to a computer-based data acquisition system. You have an 8-bit ADC with a ± 10 V range to accomplish this task.
- Because of the design of your LC detector, the maximum output voltage of the detector is 500 mV, with chromatographic peaks typically being a few tens of mV in size. Clearly describe the potential problems using your ADC system to monitor this signal.
 - Design an op-amp circuit to help address the primary problems you discussed in part a.
- a. For this ADC, we have a total of 20V split into 2^8 or 256 bits. Therefore the size of the least significant bit, and ultimately the resolution, is $20V/256$ or about 78 mV. Ultimately, this means that, on its own, the ADC cannot distinguish between signals that differ by less than 78 mV. Since our peaks are only a few mV in size, this poses a significant problem. Many of our peaks might be buried in the noise!
- b. One possible solution is to amplify the signal before it reaches the ADC. A simple voltage follower circuit can accomplish this. Note that since the ADC has a ± 10 V range, the sign of the output of the amplifier will not be an issue. Here is a circuit that would do the trick by providing a factor of 20 amplification. This effectively decreases the size of the LSB to about 4 mV, less than the size of a typical peak.



11. Below is an example chromatogram for the system described above. Each run consumes your sample and takes about 15 minutes to complete. The data below is an example of the results of one of your separations. You are unhappy with the signal to noise ratio of your data. Estimate the S/N ratio for the first peak and describe two approaches that are appropriate to this experiment that you might take to improve S/N for **this application**. Note any potential problems with these approaches. You **do not** need to have a solution to problem 10 to complete this problem.



The magnitude of the signal at the peak is ~40 mV. The average p-p noise, estimated away from the peak, is ~5 mV, giving a S/N of about 8.

For a chromatographic experiment, signal averaging is impractical because of the run-to-run variability in the measurement and the time necessary for a run. Therefore other options must be chosen. You should **discuss** how the method works and its limitations. Here are a few reasonable choices:

- **Boxcar Averaging:** Works on a single dataset, but you need to be careful so that you have enough data that when the boxcar is run, the result is still representative of the real data.
- **Polynomial Smoothing:** Same concerns as with boxcar averaging.
- **Fourier Filtering:** Math intensive, important not to filter out useful frequencies. The process would involve converting the data to a power spectrum with a fourier transform, removing the high frequency data and doing a reverse transform to get the filtered data back.

Mass Spectrometry: Complete problem 12 (12 pts)

12. Draw and label a block diagram of a generic mass spectrometry instrument. Include all major components from sample introduction to output. How, if at all, do the components in your diagram influence the resolution and sensitivity of the instrument?

A complete block diagram would have the following components:

- Ionization source
- Ion optics
- Mass analyzer
- Detector
- Vacuum system

When you consider resolution and sensitivity, you should keep the following items in mind. Better resolution comes from the ability to impart the same energy on the ions and the ability to distinguish ions of one energy (m/z) from another. Sensitivity is a result of the quantity of ions reaching the detector and its ability to convert ions in to a signal.

- Ionization source: impacts resolution by imparting kinetic energy onto the ions that are formed. Impact sensitivity by its ability to convert neutral analyte to ions.
- Ion optics: Work with the source to extract ions of a very narrow range of kinetic energies, therefore impacting resolution. The focusing ability of the optics can contribute to sensitivity as well.
- Mass analyzer: Primarily impacts resolution by determining the range of m/z that are allowed to reach the detector.
- Detector: Primarily impacts sensitivity by its ability to convert ions to signal.
- Vacuum system: Can impact sensitivity if the pressure is too high, resulting in a shorter mean free path and fewer ions reaching the detector.

Complete **TWO** of the problems 13-15. Clearly indicate which problem is not to be graded. Show all work for calculations. (12 pts each)

13. 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

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.

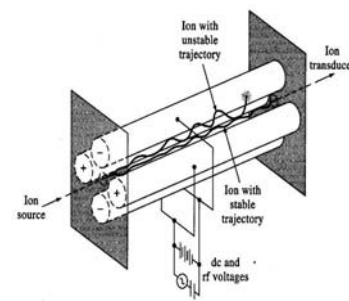


Figure 11-4 A quadrupole mass spectrometer.

Dual Sector: The flight of an ion through the magnetic sector is a balance of centripetal force of the ion with the magnetic force of the magnetic sector or the electrical force of the electrical sector. Ions with too large or too small of a centripetal force will not be able to make the bend through the magnetic sector. Only ions whose centripetal force matches the opposing force will have a stable path. Spectra can be scanned by systematically adjusting either the magnetic field or the accelerating voltage.

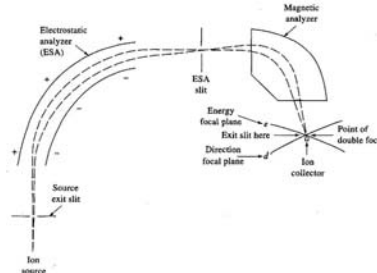


Figure 20-13 Nier-Johnson design of a double-focusing mass spectrometer.

14. 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?

You need to consider the energetics of the ionization source and the impact of these energetics on the species that form.

Electron Impact: This is an energetic or hard ionization source. As a result, parent ions that are formed possess significant internal energy. This leads to significant fragmentation for most organic compounds. Therefore we would expect to see several fragment peaks and only a small (if any) molecular ion peak.

Chemical Ionization: By using a gas such as methane in the ionization source, parent ions that are formed have much less internal energy. As a result, mass spectra from CI exhibit strong molecular ion peaks and minimal fragmentation.

ICP: The high temperature in an ICP would serve to completely decompose the small molecule, leading to essentially no signal from the sample. Remember, ICP is predominantly useful for elemental (and typically metals) analysis.

15. Describe the similarities and differences between quadrupole ion trap and Fourier transform ICR mass spectrometers. Include a description of how a mass spectrum is collected for each instrument.

A quadrupole ion trap is similar to a linear quadrupole filter except it is a spherical 3-dimensional configuration. By a combination of fields, ions are temporarily stored within the trap. They are then released sequentially by increasing the radio frequency voltage applied to the ring electrode. The ejected ions then strike a detector. A plot of detector signal vs. the radio frequency voltage, related to the m/z value, is the mass spectrum. In an FT ICR instrument, ions are trapped in a cell by an electric trapping voltage and a magnetic field. Each ion assumes a circular motion in a plane perpendicular to the direction of the field. The cyclotron frequency depends on the inverse of the m/z value. In modern instruments a radio frequency pulse that increases linearly in frequency is employed. A time domain image current is generated after termination of the pulse. Fourier transformation of the time decay signal yields the mass spectrum.

With QIT, spectrum is scanned one m/z at a time, by adjusting applied fields. With ICR, an entire spectrum is collected with each RF pulse, allowing signal averaging and greater sensitivity.

Possibly Useful Information

$\frac{dQ}{dt} = I = C \frac{dV}{dt}$	$P = IV = I^2R$
$V = IR$	$v_o = A(v_+ - v_-)$
$v_{rms} = \sqrt{4kTR\Delta f}$	$001 + 001 = 010$
$\Delta f = \frac{1}{3t_r}$	$i_{rms} = \sqrt{2ie\Delta f}$
$S_m = \bar{S}_{bl} + ks_{bl}$	$c_m = \frac{S_m - \bar{S}_{bl}}{m}$
$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P} \approx \frac{5 \text{ cm}}{\text{mtorr}}$	$\frac{m}{z} = \frac{B^2 r^2 e}{2V} = F_c$
$F_M = Bzev = \frac{mv^2}{r} = F_c$	$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$

