Determination of the Elemental Molar Masses of Chlorine and Bromine

Pre-lab Assignment:

Reading:

1. Sections 1.5, 1-8, and 2.4 in Brown, LeMay, Bursten, and Burdge.
2. This lab handout!

Questions (show all work):

1. What molecules are you using in this lab to determine the elemental masses of chlorine and bromine?
2. What *specifically* will you inject into the GC-MS?
3. How many peaks do you expect to see on the chromatograph?

INTRODUCTION:

The purpose of this lab is to give you insight into the concept of elemental molar mass. Many elements have more than one stable isotope. As a result, individual atoms of the same element can have different masses. In the laboratory we are almost always working with large numbers of atoms (moles). We are, therefore, interested in the average mass of a mixture of stable isotopes of the element, rather than the individual isotope masses. In this lab you will use a mass spectrometer to measure the masses and abundances of the isotopes of Cl (^{35}Cl and ^{37}Cl) and Br (^{79}Br and ^{81}Br). From the mass and abundance data you will be able to calculate the elemental molar mass of Cl and Br and compare your answer to the published result. This experiment is a "discovery"-type experiment. The procedure will be carefully described, but the analysis of the data is left purposely vague. You will work in small groups to decide how best to work up the data.

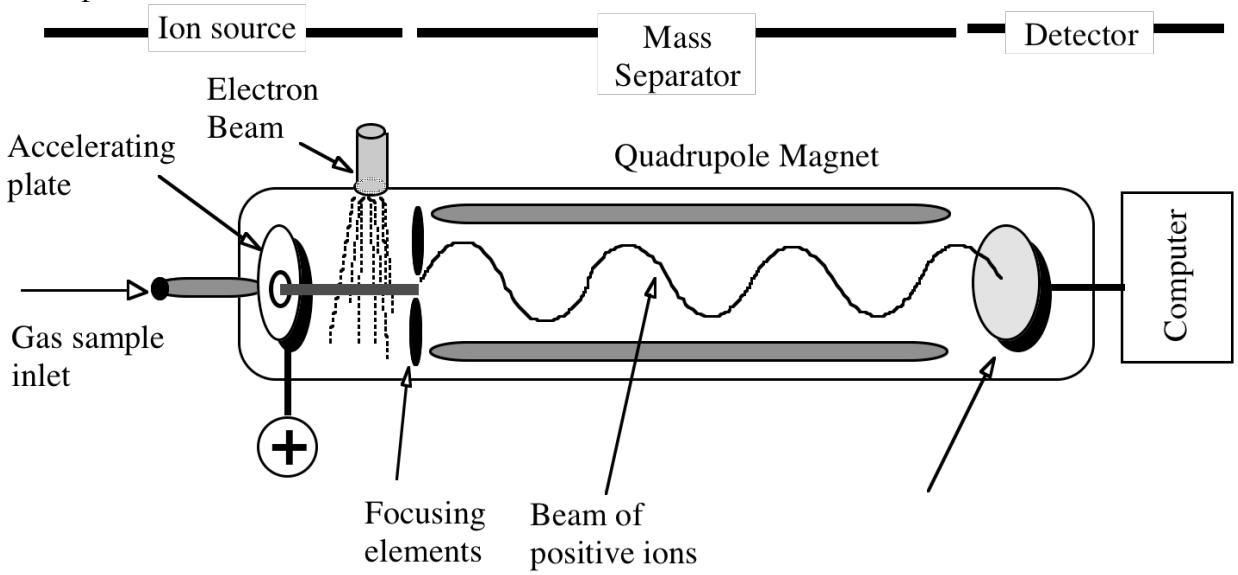


Figure 1. Schematic representation of a quadrupole mass analyzer used on our Hewlet Packard 5970 mass spectrometer.

What is a mass spectrometer? A mass spectrometer is an instrument that accurately measures the masses and relative abundances of atoms, molecules, or pieces of molecules (fragments). Figure 1 is a diagram of one of our instruments. A mass spectrometer consists of three general parts: the ion source, the mass separator, and the ion detector. In our instrument a sample is introduced into the ion source as a gas. An electron beam fragments the gas molecules into positively charged ions. The positive ions are accelerated away from the positively charged accelerator plate, through a set of charged focusing lenses and into the mass separator. A mass separator consists of a magnetic field that deflects ions toward or away from the detector.

Note: Figure 1 shows a slightly more complicated mass separator used in one of our instruments at Colby. *{In our instrument, the magnet is actually a set of four electromagnets called a quadrupole. The quadrupole magnetic field oscillates very quickly causing the positively charged fragments to travel in an oscillating path. Only fragments with the correct mass can travel the entire length of the quadrupole magnet without hitting the walls of the instrument.}* Ion fragments that pass through the mass separator hit a detector where a small current is produced and recorded by a computer. By changing the magnet field strength of the mass separator fragments of different masses can be detected. Analysis of mass spectral data is often used to determine the structure of unknown compounds.

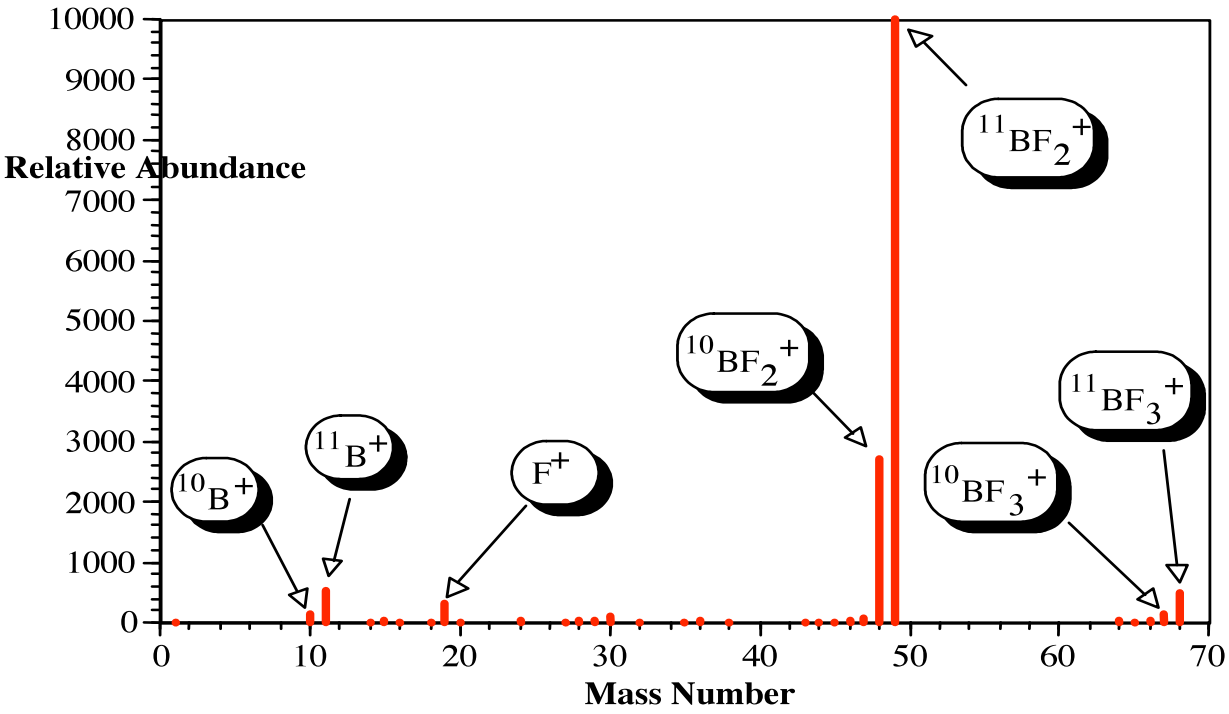


Figure 2 . Mass Spectrum of BF_3. Prominent peaks are labeled with the appropriate positively charged fragments.

Figure 2 shows the mass spectrum of the gas boron trifluoride, BF_3. The spectrum is a plot of fragment abundance as a function of mass number. Each vertical bar corresponds to a fragment ion, the position denotes its mass and the height is proportional to the abundance of the ion. Because boron has two stable isotopes, ^{10}B and ^{11}B, the BF_3^+ fragment produces peaks at 67 and 68 mass number (fluorine has only one stable isotope with a mass of 19). Similarly the BF_2^+ fragment produces two peaks with similar relative abundances at 48 and 49 mass number. The difference between the two sets of peaks is the loss of a single fluorine. Notice a fragment peak at 19 mass number due to a F^+ fragment. Using the mass spectral data, the elemental abundances of ^{10}B to ^{11}B can also be calculated.

Fragment	**Mass Number**	**Relative Abundance**
$^{10}BF_2^+$	48	2692
$^{11}BF_2^+$	49	10000
Total BF_2^+		12692

The fluorine has only one stable isotope so it plays no role in the calculations. The elemental abundance of ^{10}B is determined from the relative abundance of $^{10}BF_2^+$ divided by the total fragment abundance.

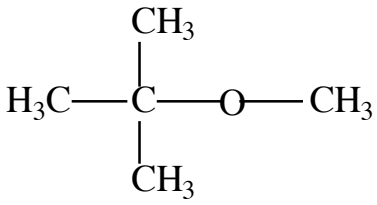
Therefore:

$$\textbf{Abundance } ^{10}\textbf{B \%} = \frac{\textbf{rel.ab. } ^{10}\textbf{BF}_2^+}{\textbf{total frag. ab.}} \textbf{ x 100} = \frac{\textbf{2692}}{\textbf{(2692 + 10000)}} \textbf{ x 100 = 21.21\%}$$

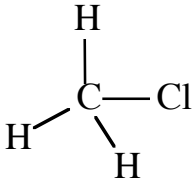
If the abundance and masses of the two boron isotopes are known, the elemental molar mass for the element can be calculated as a weighted average.

Outline of this experiment: You will work in small groups to determine the elemental molar mass for chlorine and bromine. The samples you will be using are the gasses chloromethane, CH_3Cl, and bromomethane, CH_3Br. Because the gases are very reactive in the pure form and difficult to handle, we have purchased the gases dissolved in tert-butyl methyl ether. A small amount of the gas-ether solution will be provided in a small vial. The ether rapidly evaporates in the vial so you will really have a sample of CH_3Br or CH_3Cl gas mixed with gaseous ether. The first step in the analysis will be to separate the CH_3Br or CH_3Cl from the ether. The second step of the experiment will be to take the mass spectrum of the pure CH_3Br or CH_3Cl sample.

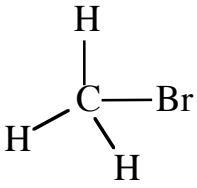
The separation of the gas mixtures will be performed using a gas chromatograph (GC). (Refer to **Figure 3**). A GC separates gas mixtures based on boiling point. High boiling compounds take longer to pass through the GC than low boiling compounds. In our experiment, CH_3Cl or CH_3Br exit the GC first. The separated gases from the GC are then automatically introduced into the mass spectrometer (MS) for analysis. The combination of a gas chromatograph and a mass spectrometer is referred to as a GC-MS. Using the mass spectral data for CH_3Br and CH_3Cl you and your partner will calculate the elemental molar mass for chlorine and bromine. You will then compare your results with literature values from your textbook.



tert-butylmethyl ether



chloromethane



bromomethane

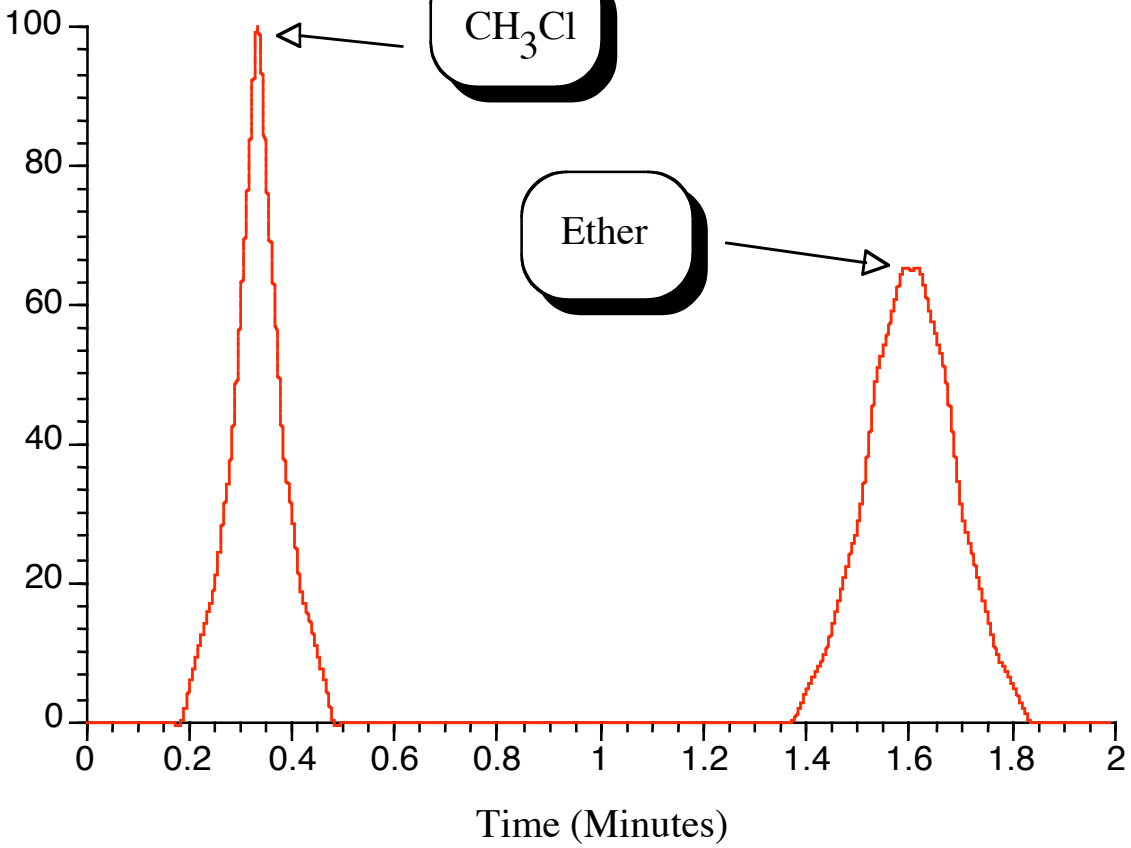


Figure 3. Total ion chromatograph for the CH_3Cl and ether mixture.

PROCEDURE:

1. Work with your assigned group.
2. You will be analyzing two samples, a CH_3Br and ether gas mixture and a CH_3Cl and ether gas mixture. The samples will be contained in labeled, 40-mL sampling vials. Check with the lab instructor to make sure the GC-MS is ready for a new sample. Check that the status indicators are ready. Select a sample and insert the needle of a 10-ul syringe through the septa on the top of the sample vial. Gently pull the plunger of the syringe upward to draw 5-10 ul of the gas mixture (not liquid) into the syringe.
3. Remove the syringe needle from the sample vial and push the syringe needle into the injection port of the GC. Inject the contents of the syringe and press the start button.
4. The instrument is automated, so stand back and watch the system acquire your data. The computer system next to the GC-MS will display a plot showing total ion counts (TIC) as a function of time similar to plot shown in Figure 3. The TIC is the sum of all fragments abundances at a given time. Different compounds come off the GC at different times and therefore produce different peaks. The samples we are interested in (CH_3Cl or CH_3Br) boil at very low temperatures and therefore come off the GC very quickly. The ether will come off the GC second.
5. Repeat steps 2-4 with the other sample.

Data Analysis:

1. Working with your partner, assign reasonable ion fragments to at least 4 significant MS peaks for both CH_3Cl and CH_3Br. Make sure these peaks correspond to ions that will allow calculation of elemental molar masses for chlorine or bromine. Several peaks could originate from two different fragments having different Cl or Br isotopes. Consider all reasonable possibilities. A useful tool for the identification of fragment peaks can be found at:
   http://www.colby.edu/chemistry/NMR/IsoClus.html
2. Working with your group, use the mass spectral data for CH_3Cl and CH_3Br to calculate the elemental molar mass for chlorine and bromine. Perform this calculation **using at least two different fragments** for each of chlorine and bromine. We encourage you to use Excel to organize your data and perform your calculations.
3. Compare your results with the reported literature values.
4. Calculate the **percent relative experimental error** in your results.
5. Speculate on important sources of the error, if any, in your experiment.

If you have difficulty with the calculations feel free to consult with your lab instructor often, but don't be frustrated if your instructor doesn't answer all of your questions or asks a question in return. You will have a better sense of accomplishment if you work out the details on your own. You will hopefully gain a better grasp of the theory of this experiment if you try many ideas, some of which might be wrong. Keep track of all measurements in your lab notebook**.**

What should be in your lab notebook:

1. Record all observations in your lab notebook. **Both members of the group should keep track of the various calculations that you tried**. **Do all of your calculations in your lab notebooks, not on a separate sheet of paper.** 4 or more peaks should be assigned with the corresponding fragment formula on each of your mass spectra.

What should be in your discussion:

1. Attach copies of ALL DATA (spectra and Excel tables) to the back of your discussion.
2. In your discussion state the final results. What was your percent relative experimental error for each element? How close were your data to literature values? What was your accuracy for Cl? For Br? Why?
3. Discuss any significant sources of experimental error and state whether they are systematic or random. If the error source was systematic, did the error cause your values to be too high or too low? If the error was a random error, state that the effect on your results will be random. [Note: the volume injected from the syringe and issues involving the separation in the GC will not have an effect on your results. Errors in the amount of sample injected or the separation will not have an effect on the relative peaks heights of a fragment ion and its related isotope peak.]