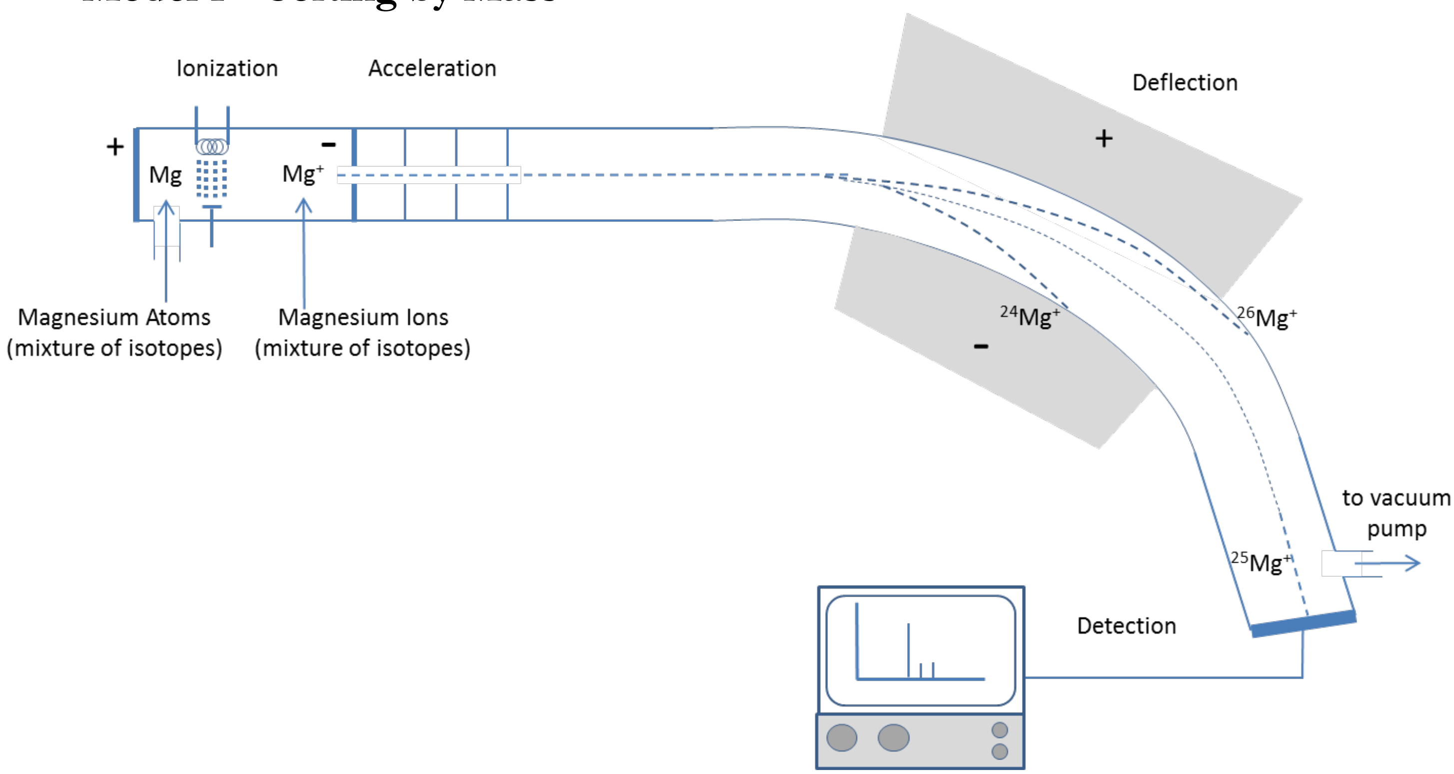
Mass Spectroscopy

How do we know isotopes exist?

Why?

When John Dalton proposed the first formal atomic theory he stated "Atoms of the same element are identical". Today we know that is not true – many elements contain several different isotopes, or atoms that differ in mass. Mass spectroscopy is the principle technique used to study isotopes. It is used to both "count" and "weigh" atoms in a sample - just not in the traditional sense.

Model 1 – Sorting by Mass



1. According to Model 1 what four processes occur inside a mass spectrometer?

2. Consider where the sample is introduced into the mass spectrometer in Model 1. Which one of the four processes you listed in Question 1 is the first process?

3. Match the four processes from Question 1 to the following descriptions.

_____________________ Ions collide with a metal plate. Electrons are transferred from the metal to the ion, producing a current and thus a signal to a computer.

_____________________ Ions are attracted to the negative side of an electromagnetic field causing separation of the mixture based on mass and charge.

_____________________ Electrons are knocked off sample particles to form (mostly) +1 ions.

_____________________ Ions move through a series of charged plates to form a narrow beam of high speed particles with equal kinetic energy.

4. When a sample is injected into the mass spectrometer, do the atoms or molecules turn into positive or negative ions? Justify your answer with at least two pieces of evidence from Model 1.

5. According to Model 1, what causes the sample mixture to become separated?

Read This!

The key to mass spectrometry is that all of the particles go into the deflection chamber with the same kinetic energy. They do not, however, have the same **mass/charge ratio (m/z)**. Although most of the ions formed are +1 ions, their masses are different. Therefore the amount of deflection they experience by the electromagnet is different. The strength of the electromagnet can be varied such that only particles with a particular mass/charge ratio make it to the detector. Other particles collide with the metallic sides of the instrument, are neutralized and removed by the vacuum pump. The machine is calibrated using carbon-12 isotopes which are, by definition, exactly 12 amu (12.0000000…amu).

6. Circle the correct phrases below to complete the sentences.

   During mass spectrometry particles with _______(more mass/less mass) are deflected more by the electromagnet.

   During mass spectrometry particles with _______ (more charge/less charge) are deflected more by the electromagnet.

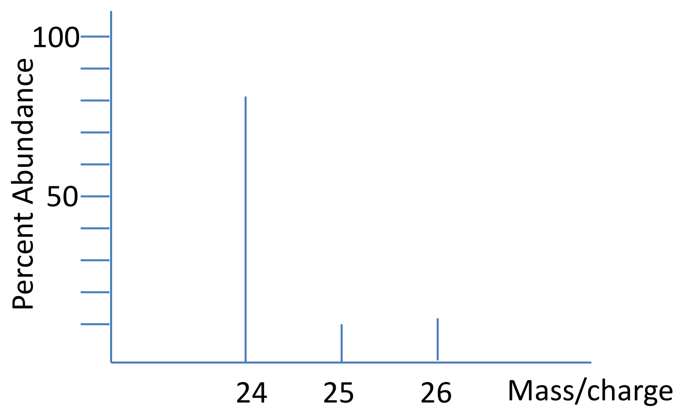
7. Consider the following ions formed in a mass spectrometer. Rank the ions in terms of their degree of deflection by the electromagnet from least to greatest. Greater deflection means a tighter turn towards the negative pole of the electromagnet.

$^{20}F^{1+}$ $^{16}O^{1+}$ $^{16}O^{2+}$ $^{17}O^{1+}$

8. Although you do not need to write an explanation for the previous question, take a minute to make sure all group members are able to explain the ranking.

9. Why is it necessary to have the mass spectrometer chamber under vacuum (very low pressure) for it to work properly?

Model 2 – A Mass Spectrum



10. Model 2 is the mass spectrum that resulted from the experiment in Model 1.
    a. What is the mass number of the most common isotope of magnesium?

    b. What is the percent abundance of the most common isotope of magnesium?

11. The average atomic mass of an element can be estimated from data on a mass spectrum.
    a. Calculate the average atomic mass of magnesium using data from Model 2. (Note: You will not get the correct answer if you add 24, 25 and 26 and divide by 3.)

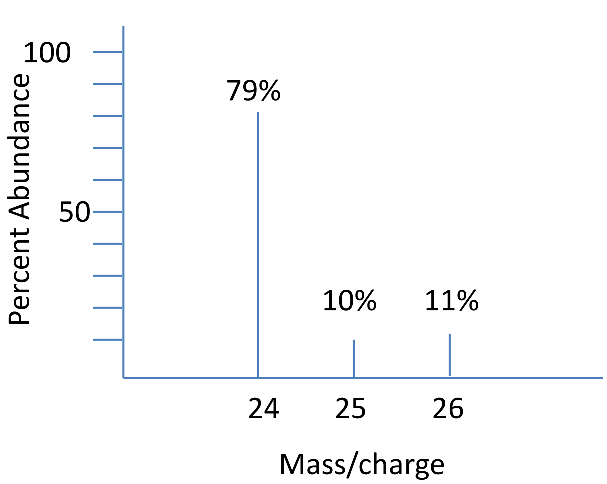
b. Give two reasons why your calculated value in part a is only an estimate of the average atomic mass of the element magnesium?

12. The table below provides mass number and percent abundance information for the element lead. Draw a mass spectrum for lead. (You can assume only +1 ions of lead are formed.)

^{204}Pb	1.4%
^{206}Pb	24.1
^{207}Pb	22.1
^{208}Pb	52.4

Read This!

The mass spectra you have been looking at in this activity used Percent Abundance on the y-axis. Typically however the spectra use relative intensity. The ions from the sample are sorted by mass/charge ratio by the mass spectrometer. The ion which hits the detector most often is assigned a relative intensity of 100. The other ions are given proportional relative intensities based on their abundance in the sample. An example of magnesium's mass spectrum shown both ways is given below.



13. Consider the two mass spectra in the Read This box on the previous page.
    a. The sum of all percent abundances for magnesium is equal to 100. Explain why this is reasonable.

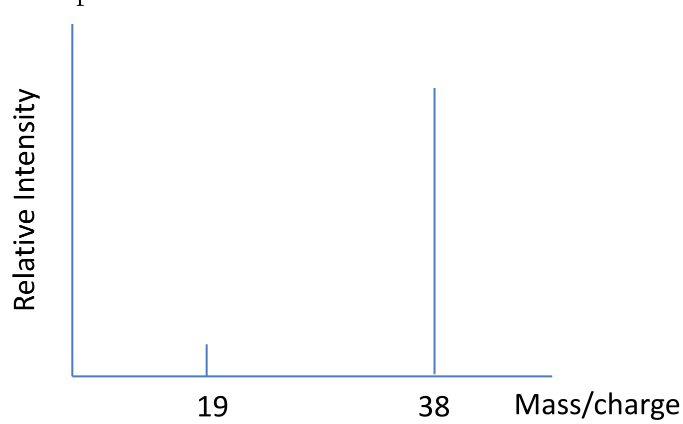
    b. The sum of all relative intensities for magnesium does not equal 100. Explain why this is reasonable.

    c. Imagine that the relative intensities are the number of particles in a sample. Theoretically, how many magnesium ions were detected by the mass spectrometer?

    d. What percentage of the ions were ^{24}Mg ions? Show mathematical work it support your answer.

    e. Show mathematically how a computer might translate the 12.7 peak in the relative intensity graph to 10.0% for the percent abundance graph.

14. The following information was gathered by mass spectroscopy for the element fluorine. Fluorine has only one natural isotope. Propose an explanation for the two lines on fluorine's mass spectrum.

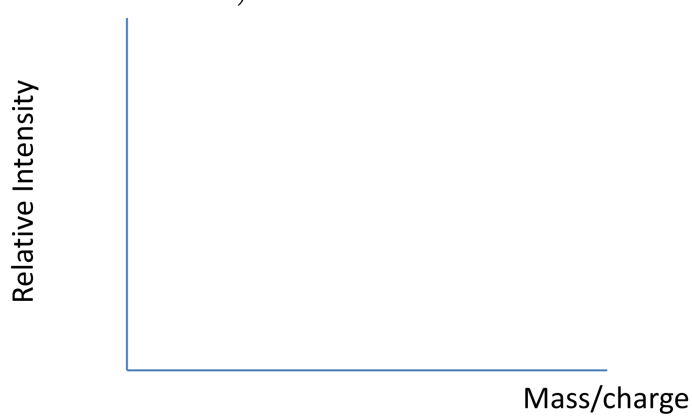


Read This!

The process of ionization inside of a mass spectrometer is quite violent. There are several methods of ionization used in industry, but many of them remove electrons from the atoms or molecules by high energy particle bombardment. In other words the electrons are knocked off the atoms or molecules by high speed particles colliding with them. Occasionally this process will break apart a molecule. This is called **fragmentation**. The pieces are analyzed by the mass spectrometer along with the whole molecules.

15. The element Chlorine has two natural isotopes – ^{35}Cl (76% abundance) and ^{37}Cl (24% abundance). The mass spectrum of diatomic chlorine has five lines.
    a. List the ions that are responsible for the five lines in chlorine's spectrum.

    b. Draw a mass spectrum that would result from diatomic chlorine. Include the mass/charge number and estimate the relative abundance of each ion. (Assume only +1 ions are formed.)



Extension Questions

Model 3 – Successive Ionization Energies

1st Ionization $Mg_{(g)} + \text{energy} \rightarrow Mg^{+}_{(g)} + e^{-}$

2nd Ionization $Mg^{+}_{(g)} + \text{energy} \rightarrow Mg^{2+}_{(g)} + e^{-}$

16. List two ways that the first ionization and second ionization of an atom are similar.

17. List two ways that the first ionization and second ionization of an atom are different.

18. Occasionally a particle introduced into a mass spectrometer is ionized twice, causing a 2+ ion to be formed. Consider the 1st and 2nd ionization energies of several atoms in the table below.

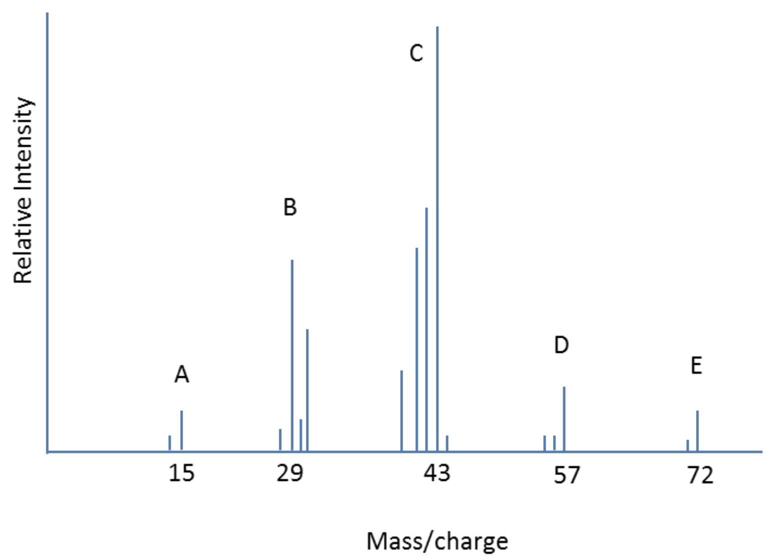
Element	1st Ionization Energy (kJ/mole)	2nd Ionization Energy (kJ/mole)
magnesium	738	1451
chlorine	1251	2298
xenon	1170	3099
oxygen	1314	3388

a. How do 1st ionization and 2nd ionization energies usually compare for an atom?

b. Propose a reason why very few 2+ ions are formed in a mass spectrometer.

c. What would the mass spectrum of magnesium look like if a small portion of atoms were ionized to 2+ ions?

19. Mass spectroscopy is also used to study large organic molecules. When a sample of a pure compound is analyzed in the instrument some of the molecules get ionized whole (molecular ions), but some are fragmented and ionized. The fragmentation occurs in predictable patterns allowing scientists to propose chemical structures for unknown substances. Consider the mass spectrum of pentane ($CH_3CH_2CH_2CH_2CH_3$) shown below.



a. Match the molecular ion and fragment ions below to each of the lettered peak clusters in the mass spectrum.

$CH_3CH_2CH_2CH_2CH_3^+$	$CH_3CH_2^+$
$CH_3CH_2CH_2CH_2^+$	CH_3^+
$CH_3CH_2CH_2^+$	

b. Why are the peaks in this spectrum clusters rather than single peaks?