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?
   
   Ionization, acceleration, deflection, and detection.

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

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

   **Detection**
   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.

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

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

   **Acceleration**
   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.

*The ions formed are positive because they are attracted to the negative terminals in the ionization chamber and of the electromagnetic field.*

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

*The mass of the ion changes the amount of deflection by the electromagnetic field. Heavier ions are not deflected as much as lighter ions.*

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 so only particles with a particular mass/charge ratio can make it to the detector. Other particles collide with the metallic sides of the instrument, are neutralized, and then removed by the vacuum pump. The machine is calibrated using carbon-12 isotopes which are, by definition, exactly 12 amu (12.0000000...amu).

6. 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. Make sure all group members are able to explain the ranking.

\[
\begin{align*}
{^{19}\text{F}^+} & < {^{16}\text{O}^+} & < {^{18}\text{O}^+} & < {^{16}\text{O}^+} \\
\text{Least deflection} & & \text{More deflection}
\end{align*}
\]

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

*The ions must travel in continuous paths toward the detector. If there were gaseous atoms in the mass spectrometer chamber, they might impede the travel of the ions in the sample.*

Model 2 – A Mass Spectrum

![Mass Spectrum Graph](image_url)
8. 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?

   24

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

   80%

9. 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. *Hint:* You will not get the correct answer if you add 24, 25 and 26 and divide by 3.

   
   \[
   \text{Average atomic mass} = (24)(0.80) + (25)(0.10) + (26)(0.10) = 24.3 \text{ amu}
   \]

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

   The mass number is not the same as the atomic mass of the isotopes. The average atomic mass would most likely not be an integral number. It is difficult to read the exact percent abundance on the graph, so they are estimated.

10. 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.)

<table>
<thead>
<tr>
<th>Mass/Charge</th>
<th>204Pb</th>
<th>206Pb</th>
<th>207Pb</th>
<th>208Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent Abundance</td>
<td>1.4%</td>
<td>24.1%</td>
<td>22.1%</td>
<td>52.4%</td>
</tr>
</tbody>
</table>

**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 that 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.
11. Consider the two mass spectra in the Read This! box.
   
   a. The sum of all percent abundances for magnesium is equal to 100. Explain why this is reasonable.
      
      *If all of the isotopes are accounted for, you must have 100% of the atoms.*
   
   b. The sum of all relative intensities for magnesium does not equal 100. Explain why this is reasonable.
      
      *Since the tallest peak is assigned 100, the total of all peaks will be greater than 100 unless there is only one isotope (one peak).*

12. Imagine that the relative intensities on the mass spectra in the Read This! box represent the number of particles in a sample.
   
   a. Theoretically, how many magnesium ions were detected by the mass spectrometer?
      
      \[100 + 13 + 14 = 127\]
   
   b. What percentage of the ions were \(^{24}\text{Mg}\) ions? Show mathematical work to support your answer.
      
      \[\frac{100}{127} = 78.7\% = 79\%\]
   
   c. Show mathematically how a computer might translate the 13 peak in the relative intensity graph to 10% for the percent abundance graph.
      
      \[\frac{13}{127} = 10.2\% = 10\%\]

---

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.

13. The following information was gathered by mass spectroscopy for the element fluorine. Fluorine has only one natural isotope, but it does form diatomic molecules naturally. Propose an explanation for the two lines on fluorine's mass spectrum.

   ![Mass Spectrum Graph](image)

   The mass number for atomic fluorine is 19. A diatomic molecule of fluorine would have an approximate mass of 38. Since most of the fluorine would be diatomic, that peak is larger. Some of the molecules would be fragmented to give the atomic peak at 19. This happens only occasionally, so the 19 peak is much smaller.
14. The element chlorine has two natural isotopes: $^{35}\text{Cl}$ (76% abundance) and $^{37}\text{Cl}$ (24% abundance). The mass spectrum of chlorine has five lines.

a. Three of the lines in the mass spectrum are from diatomic molecules of chlorine. List the three possible combinations of the two isotopes and their total mass number.

$$^{35}\text{Cl}_2^+ = 70 \quad ^{37}\text{Cl}_2^+ = 74 \quad ^{35}\text{Cl} - ^{37}\text{Cl}^+ = 72$$

b. Explain the remaining two lines in the spectrum.

_The other lines would be from the fragments (single atoms) of chlorine: $^{35}\text{Cl}^+$ and $^{37}\text{Cl}^+$._

c. 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.) Although the heights of the peaks are difficult to predict you should be able to determine which will be taller or shorter based on the abundance of each chlorine isotope.

![Mass Spectrum Diagram]

_A answers will vary. Students should be able to show understanding by including both the single atom peaks and the molecular peaks. The heights of the peaks are more difficult to predict, but there should be some indication that the $^{35}\text{Cl}$ is more common, and therefore those peaks will be higher._
Extension Questions

Model 3 – Successive Ionization Energies

<table>
<thead>
<tr>
<th>1st Ionization</th>
<th>Mg (g) + energy → Mg(^{1+}) (g) + e(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2nd Ionization</td>
<td>Mg(^{1+}) (g) + energy → Mg(^{2+}) (g) + e(^-)</td>
</tr>
</tbody>
</table>

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

*Answer may include: both require energy, both remove one electron, both result in a positive ion being formed, and both remove electrons from gaseous particles.*

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

*First ionization removes an electron from a neutral atom while second ionization removes an electron from a \(1^+\) ion. Second ionization results in a \(2^+\) ion while first ionization results in a \(1^+\) ion.*

17. 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.

<table>
<thead>
<tr>
<th>Element</th>
<th>1st Ionization Energy (kJ/mole)</th>
<th>2nd Ionization Energy (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>738</td>
<td>1451</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1251</td>
<td>2298</td>
</tr>
<tr>
<td>Xenon</td>
<td>1170</td>
<td>2046</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1314</td>
<td>3388</td>
</tr>
</tbody>
</table>

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

*The second ionization energies are always higher than the 1st ionization energies.*

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

*Since more energy is required to remove the second electron, this process happens successfully less often.*

c. If \(2^+\) ions of magnesium were formed in the mass spectrometer chamber illustrated in Model 1, would they be deflected more or less than the \(1^+\) ions by the electromagnet?

*The \(2^+\) ions would be attracted to the negative pole of the magnet more than the \(1^+\) ions, so there would be more deflection.*
18. What would the mass spectrum of magnesium look like if a small portion of atoms were ionized to 2+ ions?

![Mass Spectrum of Magnesium](image)

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), while 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 (CH₃CH₂CH₃CH₂CH₃) shown below.

![Mass Spectrum of Pentane](image)

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

CH₃CH₂CH₃CH₂CH₃⁺  E
CH₃CH₂CH₃⁺  D
CH₃CH₂⁺  C
CH₃⁺  B
CH₃⁺  A

b. Peak cluster A has a small peak at 14. What may have fallen of the CH₃⁺ ion to form this peak?

*Most likely a hydrogen atom fell off in the fragmentation to form a CH₂⁺ ion.*