FLINN SCIENTIFIC

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Part A. Isotopic Abundance and the Mass Spectra of Elements

1. The modern definition of isotopes is based on the subatomic particle structure of atoms. Complete the following table to show the number of protons, neutrons, and electrons in neutral atoms of Cl–35 and Cl–37.

Isotope	Cl–35	Cl–37
Protons		
Neutrons	18	20
Electrons		

2. Write a 2–3 sentence definition for isotopes that includes all of the following terms: protons, neutrons, atomic number, and mass number.

3. Which property of an atom defines the identity of an element? Explain why isotopes form the same compounds and undergo the same reactions.

4. Radioactive isotopes (radioisotopes) are widely used in medicine. Because isotopes have identical chemical properties, the reaction and distribution of radioisotopes in the body is similar to that of their natural isotopes. Iodine–131, for example, is an artificial radioisotope that is used to diagnose thyroid disorders. When administered to a patient, I–131 is taken up by the thyroid gland, where it is incorporated into the thyroid hormone, just as iodine in the diet would be. Based on where the following elements are likely to be found in the body, match each radioisotope with its medical use.

Sodium-24 — a. studies of bone formation

Phosphorus-32 — b. red blood cell studies

Calcium-47 — c. tracing blood circulation

Iron-55 — d. genetics (DNA) research

5. Regardless of its source on earth, the element chlorine always contains 75.8% chlorine-35 atoms and 24.2% chlorine-37 atoms. The atomic mass of an element is the weighted average of the masses of the isotopes. Fill in the values of *x* and *y* in the following equation to show how the atomic mass *(z)* of chlorine is calculated.

(0.758) (x amu) + (y) (37 amu) = z amu

6. Figure 3 shows an expanded mass spectrum of silicon. How many isotopes of silicon exist in nature? List the mass number and natural abundance of each isotope.

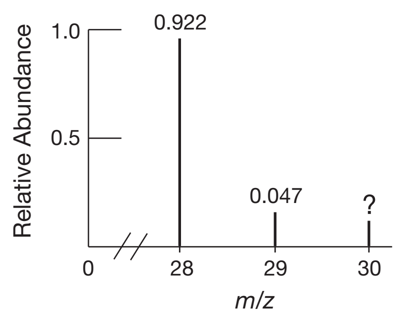


Figure 3. Mass spectrum of silicon.

7. Calculate the average atomic mass of silicon using the natural abundances obtained above and the mass number of each isotope. Compare the calculated value with the literature or reference value for the atomic mass of silicon.

8. High-resolution mass spectrometers provide masses of atoms and molecules that are precise to 4–6 decimal places. The actual mass of a Si-28 nuclide is 27.97693 amu. Define the **nuclear binding energy** of an atom and explain how it accounts for the difference in mass between the actual mass and the mass number. *Hint*: $E = mc^2$

9. *"The atomic mass of silicon represents the mass of the most common naturally occurring isotope."* Explain why this statement is false.

10. Copper occurs in nature as a mixture of two isotopes, 69.2% Cu-63 and 30.8% Cu-65. Sketch the expected mass spectrum of copper ions below.

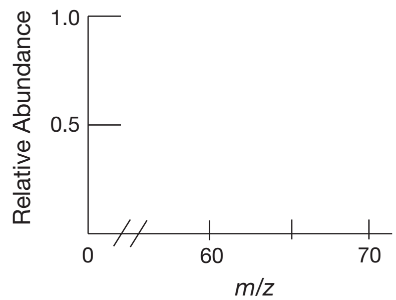
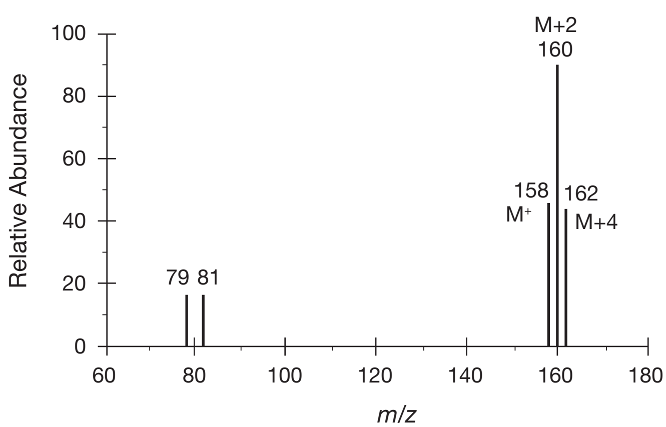


Figure 4. Mass spectrum of copper.

11. The mass spectrum of elemental bromine, a red liquid composed of diatomic molecules (Br_2), is shown below. What is the isotopic composition of individual molecules giving rise to the three ion peaks at *m/z* 158 (M^+), 160 (M+2), and 162 (M+4)?



12. Use the natural abundance of bromine isotopes to explain the 1:2:1 height ratio for the *m/z* 158, 160 and 162 peaks in the mass spectrum of bromine. *Hint*: Consider the probability of forming each molecule.

13. (*Optional*) Estimate and explain the expected height ratio of the *m/z* 70, 72, and 74 molecular ion peaks in the mass spectrum of chlorine gas (Cl_2). Recall the natural abundance of chlorine isotopes, 75% Cl–35 and 25% Cl–37.

Part B. Ionization Methods and Fragmentation Patterns in Mass Spectrometry

1. Compare and contrast electron ionization (EI) and chemical ionization (CI) in terms of the relative energies of the ions produced in mass spectrometry, the intensity of the molecular ion, and the number of fragment ions that may appear in the mass spectrum of a compound.

2. The mass spectrum of butyl methacrylate (molecular formula $C_8H_{15}O_2$) was obtained by both EI and CI. Which spectrum in Figure 5 was most likely obtained by EI? Explain your reasoning.

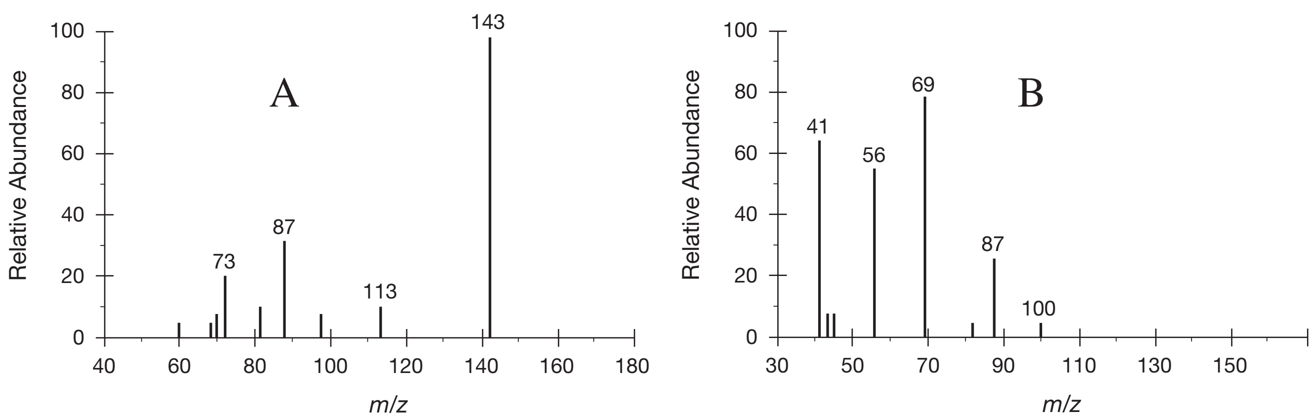


Figure 5. Mass spectra of butyl methacrylate.

3. *"The mass spectrum of a compound is unique and characteristic of its structure, much like a fingerprint."* Using the spectrum of 1-bromobutane in Figure 2 (see the *Background* section) as an example, describe why this statement is true.

4. Comparing the mass spectra of butyl methacrylate in Figure 5, describe one very important limitation to the general statement quoted in italics in Question 3.

5. Mass spectrometry is primarily a method of qualitative analysis. Why isn't it useful for quantitative analysis?

6. Mass spectrometry is a "workhorse" instrument in forensic analysis, toxicology, and drug analysis. Its use is often portrayed on television shows, where the process of forensic analysis is simplified, making it appear that a computer can instantaneously identify the names and structures of all compounds in an evidence sample. What is the minimum information that must be stored in a computer library for this process to work?

7. Proteins and other large molecules are nonvolatile and degrade when heat or energy is applied, making them unsuitable for analysis by EI or CI mass spectrometry. In 2002, the Nobel Prize in Chemistry was awarded to three individuals for their discovery of electrospray ionization (ESI) as an alternative method of ionizing proteins and obtaining their mass spectra. Look up electrospray ionization online and briefly summarize how ions are generated using this technique.

8. Figure 6 shows the structural formula and mass spectrum of 4-heptanone. Verify that the highest mass peak in the mass spectrum corresponds to the molecular ion for this compound. *Note*: Use the mass numbers for the most common isotopes of C, H and O to calculate the molecular mass.

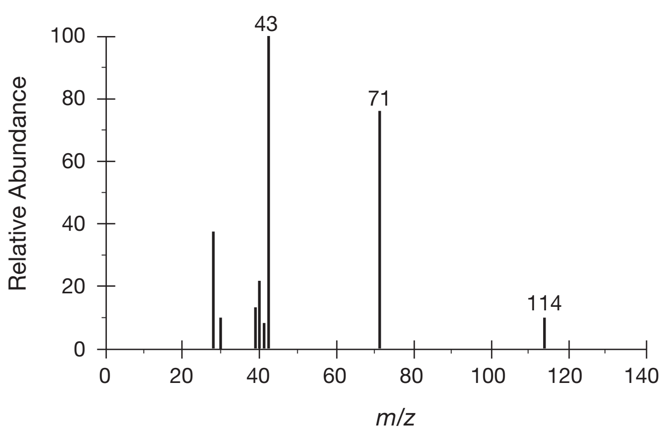


Figure 6.

4-Heptanone $CH_3–CH_2–CH_2–\overset{\overset{\displaystyle O}{\|}}{C}–CH_2–CH_2–CH_3$

9. Identify the two tallest (most intense) peaks in the mass spectrum of 4-heptanone. *(a)* How are the masses of these fragment ions related **mathematically** to the mass of the molecular ion? *(b)* What is the significance of this mathematical relationship in terms of bond breakage?

10. *(a)* Draw the structure of the molecular ion for 4-heptanone and show by means of a dashed line which bond may be broken to produce the fragment ions identified in Question 10. *(b)* The molecular ion is a radical cation. Explain how bond breakage can lead to either fragment ion.

Part C. Molecular Structures and Mass Spectra of Organic Compounds

The names and structural formulas of six organic compounds are given below (1–6). These are followed by a set of spectra A–F (page 9). Calculate the molecular mass for the most common isotopic composition of each compound, identify its mass spectrum, and explain the possible origin of at least one major fragment ion in the spectrum. All mass spectra were obtained by EI—note that spectra are not presented in order!

Name	Structure	Molecular Mass	Spectrum	Fragment Ion
Methyl bromide	CH_3–Br			
Methyl alcohol	CH_3–O–H			
Vinyl chloride	CH_2=CH–Cl			
Methylene chloride	CH_2Cl_2			
Hexane	CH_3–CH_2–CH_2–CH_2–CH_2–CH_3			
Ethyl methyl ether	CH_3–O–CH_2–CH_3			

Assign each mass spectrum A–F below to the correct compound, 1–6. The spectra are not in order!