

Mass Spectrometry Revision Notes | CIE | A-Level Chemistry

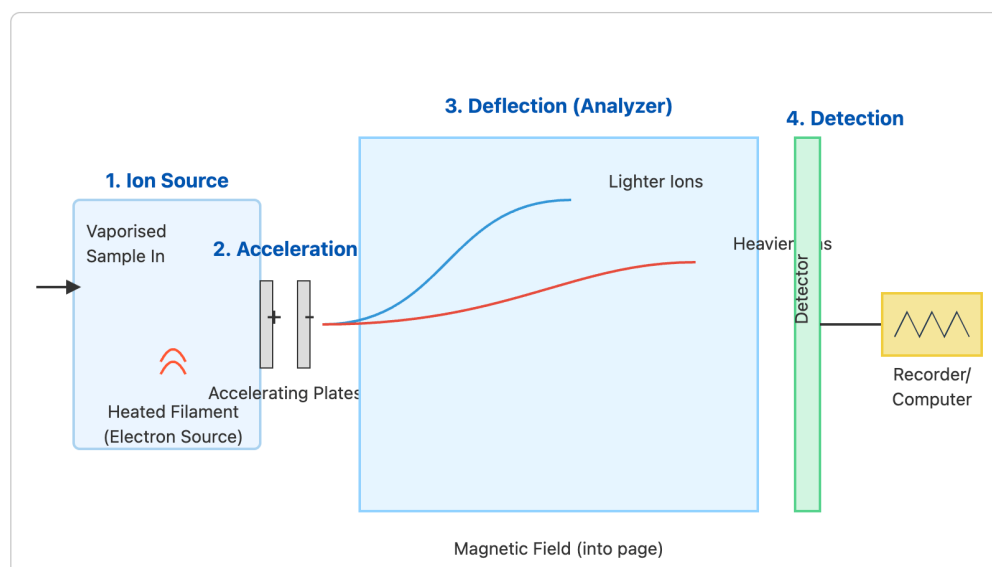
Principles of Mass Spectrometry

Mass spectrometry is a powerful analytical technique used to measure the mass-to-charge ratio of ions. It can determine the relative atomic mass of an element and is widely used in the identification of organic compounds.

The process involves several key stages:

1. **Vaporisation:** The sample is heated and vaporised to produce gaseous atoms or molecules.
2. **Ionisation:** The gaseous particles are bombarded with high-energy electrons, which knock out one or more electrons from each particle to form positive ions.
3. **Acceleration:** The positive ions are accelerated by an electric field so that they all have the same kinetic energy.
4. **Deflection:** The ions are deflected by a magnetic field. The amount of deflection depends on the mass and charge of the ion; lighter ions and ions with a higher charge are deflected more.
5. **Detection:** The deflected ions are detected by a device that measures their abundance. The detector is connected to a computer which generates a mass spectrum.

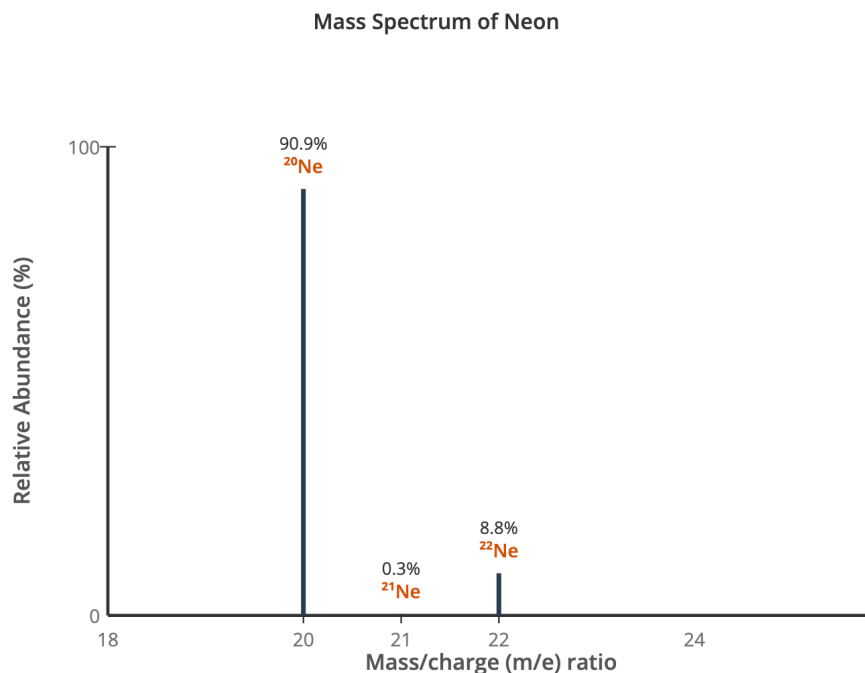
Simplified Diagram of a Mass Spectrometer



Interpreting Mass Spectra

A mass spectrum is a graph that plots the mass-to-charge ratio (m/e) on the x-axis against the relative abundance of ions on the y-axis.

- For ions with a single positive charge, the m/e ratio is equal to the relative mass of that isotope.
- The height of each peak indicates the relative abundance of each isotope present in the sample.



Calculating Relative Atomic Mass

The data from a mass spectrum allows for the precise calculation of an element's relative atomic mass (A_r). The following formula is used:

$$A_r = \Sigma (\text{isotopic mass} \times \text{relative abundance}) / 100$$

For example, using the data for neon ($^{90.9\%} {}^{20}\text{Ne}$, $^{0.3\%} {}^{21}\text{Ne}$, $^{8.8\%} {}^{22}\text{Ne}$):

$$A_r \text{ of neon} = ((20 \times 90.9) + (21 \times 0.3) + (22 \times 8.8)) / 100 = 20.2$$

Mass Spectrometry for Organic Compounds

Mass spectrometry is a vital tool for identifying organic molecules.

Molecular Ion Peak (M^+)

The peak with the highest mass-to-charge ratio is the **molecular ion peak (M^+)**. This is

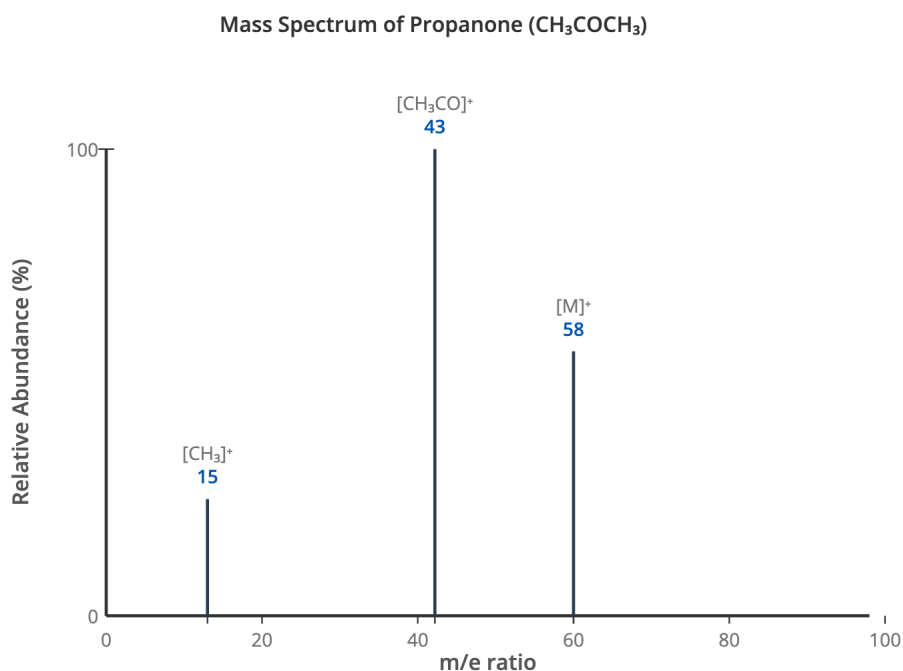
caused by the molecule losing one electron. This peak gives the relative molecular mass of the compound.

Fragmentation Patterns

The high-energy electrons in the ionisation chamber can cause covalent bonds within the organic molecule to break, creating smaller, positively charged fragments. These fragments are also detected, creating a series of peaks at lower m/e values. The fragmentation pattern is unique to a specific molecule and can be used for identification.

Common fragments include:

- **15:** $^+\text{CH}_3$
- **29:** $^+\text{C}_2\text{H}_5$
- **43:** $^+\text{C}_3\text{H}_7$ or $^+\text{CH}_3\text{CO}$



Using Isotope Peaks

High-resolution mass spectrometry can reveal additional peaks resulting from isotopes of atoms within the molecule.

- **The $[\text{M}+1]$ Peak:** A small peak is always observed one unit beyond the molecular ion peak. This is due to the presence of the carbon-13 isotope (^{13}C). The height of the $[\text{M}+1]$ peak relative to the M^+ peak can be used to determine the number of carbon atoms in the molecule.
- **The $[\text{M}+2]$ Peak:** A prominent peak two units beyond the M^+ peak indicates the presence of chlorine or bromine.

- **Chlorine:** If one chlorine atom is present, the ratio of the heights of the M^+ peak to the $[M+2]$ peak is approximately **3:1** (due to ^{35}Cl and ^{37}Cl isotopes).
- **Bromine:** If one bromine atom is present, the ratio of the heights of the M^+ peak to the $[M+2]$ peak is approximately **1:1** (due to ^{79}Br and ^{81}Br isotopes).