Lesson 1 Mass spectroscopy

Click to revise mass spectroscopy

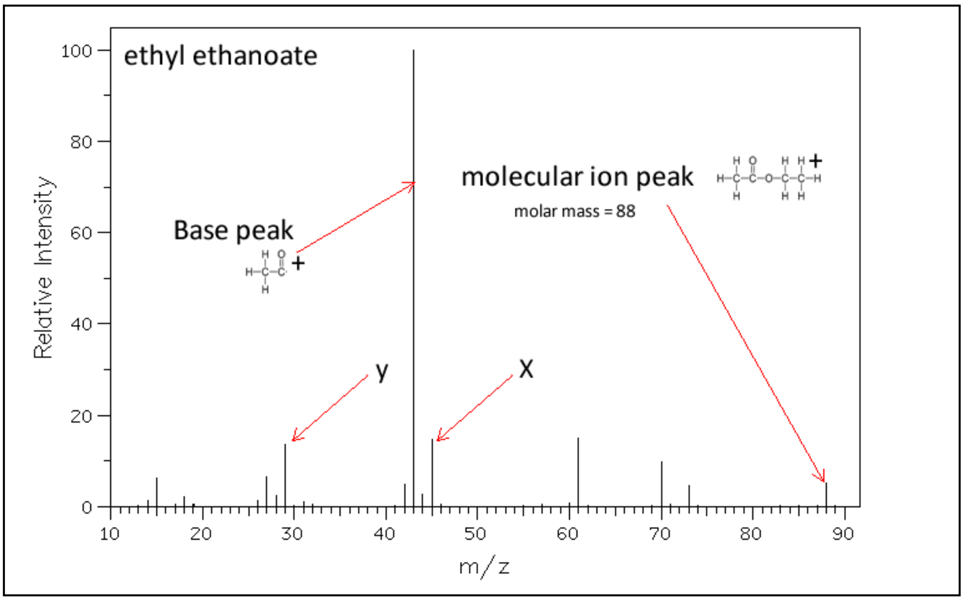
A mass spectrometer is a very sensitive instrument able to detect compounds in minute quantities. It is, however, expensive and destructive. If a small amount of substance needs to be analysed then this method will destroy the sample.

Not only can a mass spectrometer be used to derive molar masses of molecular compounds and atomic masses of elements but it is also used for:

- quantitative analysis, where the concentration of minute amounts of substance can be calculated, using a calibration curve for a unique signal at a known m/z value.
- qualitative analysis, where the mass spectrum of a compound produced by the mass spectrometer is unique and offers a fingerprint of the particular substance which can be identified from a database of mass spectra. The spectrum can also give information about the structure of an unknown compound.

This particular machine separates out the different isotopes or charged fragments according to their mass and calculates their relative abundance. The information is presented graphically as a **mass spectrum**. Its operation is as follows.

- Firstly the mass spectrometer vaporizes the compounds or elements that must be investigated.
- The vapour is then subjected to electron bombardment. When high energy electrons collide with the molecule, bonding and non-bonding electrons can be removed from the molecule creating positive charged ions.
- After electron bombardment, fragmentation of the original molecule can occur producing a variety of cations. These ions are accelerated through a magnetic field before they are collected on a photographic plate. The image given is of a set of peaks.
- Heavier particles, have a greater momentum and thus travel further along the photographic plate than the lighter ions. How quickly the charged particles bend onto the photographic plate depends on the (m/z) mass to charge ratio of the particle.
- The strength of the magnetic field can be adjusted to allow particles of different m/z ratio to be displayed.



Consider the mass spectrum of ethyl ethanoate shown on the right.

What's visible are the:

- Molar mass of the molecule 88 amu
- The base peak at 43 m/z .

a) What particle is responsible for the peak at 45 m/z ? $CH_3CH_2O^+$

b) What particle is responsible for the peak at 29 m/z ? $CH_3CH_2^+$

c) Some spectra have a smaller peak at m/z = M + 1 (where M is the molar mass of the molecule). Suggest why this is? *This is due to the presence of an atom of ^{13}C (natural abundance 1.1%) in some organic molecules.*

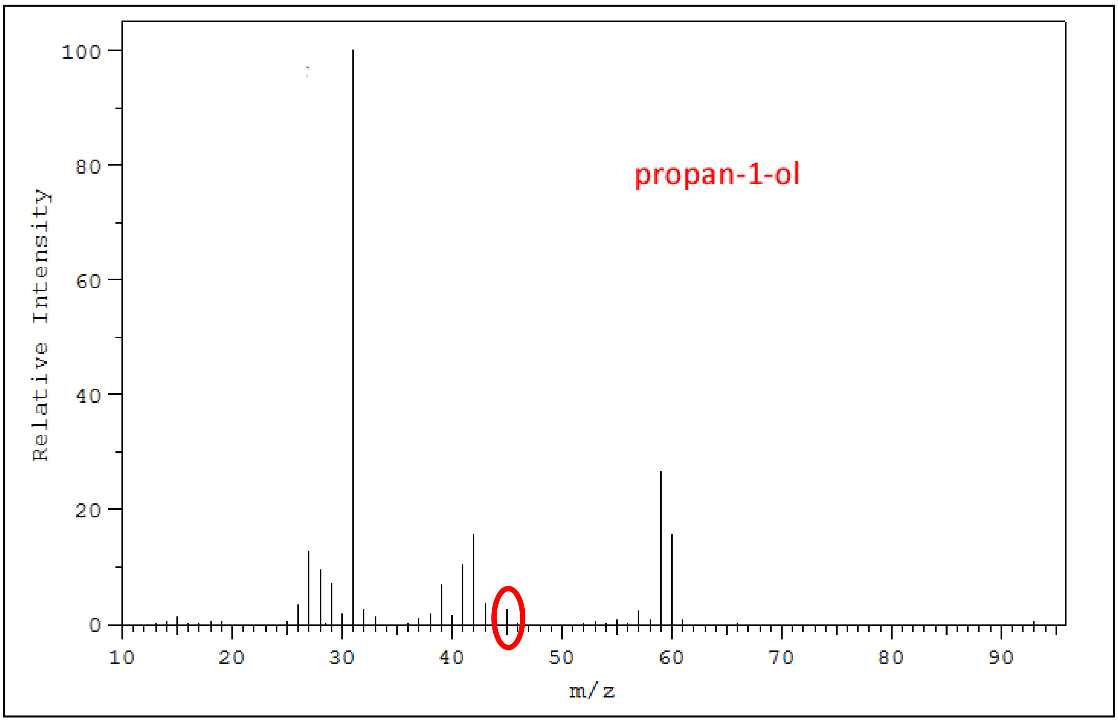
1) Consider the mass spectrum of ethanol. Which of the particles below will register a signal on the mass spectrum? Explain why
   a) OH^-
   b) CH_3^+
   c) CH_3CH_2
   d) CH_2OH^-

The mass spectrum registers only positive charged fragments.

2) Which of the equations below best represents a possible reaction as ethanol passes through the mass spectrometer?
   a) $CH_3CH_2OH \rightarrow CH_3CH_2OH^+ + e$
   b) $CH_3CH_2OH + e \rightarrow CH_3CH_2 + 2e$
   c) $CH_3CH_2OH \rightarrow CH_2OH^+ + e$
   d) $CH_3CH_2OH + e \rightarrow OH^+ + CH_3CH_2 + 2e$

The equation represents the input of an electron to remove an electron and form a positive fragment. Both sides of the equation must be balanced for charge and mass.

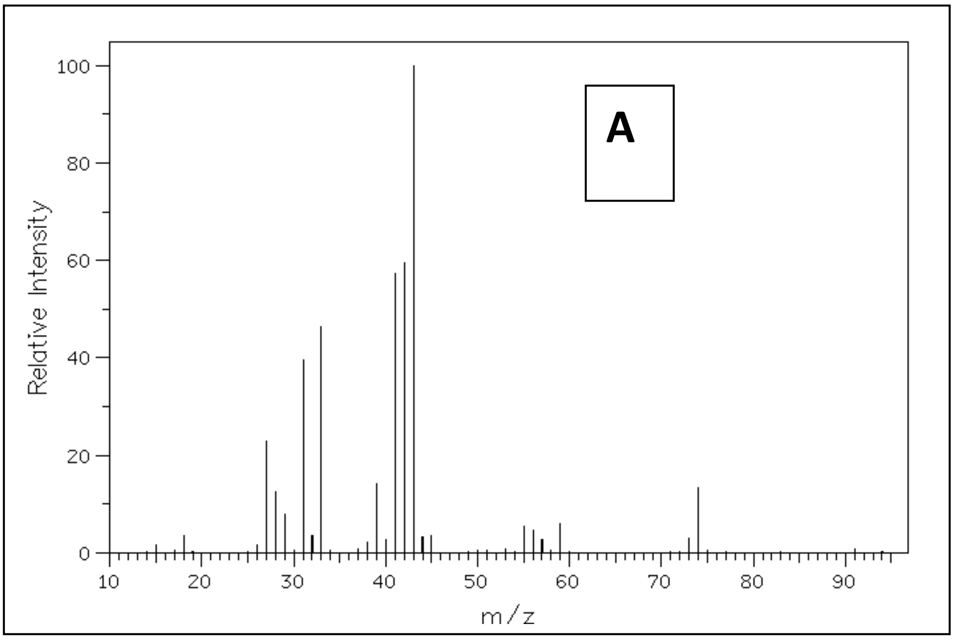
3) Consider the mass spectrum of propan-1-ol shown below.

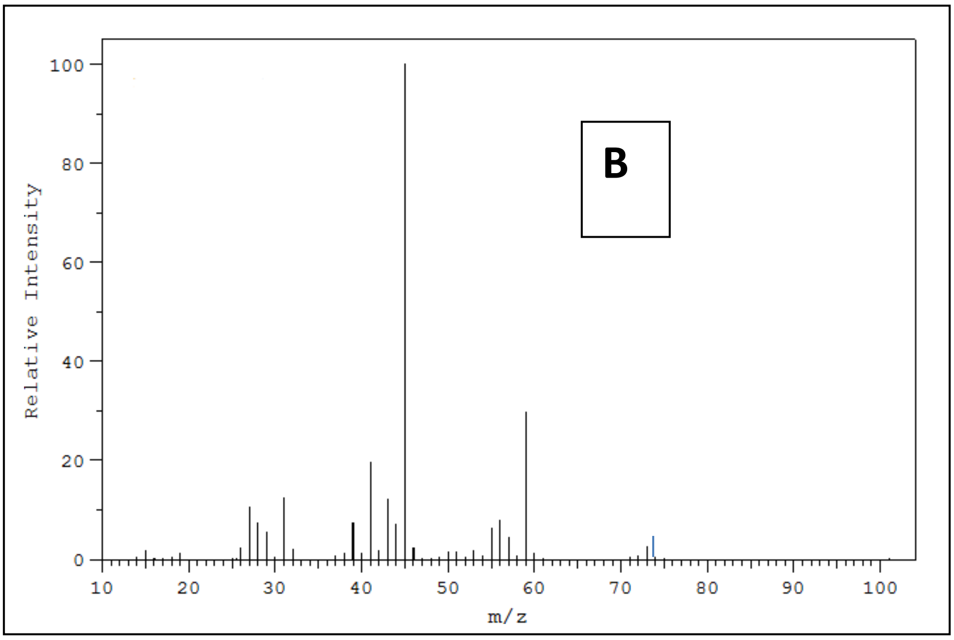


a) What possible fragment caused the base peak? *CH_2OH^+*
b) What is the m/z of the peak formed by the fragment $CH_3CH_2CH_2OH^+$? *60*
c) Circle on the spectrum above the peak formed by the fragment $CH_2CH_2OH^+$
d) What possible fragment formed the peak at m/z 61? *$CH_3{}^{13}CH_2CH_2OH^+$*

This is due to the presence of an atom of ^{13}C (natural abundance 1.1%) in some organic molecules.

4) Below are the mass spectra of 2-methylpropan-1-ol and butan-2-ol.





a) Identify the fragment that caused the base peaks in each spectrum.
Base peak in A at m/z = 43 is due to $CH_3CH(CH_3)^+$
Base peak in B at m/z = 45 is due to $OHCHCH_3^+$

b) Both spectra have a small peak at m/z 15. What possible fragment could cause this peak? CH_3^+

c) Spectrum B shows a peak at m/z 59 what possible fragment caused this peak?
$CH_3CH_2CHOH^+$