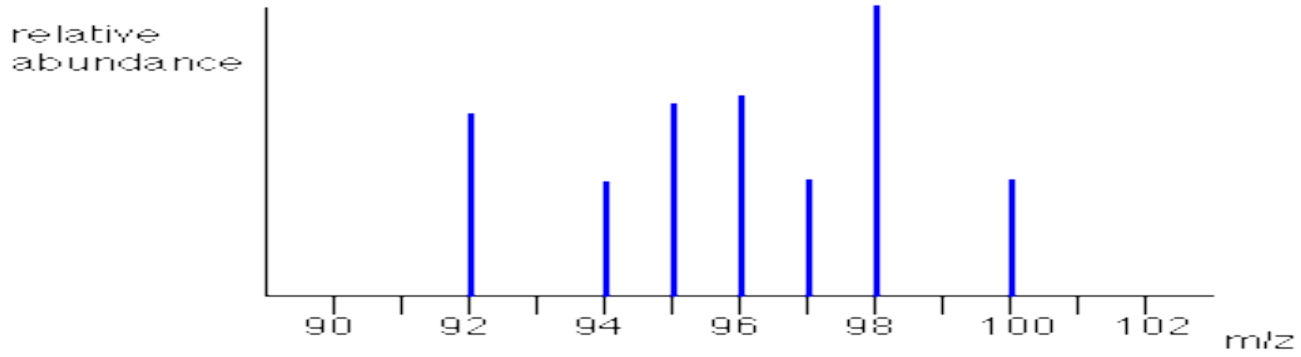
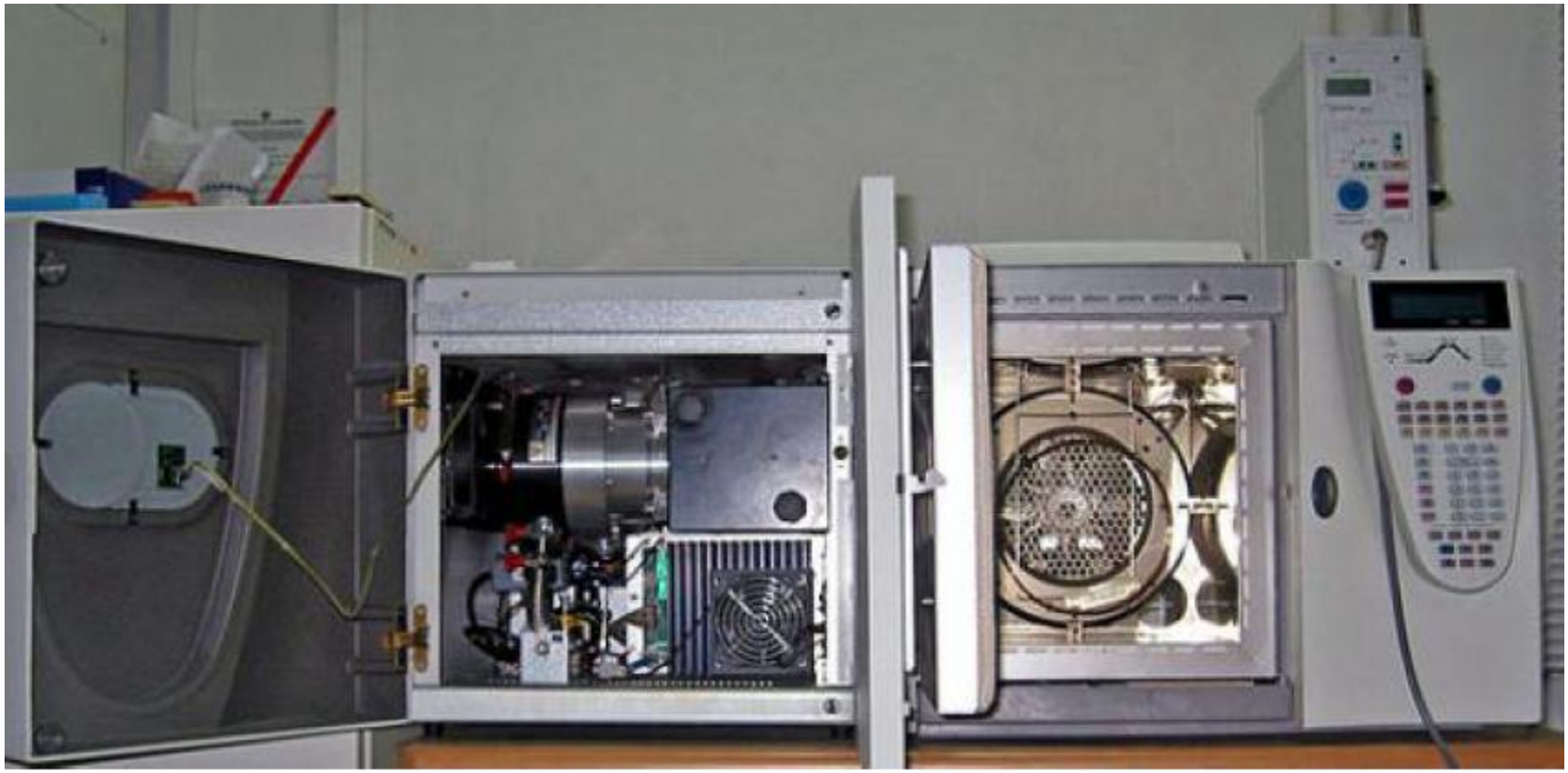
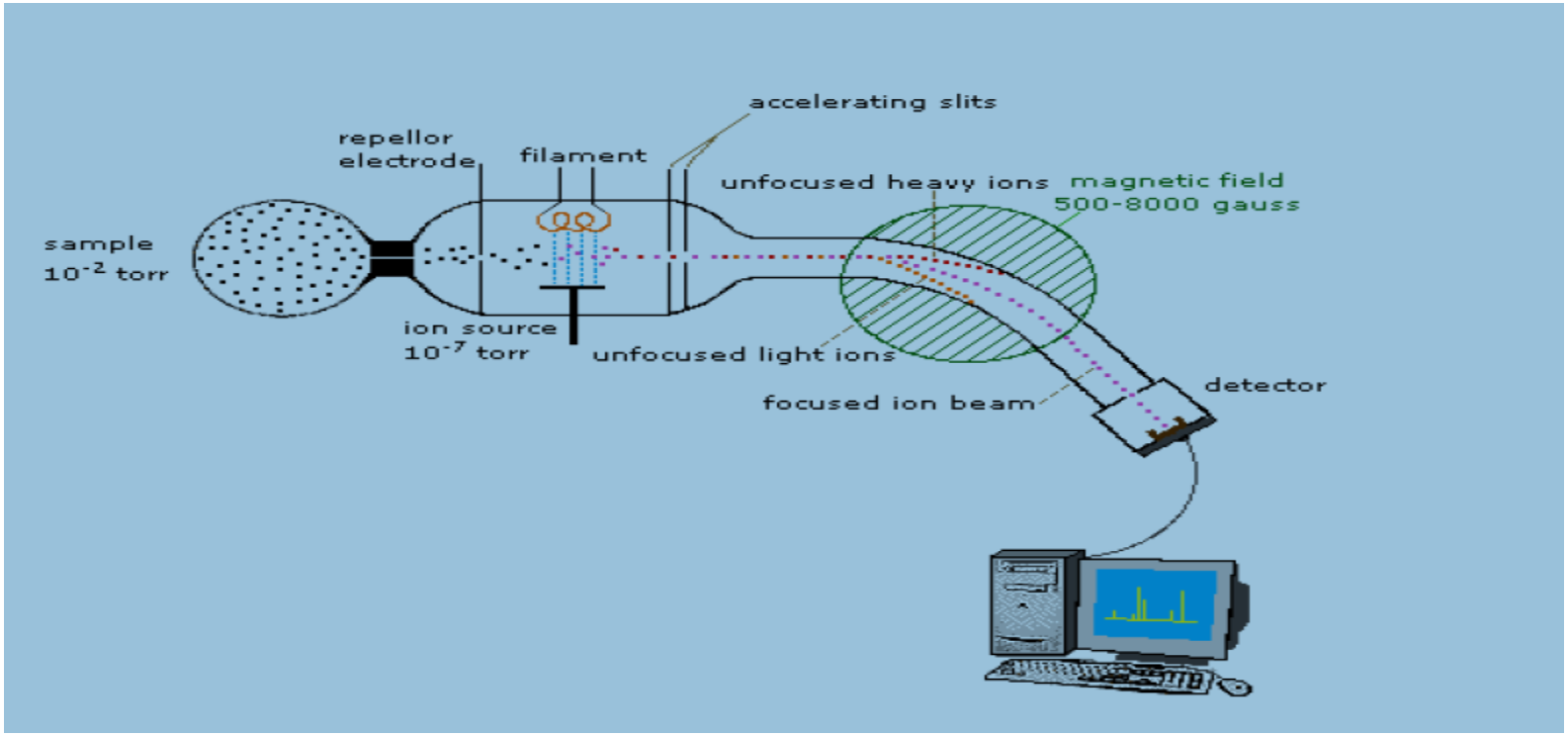
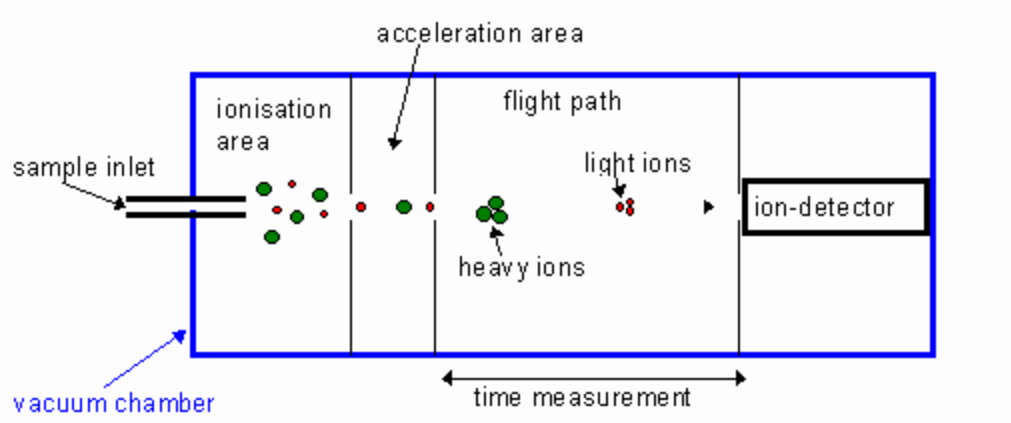
Mass Spectroscopy

Mass spectrometry (MS) is an analytical technique that ionizes chemical species and sorts the ions based on their **mass**-to-charge ratio. In simpler terms, a **mass** spectrum measures the masses within a sample. **Mass spectrometry** is used in many different fields and is applied to pure samples as well as complex mixtures.









A beam of high energy electrons (usually at 70 eV)

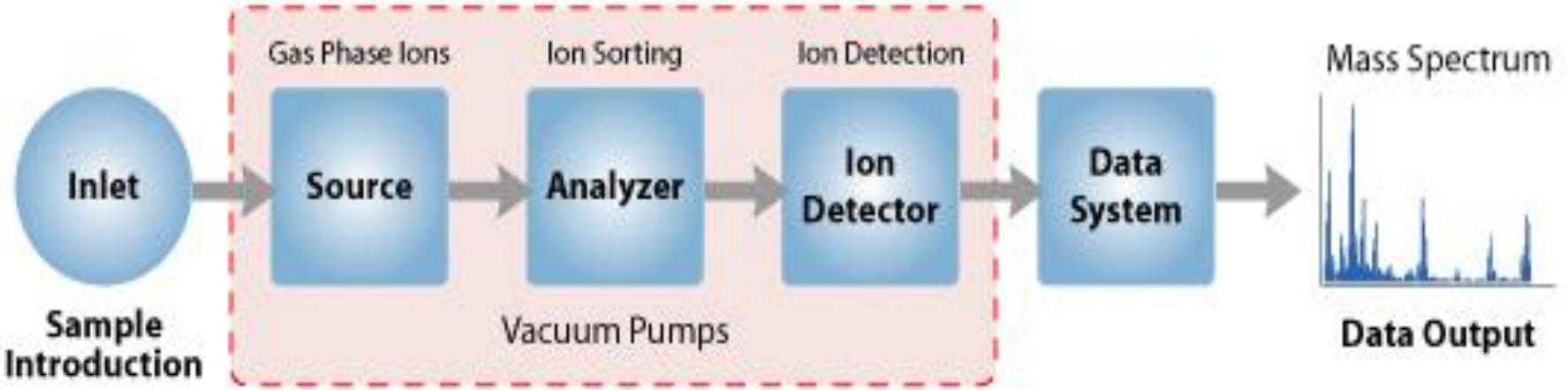
An outline of what happens in a mass spectrometer

1- Ionization: The atom is ionised by knocking one or more electrons off to give a positive ion. This is true even for things which you would normally expect to form negative ions (chlorine, for example) or never form ions at all (argon, for example). Mass spectrometers always work with positive ions.

2- Acceleration: The ions are accelerated so that they all have the same kinetic energy.

3-Deflection: The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected. The amount of deflection also depends on the number of positive charges on the ion - in other words, on how many electrons were knocked off in the first stage. The more the ion is charged, the more it gets deflected.

4- Detection: The beam of ions passing through the machine is detected electrically.

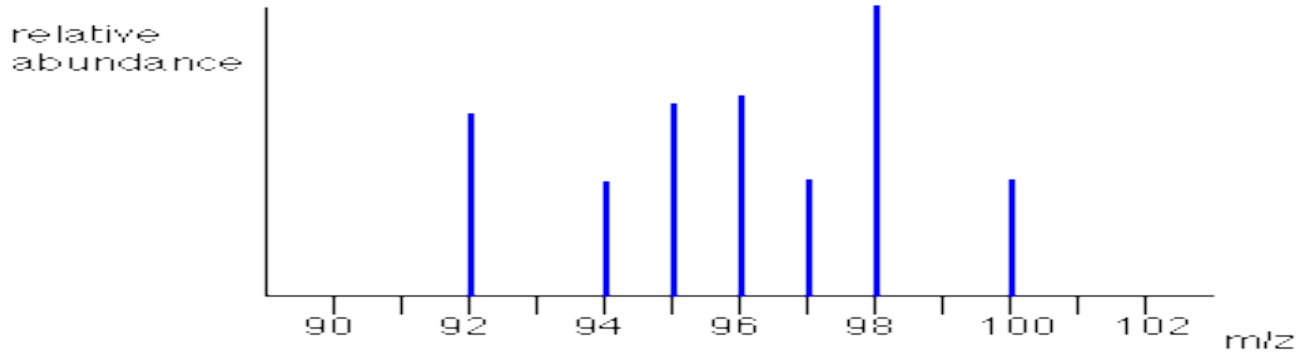

Gas Phase Ions
Ion Sorting
Ion Detection
Mass Spectrum
Inlet
Source
Analyzer
Ion Detector
Data System
Sample Introduction
Vacuum Pumps
Data Output

Basic Principle:

A **mass spectrometer** generates multiple ions from the sample under investigation, it then separates them according to their specific **mass**-to-charge ratio (m/z), and then records the relative abundance of each ion type.

A mass spectrum will usually be presented as a vertical bar graph, in which each bar represents an ion having a specific mass-to-charge ratio (m/z) and the length of the bar indicates the relative abundance of the ion.

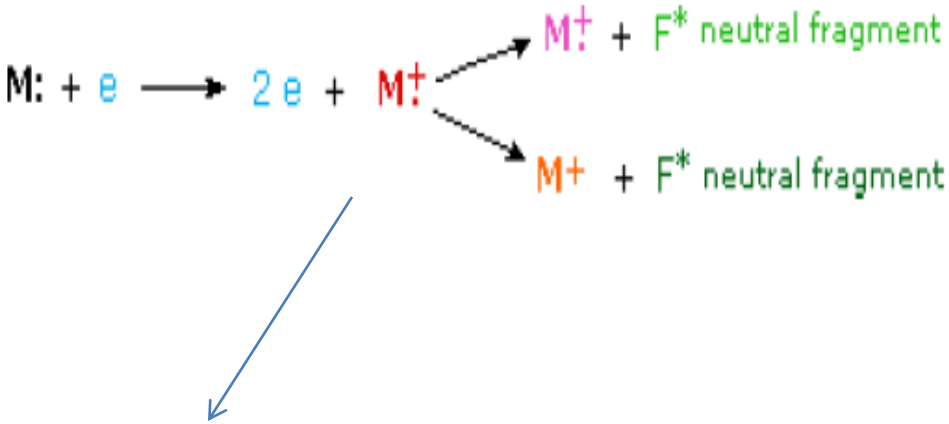
The most **intense** ion is assigned an abundance of 100, and it is referred to as the base peak.



The formation of molecular ions

When the vaporised organic sample passes into the ionisation chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the ***molecular ion*** - or sometimes the ***parent ion.***

When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.



Molecular ion (radical cation)

Fragmentation

The molecular ions are energetically unstable, and some of them will break up into smaller pieces. The simplest case is that a molecular ion breaks into two parts - one of which is another positive ion, and the other is an uncharged free radical.

Note: A free radical is an atom or group of atoms which contains a single unpaired electron.

simplified mass spectrum of pentane - $CH_3CH_2CH_2CH_2CH_3$