

1/ Mass Spectrometry:

Mass spectrometry gives accurate information on the relative masses of isotopes and their relative abundance (proportions).

Mass spectrometry is an important method of analysis in chemistry and can be used to identify elements and compounds by their characteristic mass spectrum pattern, it is an analytical tool useful for measuring the mass to charge ratio (m/z) for ions formed in a mass spectrometer. These measurements can often be used to calculate the exact molecular weight of the sample components as well.

Mass spectrometers can be used to identify unknown compounds via molecular weight determination, to quantify known compounds, and to determine structure and chemical properties of molecules.

2/ The basic components Mass spectrometer:

A mass spectrometer is an instrument of analysing particles of different relative mass. of which there are several types.

All types of mass spectrometers involve vaporising atoms or molecules in high vacuum and subjecting the vapourised particles to electron bombardment to generate a beam of positive ions, a process called ionisation.

The mass spectrometer, by several different means, separates and counts the numbers of different positive ion particles produced.

The resulting data from the detector is called a mass spectrum (plural mass spectra) which gives lots of data.

a- The Ionization Source:

High voltage electron gun which fires a beam of high speed/energy electrons from a heated 'metal element' into the vaporised sample under analysis and causes ionization of the atoms (or molecules) forming positive ions (mainly monopositive in charge).

The collision of high kinetic energy electrons with atoms or molecules causes another electron to be knocked off the particle leaving a negative deficit i.e. a positively charged particle is formed e.g.

$M_{(g)} + e^- \implies M^+_{(g)} + 2e^-$, usually written as just

$M_{(g)} \implies M^+_{(g)} + e^-$ (M might represent e.g. a metal atom or a molecule)

The ions formed should be written as $[M]^+$, a notation that is handy if you are dealing with ionised molecule fragments with an overall single positive charge e.g. $[\text{CH}_3]^+$ is seen in the mass spectrum of methane gas, CH_4 .

The low pressure (~vacuum) is needed to prevent the ions from colliding with air particles which would stop them reaching the ion detector system.

b- The Mass Analyzer:

The magnetic field that causes deflection of ions, this is can be varied to change the extent of deflection for a given mass and to focus a beam of ions of particular mass down onto the detector. Hence, by programming the mass spectrometer to 'sweep' through all likely particle masses, in terms of the right hand diagram, you can increase the strength of the magnetic field to bring into focus onto the ion detector monopositive ions of increasing mass.

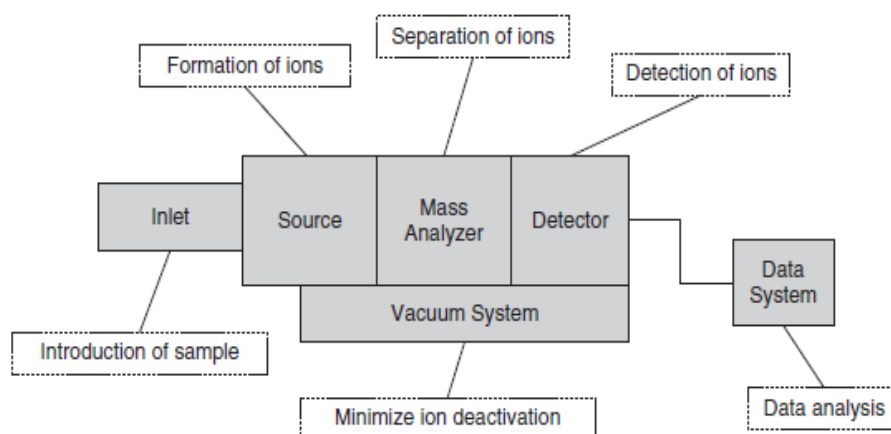
c- Ion Detection System:

An ion detection system which essentially generates a tiny electrical current when the ions hit it. The minute electric current which can be amplified. The strengths of the 'electronic' signals from the various ion peaks are sent to a computer for analysis, computation and display. They tell you the particle masses present and their relative abundance. The data is then presented as an m/z versus peak height.

m/z means the relative mass of the ion over its charge, which for our purposes the electric charge is +1 (lower case z) and the mass (lower case m) is the relative atomic/formula mass of the particle ionised. You should write the structure of the ion in square brackets and put the charge on the outside of them in the top right - this is an important and universally accepted notation in mass spectrometry.

The basic components of a mass spectrometer are shown in Figures 01 and 02.

Figure 01

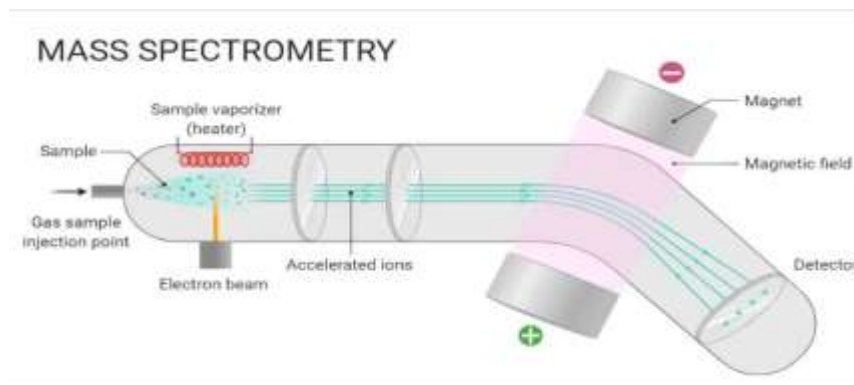


Samples are introduced into an ionization source through some type of inlet system. Depending on the phase and nature of the sample and the analytes, different inlets and ionization sources will be more or less optimal for producing ions.

Analyte molecules are typically neutral and must be ionized.

This can be accomplished in many ways. Analytes can be subjected to high-energy sources, such as electron bombardment, a laser, or an electrical discharge. Lower energy, or "softer," ionization sources also exist, such as those encountered in atmospheric pressure ionization¹.

Figure 02



¹ Analytical chemistry, Gary D Christian and all, John Wiley & Sons, 7Th Eddition, P736.

Examples of m/z values (mass/charge ratio) m/z values apply to ALL methods of mass spectrometry:

ion	relative mass (m)	positive ion charge (z)	m/z ratio
$[^{14}\text{N}]^+$	14	1	$14/1 = 14$
$[^{56}\text{Fe}]^+$	56	1	$56/1 = 56$
$[^{56}\text{Fe}]^{2+}$	56	2	$56/2 = 28$
$[^{35}\text{Cl}]^+$	37	1	$35/1 = 35$
$[^{35}\text{Cl}_2]^+$	70	1	$70/1 = 70$
$[^{35}\text{Cl}_2]^{2+}$	70	2	$70/2 = 35$
$[\text{CH}_3]^+$	15	1	$15/1 = 15$

Note that you can get multiple charged ions, but most mass spectral analysis is based on mono-positive ions.

Other terms used in mass spectroscopy:

Monatomic (mononuclear ions) are derived from single atoms eg $[^{35}\text{Cl}]^+$ or $[^{88}\text{Sr}]^+$ and a molecular ion (polynuclear ion) is derived from when the molecule is more than one atom i.e. a complete but ionised molecule (**molecular ion**) e.g. the complete molecules minus one electron to give a singly charged positive ion OR the positive residue left when one of more electrons are broken off to leave a **molecular fragment ion**)

Molecular ions: $[\text{Cl}_2]^+$ from chlorine molecules, $[\text{C}_6\text{H}_5\text{COOH}]^+$ from benzoic acid molecules

Fragment ions: $[\text{CH}_3\text{CH}_2]^+$, an ethyl fragment from the fragmentation of a hydrocarbon in a mass spectrometer.

3/Fields of Application of Mass Spectrometry²:

Key application and field of application	Explanation
Elemental and isotopic analysis. Physics Radiochemistry Geochemistry	Elemental identification and isotopic abundance measurement of both short lived and stable species in physical and radioactivity in geochemistry and more recently in the life sciences.
Organic and bio-organic analysis Organic chemistry Polymer chemistry Biochemistry and medicine	Identification and structural characterization of molecules from small to very large as provided either by chemistry, physiological processes or polymer chemistry.
Structural elucidation Organic chemistry Polymer chemistry Biochemistry and medicine	Mass spectrometric experiments can be arranged consecutively to study mass selected ions in tandem mass spectrometry. Eventually products are subjected to a third level and so fourth.
Characterization of ionic species and chemical reactions Physical chemistry Thermochemistry	Tandem MS provides an elegant means for the study of unimolecular or bimolecular reactions of gas phase ions and for the determination of ion energetics.
Mass Spectral Imaging Biomedical studies Material sciences	Mass spectra can be obtained from micrometer sized areas on surfaces, translating the lateral distribution of compounds on surfaces into images, which in turn can be correlated to optical images.

² <https://byjus.com/chemistry/mass-spectrometry/#fields-of-application-of-mass-spectrometry>,