FREE RADICAL CHEMISTRY BIOTECHNOLOGY
an ARC Centre of Excellence

Teacher Notes on: Mass Spectrometry

What is it?

Mass spectrometry is a powerful analytical technique that is used to identify unknown compounds, to quantify known compounds, and to illuminate the structure and chemical properties of molecules. Detection of compounds can be accomplished with very minute quantities (as little as 10^{-12}g, 10^{-15} moles for a compound of mass 1000 Daltons). This allows for the identification of compounds at very low concentrations (as small as one part in 10^{12}!) in chemically complex mixtures. Mass spectrometry is used by a wide range of professionals. So aprart from chemists, physicians, astronomers, biologists, and botanists use Mass Spec (as it is commonly called) for the valuable information it provides.

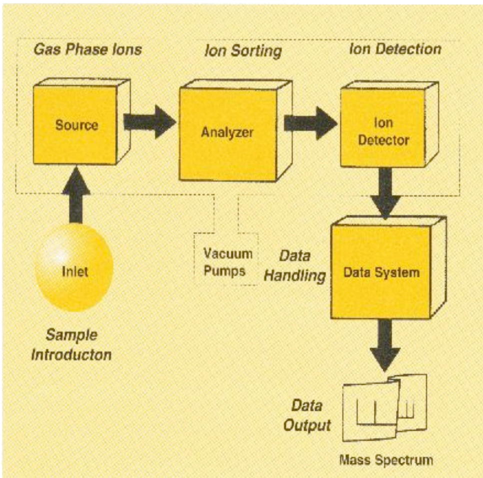
Difference between NMR and MS

MS is destructive, whereas NMR is not. However, a much smaller amount of material is needed for MS techniques. NMR and Mass Spectrometry (MS) are complementary techniques: while MS can tell the weight (and thus the molecular formula) of a molecule, NMR can differentiate between structural isomers, and provide information about connectivities between atoms within a molecule.

What is it used for?

To identify, quantify, and elucidate structures of chemical compounds.
For example:

- Detect and identify the use of steroids in athletes
- Determine the composition of molecular species found in space
- Determine whether honey is adulterated with corn syrup
- Locate oil deposits by measuring petroleum precursors in rock
- Monitor fermentation processes for the biotechnology industry
- Detect dioxins in contaminated fish
- Determine gene damage from environmental causes
- Establish the elemental composition of semiconductor materials
- Sequence biopolymers such as proteins and oligosaccharides
- Determine how drugs are used by the body
- Perform forensic analyses such as conformation of drugs
- Analyze for environmental pollutants
- Determine the age and origins of specimens in geochemistry
- Identify and quantitate compounds of complex organic mixtures
- Perform ultrasensitive multielement inorganic analyses
- Identify structures of biomolecules, such as carbohydrates,



Source: American Society for Mass Spectrometry web page (www.asms.org)

Figure 1: different functional units of a mass spectrometer

What is a Mass Spectrometer?

A mass spectrometer is an instrument that measures the masses of individual molecules that have been converted into ions, i.e., molecules that have been electrically charged. As molecules are very, very small it is not practical or convenient to measure their masses in kilograms, or grams. For example, the mass of a single hydrogen atom is approximately 0.00000000000000000000000166 grams (1.66×10^{-24} grams).

To overcome the difficulties of using conventional measurement units, chemists and biochemists use the unit of mass called the Dalton (Da for short). This is a convenient unit for the mass of individual molecules. It is defined as follows: 1 Da=(1/12) of the mass of a single atom of the isotope of carbon-12 (^{12}C). Accepted convention defines the ^{12}C isotope as having exactly 12 mass units.

Da=1/12 of the mass of a single atom of the isotope of carbon ^{12}C

The actual size of a Mass Spec ranges varies from the size of a microwave oven to that of a whole room

A mass spectrometer measures the mass-to-charge ratio of the ions formed from the molecules—not the molecular mass.

How does it work?

A sample, which may be a liquid or vapor, enters the vacuum chamber through an inlet. Depending on the type of inlet and ionization techniques used, the sample may already exist as ions in solution, or it may be ionized in conjunction with its volatilization or by other methods in the ion source.

Atoms or molecules are passed into a beam of high-speed electrons. The high-speed electrons knock electrons off the atoms or molecules being analysed and change them to positive ions. An applied electric field then accelerates these ions through a magnetic field, which deflects the paths of the ions. The amount of path deflection for each ion depends on its mass with the most massive ions are deflected the smallest amount, which causes the ions to separate.

m/z ratio

The charge on an ion is denoted by the integer number z of the fundamental unit of charge and the mass-to-charge ratio m/z therefore represents Daltons per fundamental unit of charge. In many cases, the ions encountered in mass spectrometry have just one charge (z=1) so the m/z value is numerically equal to the molecular (ionic) mass in Da. Mass spectrometrists often speak loosely of the "mass of an ion" when they really mean the m/z ratio, but this convenient way of speaking is useful only for the case of singly-charged ions.

Adapted from: Seven Zumdahl (2005) *Chemical Principles* Houghton Mifflin Company and American Society for Mass Spectrometry web page (www.asms.org)

The gas phase ions are sorted in the mass analyzer according to their mass-to-charge (m/z) ratios and then collected by a detector. In the detector the ion flux is converted to a proportional electrical current. The data system records the magnitude of these electrical signals as a function of m/z and converts this information into a mass spectrum. A comparison of the positions where the ions hit the detector plate gives very accurate values of their relative masses.

For example, when ^{12}C and ^{13}C are analysed in a mass spectrometer, the ratio of their masses is found to be

$$\frac{\text{Mass } ^{13}C}{\text{Mass } ^{12}C} = 1.0836129$$

Since the atomic mass unit is defined such that the mass of ^{12}C is *exactly* 12 atomic mass units, then on this same scale,

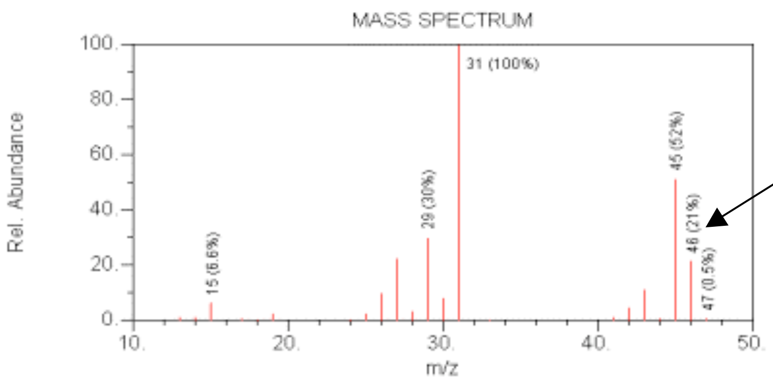
$$\text{Mass of } ^{13}C = (1.0836129)(12 \text{ amu}) = 13.003355 \text{ amu}$$

The mass of other atoms can be determined in a similar manner.

How to read the spectrum

A Mass spectrum appears as a series of peaks/signals distributed along the x-axis of the spectrum (Figure 1). Each of these signals corresponds to the relative abundance of an atom within the molecule being observed. The position of each signal in the spectrum gives the m/z ratio.

Fig. 1: EI mass spectrum of ethanol



Molecular weight of Ethanol

The fragmentation pattern acts as a finger print for this compound and so allows its unique identification.