Mass Spectroscopy

Parand Samadi

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Introduction

Mass spectrometry is an analytical chemistry technique that helps identify the amount and type of chemicals present in a sample by measuring the mass-to-charge ratio and abundance of gas-phase ions. A mass spectrum (plural spectra) is a plot of the ion signal as a function of the mass-to-charge ratio. The spectra are used to determine the elemental or isotopic signature of a sample, the masses of particles and of molecules, and to elucidate the chemical structures of molecules, such as peptides and other chemical compounds. Mass spectrometry works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios.

Procedure

Mass spectrometers can be divided into three fundamental parts, namely the ionisation source , the analyser , and the detector.

The sample has to be introduced into the ionisation source of the instrument. Once inside the ionisation source, the sample molecules are ionised, because ions are easier to manipulate than neutral molecules. These ions are extracted into the analyser region of the mass spectrometer where they are separated according to their mass (m) -to-charge (z) ratios (m/z) . The separated ions are detected and this signal sent to a data system where the m/z ratios are stored together with their relative abundance for presentation in the format of a m/z spectrum

The analyser and detector of the mass spectrometer, and often the ionisation source too, are maintained under high vacuum to give the ions a reasonable chance of travelling from one end of the instrument to the other without any hindrance from air molecules. The entire operation of the mass spectrometer, and often the sample introduction process also, is under complete data system control on modern mass spectrometers.

Methods of sample ionisation

The method of sample introduction to the ionisation source often depends on the ionisation method being used, as well as the type and complexity of the sample.

The sample can be inserted directly into the ionisation source, or can undergo some type of chromatography en route to the ionisation source. This latter method of sample introduction usually involves the mass spectrometer being coupled directly to a high pressure liquid chromatography (HPLC), gas chromatography (GC) or capillary electrophoresis (CE) separation column, and

hence the sample is separated into a series of components which then enter the mass spectrometer sequentially for individual analysis.
Many ionisation methods are available and each has its own advantages and disadvantages ("Ionization Methods in Organic Mass Spectrometry", Alison E. Ashcroft, The Royal Society of Chemistry, UK, 1997; and references cited therein). The ionisation method to be used should depend on the type of sample under investigation and the mass spectrometer available.
Ionisation methods include the following:

Atmospheric Pressure Chemical Ionisation (APCI)

Chemical Ionisation (CI)

Electron Impact (EI)

Electrospray Ionisation (ESI)

Fast Atom Bombardment (FAB)

Field Desorption / Field Ionisation (FD/FI)

Matrix Assisted Laser Desorption Ionisation (MALDI)

Thermospray Ionisation (TSP)

The ionisation methods used for the majority of biochemical analyses are Electrospray Ionisation (ESI) and Matrix Assisted Laser Desorption Ionisation (MALDI) , and these are described in more detail in Sections 5 and 6 respectively.

With most ionisation methods there is the possibility of creating both positively and negatively charged sample ions, depending on the proton affinity of the sample. Before embarking on an analysis, the user must decide whether to detect the positively or negatively charged ions.
Mass analyzers separate the ions according to their mass-to-charge ratio. The following two laws govern the dynamics of charged particles in electric and magnetic fields in vacuum:

$$F = Q * (E + v * B)$$

(Lorentz force law)

$$F = m * a$$

(Newton's second law)

$$a = E + v * B$$

This differential equation is the classic equation of motion for charged particles. Together with the particle's initial conditions, it completely determines the par-

ticle's motion in space and time in terms of m/Q. Thus mass spectrometers could be thought of as "mass-to-charge spectrometer.