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Mass Spectrometry

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Introduction

Mass spectrometry started with the discovery of isotopic form of stable elements by Thomson in the year 1911 during his outstanding work on positive rays. The pioneering work by Thomson, Aston, Dempster and Nier led to the construction of mass spectrometers for precise measurement of ionic masses using magnetic and electrostatic analysers. Today mass spectrometers are widely used to identify unknown compounds by way of determining their molecular weight at the expense of negligible amount of sample. The Nobel Prize in Chemistry for 2002 has been awarded to John B Fenn, USA, Koichi Tanaka, Japan and Kurt Wuthrich, Germany for pioneering in electrospray ionisation mass spectrometry, soft laser desorption ionisation mass spectrometry and nuclear magnetic resonance, respectively for the analysis of biological macromolecules. The mass spectrum of a compound is given in the form of a bar graph representing the abundance of various ions with respect to their mass (m) to charge (z) ratio \((m/z)\). In addition to the molecular ion, which infers the molecular weight of the sample, the other ions present in the mass spectrum are very characteristic of the compound, thus the mass spectrum of a compound becomes the fingerprint of it in most of the cases.

Principles

Mass spectrometry deals with the study of gas-phase ions and the mass spectrometers are used to determine the mass to charge ratio \((m/z)\) of ions and measure their concentration. Hence, the basic principle in getting a mass spectrum can be divided into three parts, namely, production of ions, separation of ions according to their mass to charge ratio and their detection. A simple mass spectrometer, in general, consists of a source for producing ions, an analyser for the separation of ions and a detector to measure their abundance. The block diagram of a mass spectrometer is given in Figure 1.

Positive and negative ions when produced in the gas-phase will have the tendency to be neutralised by collision with other species around. Hence, the ions produced in gas-phase are always analysed at low pressure ranging from \(10^{-6}\) Torr to \(10^{-8}\) Torr (1 Torr = 1mm of Hg) in a mass spectrometer (Figure 1).

Ions can be produced by different ionisation techniques and for the study of organic molecules of low molecular weight (~800 Da) electron impact ionisation is more suitable.

Electron Impact Ionisation

In an electron impact (EI) source, ionisation of neutral molecules \((M)\) is effected by electrons \((e)\). Electrons are produced in vacuum by thermionic emission from heated filaments that are usually made of tungsten or rhenium. Three processes can occur during
electron impact and they are represented in the following equations.

\[ M + e^- \rightarrow M^+ + 2e^- \]  
\[ M + e^- \rightarrow M^- \]  
\[ M + e^- \rightarrow M^{n+} + (n+1)e \]

The probability of the first reaction namely removal of one electron from the molecule (M) is very high compared to the other two reactions and hence, singly charged positive ions are produced in high abundance when compared to the negative (2) and multiply charged ions (3). The energy required for the first reaction which equals the first ionisation potential of the molecule lies between 8 and 12 eV for most of the organic compounds. Nevertheless, ionisation efficiency reaches a steady state only with electrons of 50-90 eV energy and hence, use of electrons of 70 eV energy is universally accepted for EI ionisation. Hence, under EI molecular ions (M^+) are produced with high energy. Ions thus produced cannot dissipate their energy in the EI source as the source is operated under high vacuum (10^{-6} - 10^{-7} Torr). Therefore, the ions produced in the primary step (1) undergo unimolecular fragmentation leading to different ions (equations 5-10) for a hypothetical molecule ABCD.

\[ ABCD + e^- \rightarrow ABCD^+ + 2e^- \]  
\[ ABCD^+ \rightarrow ABC^+ + D \]  
\[ ABCD^+ \rightarrow AB^+ + CD \]  
\[ ABCD^+ \rightarrow A^+ + BCD \]  
\[ ABCD^+ \rightarrow AD^+ + BC \]  
\[ ABC^+ \rightarrow AB^+ + BC \]  
\[ AD^+ \rightarrow A^+ + D \]

Ionisation of neutral molecule (ABCD) by removal of one electron (4) takes place in 10^{-14} - 10^{-16} seconds and the other fragmentation process occurs in 10^{-8} seconds. Therefore, ions of different mass to charge ratio are produced in the source of the mass spectrometer the moment sample is introduced into the source of the mass spectrometer and when sample molecules collide in the high-energy electrons. Ions thus formed are separated according to their mass to charge ratio in the