

PRINCIPLES OF ELECTRON-IONIZATION MASS SPECTROSCOPY¹:

Once the individual components of a mixture elute from the GC column in the gas phase, they can be directly introduced into the vacuum chamber of a mass spectrometer. This allows for implementing structural information to the detection a mixture's components.

The vaporized sample is ionized in a vacuum chamber with a bombarding beam of electrons of much higher energy (70 eV) than the ionization potential of organic molecules. Collisions between sample molecules and electrons impart enough energy to the sample to produce a molecular ion by abstraction of one electron. Given the negligible mass of the electron, the molecular ion is identical in mass to the parent molecule, with a charge of +1. The radical cation thus obtained has a mass over charge ratio (m/z) equal to the mass of the parent molecule. The ions formed are accelerated by a small applied potential through a mass analyzer and identified by an ion detector. The ions are sorted according to their mass and charge by electric or magnetic field applied. In the spectra obtained, the abundance of the ions detected is plotted versus the m/z ratio. Thus only ions are detected by mass spectrometry, while neutral molecules give rise to no signals in the spectra.

The residual energy imparted on the sample molecule leaves them in highly excited states that result in extensive fragmentation. This gives rise to cations with m/z values that are a portion of the parent molecule. Fragmentation patterns are characteristic of a given molecule and give rise to complex mass spectra useful for compound identification. Many bond-breaking mechanisms are predictable, in particular for functional groups, and they give rise to fragmentation patterns that are the result of expected α -cleavage and β -cleavage or McLafferty rearrangements.

Peak intensity is proportional to the stability of the fragments obtained. As a result, when there are few pathways for fragmentation of the molecular ion, its relative abundance will be significant. On the other hand, when many low energy bond-breaking options for energy dissipation are available, the abundance of the molecular ion will be lower, in certain cases undetectable. The tallest peak (base peak) in the spectrum corresponds to the most abundant molecular ion. The base peak is set to a relative abundance of 100% and all other signals are reported in relation to it.

Characteristic features of mass spectra can aid in the identification of unknown samples: given the valence of nitrogen, molecules that contain an odd number of nitrogen give rise to molecular ion with odd m/z value. An even m/z values reflects an even number or the absence of nitrogen. Isotopic effect can also help in mass spectra analysis since isotopic peaks reflect the

relative abundance of natural occurring isotopes. This gives rise to additional peaks reflective of the mass distribution of the various isotopes. With a relative abundance of 1% ^{13}C gives rise to M+1 peak that is proportional to the number of carbons in the sample molecule. Isotopes of higher abundance give rise to characteristic patterns in the mass spectra. Molecules containing chlorine or bromine atoms give rise to M and M+2 peaks in ratios of 3:1 for ^{35}Cl : ^{37}Cl and 1:1 for ^{79}Br : ^{81}Br .

Used in tandem with gas chromatography mass spectrometry is a powerful tool for separating and identifying individual components of organic mixtures.

Useful links:

Scripps Center for Mass Spectrometry: <http://masspec.scripps.edu/MSHistory/whatisms.php>

SCIMEDIA: Analytical Chemistry and Instrumentation: <http://elchem.kaist.ac.kr/vt/chem-ed/analytic/ac-meths.htm#mass-spec>