

Study Notes on Mass Spectrometry

Mass spectrometry

Mass spectrometry is a technique which is used to determine the mass of a molecule and its fragments. This spectrometry tends to measure the mass-to-charge ratio of gaseous ions. The ions can be either positively or negatively charged. It is considered to be a destructive analytical technique because the sample cannot be recovered for further analysis. To determine the mass of individual atoms, the mass defect can be determined, the precision must approach 1 part in 10^4 . With a mass spectrometer of this precision, molecules of nominally the same mass such as $^{12}\text{C}^{16}\text{O}$ (of mass $27.9949m_u$) can be distinguished from $^{14}\text{N}_2$ (of mass $28.0061m_u$) and the elemental and isotopic composition of ions of nominal mass less than $1000 m_u$ may be determined unambiguously.

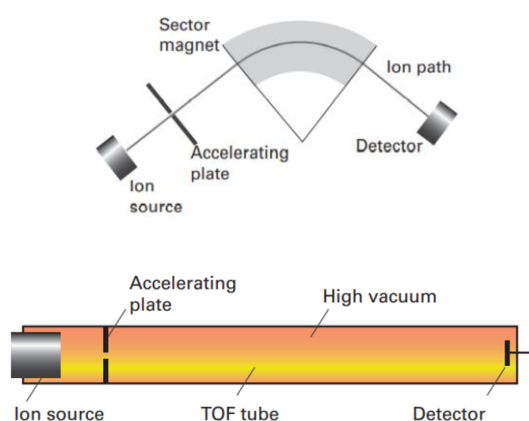
(a). Ionization and detection methods:

The major practical challenge with mass spectrometry deals with the conversion of a sample into gaseous ions. Many different experimental arrangements have been devised to produce gas-phase ions, but all suffer from a tendency to fragment the compound of interest. Electron impact ionization (EI) mainly relies on bombarding a sample with high-energy electrons that cause both vaporization and ionization. One of the disadvantages is that EI tends to induce considerable decomposition in larger molecules. Fast atom bombardment (FAB) is like EI, but bombardment of the sample with fast neutral atoms is used to vaporize and ionize the sample; it induces less fragmentation than EI. Matrix-assisted laser desorption/ionization (MALDI) is like EI, but a short laser pulse is used to the same effect; this technique is particularly effective with polymeric samples. In electrospray ionization (ESI), charged droplets of solution are sprayed into a vacuum chamber where solvent evaporation results in generation of individually charged ions; ESI mass spectrometry is now becoming more widely used and is often the method of choice for ionic compounds in solution.

The traditional method of ion separation depends on the acceleration of ions with an electric field and then using a magnetic field to deflect the moving ions: ions with a lower mass-to-charge ratio are deflected more as compared to heavier ions. As the magnetic field gets changed, ions with different mass-to-charge ratio are directed on to the detector. In a time-of-flight (TOF) mass spectrometer, the ion from a sample gets accelerated by an electric field for a fixed time and then

allowed to fly freely. Because the force on all the ions of the same charge remains the same, the lighter ions are accelerated to higher speeds than the heavier ions and strike a detector sooner. In an ion cyclotron resonance (ICR) mass spectrometer (often denoted FTICR, for Fourier transform-ICR), ions get collected in a small cyclotron cell inside a strong magnetic field. The ions circle round in the magnetic field, effectively behaving as an electric current. Because an accelerated current generates electromagnetic radiation, the signal generated by the ions can be detected and used to establish their mass-to-charge ratio.

Mass spectrometry is most widely used in organic chemistry but is also very useful for the analysis of inorganic compounds. However, many inorganic compounds, such as those with ionic structures or covalently bonded networks (for example SiO_2), are not volatile and do not fragment into molecular ion units (even with the MALDI technique) due to which, these cannot be analysed by this method. Conversely, the weaker bonding in some inorganic coordination compounds means that they fragment much more easily than organic compounds in the mass spectrometer.



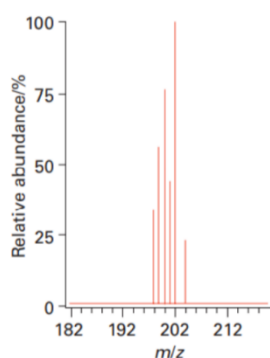
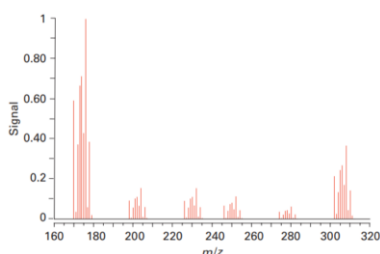
(b). Interpretation

The given below figure shows a typical mass spectrum. To interpret a spectrum, it is helpful to detect a peak which corresponds to the singly charged, intact molecular ion. Sometimes a peak occurs at half the molecular mass and is then ascribed to a doubly charged ion. Peaks from multiply charged ions are usually easy to identify because the separation between the peaks from the different isotopomers is no longer m , but fractions of that mass. For instance, in a doubly

charged ion, isotopic peaks are $\frac{1}{2}m_u$, apart, in a triply charged ion they are $\frac{1}{2}m_u$, apart, and so on.

In addition to indicating the mass of the molecule or ion that is being studied (and hence its molar mass), a mass spectrum also provides information about fragmentation pathways of molecules. This information can be used to confirm structural assignments.

Multiple peaks are observed when an element is present as several isotopes (for instance, chlorine is 75.5 percent ^{35}Cl and 24.5 percent ^{37}Cl). Thus, for a molecule containing chlorine, the mass spectrum will show two peaks $2m_u$ apart in an intensity ratio of about 3:1. Different patterns of peaks are obtained for elements having more complex isotopic composition and can be used to identify the presence of an element in compounds of unknown composition. An Hg atom, for instance, has six isotopes in significant abundance. The actual proportion of isotopes of an element varies according to its geographic source, and this subtle aspect is easily identified with high-resolution mass spectrometers. Thus, the precise determination of the proportions of isotopes can be used to determine the source of a sample.



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