

Mass Spectroscopy

The following example describes the operation of a spectrometer mass analyzer, which is of the sector type. Other analyzer types are treated below. Consider a sample of sodium chloride, table salt. In the ion source, the sample is vaporized, turned into gas, and ionized, transformed into electrically charged particles, into sodium (Na^+) and chloride (Cl) ions. Sodium atoms and ions are monoisotopic, with a mass of about 23 u. Chloride atoms and ions come in two isotopes with masses of approximately 35u at a natural abundance of about 75 percent and approximately 37u at a natural abundance of about 25 percent. The analyzer part of the spectrometer contains electric and magnetic fields, which exert forces on ions traveling through these fields. The speed of a charged particle may be increased or decreased while passing through the electric field, and its direction may be altered by the magnetic field. The magnitude of the deflection of the moving ion's trajectory depends on its mass-to-charge ratio. Lighter ions get deflected by the magnetic force more than heavier ions based on Newton's second law of motion, $F = ma$. The streams of sorted ions pass from the analyzer to the detector, which records the relative abundance of each ion type. This information is used to determine the chemical element composition of the original and the isotopic composition of its constituents, the ratio of ^{35}Cl to ^{37}Cl .

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)

$$F = ma$$

(Newton's second law of motion in non-relativistic case, i.e. valid only at ion velocity much lower than the speed of light). Here F is the force applied to the ion, m is the mass of the ion, a is the acceleration, Q is the ion charge, E is the electric field, and $v * B$ is the vector cross product of the ion velocity and the magnetic field. Equating the above expressions for the force applied to the ion yields:

$$\left(\frac{m}{Q}\right) * a = E + v * B$$

This differential equation is the classic equation of motion for charged particles. Together with the

particle's initial conditions, it completely determines the particle's motion in space and time in terms of m/Q . Thus mass spectrometers could be thought of as "mass-to-charge spectrometers". When presenting data, it is common to use the dimensionless m/z , where z is the number of elementary charges (e) on the ion ($z=Q/e$). This quantity, although it is informally called the mass-to-charge ratio, more accurately speaking represents the ratio of the mass number and the charge number, z . Field ionization and desorption are two closely related techniques which use quantum tunneling of electrons to generate ions. Typically, a highly positive potential is applied to an electrode with a sharp point, resulting in a high potential gradient at the tip. As the sample reaches this field, electron tunneling occurs to generate the action, which is repelled into the mass analyzer. Field ionization utilizes gaseous samples whereas in field desorption the sample is adsorbed directly onto the electrode. Both of these techniques are soft, resulting in low energy ions, which do not easily fragment. In ESI, a highly charged aerosol is generated from a sample in solution. As the droplets shrink due to evaporation, the charge density increases until a columbic explosion occurs, producing daughter droplets that repeat the process until individualized sample ions are generated. One of the limitations of ESI is the requirement that the sample be soluble. ESI is best applied to charged, polar, or basic compounds.

In electron impact ionization, a vaporized sample is passed through a beam of electrons. High energy (typically 70 eV) beams strips electrons from the sample molecules leaving a positively charged radical species. The molecular ion is typically unstable and undergoes decomposition or rearrangement to produce fragment ions. Because of this, electron impact is classified as a hard ionization technique. With regards to metal-containing compounds, fragments in EI will almost always contain the metal atom (i.e., $[ML_n]^+$ fragments to $[ML_{n-1}]^+ + L$, not $ML_{n-1} + L^+$). One of the main limitations of EI is that the sample must be volatile and thermally stable.