

Quick Guide to Interpreting an EI Mass Spectrum

This guide is based on McLafferty and Turecek, *Interpretation of Mass Spectra*, which is available in the WCU library. Please consult it for more detail.

Before you begin, convert your spectrum from raw abundance (counts) into relative abundance (% of base peak).

1. Look for the M^+ (molecular ion) peak.

The molecular ion, sometimes called the *parent peak*, is the highest mass peak of significance in the spectrum (except for the $M^+ + 1$, \dots , etc. peaks). It represents the unfragmented molecule, and can therefore tell you the *monoisotopic* mass of the analyte. Not all compounds yield an M^+ peak; some are too unstable. Some compounds yield very abundant M^+ peaks; this stability can be a clue to the structure.

2. Use $M^+ + 1$ peak to figure out C count.

Zoom in on the M^+ peak and look for a very small, but real, peak 1 m/z unit above your molecular ion peak. This peak is usually present for small, organic molecules and represents the fraction of the molecules containing one ^{13}C atom. Take the ratio of these two abundances and divide by the natural abundance of ^{13}C to find the approximate number (± 1) of carbon atoms in the molecule. (Or, remember, a ratio of $1.1 = 1\text{C}$, $2.2 = 2\text{C}$, $3.3 = 3\text{C}$, \dots)

The $M^+ + 1$ peak must be the highest mass in the spectrum, an odd-electron ion, and give logical, neutral losses (see 4 and 6 below). If you don't see an obvious $M^+ + 1$ peak or see multiple peaks in distinct patterns, you may have halogens or other non-C,H,O,N atoms in your molecule.

3. Apply the nitrogen rule.

Is M^+ odd or even? For small, organic molecules an even M^+ strongly suggests an even number of nitrogen atoms (0 is even), and an odd molecular weight (M^+) suggests an odd number of nitrogen atoms.

4. Calculate rings and double bonds (degree of unsaturation).

$\text{C}_x\text{H}_y\text{N}_z\text{O}_n$ will have $x - 0.5y + 0.5z + 1$ rings and/or double bonds. Integers represent odd-electron ions; results ending in 0.5 represent even-electron ions.

5. Look for the base peak.

The base peak is the largest peak in the spectrum (relative abundance = 100%). It represents the most stable fragment (keeping in mind that some "fragments" are actually rearrangements).

6. Calculate the identity of each peak using steps 2-4.

Attempt to identify any peaks possible. Look for logical losses (e.g. $-\text{OH}$ or $-\text{CH}_3$) and series of logical losses (e.g. $-\text{CH}_3$, $-\text{CH}_2$). Look for isotopic abundances of fragments and assign compositions. The nitrogen rule still applies to fragments, but keep in mind any odd-mass element could cause the same result. When you've identified as many peaks as you can, attempt to deduce a structure.