Interpreting mass spectral data – Primer

Molecular masses in LCMS: M, [M-H]-, & [M+H]+

When interpreting mass spectral (MS) data, you will need to know the m/z (molecular weight to charge) value for a particular ion in order to view the correct EIC (extracted ion chromatogram) for that ion. In most MS data software, you can input the molecular formula of the intact neutral molecule, M, and obtain the exact masses of not only M but also commonly observed ions.

The most common ions are $[M + H]^+$ for positive mode and $[M – H]^-$ for negative mode. There are a few **rules of thumb** on molecular masses that can be used to verify that a particular m/z appears to be right. One example is the "Nitrogen Rule." In an organic compound containing hydrogen, carbon, oxygen, nitrogen, silicon, phosphorus, sulfur, or a halogen, there must be an odd number of nitrogens if the molecular mass is odd. Conversely, if you have an even molecular mass, there are either no nitogens or an even number of nitrogens in the neutral molecule. The reason has to do with nitrogen's odd atomic mass in conjunction with its bonding properties.

If you are given a formula, for example $C_2H_6O_4P$, how can you tell whether this is for the neutral molecule M or the anion $[M – H]^-$? Using a mass calculator (available from your MS data analysis software or free web sources), you can get a mass of 125.000370. Since it is odd and there are no nitrogens in the formula, we know this cannot be the mass of the neutral molecule. Therefore it must be the anion $[M – H]^-$.

Generally the formula of the neutral molecule is provided rather than the ions. This is typically the convention since the analyst inputs this

formula into the data analysis software and from there the masses of M, $[M + H]^+$, $[M – H]^-$, and other ions can all be calculated.