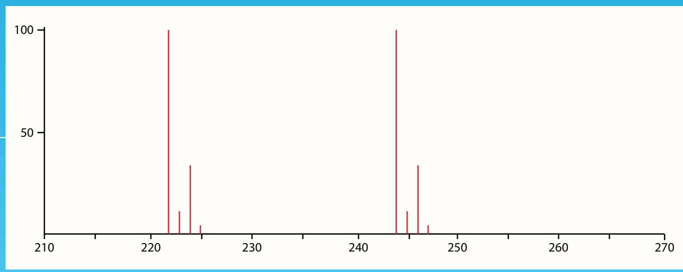
MORE THAN MEETS THE EYE

HOW MUCH INFORMATION CAN BE GLEANED FROM A MASS SPECTRUM?

A spectrum from a simple analyser, such as a quadrupole, can contain much more information than initially meets the eye. Having access to this information allows many informed assumptions to be made about the analyte in question.

This is an example spectrum of an unknown compound — what information can we take from it?



Charge State

Multiple charges can be picked up by the analyte during the ionisation process. The nominal mass difference between isotopes is 1Da, so it is possible to calculate the charge state by 1 / observed m/z difference. A doubly charged species will have an m/z difference of 0.5, triply charged 0.333 etc.

Adducts

One of the first things to do when looking at a spectrum is look +- 22 m/z units around what is believed to be the pseudo-molecular ion. Adducts are very common in electrospray ionisation spectra — Na+ is one of the most common. This allows a greater degree of confidence in assessing the molecular weight of the analyte.

Nitrogen Rule

Molecules with an odd molecular weight will contain an odd number of nitrogens, with even molecular weights containing either an even number of nitrogens or none at all. This is especially useful in MSMS analysis as, if the number of observed m/z switches from odd to even (or vice versa) it's indicative of the location of nitrogen(s) in the structure.

Carbon number

The A+1 peak can be used to narrow the possible number of carbon atoms there are in the molecule. 13C has a natural abundance of 1.1%, so if we observe an A+1 height of 6.6%, the molecule will contain 6 carbons. For larger molecules, this can be used to limit the possible formula for confirmation.

Isotope Pattern

With organic molecules, the presence of C, H, N, and O is assumed. But is there evidence of any other elements? The +2 peak has a height of approx. 33% of the mono-isotopic peak, which is characteristic of chlorine. Other A+2 elements, such as bromine and sulphur, also have different peak heights which can be used diagnostically.

The example spectrum has peaks at m/z 221 and at m/z 243. The m/z difference between the isotope peaks is 1. This information combines to indicate that the peaks are singly charged and that they are the [M+H] and [M+Na] ions. We can therefore determine that the molecular weight is 220 Da. An even molecular weight means there is either an even number of nitrogens or none at all in the molecular formula. Finally, the height of the A+1 peak suggests 10 carbons while the height of the A+2 peak suggests the presence of chlorine...

Now that's a lot of information from a slightly closer look!

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