What is “Spectral Accuracy”?

Mass spectrometry is an important tool for compound identification or confirmation by virtue of its ability to obtain elemental composition information (formula ID) by accurate mass measurements. This simple but elegant method of formula ID relies on the fact that each unique formula has a unique mass. Mass Accuracy is a measure of an instruments error in determining the theoretical (exact) mass of an ion and is usually expressed in parts-per-million (PPM) relative to the measure mass values or in absolute units of milli-Daltons (mDa) (Figure 1). Unfortunately, due to this measurement error, mass accuracy alone can rarely provide a unique formula, particularly at higher mass values (above 400Da).

An ions isotope pattern is also unique for every unique formula and significantly richer in information than the measurement of a single peak position, as with accurate mass measurements. It is composed of many peaks each with unique relative intensities based on their isotopic abundances, and unique relative mass positions based upon the mass of each isotope. Spectral Accuracy is a measure of the similarity between the measured spectra (the entire ions isotope pattern) against that of the theoretical spectrum. However, since the line-shape of the measured spectrum is unknown, measures of Spectral Accuracy are generally not high enough to provide a unique formula ID (Figure 2). Cerno’s MassWorks software elegantly addresses this problem by not only calibrating the mass position of the peak, but by also calibrating the line-shape to a mathematically defined function. This allows extremely accurate comparisons to be made between measured and theoretical spectra with Spectral Accuracy values capable of uniquely identifying an unknown ion formula (Figure 3).

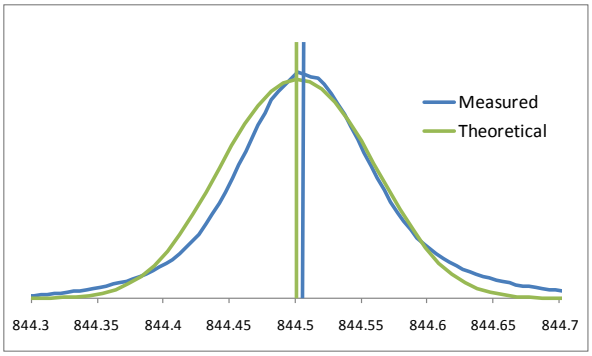

Figure 1. Mass Accuracy is a measure of the difference between the measured mass value and the theoretical value for a given ion formula. Uncertainty of the true mass value usually prohibits unambiguous formula ID.

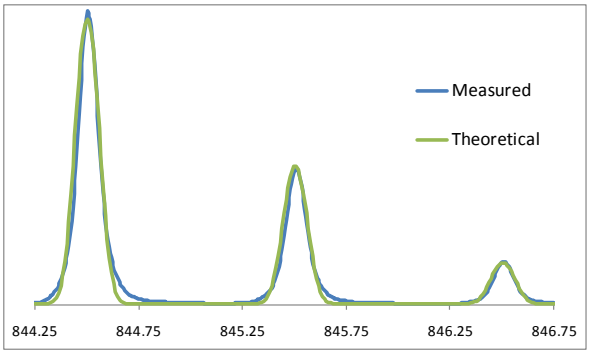

Figure 2. Spectral Accuracy is a measure of the similarity between the measured isotope pattern (ion spectrum) and the theoretical ion spectrum. Without proper line-shape calibration, Spectral Accuracy values are of limited use in identifying the unknown formula.

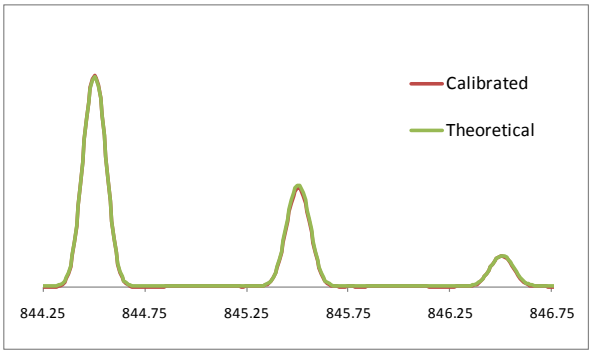

Figure 3. MassWorks software calibrates for spectral line-shape as well as for mass position allowing highly accurate comparisons between calibrated and theoretical spectra with Spectral Accuracy as great as 99.9%. This allows for enhanced formula ID for high resolution instruments, and, when combined with the improved mass accuracy of the MassWorks calibration, enables formula ID on unit resolution GC and LC/MS quadrupole instruments.