NIST 14 – MS/MS Notes

[Excerpt from User's Guide: NIST Standard Reference Database 1A; NIST/EPA/NIH Mass Spectral Library (NIST 14) and NIST Mass Spectral Search Program (Version 2.2) June 2014; The NIST Mass Spectrometry Data Center, Stephen E. Stein, Director]

The NIST MS/MS Library

MS/MS spectra, along with an increased number of fields relevant to MS/MS data, are provided in a set of files separate from the Main and Replicates data files that comprise the Library of EI spectra. The MS/MS spectra have been provided by contributors, measured at NIST, and extracted from the literature. The preparation of the MS/MS Library revealed that at sufficiently high signal-to-noise measurement conditions, modern instruments are capable of providing very reproducible "library-searchable" spectra. Although collision energy is an important variable in Q-tof and related instruments, spectra vary in an understandable way depending on the compound and instrument type as well as collision-energy conditions. Energy-dependent variation is accounted for by including spectra for most compounds over a wide range of collision energies, ranging from slight to complete dissociation of the precursor ion.

The MS/MS spectra in NIST 14 are provided in two libraries, nist_msms and nist_msms2. The nist_msms library is described in detail below. The second MS/MS library, nist_msms2, contains spectra of compounds that do not have chemical structures displayed. They mostly are commercially available peptides. Spectra from the nist_msms2 library are not displayed in the **MSMS** tab. Otherwise, the format of the two libraries is similar.

The **MSMS** tab allows access to the spectra in the nist_msms library. The first time this tab is selected, the three panes of the display are blank with the exception of a single entry in the **ion list** pane, which is on the left of the tab's display. This entry is the **MS/MS Library**. There is a box on the left that has a plus sign . Placing the Mouse pointer on this box and clicking expands to the first two levels (Positive Ions and Negative Ions). There are *plus boxes* next to both the Positive Ion and the Negative Ion. Clicking on one of these *plus boxes* results in the display of the next level. This is a list of molecular weights of analytes for which a spectrum was obtained by MS/MS. Clicking on the *plus box* next to one of these molecular weight listings results in the display of a list of elemental compositions that will also have *plus boxes* next to them. Clicking on one of the elemental composition *plus boxes* will result in a display of a list of the compound names that have that elemental composition. In most cases, this is only a single compound. Clicking on the *plus box* next to the compound name will result in the display of a list of the spectra acquired under MS/MS conditions for this compound. If more than one spectrum was acquired, there is a separate entry for each spectrum. Clicking on the spectrum entry will result in displaying the spectrum information.

The listing of each spectrum begins with **MS2**.

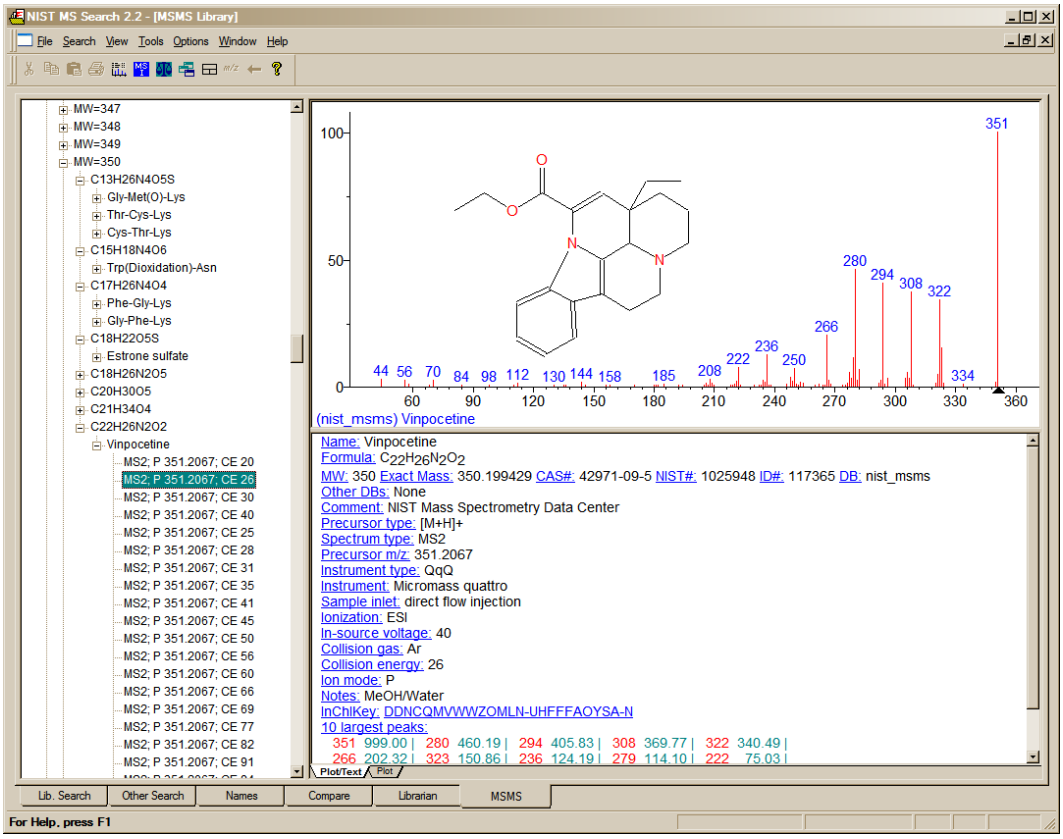

Figure 1. MSMS tab for data acquired using "triple quad".

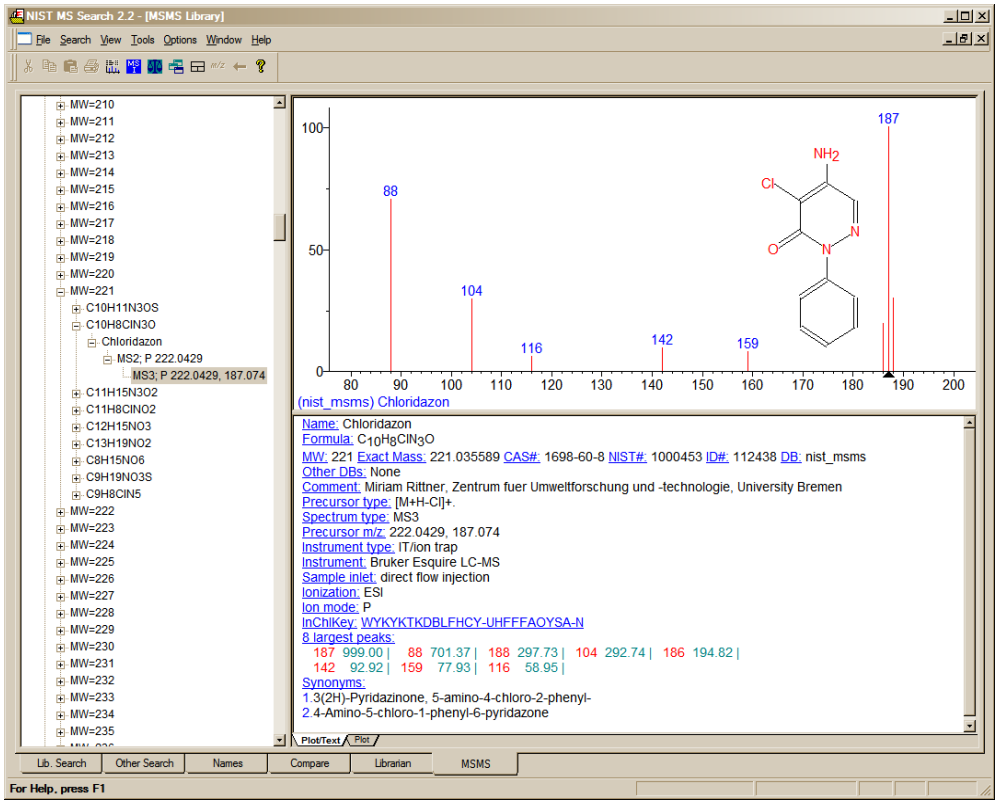

Figure 2. MSMS tab for data acquired using "ion trap MS^3".

For beam-type instruments (e.g., triple quadrupoles, HCD, and Q-tof instruments), the **MS2** designation refers to spectra generated by dissociation in a collision cell of a selected precursor ion. For ion trap instruments, the **MS2** designation refers to dissociation in the trap after following the isolation of the precursor ion.

In the case of data acquired using an ion trap mass spectrometer, the **MS2** may have a *plus box* next to it. Clicking on this *plus box* results in a subsequent spectrum listed as **MS3**, which may also have a *plus box*. Selection of the *plus box* next to the **MS3** spectrum can result in an **MS4** spectrum, which is obtained by the isolation of a product ion as a precursor ion for a subsequent iteration of MS/MS.

Clicking on the **MS3** results in the display of the spectrum as seen in Figure 2. The **MS2** designation is followed with the precursor ion *m/z* value and the collision energy for beam-type instruments (Figure 1).

As can be seen from Figure 1 and Figure 2, there is a great deal more information provided in a text format for the spectra in the nist_msms library.

The MS/MS Library can be searched with any of the **Other Searches** or the **Incremental Name Search**. All that is necessary is to include the nist_msms library in the **Include Libs** column of the **Search** dialog box for the **Other Searches** or as the single library to be searched in the **Incremental Name Search**. The **Library Spectrum Search** and **Structure Similarity Search** are also applicable. However, the user must understand that MS/MS spectra in general are different from EI spectra as well as the fact that structures in the MS/MS Library refer to the neutral form of the precursor ions.

If the nist_msms library is not present, the **MSMS** tab is not displayed.

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