

New Features in NIST 08 and the MS Search Program

Version 2.0f of the MS Search Program

The basic software of the NIST MS Search Program for Windows **Version 2.0** is unchanged. A number of new features have been added.

- A new spectrum search for MS/MS spectra in MS/MS libraries, including the NIST MS/MS library.
- Five new Constraints have been added; Tags in Comment, Peptide Sequences, Peptide Mobile Protons, Peptide Charge, and Peptide Number of Residues. Tags in comment, for example, allows searching for the name of the contributor in the EI library.
- A search for information in the Contributor/Comment field which may be particularly useful for certain types of information relevant to MS/MS.
- Flexibility has been added to searches using a Name Fragment in Constraints. It is now possible to specify the presence or absence of any arbitrary part or parts of a name.
- The program does not use or require the installation of NIST fonts.

NIST 08

The 2008 version of the NIST/EPA/NIH Mass Spectral Library (NIST 08) contains four libraries and a database of retention index values. There are three EI libraries, mainlib, replib, and nist_salts. Together they contain 220,460 spectra of 192,108 different chemical compounds. This is an increase of about 29,600 compounds (~18%). The EI Salt library contains 717 spectra of 672 compounds of low volatility not expected to be measurable by GC/MS. Limited annotation has been added indicating if a monomeric molecular ion is observed and the identities of polymeric species. The MS/MS library contains 14,802 spectra of 3,898 positive ions and 1,410 negative ions. The features of this library are described in more detail below.

Contents of the NIST/EPA/NIH (NIST 08) Mass Spectral Library		
Library Name	Library Description	Library Contents
mainlib	Main EI MS library	191,436 spectra
replib	Replicate spectra	28,307 spectra
nist_salts	EI Salt Library	717 spectra
nist_msms	MS/MS Library	14,802 spectra of 3,898 positive and 1,410 negative ions
nist_ri	Retention Index Library	293,247 Kovats RI values for 44,008 compounds

Retention Indices

One of the items in the Text Info tab under Properties is **Retention Indices**. Having a check in the box next to **Retention Index** will cause the experimental data for the retention index to be displayed with the spectra. The number of retention indices displayed is controlled by selecting All or First and entering the number of values to be displayed. The default is to display the first two values. Displaying all values will cause the display to be rather slow in cases where there are a very large number of literature values. There are literature data for 21,940 compounds that are in the **mainlib** Library, and a total of 237,206 annotated Kovats Retention Index values, including literature source and measurement conditions. In addition, for many compounds in the database an **Estimated Kovats Retention Index (RI)** will be displayed based on the structure associated with the spectrum. These values are reported in index units (**iu**) with a confidence interval, e.g. "Confidence interval (Ketones): 57(50%) 246(95%) iu" reported for acetone. This means that there is a 50% probability true value falls within 57 iu

of the estimated value and 95% of the time the true value falls within 246 u of the estimated value. The analysis is based on error measurements of all the data for the class of the compound given; i.e. in this example, ketones. Provided the text pane view has been set to display Retention Indices, these data will be displayed with the results of any search.

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. In view of the relatively small size of the library, it is intended primarily to serve as a “starter set”. It also documents spectrum variations between instrument classes under different conditions. 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 can be an important variable, spectra vary in an understandable way depending on the compound and instrument type as well as collision-energy conditions.

The **MSMS** tab allows access to the spectra in the NIST_MSMS Library. Each 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 Positive Ion and 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. Click on one of the elemental composition check 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.

The listing of each spectrum begins with **ms1** or **ms2**. An **ms1** spectrum is composed of ions arising directly from the ion source region. They can arise from electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI). These ions are not subjected to collision-induced dissociation after exiting the ion source.

For beam-type instruments (e.g., triple quadrupoles 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 **ms1** may have a plus box next to it. Clicking on this plus box results in a subsequent spectrum listed as **ms2**, which may also have a plus box. Selection of the plus box next to the **ms2** spectrum can result in an **ms3** 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 **ms2** results in the display of the spectrum as seen in Figure 1. The **ms2** designation is followed with the precursor ion *m/z* value and the collision energy for beam-type instruments.

As can be seen from Figure 1 and Figure 2 on the following page, 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 Unknown 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.

In absence of **nist_msms** library, the MSMS tab is not displayed.

