What's New in MS Search Program

The following features were added to the current version 4.0 (2026), distributed with NIST 26, compared to version 3.0 (2023).

1. Hybrid Search now reports the most probable chemical formula difference between query and each library compound (dForm) along with the relative likelihood of each dForm.
2. Hybrid Search (EI only) Kovats retention index (semi-standard non-polar columns) differences between the query compound and each library compound is estimated (dRI) as well as the difference in observed and estimated retention index values (ddRI).
3. Retention index (EI only) differences and their resulting score corrections are computed for each library hit, using AIRI estimates for library compounds without experimental values.
4. Chromatogram window - Using AMDIS for GC/MS analysis and NIST mspepsearch for LC/MS-MS Tandem analysis, full chromatograms are shown in a new Tab display along with a complete list of the highest scoring library identifications. From this list, individual query spectra can be selected, compared to the best matching library spectrum and employed for any of the multiple NIST library searches, including the Hybrid Search for compounds not confidently identified in the hit list. Multiple controls are available to filter identifications to focus on most relevant results. Each hit is identified in the chromatographic display and provided with a range of relevant data.
5. Chromatogram Analysis values include Purity, multiple score types, signal to noise, relative abundance, and agreement with isotope abundances (Tandem only).
6. XIC analysis (Tandem/Chromatogram) allows examination of the MS1 precursor m/z and retention region in the vicinity of each MS2 fragmentation scan.
7. The chemical structure of the current hit may be displayed in a separate, moveable window by selecting View/Show Structure in the top menu.
8. Multiple features were added to the right mouse button for selected spectra, including:

   o Switching to the matching name entry of the library identification in the Name tab of the current library

   o Exporting selected identifications to an Excel compatible .tsv file or to the Windows Clipboard

9. Simplified Properties and other Control boxes and their dependence on search type.
10. Penalize rare compounds added for scoring based on new algorithm

The following features were added to the version 3.0 (2023), distributed with NIST 23 as compared to ver. 2.4, distributed with NIST 20.

- Major Spectrum Type choice (EI, Tandem, Peptide, All) helps to suppress display of search parameters most probably not used.

- Name search sorting has been increased from 16 to 249 characters; the list of names has been split into two panes: compound list in the upper pane and spectrum list in the lower pane. All spectra derived from a selected compound are shown in the spectrum list (EI: replicate, derivatives, stereoisomers; Tandem: energy, instrument, fragmentation type).

- A list of 'Other Databases' (compound references) for each compound has been significantly extended.

- Added a new search method - Partial Spectrum Search - for searching with abbreviated spectra.
- All retention indices are displayed in the EI hit list. They used for EI search with RI match factor correction. If experimental data is not available for a compound, a reliable AI predicted value is used in its place.
- Hovering a mouse pointer around a peak in a spectrum plot displays peak annotation.

Changes

- Term "In-source/EI with accurate ion m/z" replaced with "HiRes No Precursor"
- "Penalize rare compounds" EI library search option has been retired.
- PubChem search has been replaced with Google search.
- Major mass spectral text file extension has been changed from .MSP to .MSPEC. Extension .MSP is still recognized.

The following features were added to the version 2.4 (2020), distributed with NIST 20 as compared to ver. 2.3, distributed with NIST 17.

For Tandem Spectrum Searching

- The following greatly aid the examination of hit lists containing many spectra that may arise from the same compound (using any type of search):
  - New columns in hit lists (selectable from Properties menu): Precursor Ion, Instrument, Energy;
  - Filter button  (refine hit list using Instrument and Precursor Ion Type settings);
  - Constraints have been enhanced to correspond to Filter button.
- When searching with high mass accuracy spectra, the NIST low resolution library (lr_msms_nist) is searched using wide m/z tolerances (unit mass resolution)
  - This ensures that compounds with only low resolution spectra can be found when searching with high mass accuracy spectra.
  - If searching with low resolution spectra, simply specify a wide m/z product ion tolerance for searching any library.

GC Retention Index

- New artificial intelligence predicted values roughly twice as accurate as earlier version
- RI columns optionally shown in hit lists for any EI search.

In the Librarian tab, a replace button was added. This replaces a spectrum in a selected library without changing its ID number.

The MS Interpreter included with NIST 2020 has been greatly improved from prior versions. It

processes EI and positive and negative ion tandem spectra of any mass accuracy.

The following features were added to the version 2.3 (2017), distributed with NIST 17 as compared to ver. 2.2, distributed with NIST 14.

HiRes MS/MS Hybrid Search

EI Hybrid search

presearch for EI Loss search

Types of Any Peak search: HiRes peak and HiRes loss

InChIKey presearch for all Library spectrum searches (finds all spectra, which have the same first InChIKey segment as the search spectrum, and compares them to the search spectrum)

Indexing old libraries for EI Hybrid and EI Loss, HiRes Any peaks Peak and Loss searches, InChIKey presearch (to index an MS/MS library for HiRes MS/MS Hybrid search, rebuild it with the library converter Lib2NIST.)

MS/MS Precursor m/z search

Precursor type constraint

Spectrum polarity filter

New Library Search output columns selection control for all Library spectrum searches.

Updating list of libraries may be performed without exiting MS Search (Tools menu)

Movable column headers in Hit Lists and Spec List and a new column selection method located in Properties of a list, Items to Display.

The following features were added to the version 2.2, distributed with NIST 14 as compared to ver. 2.0g, distributed with NIST 11 or with NIST 12 MS/MS library.

Using Retention Index in library searching: RI deviation of a hit from the search spectrum is used to penalize the Match Factor.

Indexing older user libraries to use saved in them RI values for library searching

Displaying relevant RI values in the hit list

New definitions of derivatives are used for finding replicate spectra

Displaying derivative precursor in the Lib. Search hit list

Displaying additional MS/MS information in hit lists

Editing accurate peak m/z, intensities, peak annotations and compound RI in the built-in mass spectrum editor

All small molecule mass spectra in NIST libraries have InChIKeys linked to PubChem. These InChIKeys may also be used for searching compound information on the Web or for exact structure search in libraries.

Importing and displaying Glycan structures in KCF format; adding them to mass spectra in a user library

In-source/EI with accurate ion m/z spectra [since MS Search v.3.0 called HiRes No Precursor spectra] - High resolution mass spectra

- Import of 'in-source' tandem spectra, or EI with accurate ion m/z spectra, which do not include a defined m/z of the precursor ion. To import these spectra, select "in-source / EI (accurate m/z)" in Spectrum Import Options.
- In-source/EI with accurate ion m/z spectra have accurate ion peak m/z and intensities. The accuracy is set in Spectrum Import Options.
- In-source/EI with accurate ion m/z spectra may be searched in In-source/EI with accurate ion m/z and/or MS/MS library with the new In-source HiRes search (ion peak m/z tolerance down to 0.015 ppm or $6x10^{-5}$ m/z units), Similarity Simple, Identity Normal or MS/MS Presearch OFF search options. For this purpose, adding Reverse Search option may be useful.
- In-source/EI with accurate ion m/z spectra may be added to a user library. Currently, in-source/EI with accurate ion m/z spectra added with NIST MS Search to a user library may be searched with In-source HiRes search only with Presearch OFF option. Rebuild the library with Lib2NIST to get in-source HiRes search benefits.

A number of new features have been added to the version distributed with the 2012 release of NIST MS/MS Libraries.

A new MS/MS search for small molecules

- Improved ability to identify compounds with a few dominant peaks – a common situation for Tandem MS.
- More robust scoring for spectra acquired on imperfectly-tuned instruments

New Mass Spectrum Import Options

- Control the number of decimal places in the input m/z
- Set peak intensity threshold
- Set Prepend/Overwrite/Ask automatic mass spectrum import option
- Import in-source or EI spectrum with accurate ion peak m/z and intensities.
- Import MS/MS and in-source spectra from JCAMP files (October 2012, nistms32.dll version 2.1.5.3 or later)

Note that the following features were added to the previous version (distributed with NIST 11, version 2.0g)

A new Exact Mass Search and similar to it Exact Mass Constraint allow searching for an exact mass of a precursor using its mass or formula or m/z of the precursor ion. This search and constraint take into account the presence or absence of an electron, adducts or losses; accepts uncertainty in ppm or

millimass units; and allows searching for isotopic or monoisotopic peaks.

Ability to use accurate mass to search exact fragment ion mass values in NIST libraries mainlib, replib, and nist_msms using Exact Mass in the Any Peaks Search.

Display of the exact mass with any spectrum that has an associated chemical formula.

Manage and search as many as 127 separate MS libraries instead of 16, which was the limit in previous versions.

Optional display of columns in Hit Lists containing the number of synonyms and the number of other databases in which the hit appears. The hit list can be sorted according to the values in these columns.

Maximum number of spectra in a database has been increased from 786,420 to 1,048,560.

Full compatibility with most recent NIST Peptide MS/MS libraries.

Copy selected lines from Hit List or Spec List into Windows Clipboard as tab-delimited Unicode text; this may be conveniently pasted into Excel.

Spectra in the MSP text format can be imported from the Windows clipboard into the Spec List via a Right Mouse button (RMB) menu option.

Searching for words in mass spectrum text information window (use context menu).

Optional exclusion of Homologues from the results of Structure Similarity search.

Import spectra from mzXML and mzData files.

Multiple CAS Registry numbers for a spectrum. A small fraction of spectra in NIST 14 has more than one CAS r.n. Each CAS r.n. may be found in the CAS Number search.

Tags for searching in Spectrum Text Info have been added to Tags in Comment constraint

New MS/MS Instrument Type Constraint

An alternative peak matching method to improve the reliability of the score when searching noisy MS/MS spectra.

When a Tag from the "Comment" field is displayed separately, its display in the "Comment" field is suppressed.