Wiley Spectral Webinar
Part V: Creating and Sharing User EI and MS/MS Libraries
12/27/20

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- *Retired* Research Fellow, Eastman Chem. Co.*
- *42 years experience unknown identification*
- *Now Consultant, MS Interpretation Services*
- *Specialties[1] EI GC-MS, LC-MS/MS, Chemical Ionization,[7] Accurate Mass, Derivatization,[8,9] MS library management, SciFinder,[10] Chemspider,[10] Surfactant ID,[11] NMR, GC-IR, organic synthesis, matrix ionization effects,[21] etc.*

Eastman Chemical Company, Main Site, Kingsport, TN
50 Manufacturing Sites Worldwide, ~14,500 Employees

>50 Mass Specs Networked
Worldwide

* https://en.wikipedia.org/wiki/Eastman_Chemical_Company

Wiley Webinar Series on Effective Use of Mass Spectral Libraries

Part I: Spectral Searches[2] with NIST MS Search
Part II: Structure Searches[2] with NIST MS Search and Using MS Interpreter[2,13-15]
Part III: AMDIS[3,4,12](NIST) for Processing EI Mass Spectral Data Files
Part IV: Advanced NIST Hybrid Search[16-19,22] of EI and MS/MS Spectra
Part V: Creating and Sharing[5] User EI and MS/MS Libraries

Note:[20] Handouts for ***All*** Sessions ***Now Online***!
Google Search "little mass spec and sailing"

Table of Contents

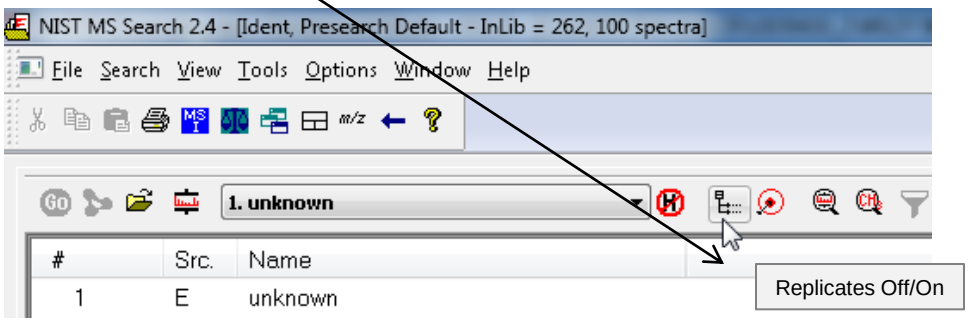
Part V: Creating and Sharing User EI and MS/MS Libraries[5]

Webinar Topics:

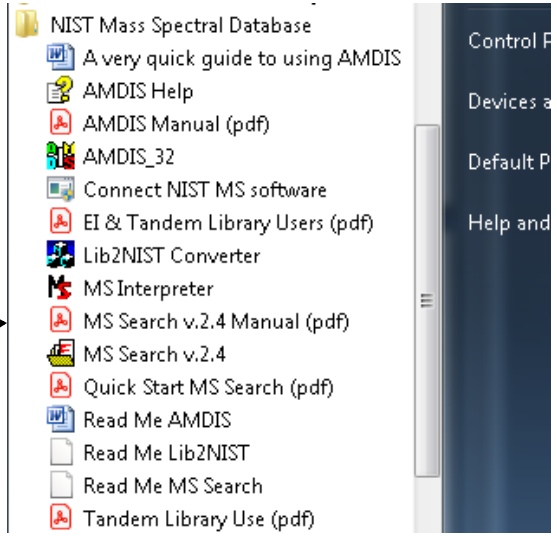
-Adding fields in preparation to add spectrum
-Special Tags in User and Wiley Libraries[23]
-Checking quality of spectrum
-Adding spectrum to current on new user library
-Updating indices for structure, InChIKey, etc.
-Sharing user libraries on corporate networks[5]

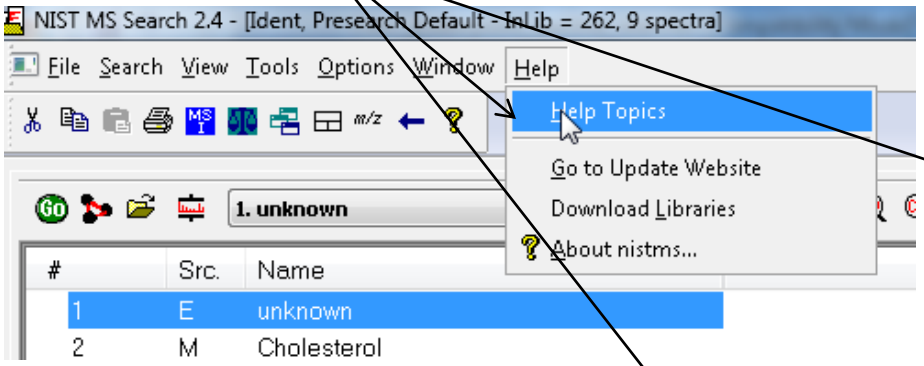
Help Files for NIST Search

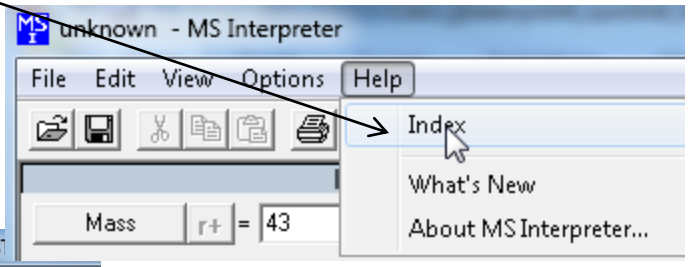
-"Hover" over Program Icon with mouse and function description displayed

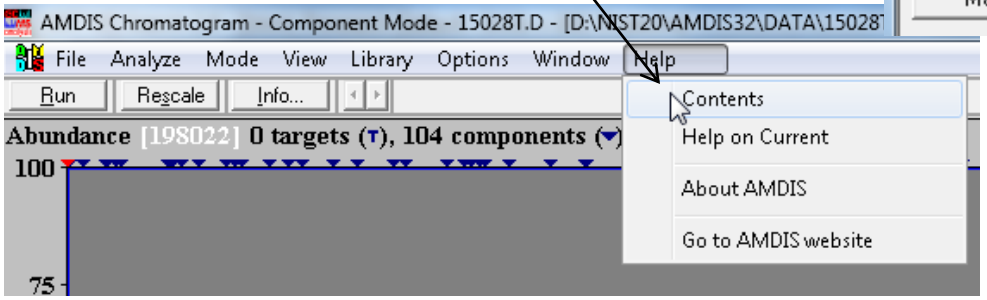


-Detailed documentation for NIST Search[2] and AMDIS[3,4,12]
-MS Interpreter included in NIST manual[2] and in posters[13-15]
-Windows Program Group
-"In program" assistance for all three programs





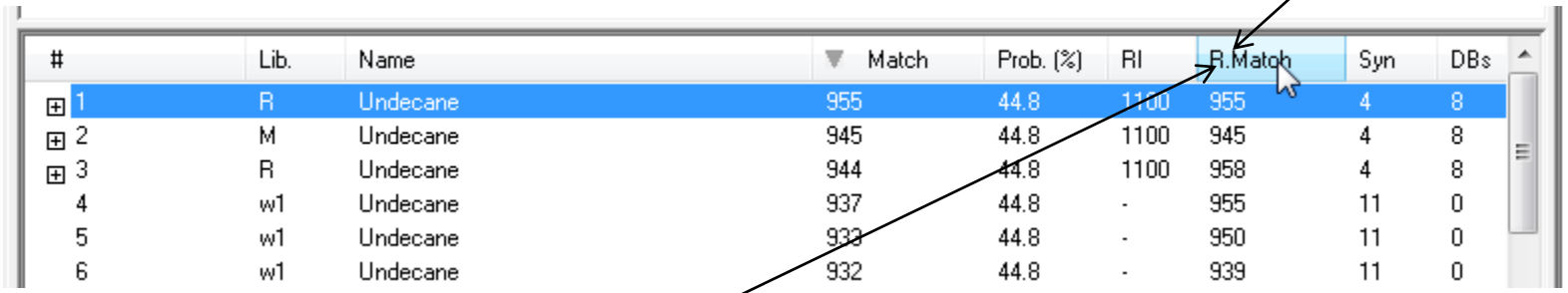




NIST Software in General is "Windows Compliant"

-***left click (LMB)*** to select an item, ***double LMB*** on that item to perform operation
-***right click (RMB)*** in area or item to see operations that can be performed or to change properties of window
-***LMB*** on first item and last item to select group ***while*** holding ***shift key***
-***LMB*** to select/deselect individual items ***while*** holding ***Ctrl button***
-use up and down arrows ***on keyboard*** to step between entries
-some NIST windows such as librarian have no delete button to delete ions, ***must*** use delete key on keyboard!
-***control a*** (select all), ***control x*** (delete selected), ***control c*** (copy); ***control v*** (paste)
-***control k*** copies entries into windows in tab-separated text format, e.g., ***paste*** into Excel
-F1 MS Search help
-F9 send spectrum to MS Interpreter
-***LMB*** and ***zoom*** mass spectral windows, ***RMB*** then ***LMB*** to ***zoom out***

Tip 3: ***LMB*** and **drag** to rearrange order of column headers



#	Lib.	Name	Match	Prob. (%)	RI	R.Match	Syn	DBs
1	R	Undecane	955	44.8	1100	955	4	8
2	M	Undecane	945	44.8	1100	945	4	8
3	R	Undecane	944	44.8	1100	958	4	8
4	w1	Undecane	937	44.8	-	955	11	0
5	w1	Undecane	933	44.8	-	950	11	0
6	w1	Undecane	932	44.8	-	939	11	0

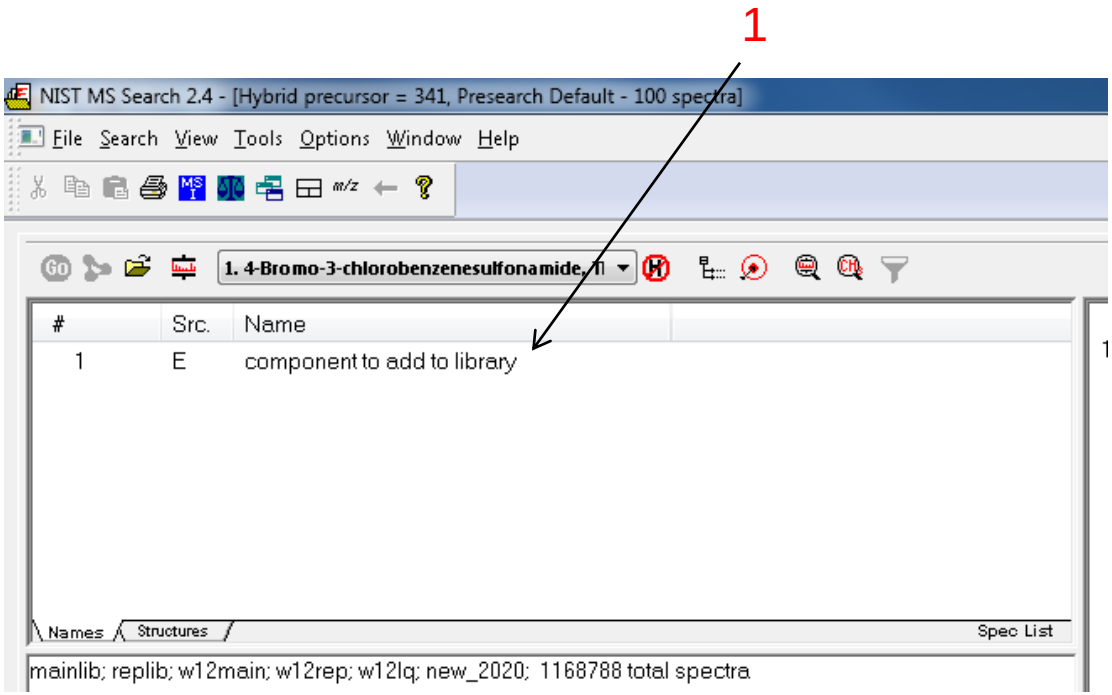
-***LMB*** on column of interest
-Can sort in lower value first or higher
-Will show use in mixtures in example later in presentation

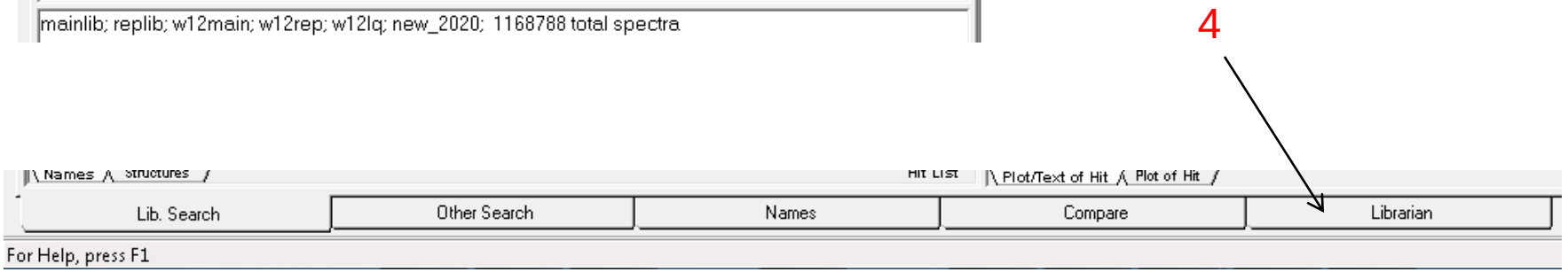
Tip 1: When reviewing search results, use up and down arrows on keyboard to quickly step through results!

Tip 2: When viewing structures in MS Interpreter, use left and right arrows on keyboard to quickly review results!

Creating a User Library Spectrum

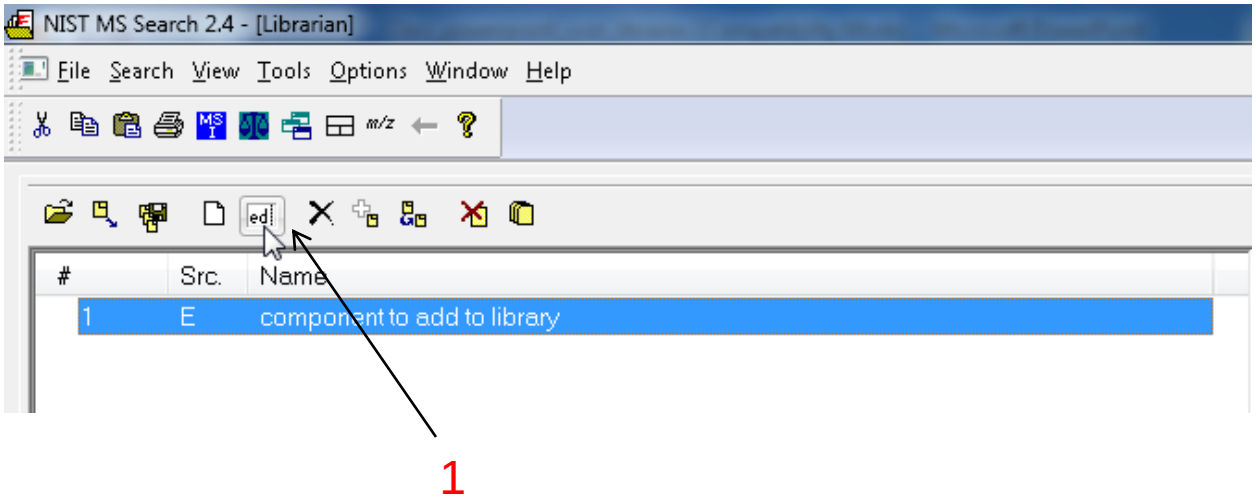
1) Import the spectrum from data processing application from manufacturer
2) Spectrum will be in the Spec List Window
3) Draw the structure in drawing program and copy into windows clipboard
4) **LMB** Librarian Tab





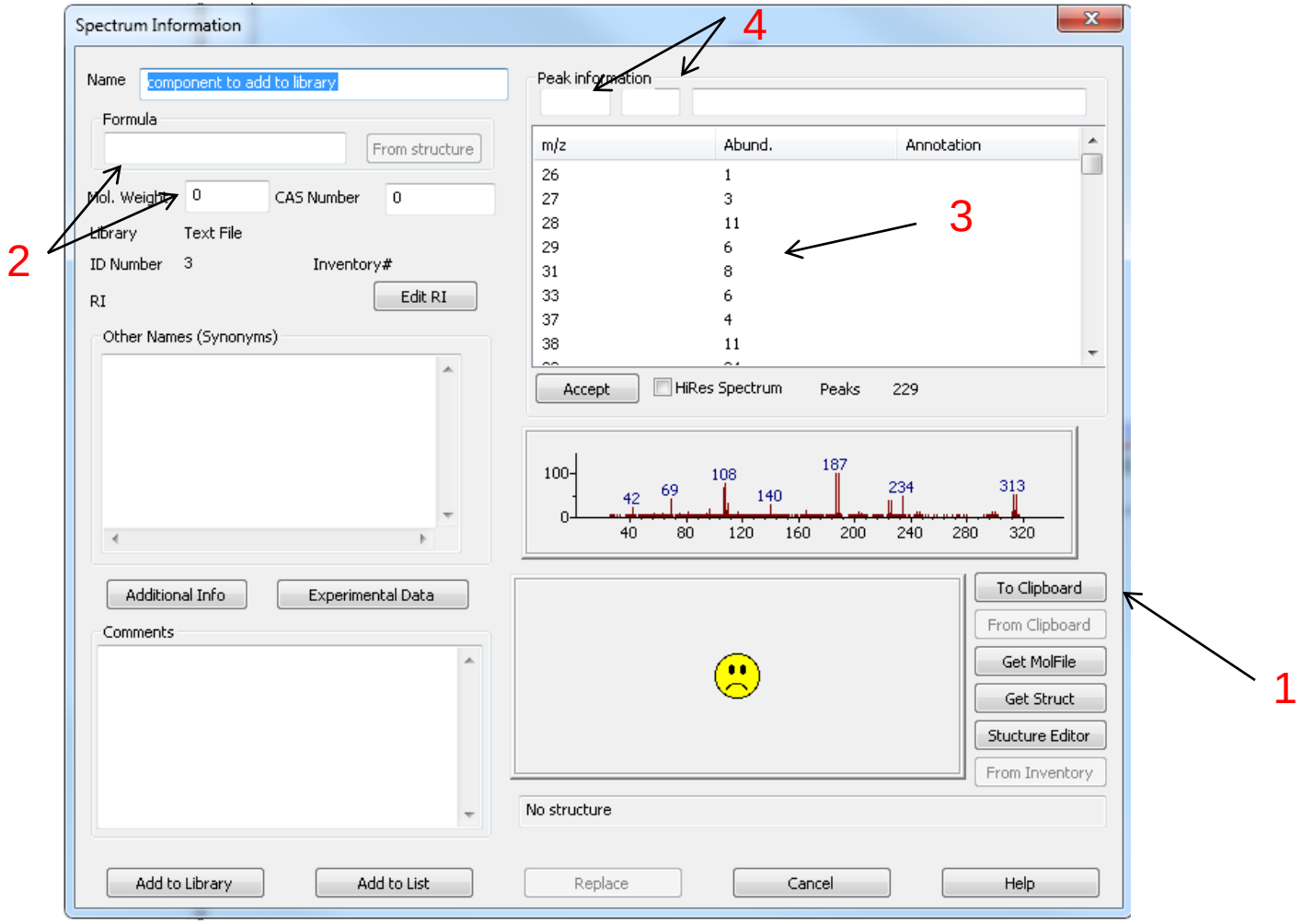
Creating a User Library Spectrum: Opening Edit Spectrum

1) **LMB** “ed” (edit spectrum) button on toolbar



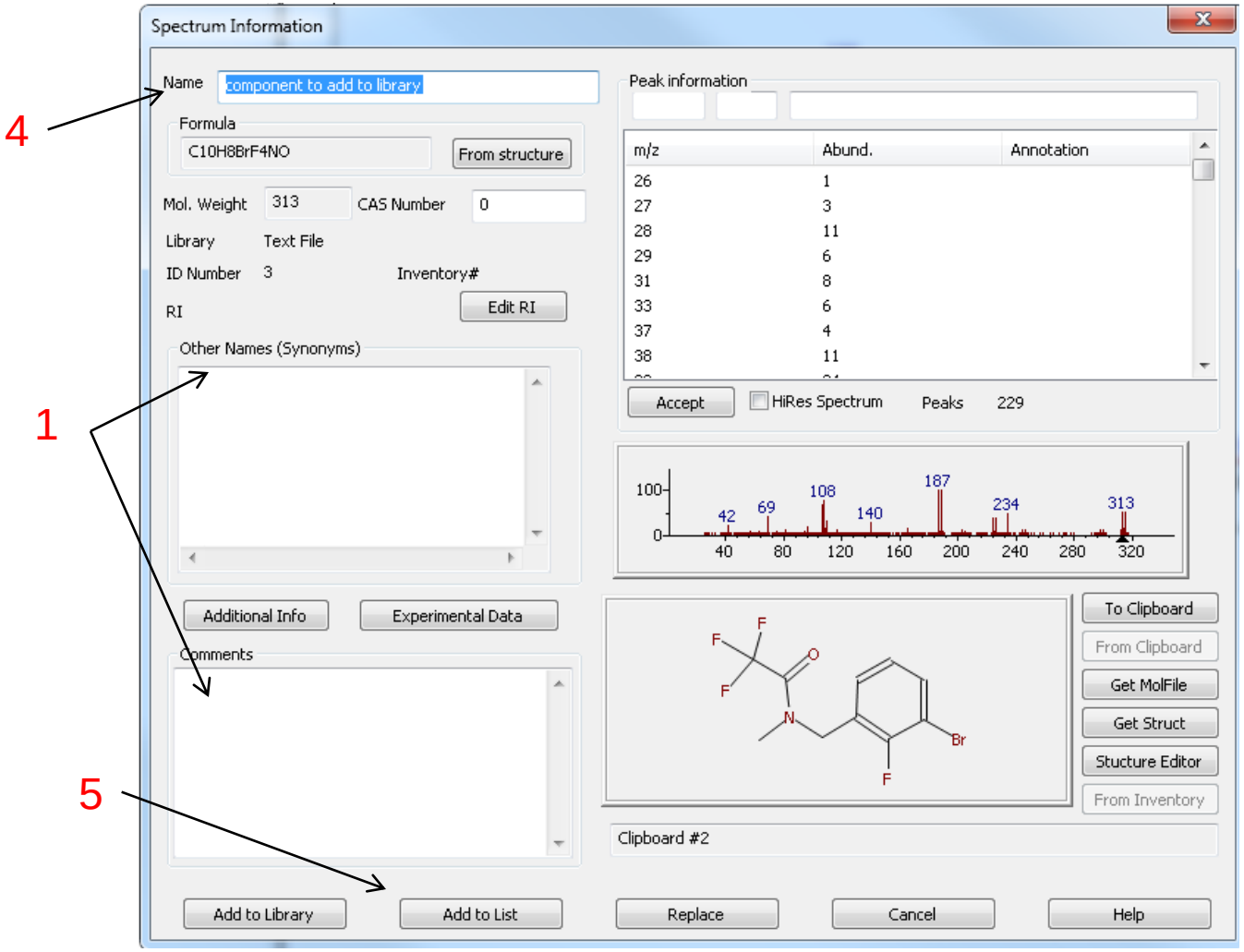
Creating a User Library Spectrum: Spectrum Information Window

1) ***LMB "***To Clipboard" to paste structure from windows clipboard into window
2) Mol. Weight and Formula will be automatically calculated
3) To delete peaks, **LMB** to select peaks and then must push ***Delete*** key on keyboard to delete, ***no*** button within NIST program
4) To add peaks, type in peak information, *m/z* and Abund., and accept; annotation not needed



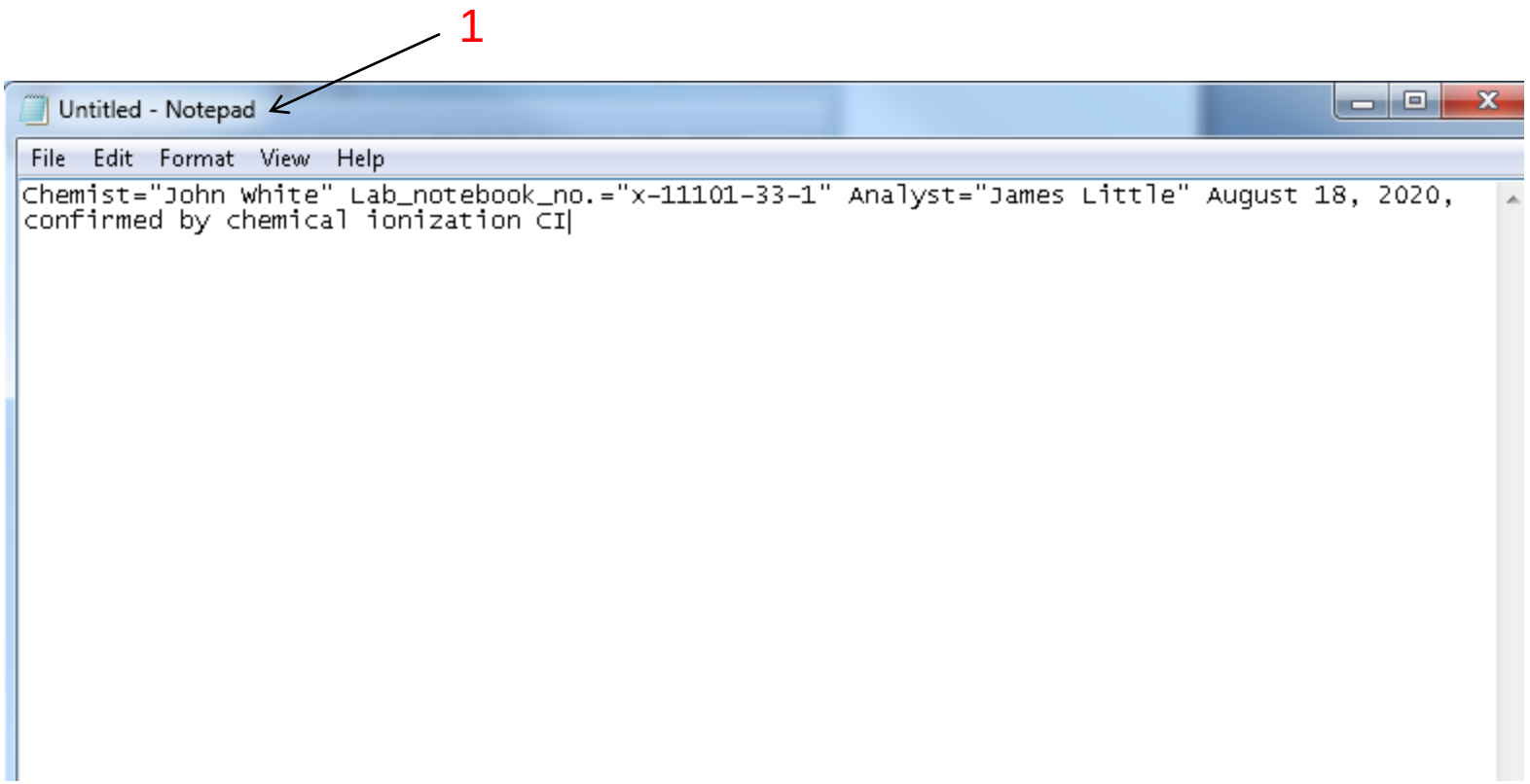
Creating a User Library: Adding Comments and Synonyms

1) Add **Comments** and **Other Names (Synonyms)** to Spectrum Information window
2) User can create Tags that will be displayed on a separate line for the library entry
3) Format for tag such as notebook number would be lab_notebook_no= "x-11101-33-1“
4) Generate name with drawing program and paste into field
5) After complete, select “Add to List”



Creating a User Library: Using Windows Notepad and Tags

1) ***Tip:*** If adding the same comment many times to different spectra, **create in Windows Notepad** and paste into Spectrum Information Window using **Ctrl V** on keyboard
2) My Tags below are chemist, lab_notebook_no., and Analyst
3) When ultimately displayed, they will show up as ***separate line items*** and are removed from the Comments display

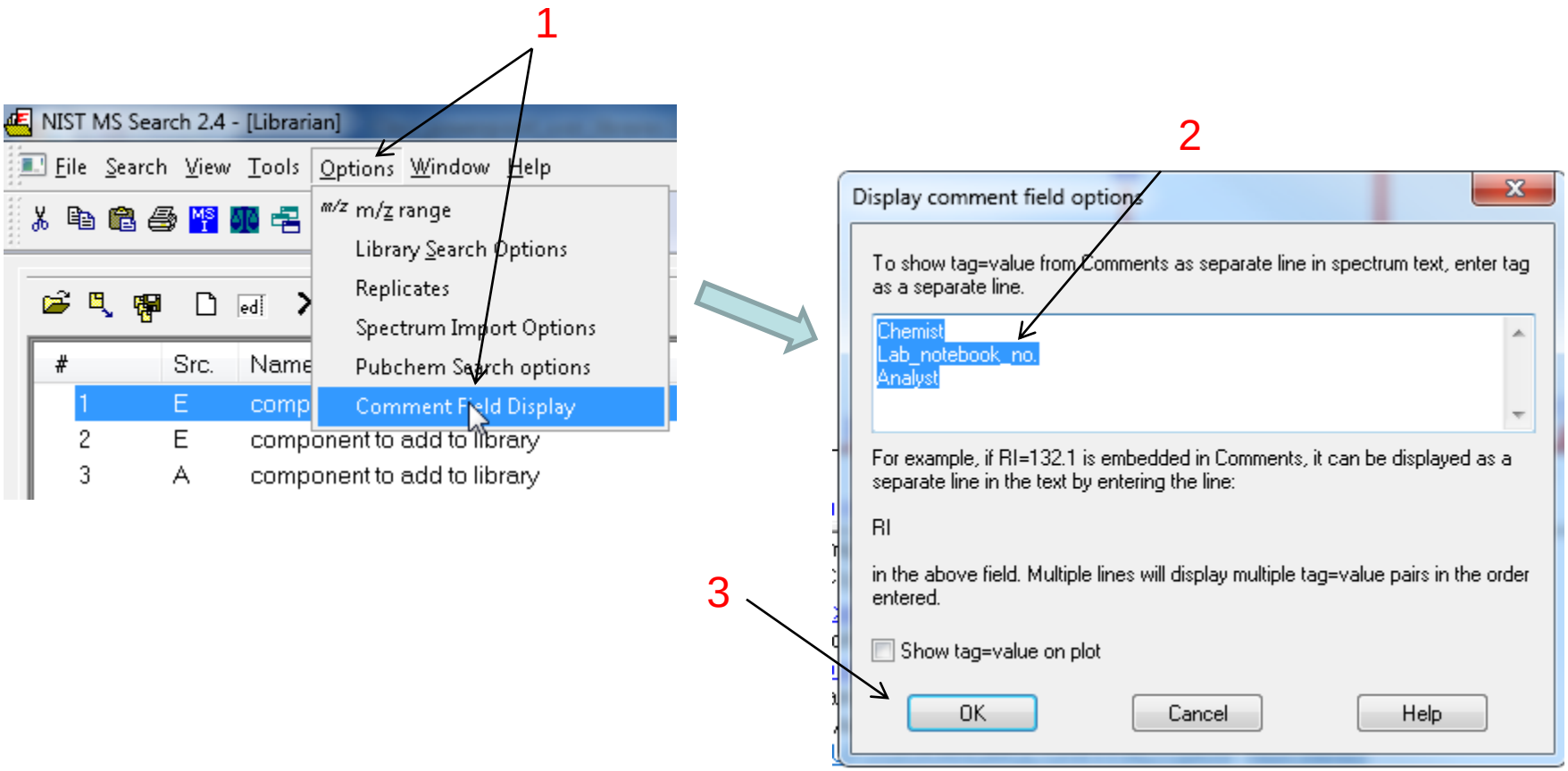


Creating a User Library: Comment Field Display with User Tags

1) ***LMB*** on Options, Comment Field Display

2) Add the ***user defined Tags*** Chemist, Lab_notebook_no., and Analyst to ***Display comment field options*** window

3) **LMB OK** to accept values



Creating a User Library: Comment Field Display Showing User Tags

1) User library comments ***without*** Tags
2) User library comments ***with*** Tags
3) The InChIKey and Estimated retention index automatically added by NIST program

1

Name: component to add to library
Formula: $C_{10}H_8BrF_4NO$
MW: 313 Exact Mass: 312.972538 ID#: 6 DB: Spec. Edit
Comment: Chemist="John White" Lab_notebook_no.="x-11101-33-1" Analyst="James Little" August 18, 2020, confirmed by chemical ionization CI
InChIKey: IUFOQIOKANQMQL-UHFFFAOYSA-N Non-stereo
Synonyms:
1.PM 2201 derivative
2.TFA derivative of PM 2201
3.Morrison's Amine, TFA derivative

Estimated non-polar retention index (n-alkane scale):
Value: 1422 iu
Confidence interval (Diverse functional groups): 89(50%) 382(95%) iu

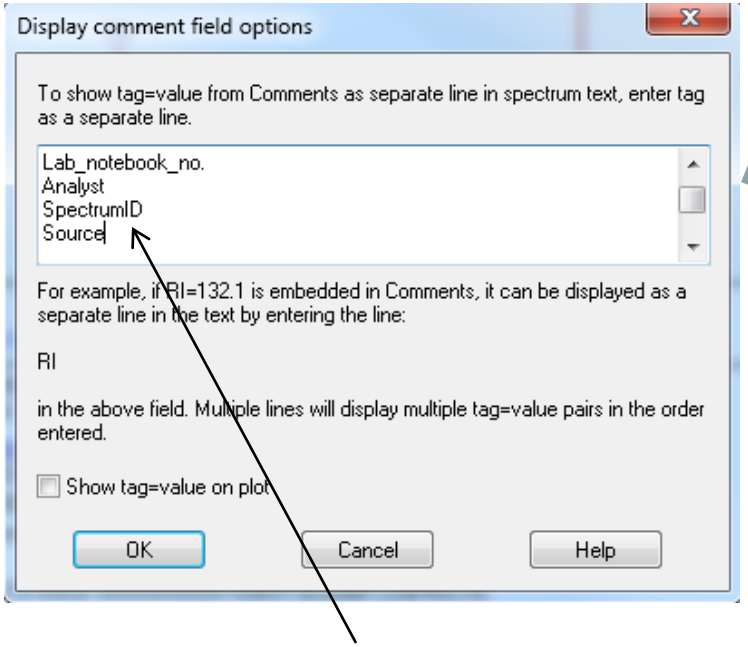
2

Name: component to add to library
Formula: $C_{10}H_8BrF_4NO$
MW: 313 Exact Mass: 312.972538 ID#: 6 DB: Spec. Edit
Chemist: John White
Lab_notebook_no.: x-11101-33-1
Analyst: James Little
Comment: August 18, 2020, confirmed by chemical ionization CI
InChIKey: IUFOQIOKANQMQL-UHFFFAOYSA-N Non-stereo
Synonyms:
1.PM 2201 derivative
2.TFA derivative of PM 2201
3.Morrison's Amine, TFA derivative

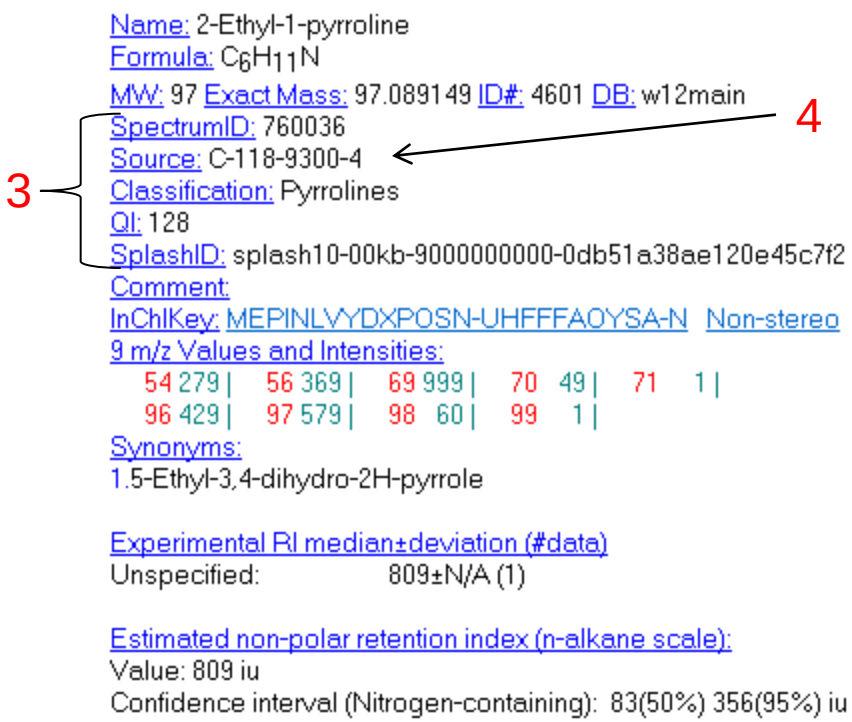
Estimated non-polar retention index (n-alkane scale):
Value: 1422 iu
Confidence interval (Diverse functional groups): 89(50%) 382(95%) iu

Tags[23] Included with Wiley Libraries

1) Tags included with Wiley Library Entries: SpectrumID, Source, Classification, QI, SplashID
2) Tags must be added ***by user*** *to* ***Display comment field options*** window
3) Tags properly displayed on typical Wiley library entry
4) Codes for Source of spectra found in Wiley User Manual[23]



2

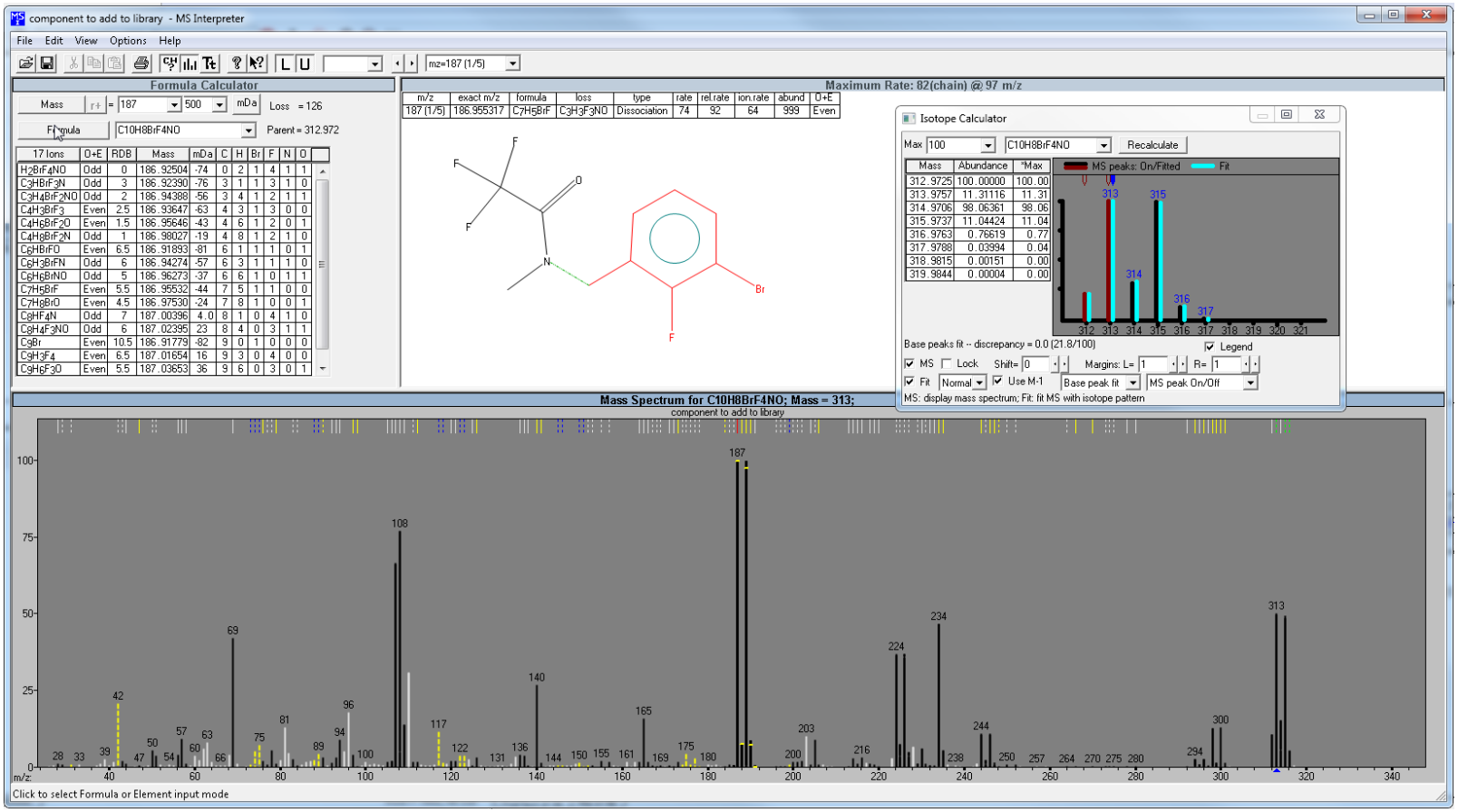


Note: "Contributor" tag is set by NIST to display as field in nist_msms2 library. One cannot see all the tags that I have added due to limited scrolling of window in above display.

Possible Quality Checks Before Adding Spectra to User Library

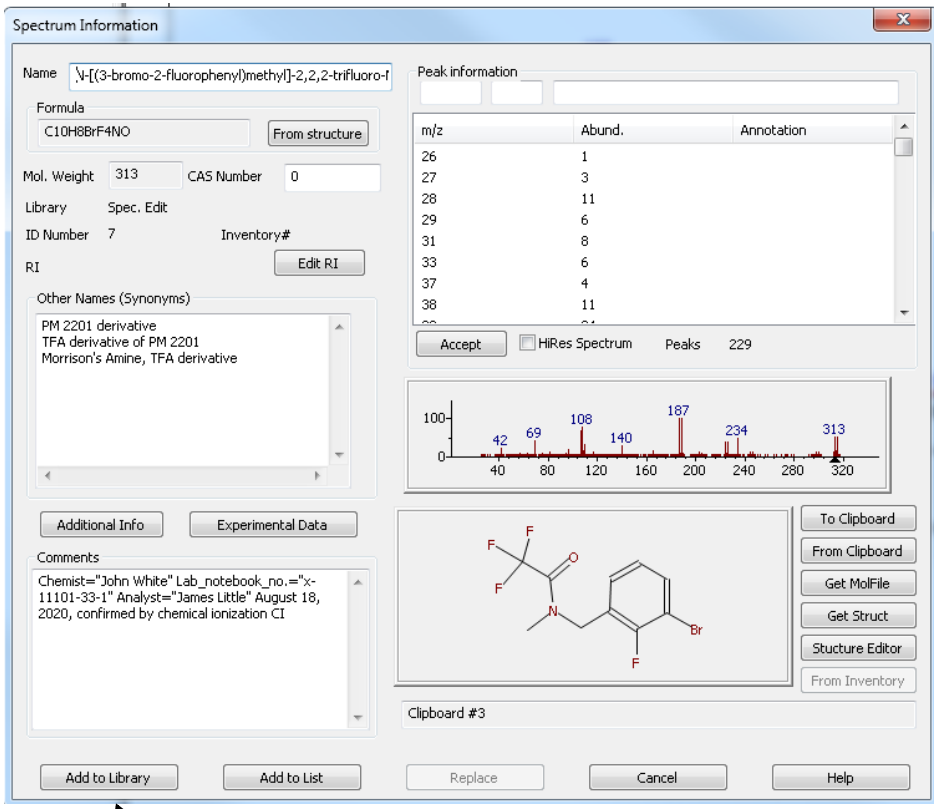
I ***always*** as a minimum do options 2 and 5

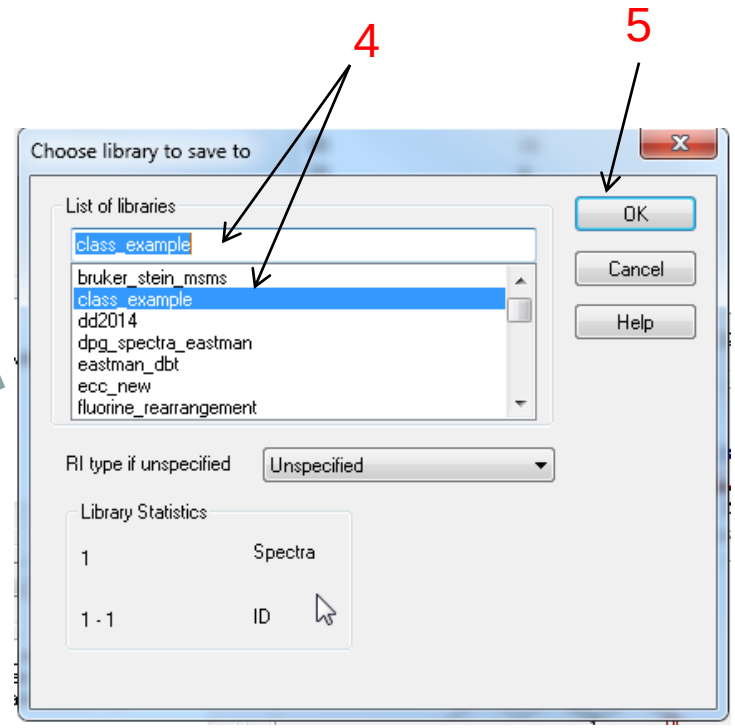
1) Use entry added to SpecList
2) Check to see if exact spectrum present using InChIKey exact structure search
3) Similarity structure search to find model compounds
4) ***Hybrid*** or ***Identity EI Normal*** library searches
5) Send to MS interpreter, see if major peaks "***in the black***," thus explained



Addition of Spectrum to User Library or Creating New Library

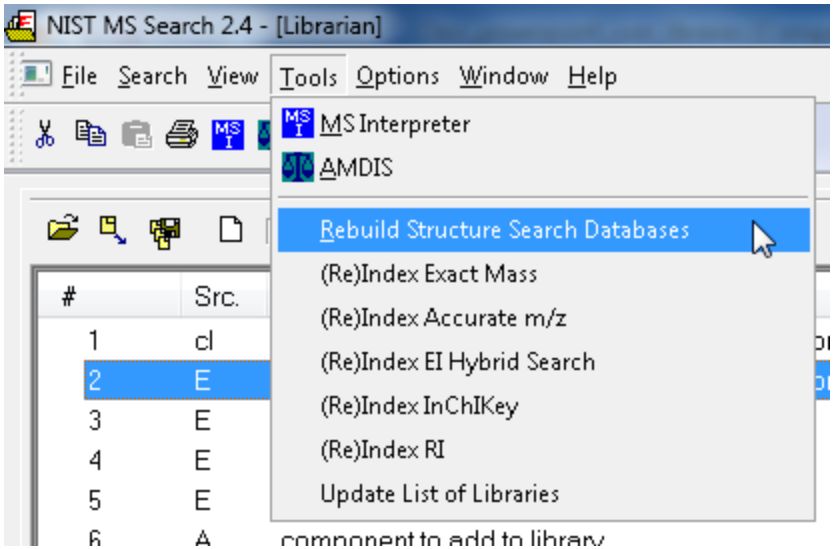
1) **LMB** to select entry to be added
2) **LMB** “ed” button in Librarian Tab to display Spectrum Information window
3) **LMB** “**Add to Library**”
4) Then add to a current user library, ***or*** if creating ***new*** library, type in its name
5) **LMB OK**





After Additions or Creating a New User Library
(Re)Index Indices for Structure, Hybrid Search, InChIKey for User Libraries

-This is ***critical step*** to create index files needed for proper searching
-***Only*** the “simple” library identity search will work ***without*** this step
-“Update of List of Libraries” makes newly created library appear in NIST program ***without*** first having to close program



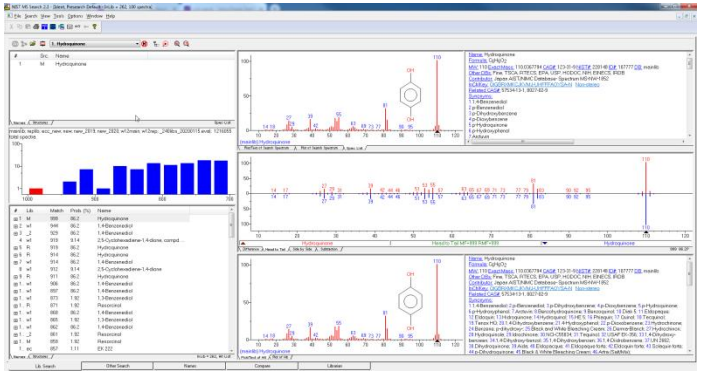
NIST User Libraries at Eastman Chemical Company

Started circa 2000

Eastman Chemical Co., Main Site, Kingsport, TN

50 Manufacturing Sites Worldwide, ~14,500 Employees

~50 GC/MS's, LC/MS's Networked *Worldwide*



NIST Search of EI and MS/MS User Libraries

~60,000 EI and ~3,000 MS/MS spectra/structures

Types of Components Added to Library

Anything a user would find useful, thus ***much more*** "diverse" than purchased commercial EI and MS/MS databases

Thus, ***users must realize*** Eastman database is an ***aid to identification*** and should be used accordingly.

- ***Most entries*** high quality with ***high confidence*** and exact structure

- Some entries will have "?" or "??" in front of name to show best educated guess

- Many components added with reference to common names for commercial plasticizers, lubricants, surfactants, antioxidants, UV stabilizers, polyesters, *etc.*

- Many entries added with reference to plant and R&D processes with unknown structure, but do include accurate mass and confirmation of MW by CI

Importance of Library Search and Comments in User Library

- GC-MS and LC-MS used in conjunction with TOC (total organic carbon) water monitors
- Quickly determine source of spills in manufacturing or breaches from water treatment plant
- Exact structure useful, but not necessary
- Comments in unknown spectrum used to determine process and pinpoint location

Google Aerial View of Kingsport Site
(~2.3 x 1.3 miles)

Software Essentials and Approach

No Expensive Hardware, Software, or Licenses!

- DOS files written by user[5] such as Get Lib, Send Lib, etc.
- DOS files interact with Lib2NIST utility supplied by NIST
- Process managed by inexpensive Windows scheduling program
- Individual User libraries ***automatically*** merged, distributed and archived ***daily***
- Additions and any new entries available to all users worldwide

Users

Standard Corporate Network and Servers

Get Lib

1) Users send files for help
2) MS Expert sends results in PDF files, adds new entries to library

1) Get Lib
2) Send Lib

Standard Computer automatically merges and archives corporate Library using DOS batch files

1) Merges user libraries
2) Sends merged library to server
3) Sends archive copy to server

MS expert

Excerpt of Typical DOS Script[5]

```
:    Get_Bat Batch File written by James Little at Eastman
:    Chemical Company, 1/14/2002 for Windows NT/2000
:    Another version needed for Windows 95/98!
:    Automatically closes
:    NIST search if open! Program copies/updates user
:    libraries ECC, NEW, TSCA, and PM.  Also updates
:    iontrap library if iontrap already exists on user system.
:    Not everyone wants or needs the iontrap library.

cls

@echo off

:    **Setting default directory for NIST98 Software and libraries
:    Change if different on your systems!  Removed in this file
:    because on Windows 95 systems gives "out of environment space"
:    errors!  Would be nice to include in future versions.  Would
:    need to use %nist% in the place of the path for NIST98 in all
:    copy commands!

:    set nist=c:\nist98

:    **Setting default location of server where libraries are stored
:    Change if needed!  Removed in this file because on Windows 95 systems
:    gives "out of environment space" errors!  Would be nice to include
:    in future versions.  Would need to use %server% in the place of the
:    path for server in all copy commands!

:    set server=\\ntresapp03\mspec2\NIST98\up_lib

@echo off
:
:    **This batch file needs closeprog.exe (program written by
:    Dmitrii Tchekhovskoi [Dmitrii.Tchekhovskoi@nist.gov].  The
:    program is expected to be found at c:\filestat\filestat.exe

if not exist c:\ms_utilities\closeprog.exe goto close_error
if exist c:\nist98\wiley6\alias.msd goto alias_error
if exist c:\nist98\wiley7\alias.msd goto alias_error

:    **Closing NIST program so libraries can be updated!

start /b /wait c:\ms_utilities\CLOSEPROG "NIST MS 2.0" "" 10000

:    **Copying libraries from server to user's library directory
cls
xcopy \\ntresapp03\mspec2\NIST98\up_lib\PM\*.* c:\nist98\pm\*.* /s /h /f /r /d
xcopy \\ntresapp03\mspec2\NIST98\up_lib\ecc\*.* c:\nist98\ecc\*.* /s /h /f /r /d
xcopy \\ntresapp03\mspec2\NIST98\up_lib\TSCA\*.* c:\nist98\TSCA\*.* /s /h /f /r /d
xcopy \\ntresapp03\mspec2\NIST98\up_lib\new\*.* c:\nist98\new\*.* /s /h /f /r /d
rem xcopy \\ntresapp03\mspec2\NIST98\up_lib\wiley6\*.* c:\nist98\wiley6\*.* /s /h /f /r /d

:    **Not everyone wants iontrap libraries, batch file checks
:    to see if installed on system, if it is, then it will copy

if not exist c:\nist98\iontrap\user.dbu goto skip_iontrap
xcopy \\ntresapp03\mspec2\NIST98\up_lib\iontrap\*.* c:\nist98\iontrap\*.* /s /h /f /r /d

:skip_iontrap

echo.
echo    **THIS PROCEDURE UPDATED YOUR USER LIBRARIES
echo.
echo    **If (0) files were copied, no library updates were needed
echo.
echo    **If you get tired of always having to close this window, edit
echo    Get_Lib.bat text file with Notepad program or Word and place
echo    a ":" before the "pause" command below.
echo.

:pause
```

Webinar References (*Internet Links*)

1. *James Little Mass Spectral Resource Website*
2. *NIST Search Software Detailed Manual*
3. *AMDIS Program for Data Processing Detailed Manual*
4. *Basic Instructions for Using AMDIS with NIST Search*
5. *Nightly Automatic Update of Users' Libraries*
6. *Using NIST Search from Instrument Manufacturers' Software*
7. *Chemical Ionization for MW Determination*
8. *Trimethylsilyl Derivatives for GC-MS*
9. *Methyl Ester Derivatives for GC-MS*
10. *SciFinder/ChemSpider and Accurate Mass LC-MS Data for Unknown ID's*
11. *Surfactant Identification*
12. *QuickGuide.rtf Supplied with AMDIS Software Installation for Retention Indices*
13. *New Developments in the Modeling of Ion Fragmentation by MS Interpreter Software*
14. *Enhancements to NIST MS Interpreter for Modeling High Mass Accuracy Tandem Mass Spectra*
15. *An Automated Method for Verifying Structure-Spectral Consistency Based on Ion Thermochemistry*
16. *Combining Fragment-Ion and Neutral-Loss Matching during Mass Spectral Library Searching: A New General Purpose Algorithm Applicable to Illicit Drug Identification*
17. *The Hybrid Search: A Mass Spectral Library Search Method for Discovery of Modifications in Proteomics*
18. *Hybrid Search: A Method for Identifying Metabolites Absent from Tandem Mass Spectrometry Libraries*
19. *Structure Annotation of All Mass Spectra in Untargeted Metabolomics*
20. *Most Current Handouts for Webinar Series, Parts I-V*
21. *Lipid Matrix Ionization Effects in LC-MS*
22. Mass Spectral Similarity Mapping in Hybrid Searches Applied to Fentanyl Analogs
23. User Manual for Wiley Libraries

Acknowledgements

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- Adam Howard[c]
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[a]NIST, [b]Agilent, [c]Eastman Chemical Company