

Wiley Spectral Webinar

Part V: Creating and Sharing User EI and MS/MS Libraries

12/27/20

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Kingsport, TN

- *Retired* Research Fellow, Eastman Chem. Co.*
- *42 years experience unknown identification*
- *Now Consultant, MS Interpretation Services*
- *Specialties¹ 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,^{2,1} etc.*



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

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



>50 Mass Specs Networked
Worldwide

Wiley Webinar Series on Effective Use of Mass Spectral Libraries

Part I: Spectral Searches² with NIST MS Search

Part II: Structure Searches² 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 Sharing⁵ User EI and MS/MS Libraries

Note:²⁰ Handouts for *All Sessions Now Online!*
Google Search “little mass spec and sailing”

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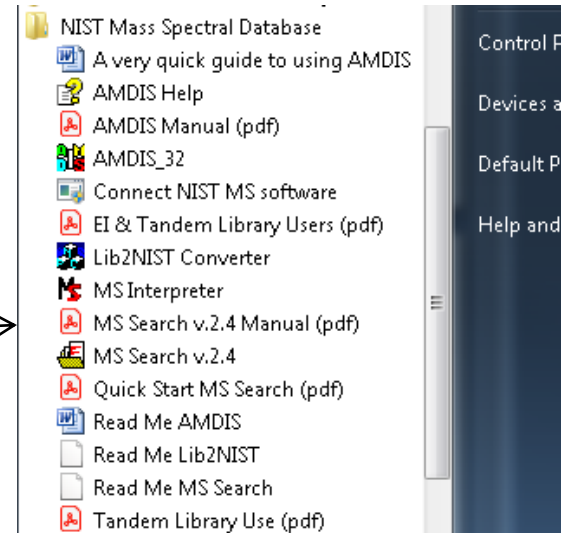
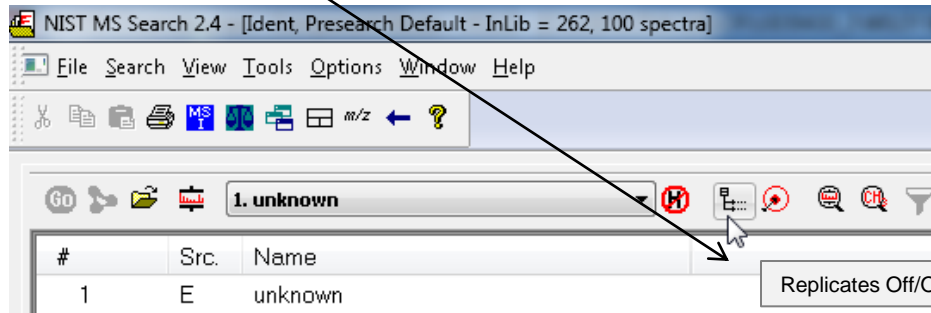
Part V: Creating and Sharing User EI and MS/MS Libraries⁵

Webinar Topics:

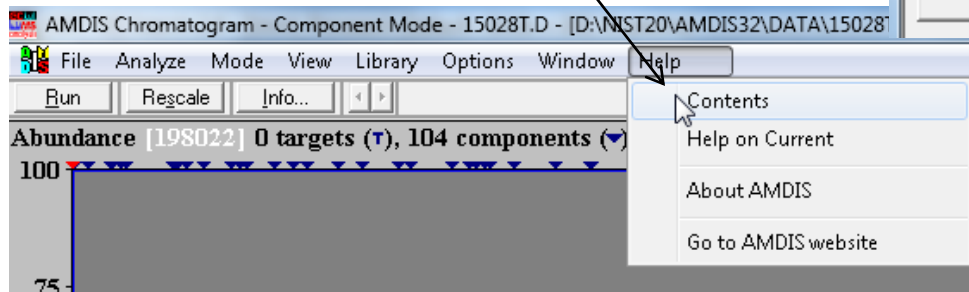
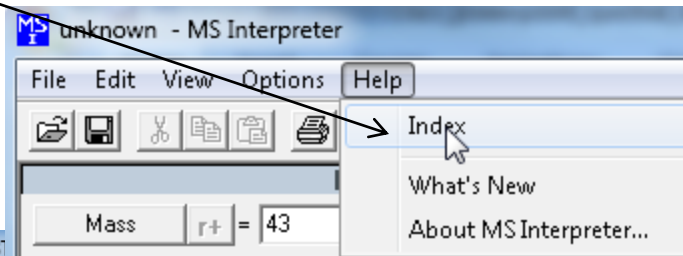
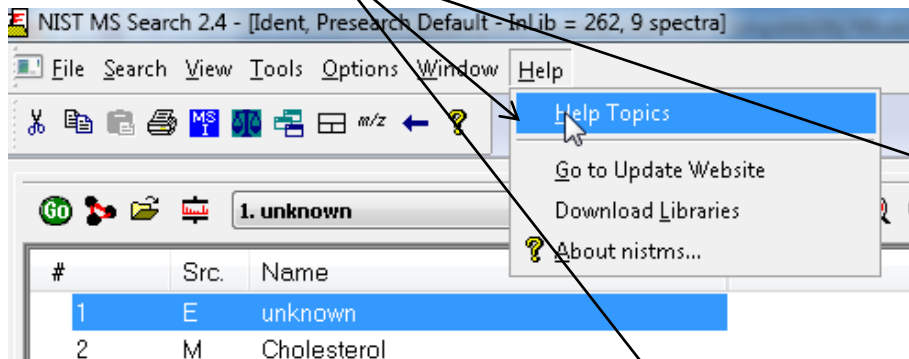
- Adding fields in preparation to add spectrum
- Special Tags in User and Wiley Libraries²³
- Checking quality of spectrum
- Adding spectrum to current on new user library
- Updating indices for structure, InChIKey, etc.
- Sharing user libraries on corporate networks⁵

Help Files for NIST Search

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



- Detailed documentation for NIST Search² and AMDIS^{3,4,12}
- MS Interpreter included in NIST manual² and in posters¹³⁻¹⁵
- 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

The screenshot displays the NIST MS Search 2.4 software interface. The main window is titled "NIST MS Search 2.4 - [Hybrid precursor = 341, Presearch Default - 100 spectra]". The menu bar includes File, Search, View, Tools, Options, Window, and Help. The toolbar contains various icons for file operations and search. The main area shows a table with the following data:

#	Src.	Name
1	E	component to add to library

Below the table, there are tabs for "Names" and "Structures", and a "Spec List" button. The status bar at the bottom indicates "mainlib; replib; w12main; w12rep; w12lq; new_2020; 1168788 total spectra".

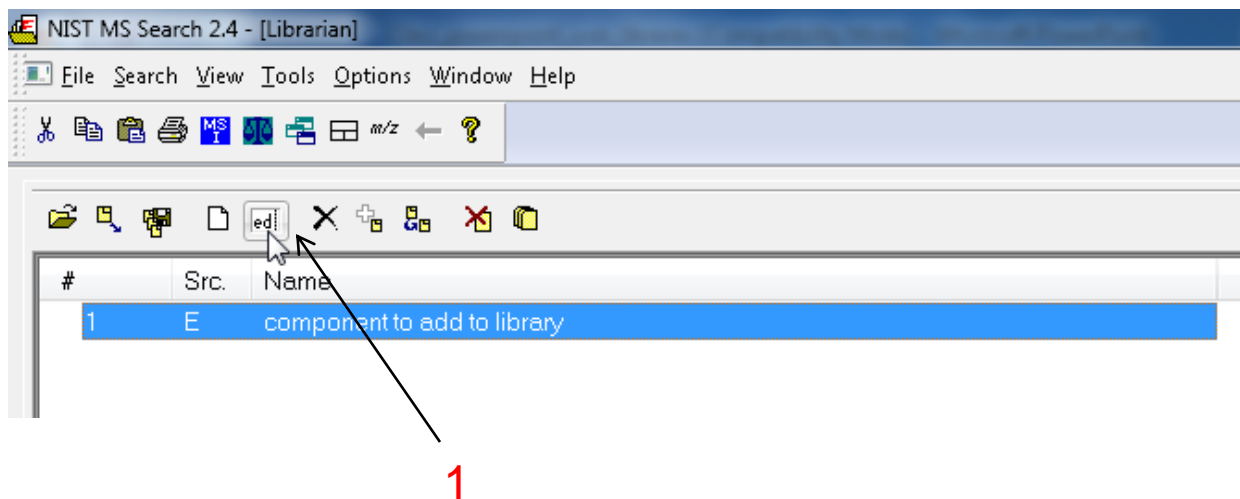
A red arrow labeled "1" points to the "component to add to library" entry in the table. Another red arrow labeled "4" points to the "Librarian" tab in the bottom navigation bar.

The bottom navigation bar includes tabs for "Lib. Search", "Other Search", "Names", "Compare", and "Librarian". The "Librarian" tab is highlighted, and a red arrow labeled "4" points to it.

For Help, press F1

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

Spectrum Information

Name: component to add to library

Formula: [] From structure

Mol. Weight: 0 CAS Number: 0

Library: Text File

ID Number: 3 Inventory#: []

RI: [] Edit RI

Other Names (Synonyms): []

Additional Info Experimental Data

Comments: []

To Clipboard From Clipboard Get MolFile Get Struct Structure Editor From Inventory

Peak information

m/z	Abund.	Annotation
26	1	
27	3	
28	11	
29	6	
31	8	
33	6	
37	4	
38	11	
42		
69		
108		
140		
187		
234		
313		

Accept HiRes Spectrum Peaks: 229

100 0 40 80 120 160 200 240 280 320

No structure

Add to Library Add to List Replace Cancel Help

1 2 3 4

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"

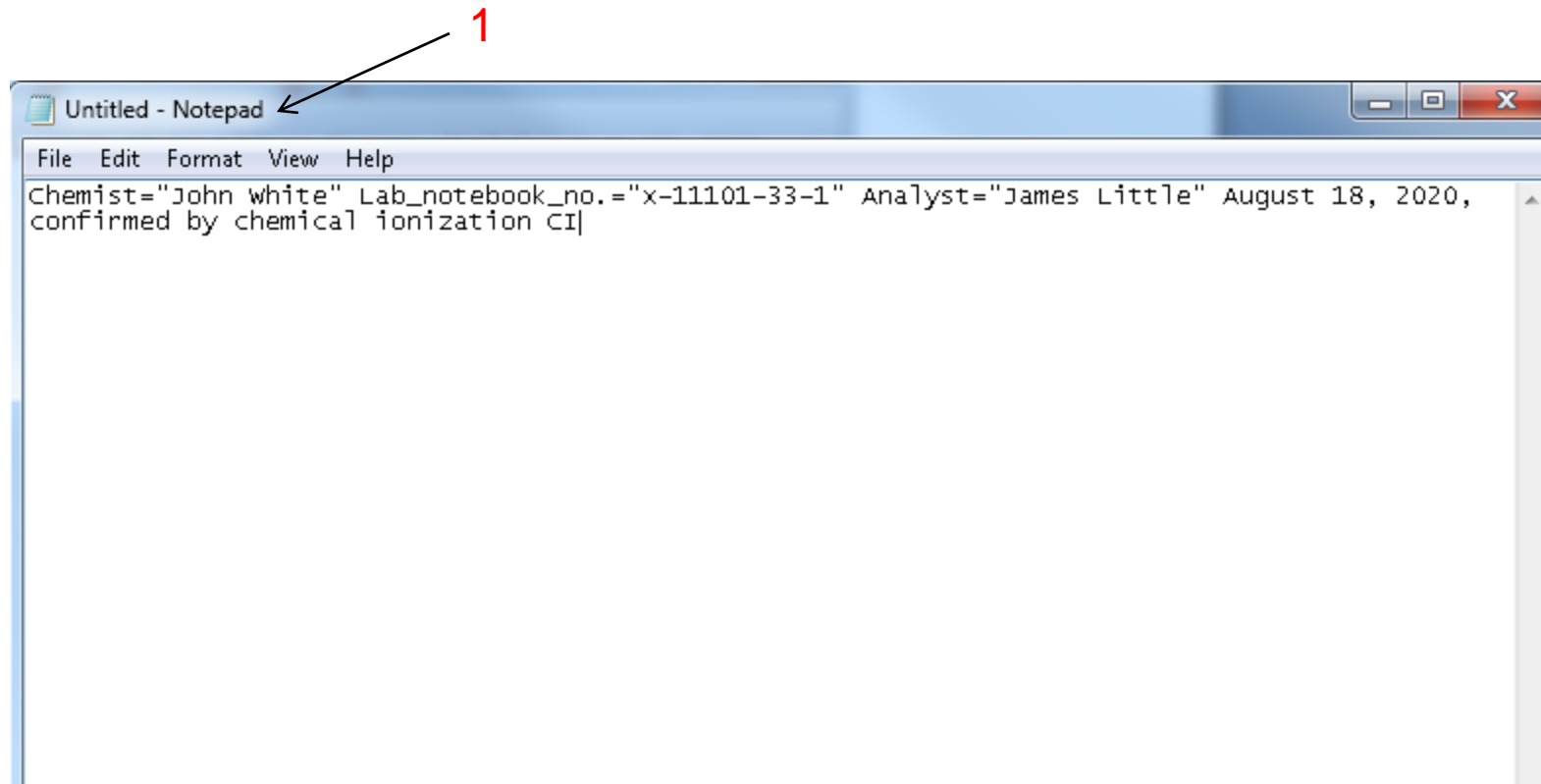
The screenshot shows the 'Spectrum Information' dialog box with the following fields and controls:

- Name:** component to add to library (Annotation 4 points to this field)
- Formula:** C10H8BrF4NO (with a 'From structure' button)
- Mol. Weight:** 313
- CAS Number:** 0
- Library:** Text File
- ID Number:** 3
- Inventory#:** (empty)
- RI:** (with an 'Edit RI' button)
- Other Names (Synonyms):** (empty text area, Annotation 1 points to this area)
- Additional Info:** (button)
- Experimental Data:** (button)
- Comments:** (empty text area, Annotation 5 points to this area)
- Peak information:** Table with columns m/z, Abund., and Annotation.

m/z	Abund.	Annotation
26	1	
27	3	
28	11	
29	6	
31	8	
33	6	
37	4	
38	11	
...
- Mass Spectrum:** A plot showing relative abundance (0-100) versus m/z (40-320). Key peaks are labeled at m/z 42, 69, 108, 140, 187, 234, and 313.
- Chemical Structure:** A 2D chemical structure of a brominated amide derivative.
- Clipboard #2:** (empty)
- Buttons:** 'Accept', 'HiRes Spectrum' (checkbox), 'Peaks 229', 'To Clipboard', 'From Clipboard', 'Get MolFile', 'Get Struct', 'Structure Editor', 'From Inventory', 'Add to Library', 'Add to List', 'Replace', 'Cancel', 'Help'.

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



```
File Edit Format View Help
Chemist="John white" Lab_notebook_no.="x-11101-33-1" Analyst="James Little" August 18, 2020,
confirmed by chemical ionization CI
```

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

The screenshot shows the NIST MS Search 2.4 interface. The 'Options' menu is open, and 'Comment Field Display' is selected. A dialog box titled 'Display comment field options' is open, showing a list of tags: 'Chemist', 'Lab_notebook_no.', and 'Analyst'. The 'OK' button is highlighted.

1

2

3

#	Src.	Name
1	E	comp
2	E	component to add to library
3	A	component to add to library

Display comment field options

To show tag=value from Comments as separate line in spectrum text, enter tag as a separate line.

Chemist
Lab_notebook_no.
Analyst

For example, if RI=132.1 is embedded in Comments, it can be displayed as a separate line in the text by entering the line:

RI

in the above field. Multiple lines will display multiple tag=value pairs in the order entered.

Show tag=value on plot

OK Cancel Help

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: C₁₀H₈BrF₄NO
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

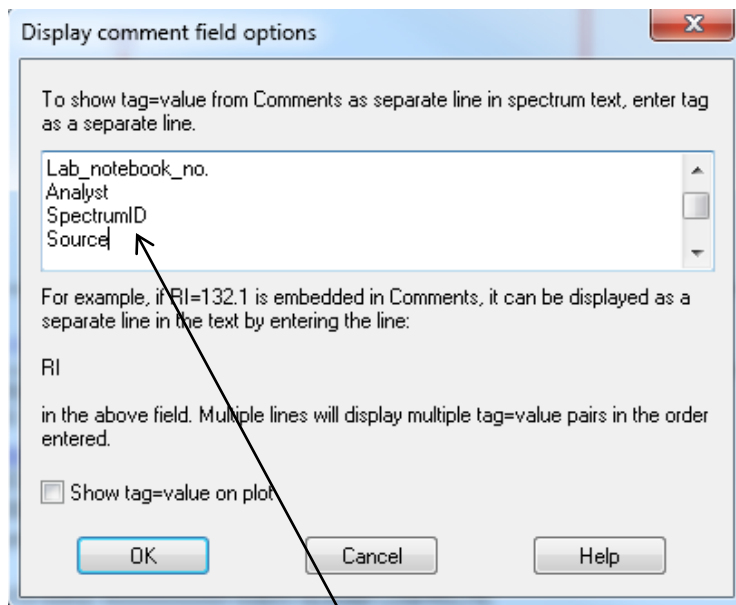
2

Name: component to add to library
Formula: C₁₀H₈BrF₄NO
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

Tags²³ 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 Manual²³



3

4

[Name:](#) 2-Ethyl-1-pyrroline
[Formula:](#) C₆H₁₁N
[MW:](#) 97 [Exact Mass:](#) 97.089149 [ID#:](#) 4601 [DB:](#) w12main
[SpectrumID:](#) 760036
[Source:](#) C-118-9300-4
[Classification:](#) Pyrrolines
[QI:](#) 128
[SplashID:](#) splash10-00kb-9000000000-0db51a38ae120e45c7f2
[Comment:](#)
[InChIKey:](#) MEPINLVYDXPOSN-UHFFFAOYSA-N [Non-stereo](#)
[9 m/z Values and Intensities:](#)
54 279 | 56 369 | 69 999 | 70 49 | 71 1 |
96 429 | 97 579 | 98 60 | 99 1 |
[Synonyms:](#)
1.5-Ethyl-3,4-dihydro-2H-pyrrole
[Experimental RI median+deviation \(#data\)](#)
Unspecified: 809±N/A (1)

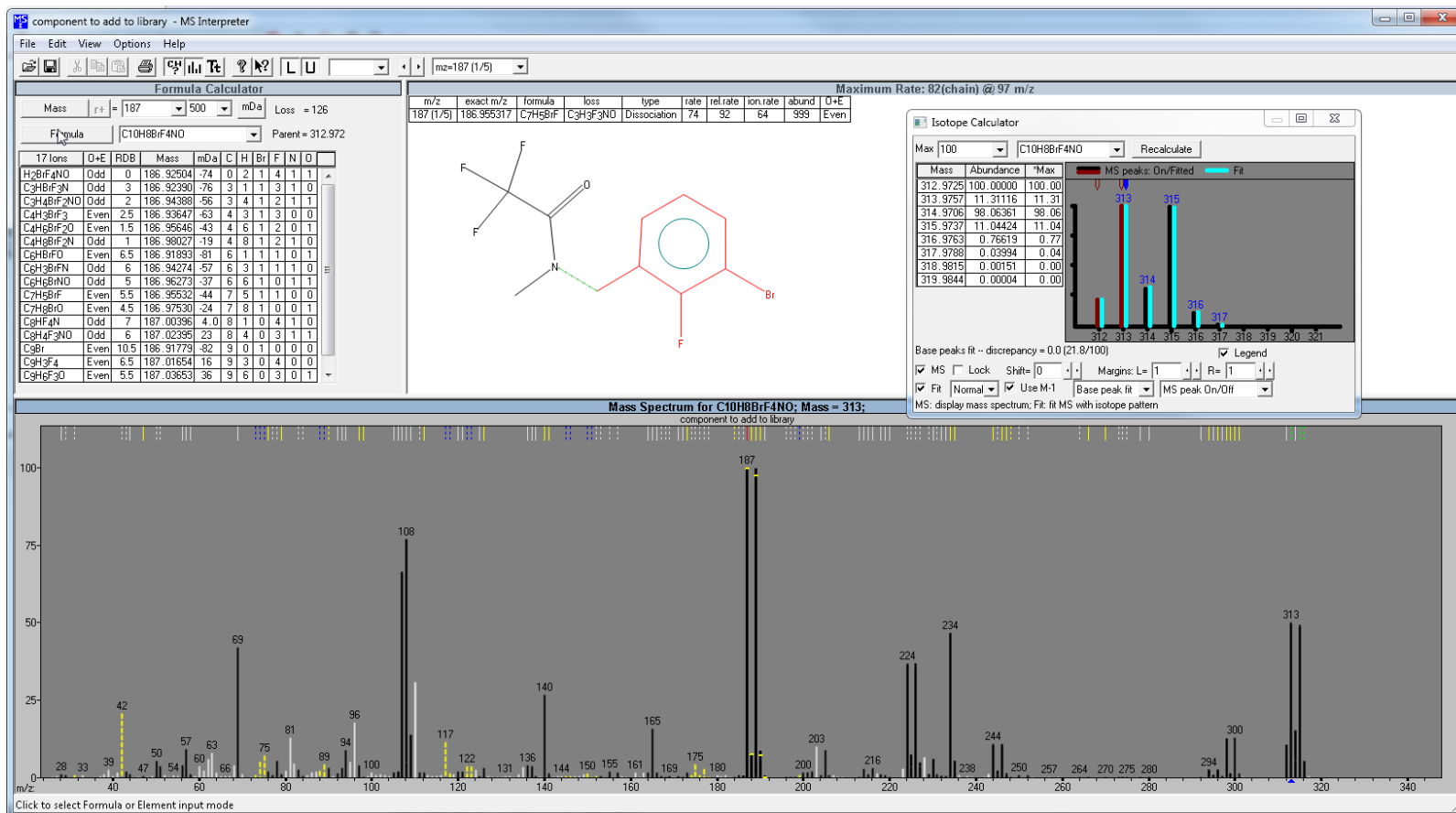
2

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

Spectrum Information

Name: \V-[(3-bromo-2-fluorophenyl)methyl]-2,2,2-trifluoro-f

Formula: C10H8BrF4NO

Mol. Weight: 313 CAS Number: 0

Library: Spec. Edit

ID Number: 7 Inventory#:

RI:

Other Names (Synonyms): PM 2201 derivative, TFA derivative of PM 2201, Morrison's Amine, TFA derivative

m/z	Abund.	Annotation
26	1	
27	3	
28	11	
29	6	
31	8	
33	6	
37	4	
38	11	

Mass Spectrum Plot: Peaks at m/z 42, 69, 108, 140, 187, 234, 313

Chemical Structure: CN(C)C(=O)C1=CC=C(C=C1)C(F)=C

Clipboard #3

Buttons: Add to Library, Add to List, Replace, Cancel, Help

Choose library to save to

List of libraries:

- class_example
- bruker_stein_msms
- class_example
- dd2014
- dpg_spectra_eastman
- eastman_dbt
- ecc_new
- fluorine_rearrangement

RI type if unspecified: Unspecified

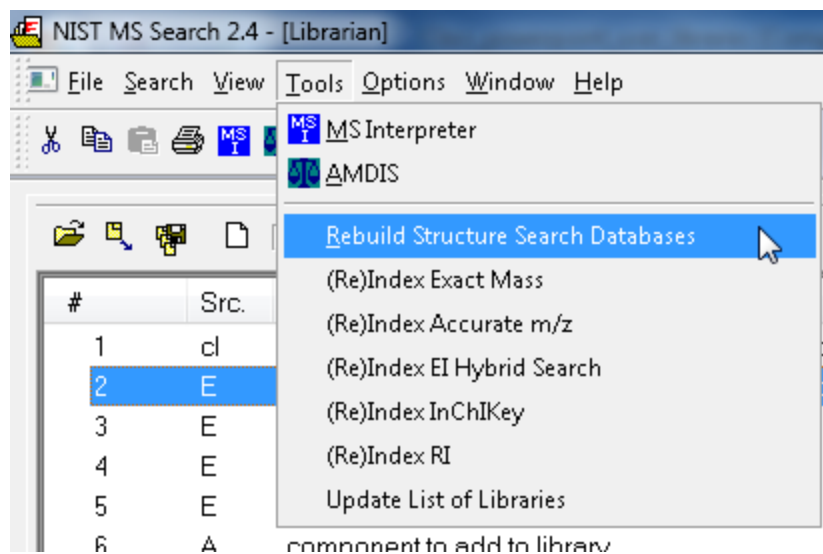
Library Statistics	Spectra	ID
1	Spectra	
1 - 1		ID

Buttons: OK, Cancel, Help

3

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

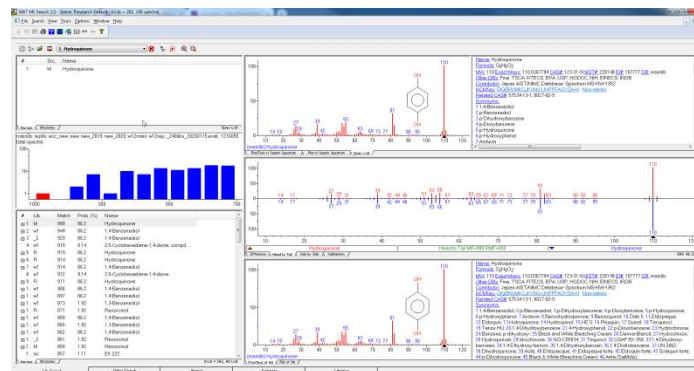
Started circa 2000



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

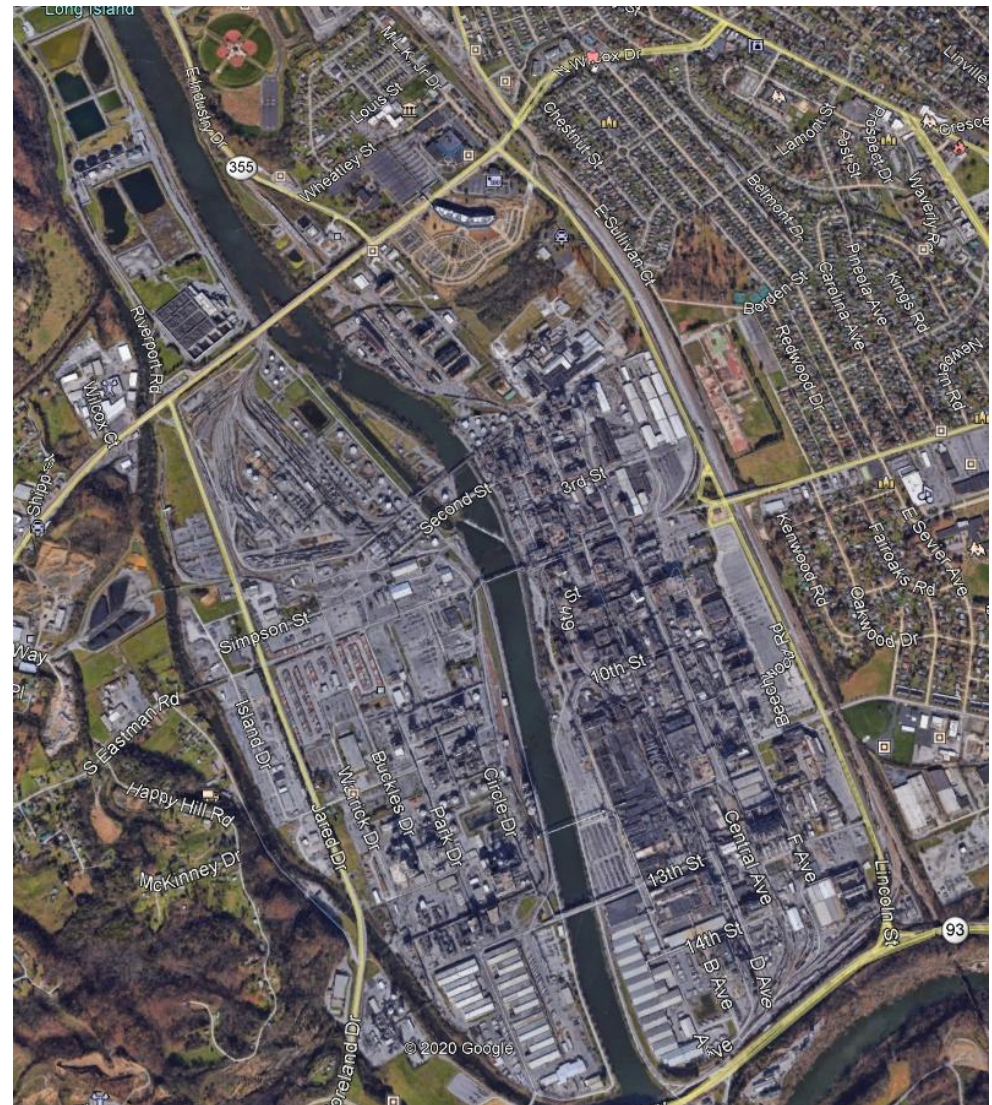
Thus, ***users must realize*** Eastman database is an ***aid to identification*** and should be used accordingly.

- ***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

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

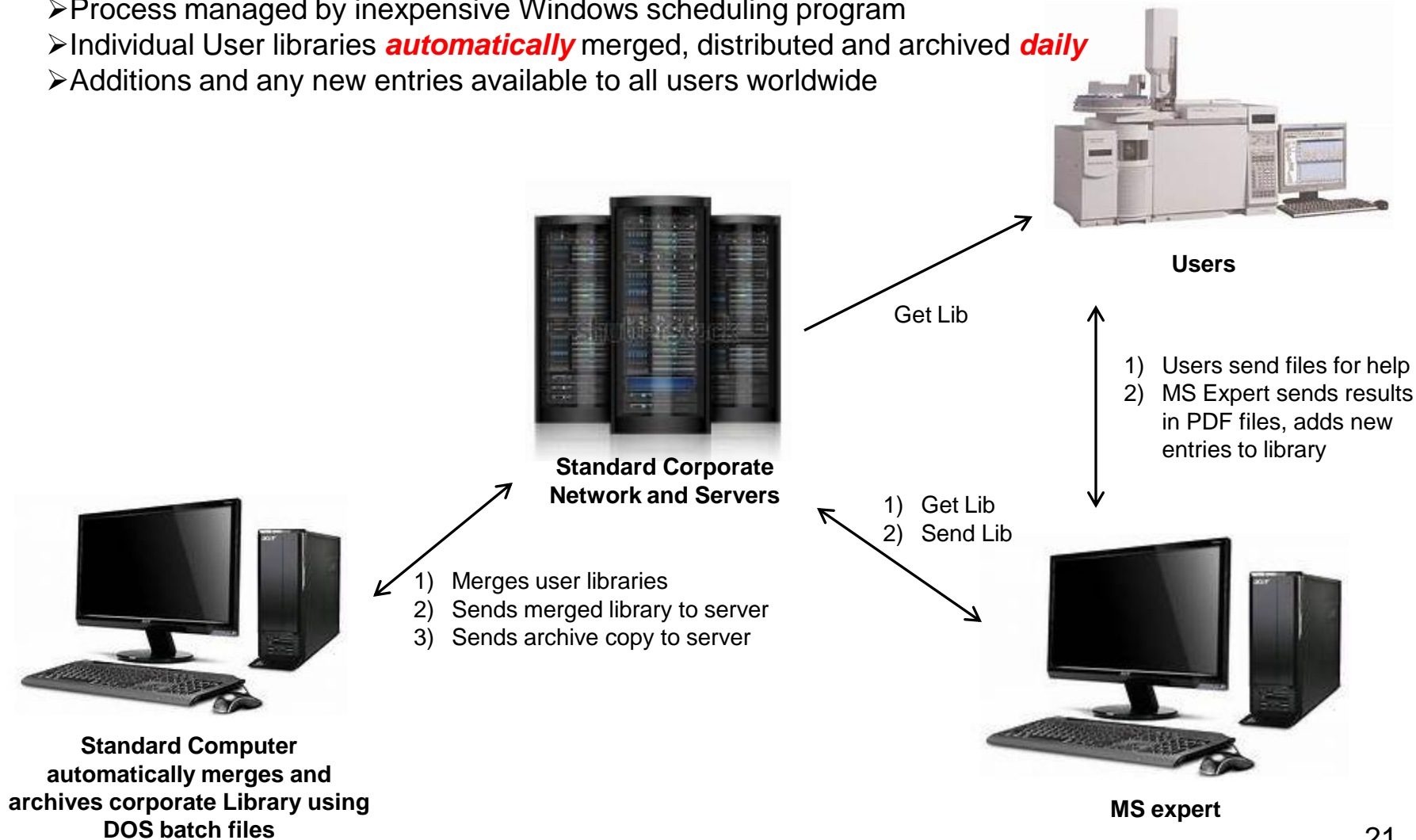
- GC-MS and LC-MS used in conjunction with TOC (total organic carbon) water monitors
- Quickly determine source of spills in manufacturing or breaches from water treatment plant
- Exact structure useful, but not necessary
- Comments in unknown spectrum used to determine process and pinpoint location



Software Essentials and Approach

No Expensive Hardware, Software, or Licenses!

- DOS files written by user⁵ 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



Excerpt of Typical DOS Script⁵

```
: 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.ms2 goto alias_error
if exist c:\nist98\wiley7\alias.ms2 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.
```

```
:nause
```

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](#)

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- Adam Howard^c
- Curt Clevon^c

^aNIST, ^bAgilent, ^cEastman Chemical Company