# NIST/EPA/NIH EI-MS LIBRARY

## 2023 Release

### *40K New NIST Measured/Evaluated Compounds*

**394K Electron Ionization (EI) Spectra**

- 347,100 Compounds, 46,954 Replicate Spectra
- 40 K More Compounds than NIST 20

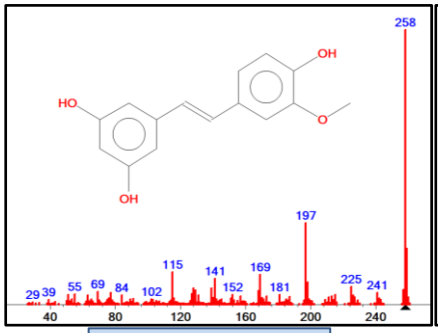
**492K Retention Index (RI) Values**

- 153K RI Compounds with EI, >40 K Increase
- AI-RI Estimates for All EI Compounds

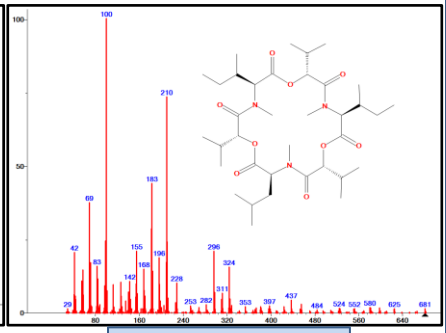
## Compounds Selected for Analytical Relevance

### Fully Evaluated with Derivatives, Retention Indices & Class Information

| Citation | New | Total |
|---|---|---|
| Wikipedia | 1570 | 6227 |
| EPA Tox | 2969 | 7117 |
| Food DB | 582 | 4273 |
| EU Contaminants | 6263 | 15149 |
| Protein Data Bank | 1194 | 4716 |
| Human Metabolite DB | 1992 | 9393 |
| PFAS | 161 | 749 |
| Adams (Essential Oils) | 2136 | 2136 |




Plant Stilbenoid




Myocotoxin ENN A

**Compound Data**

Name: Valeryl fentanyl
Formula: $C_{24}H_{32}N_2O$
MW: 364 Exact Mass: 364.251463 CAS#: 122882-90-0 NIST#: 463844 ID#: 18711
Contributor: NIST Mass Spectrometry Data Center
InChIKey: VCCPXHWAJYWQMR-UHFFFAOYSA-N Non-stereo
Synonyms:
1.Pentanamide, N-phenyl-N-[1-(2-phenylethyl)-4-piperidinyl]-; 2.N-Phenyl-N-[1-(2-pi
Other DBs:
——Wikipedia——
wikipedia2021_via_cheminfo_SMILES
——Environmental——
SUSDATFY22

Collections →

Experimental RI median±deviation (#data)
Semi-standard non-polar: 2962±18 (2)
Standard non-polar: 2958±N/A (1)

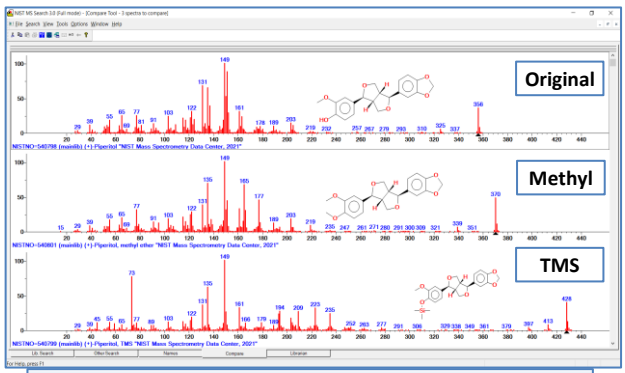
RI Averages →

Estimated non-polar retention index (n-alkane scale):
Value: 2938 iu
Confidence interval (Nitrogen-containing): 83(50%) 356(95%) iu

AI-RI Estimates →

Retention index
1. Value: 2980.5 iu
Column Type: Capillary
Column Class: Semi-standard non-polar
Active Phase: HP-5MS
Column Length: 30 m

RI Measured →




Piperitol with TMS/Me Derivatives (TFA, Acetyl not shown)

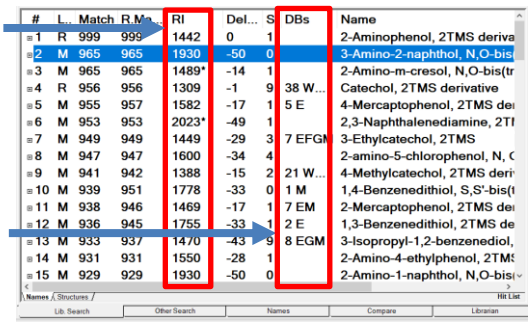
## Enhancements

### Hit List

*New*: Retention Index For All Hits (Expt'l or AI-RI*)

*Select Columns* Mass Difference, Reverse Score, Probability, …

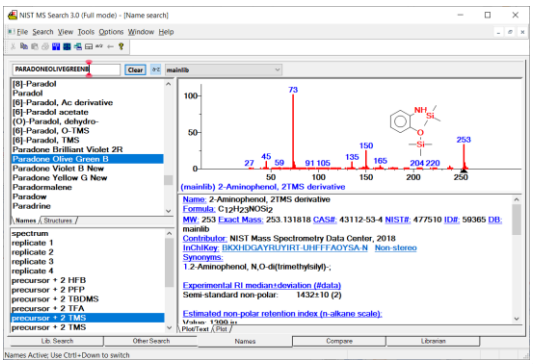
*New*: Expanded Compound Classes




### Compound/Spectrum Lookup

Names

Spectra
Replicates
Derivatives
Stereo



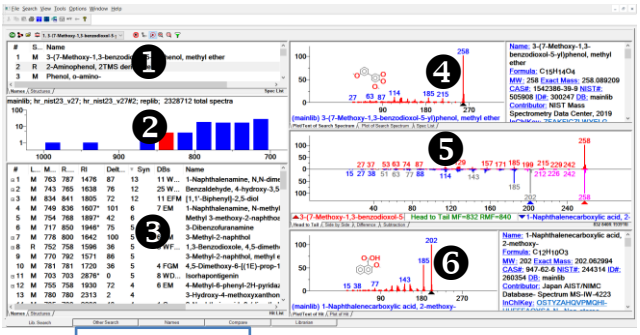
# NIST EI LIBRARY SOFTWARE

## 2023 EI Release

### *EI MS Analysis Tools*

## NISTMS

- Full Featured MS Library Search/Display Program
- Multiple Search Types & Display Modes
- 5 Views: Spectrum Search, Feature Search, Compare, Name/Spectrum, User Library



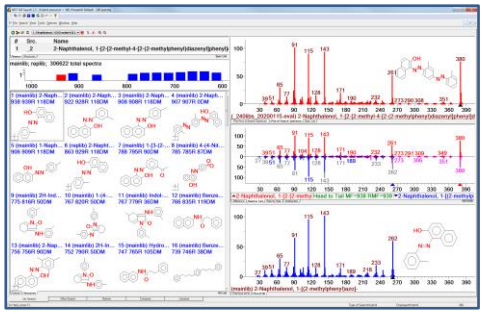

5 Tab Views

1. Query spectrum list
2. Score Histogram
3. Hit List –multiple values
4. Query spectrum
5. Query/Library Compare
6. Library Spectrum

## Hybrid Search

- For Compounds Not Found in Library & ID Confirmation
- Finds 'Modified' Library IDs and Masses of Modifications With Their Shifted Peaks
- Uses MW Estimate

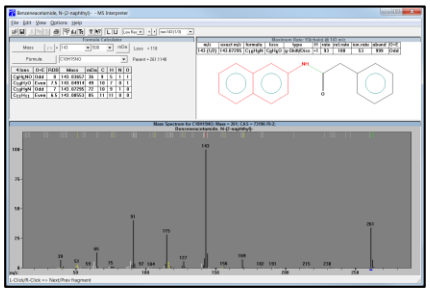
**Delta Mass => Chemical Formula**



| DMass | Replace or Insert |
|---|---|
| 1 | H->D, C->C13, NH->O,CH->N |
| 2 | CH2->O, C=C->C-C |
| 12 | CH2->C=CH2 |
| 14 | X-Y->X-CH2-Y |
| 16 | X-Y->X-O-Y |
| 17 | NH->S |
| 18 | H->F |
| 28 | X-Y->X-CO-Y |
| 30 | H->CH3O-H |
| 32 | X-Y->X-S-Y |
| 34 | H->Cl |
| 50 | Phenyl->Naphthyl |
| 76 | H->Phenyl |
| 162 | H->Glucose |

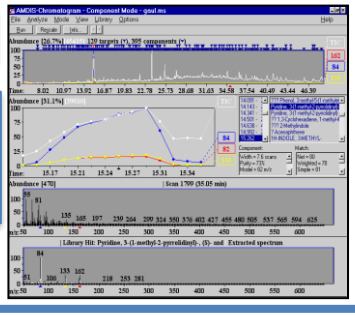
## MS Interpreter

- Connect Peaks to Plausible Fragments (in Red)
- Confirm ID
  Compute Fragment Masses
  Connect Peaks to Structures



## AMDIS

- 'Purifies' Spectra and Connects to NISTMS



## NIST Website *chemdata.nist.gov*

**Libraries, Tools, Service**

This site provides information and access to NIST mass spectral data products. A variety of data products are available, including EI and tandem MS libraries (small molecule and peptide), a GC retention index collection as well as certain freely available, specialized spectral libraries. Freely available data analysis tools include AMDIS (Automated Mass Spectral Deconvolution and Identification System for GC/MS), the Mass Spectrum Interpreter (connects chemical structures with mass spectra), and the Mass Spectral Digitizer Program. Also available is a fully functional, version of NIST MS Search Program v.2.0f with a small demonstration library.

**Recurrent Unidentified Spectral Libraries**

There are three NIST user libraries of recurrent unidentified spectra (RUS):

- **Food**: A set of 650+ spectra extracted from a set of dried food material, some of these spectra have tentative identifications. These experiments were done with methoxiamation and TMS derivatization. Data
- **PedUrine**: A set of 200+ spectra from a large set of pediatric urine samples. All of these samples were derivatized with TMS after forming the ethyloxime for the non-acid carbonyl groups; the majority of this
- **EssOil**: A set of 1000+ spectra derived from a large set of essential oils (both commercial and laboratory distilled), solvent extract of various plant materials (leaves, flowers, roots, etc). Most of these data were

**Freely Available Data and Software**

**Tools**

- Mass Spectrum Interpreter – Major New Release – February 2019 (v. 3.4). Information and downloads for version 3.4 of this program which connects mass spectral peaks to their probable chemical structure origin (EI and MS/MS, both nominal and accurate mass).
- NIST MS Software and Data - updates, demo, documentation, MSPepSearch, Lib2NIST, RUS libraries and support programs.
- AMDIS – computer program that extracts spectra for individual components in a GC/MS data file (Instructions for using AMDIS with MS Search – 11-25-2019)
- Mass Spectrum Digitizer Program – a tutorial on how to use the program (includes program download) that allows the digitization of graphical spectra
- The NIST Glyco Mass Calculator - a tool to aid in the analysis of glycoforms
- DIMEDR - A Novel Algorithm for Agglomerating Incongruent LC-MS Metabolomics Datasets.
- MS_Piano (New, 2021) - A new software tool for annotating peaks in collision induced dissociation (CID) tandem mass spectra of peptides and N-glycopeptides.

# NIST Tandem Mass Spectral Library

## 2023 Release

**51,501 Compounds, 60% More than 2020**
**400 K Precursor Ions – 2.4 M Spectra**

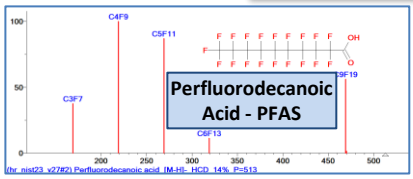
### Fragmentation Methods

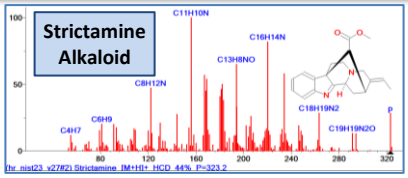
- 49,590 HRAM (High Res Accurate Mass) Compounds
- 50,071 QTOF, HCD, IT-HRAM, QqQ Compounds
- 49,561 Ion Trap Compounds (Low Res., up to $MS^4$)
- 561 APCI HRAM Compounds

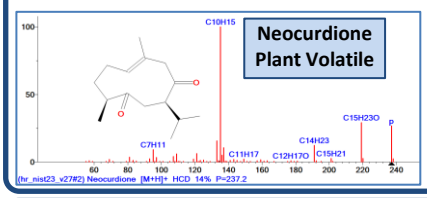
### Precursor Ion Types

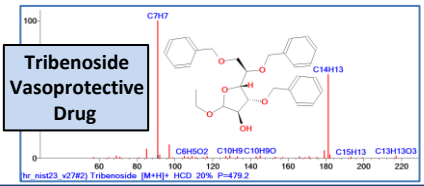
- 44,191 Protonated
- 19,620 Deprotonated
- 14,318 Water/Ammonia Loss
- 44,547 Other In-Source Generated

### All Compounds Selected for Relevance
### Measured at NIST, Thoroughly Evaluated



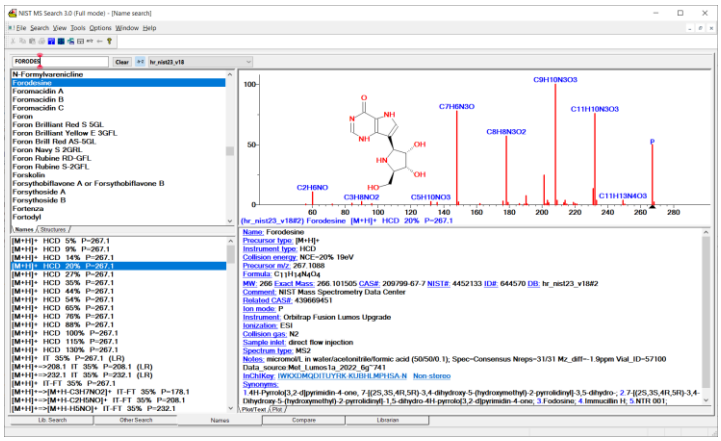




| Citation | New | Total |
|---|---|---|
| Wikipedia | 1618 | 6424 |
| EPA Tox | 3181 | 8146 |
| Food DB | 602 | 4491 |
| EU Contaminants | 6553 | 15818 |
| Protein Data Bank | 1246 | 4945 |
| Human Metabolite DB | 2071 | 9686 |
| PFAS | 90 | 116 |

**All Spectra Shown for Each Compound**

1. Compound Name Many Synonyms

2. All Related Spectra All Energies Fragmentation Types In-Source Ions, …



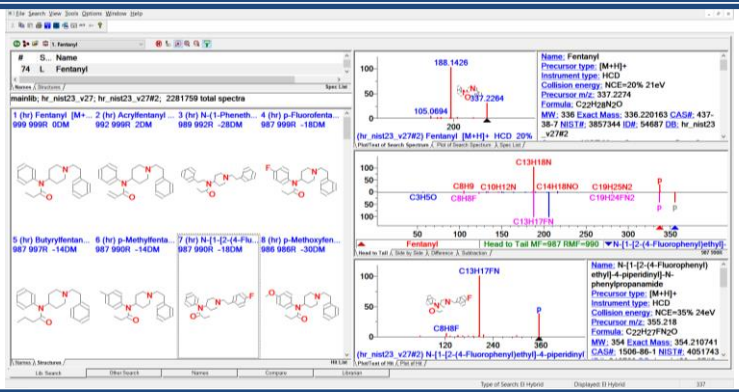
Full Spectrum Selected from List at Lower Left

All Spectrum Text Information

***Hybrid Search***
Recommended for All Tandem MS Searches

Find Related Compounds Even if Query is not in Library

Differences in masses are 'Modifications'



Query Spectrum

Shifted Library Peaks (gray->red) Contain Modification

Library Spectrum

# NIST TANDEM LIBRARY SOFTWARE

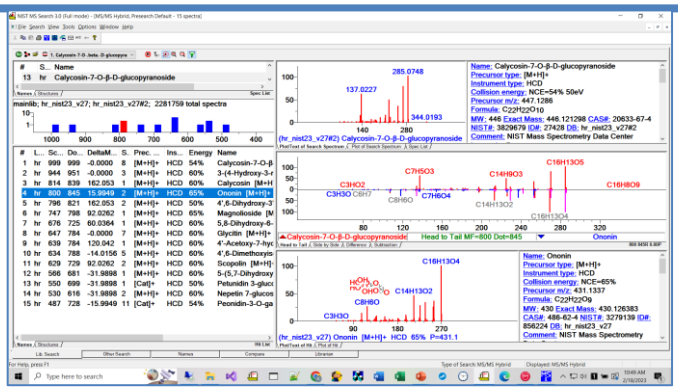
## 2023 Tandem Release

### *Tandem (MS/MS) Analysis Tools*

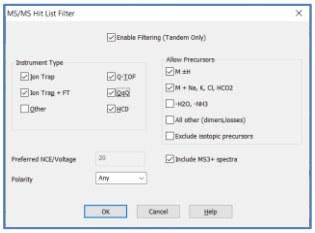
## NISTMS

All Spectra for Each Compound in One List

Multiple Energies Ion Modes Fragmentation Type In Source Ions



Filter IDs by Spectrum Type



## Hybrid Search

-Finds Compounds Not in Library and Confirms IDs
-Uses Peaks and Losses
-Shows Shifted Peaks

Recommended For Routine Use

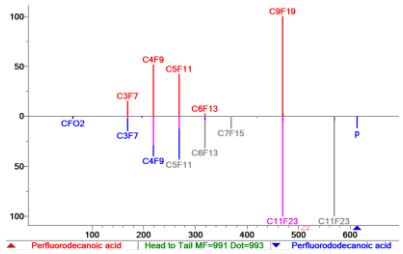
| # | L.. | S... | D... | DeltaMa... | DBs | Prec. ... | Inst... | En... | Name |
|---|---|---|---|---|---|---|---|---|---|
| 1 | hr | 935 | 999 | -0.0000 | 20 EGM | [M-H]- | HCD | 20% | Perfluoroheptanoic acid [M-H]- |
| 2 | hr | 891 | 976 | -49.9968 | 27 WC... | [M-H]- | HCD | 20% | Perfluorooctanoic acid [M-H]- |
| 3 | hr | 866 | 938 | -99.9936 | 24 WC... | [M-H]- | HCD | 14% | Perfluorononanoic acid [M-H]- |
| 4 | hr | 511 | 796 | -249.984 | 18 CE... | [M-H]- | HCD | 27% | Perfluorododecanoic acid [M-H |
| 5 | hr | 466 | 714 | -149.990 | 22 WC... | [M-H]- | HCD | 9% | Perfluorodecanoic acid [M-H]- |
| 6 | hr | 460 | 828 | -199.987 | 18 CE... | [M-H]- | HCD | 44% | Perfluoroundecanoic acid [M-H |

1 (hr) Perfluorodecanoic acid [...
999 999R 0.00P -0.0000DM

2 (hr) Perfluorododecanoic acid...
991 993R 0.00P -99.9937DM

3 (hr) Perfluoroundecanoic acid
985 985R 0.00P -49.9968DM

PFAS Illustration: Applicable to Many Classes




## MS Interpreter

Direct Access From NISTMS

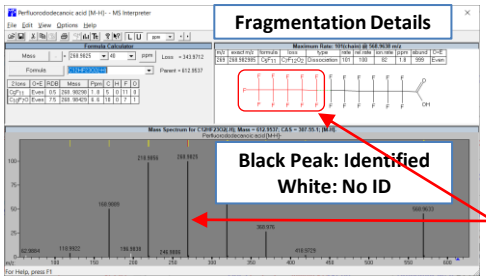
Connect Peaks to Structure

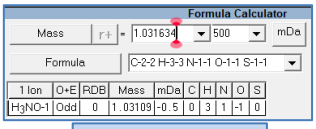
Chemical Formula Calculator

Isotope Calculator

Any resolution +/- Charge

Multiple Display Options




Find Formula from Delta Mass

## NIST Website Chemdata.nist.gov

Freely Available Libraries and Software

**Downloadable Libraries**

Annotated Recurrent Unidentified Spectra
Urine, Plasma/Serum (ARUS)
Tryptic Peptides (Human, ...)
Oligosaccharide Libraries (Milk)
Glycopeptides (mAb, Glycan Distributions)
Acyl Carnitines

**Software**

NISTMS (2019)
MS Piano (Peptide a\Annotation)
MS Pepsearch – General Search Utility for NIST Libraries
MS Interpreter
Lib2NIST – Library Conversion

http://chemdata.nist.gov

NIST National Institute of Standards and Technology U.S. Department of Commerce