Enhancing the Coverage and Quality of Spectra of Per- and Polyfluoroalkyl Substances in a Comprehensive Electron Ionization Mass Spectral Library

Yufang Zheng

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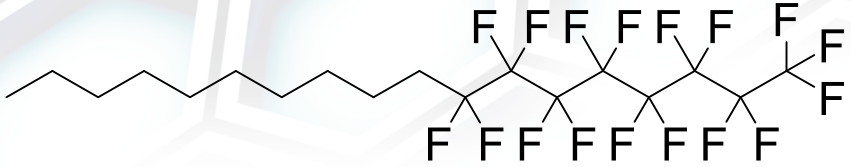
National Institute of Standards and Technology
U.S. Department of Commerce

Mass Spectrometry Data Center

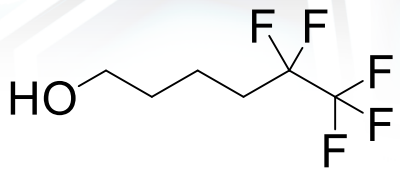
INTRODUCTION

- The NIST/EPA/NIH EI MS Library is a world's most widely used and trusted mass spectral reference library.
- The 2023 release EI library includes 394,000 carefully-evaluated spectra of 347,100 unique compounds. 40,200 compounds were added to the NIST 2020.
- It includes a GC retention index library (153K compounds with RI), LC-MS tandem MS libraries (51K compounds), as well as certain freely-available, specialized spectral libraries.
- This library provides a fast and reliable way to assist the identification of PFAS.

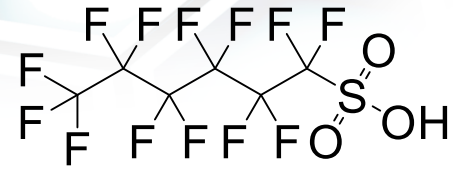
Overview



1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorooctadecane



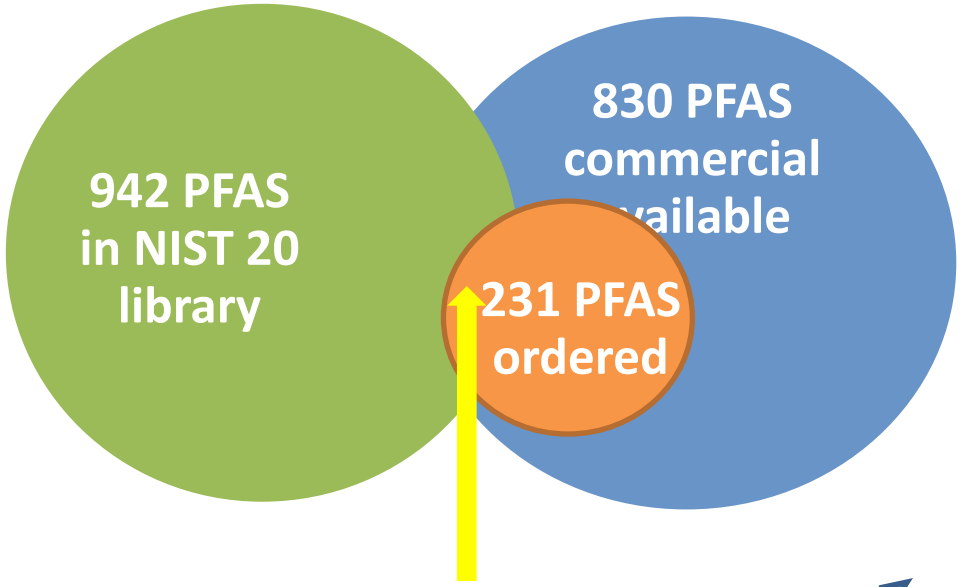
5,5,6,6,6-pentafluorohexan-1-ol



1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexane-1-sulfonic acid

- PFAS are environmental contaminants characterized by extensive fluorination along extended aliphatic chains.
- The procedure for expanding a PFAS EI mass spectral library includes sorting out PFAS not in the current library for purchase with computational methods, chemical derivatization when needed and measurement by Headspace GC or GC/MS.
- Data processing involves extraction of spectra from the raw data, application of new evaluation algorithms to confirm the identity of PFAS and the quality of spectra.
- With this new approach, about 400 high-quality PFAS spectra for 231 PFAS have been added to the 2023 library.

PFAS Selection



201 Compounds with low quality spectra or no retention index (RI) data

Over 9000 Compounds from PFAS Master List of EPA

Remove polymers and salts via ACD

6695 Compounds of Interest

Search InChIKey against NIST 2020 lib

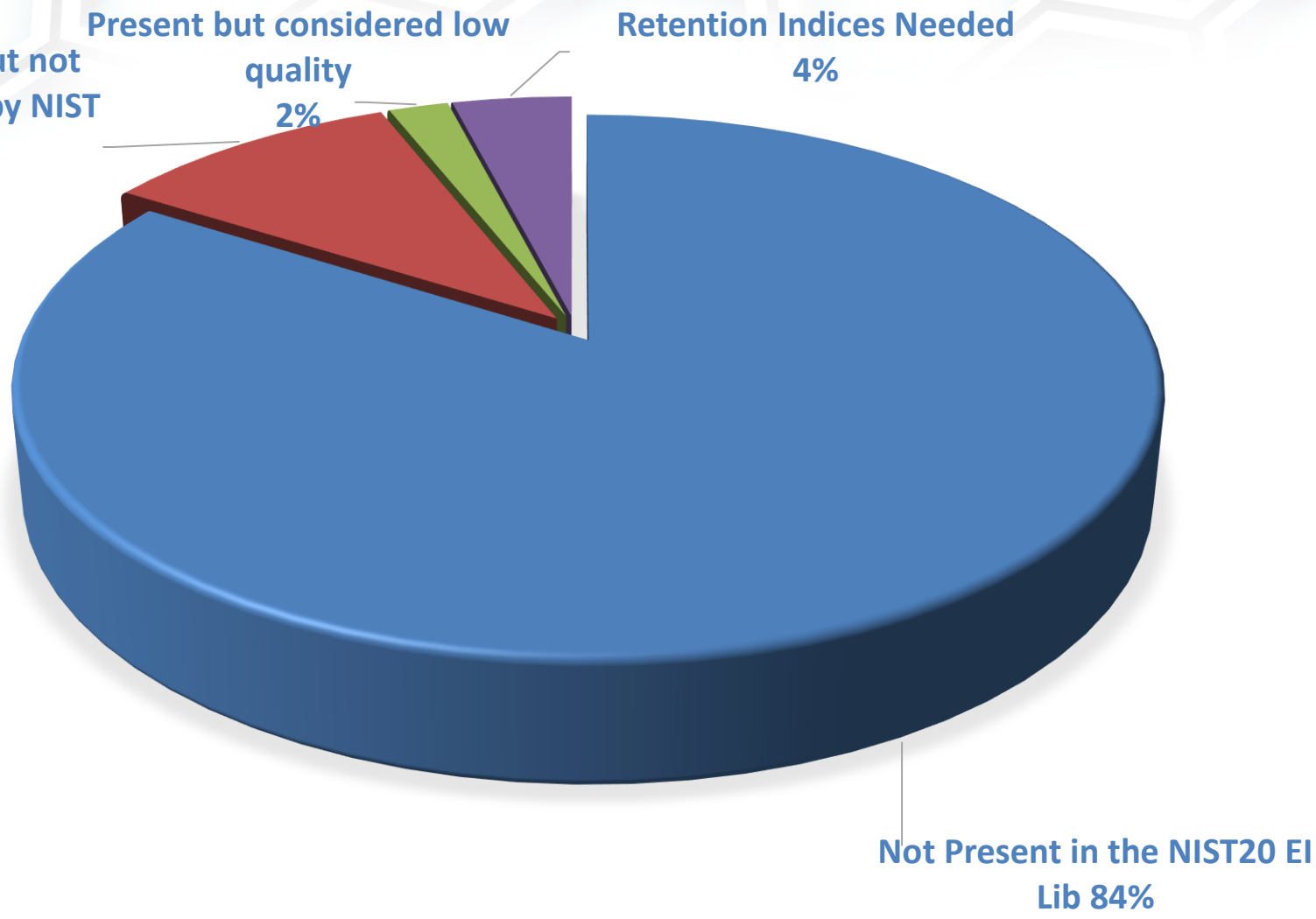
Search commercial resources

Generate a list of 830 PFAS

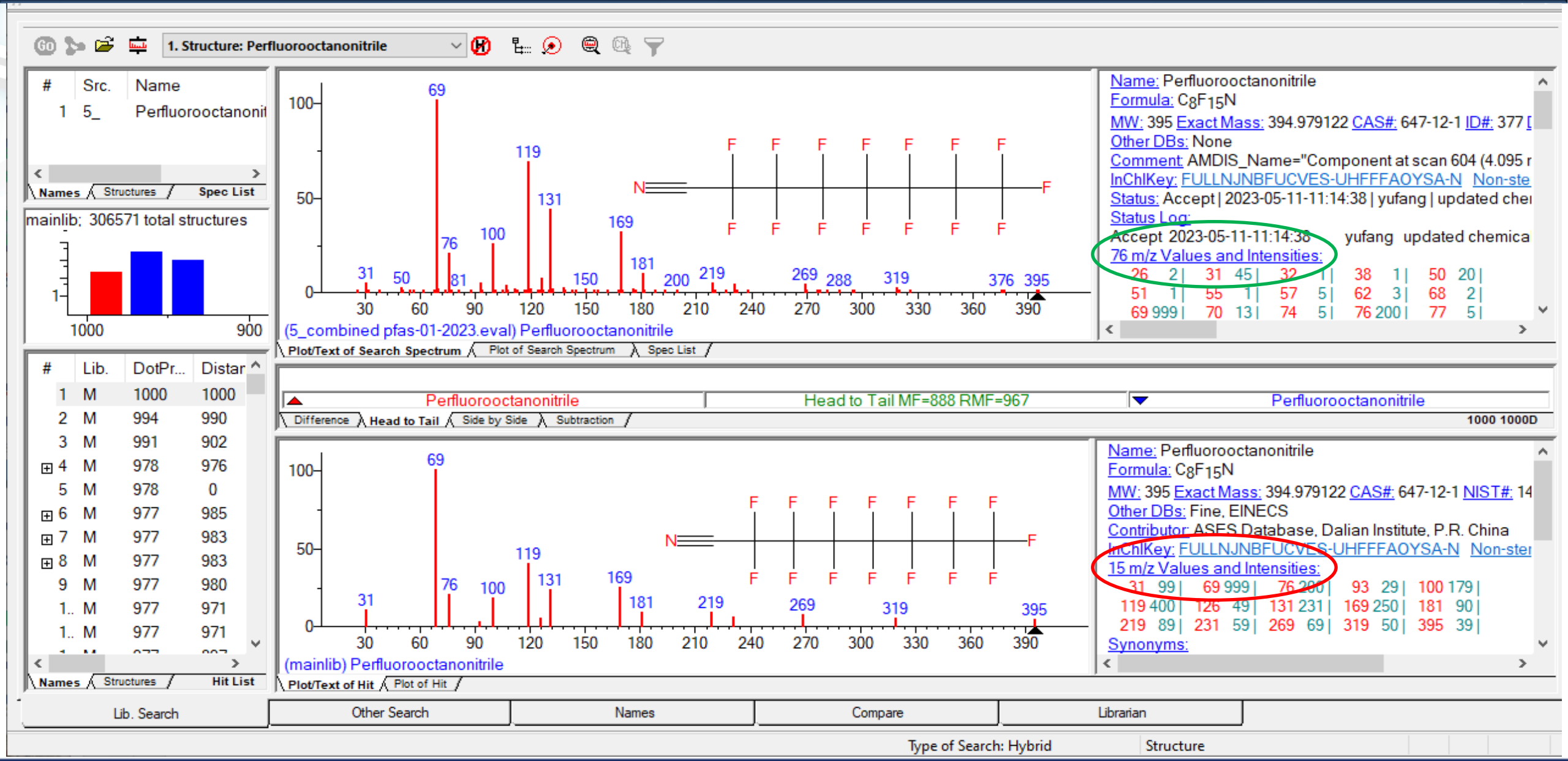
Ordered from commercial resources

1st Batch of 231 PFAS Obtained

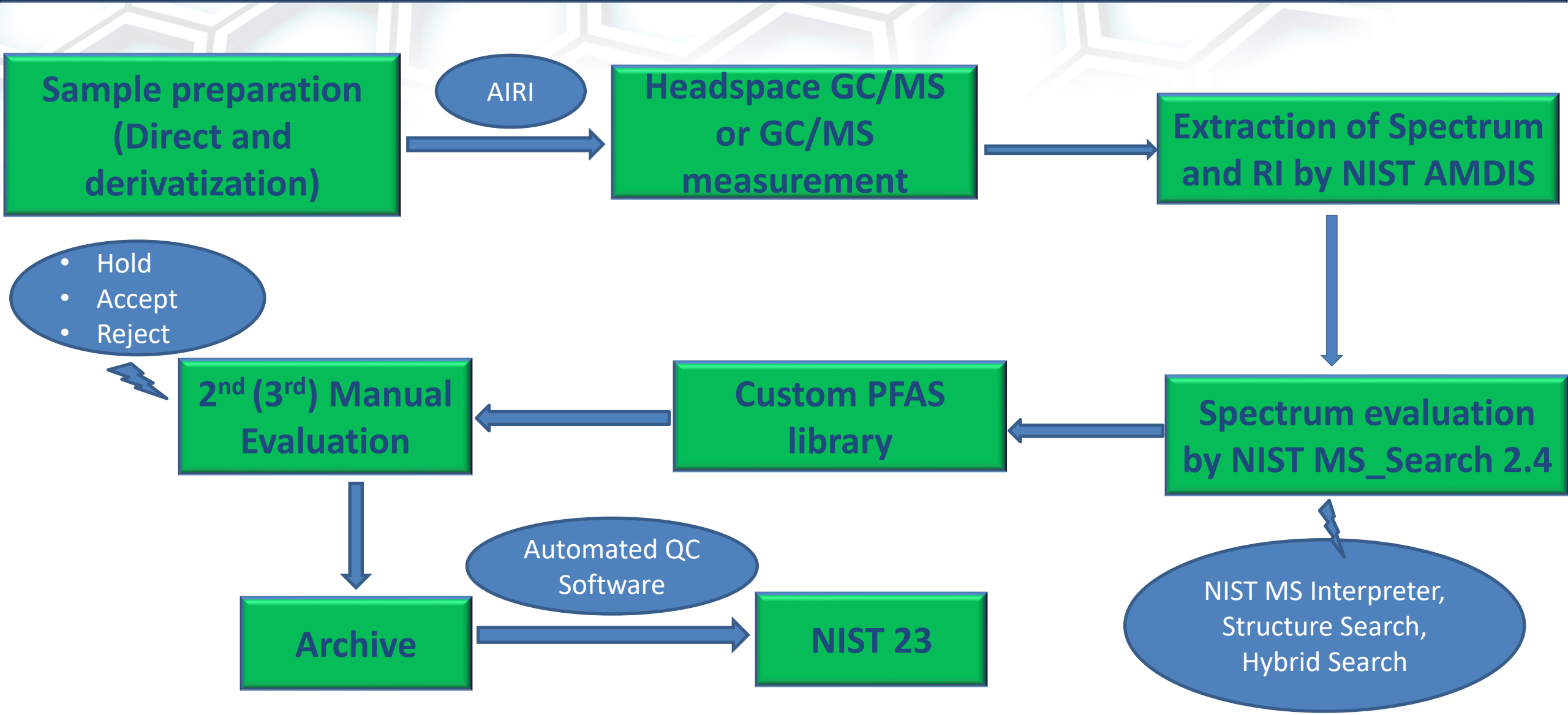
Distribution of 231 PFAS



Replacement with an high quality spectrum with RI



Workflow for Expanding PFAS EI Library



Artificial Intelligence prediction of Retention Indices to Aid in Experiment Design

1,1,2,2,3,4-hexafluorocyclobutane
Chemical Formula: $C_4H_2F_6$
Exact Mass: 164.01

Predicts RI of 231 PFAS using AIRI Program

RI<850

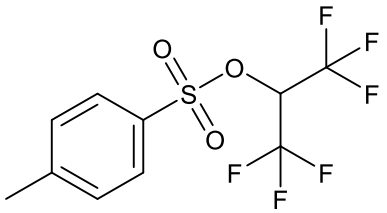
RI>850

35% of PFAS measured on Headspace GC/MS method

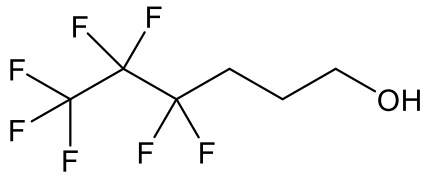
65% of PFAS measured on GC/MS by liquid injection

Functional Group

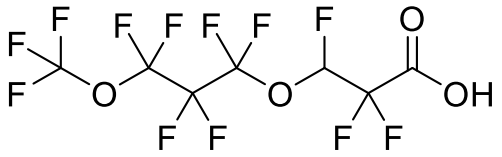
(sulfonates , alcohols, acids, and sulfur acid)



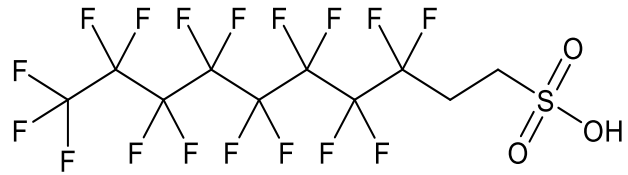
EI direct Analysis



EI direct, Silylation, Acetylation and Methylation



EI direct, Silylation, and Methylation



ESI MS analysis

HeadSpace GC-MS Method

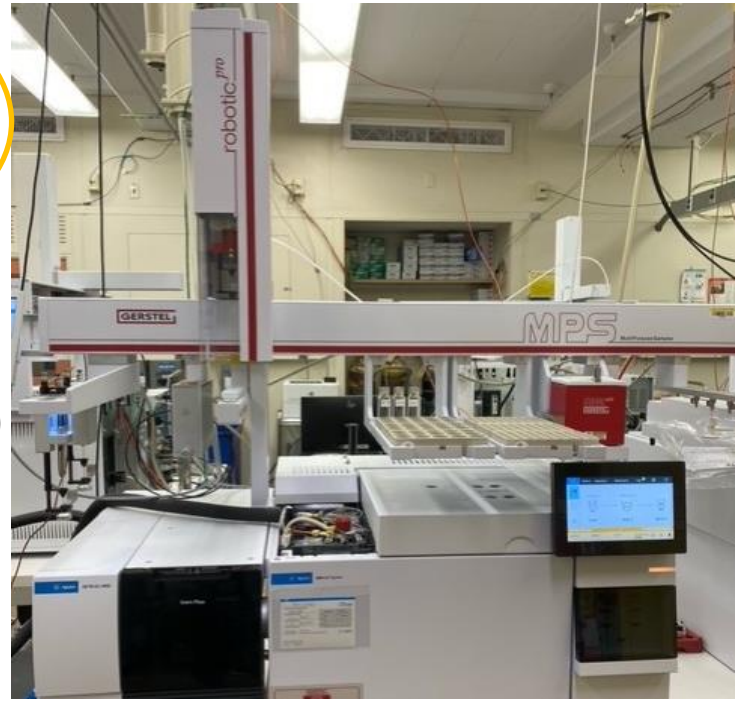
- **Sample Preparation:** All PFAS were dissolved in acetonitrile at a concentration of 1 mg/ml. Different chemical derivatization were done for compounds containing polar function groups.
- **Headspace method parameters:**

  Incubation Temp & time: 70 °C & 5-15 mins

  Syringe T: 70 °C

  Injection Volume: 100 ul

One single run is completed in 15 mins



- **GC Conditions:**

  Inlet T: 150 °C (0min) -> 12 °C /min to 250 °C (3 min)

  Oven T: -35 °C (0min) -> 5 °C /min to 75 °C (0 min) -> 20 °C /min to 200 °C(0 min)

  GC Column: 30 m x 250 µm x 0.25 µm

  Gas flow: 1 ml/min

  Split Ratio: 100:1

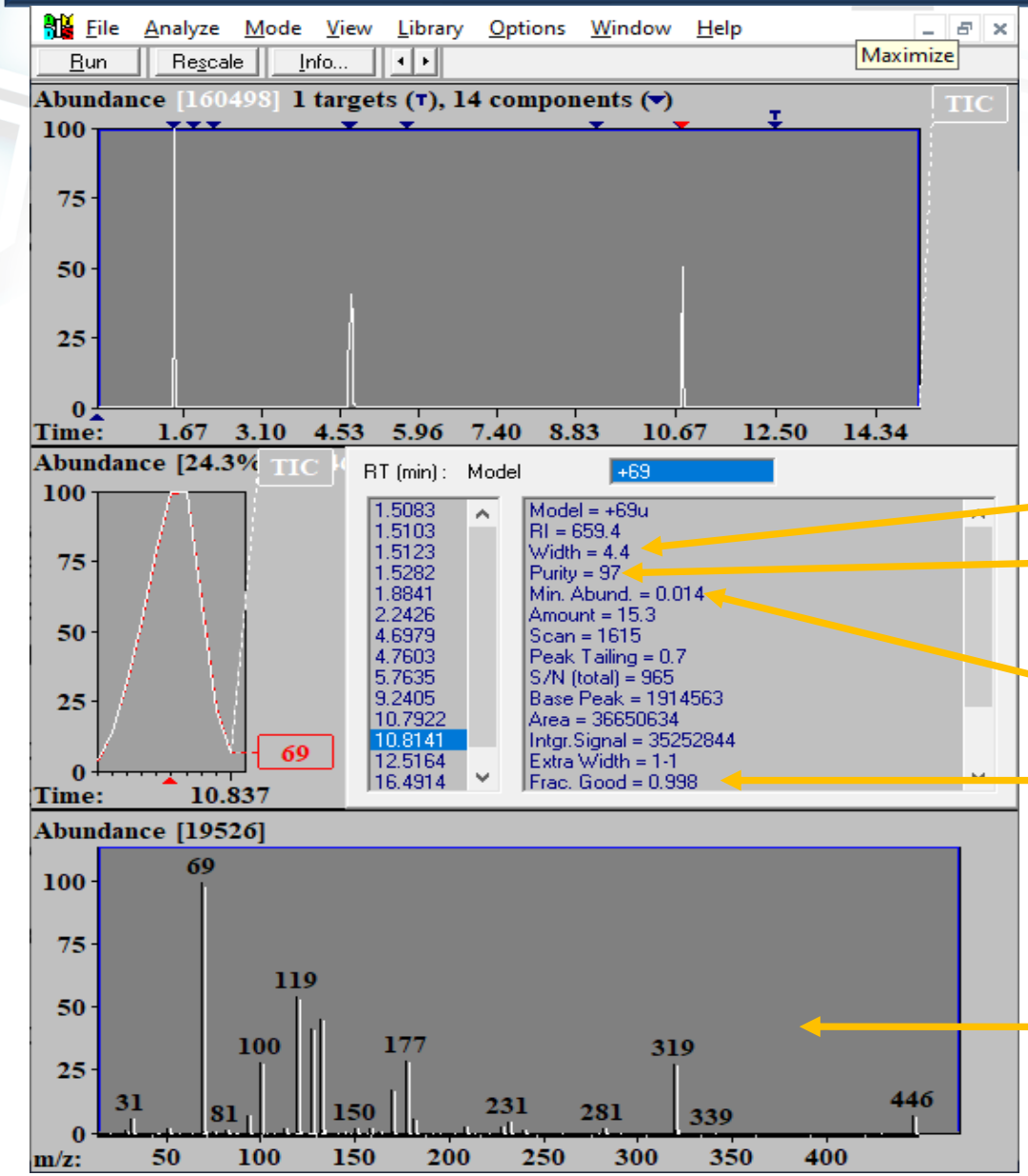
  Saturated Alkanes standard C3-C9 used as RI calibration mix

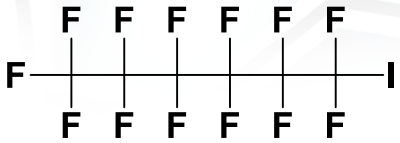
- **MS Conditions:**

  MS Acquisition Type: Scan Mode; MS Range: *m/z* 14-600

  MS instrument was tuned by standard tune method prior to analysis of samples.

Spectrum Quality Control by NIST AMDIS





Perfluorohexyl iodide
Chemical Formula: $C_6F_{13}I$
Exact Mass: 445.88

Chromatographic peak meets the following requirements:

a) Peak Width: 3-10 scans

b) Purity > 90%
(90% ion current is accounted for in extracted spectrum)

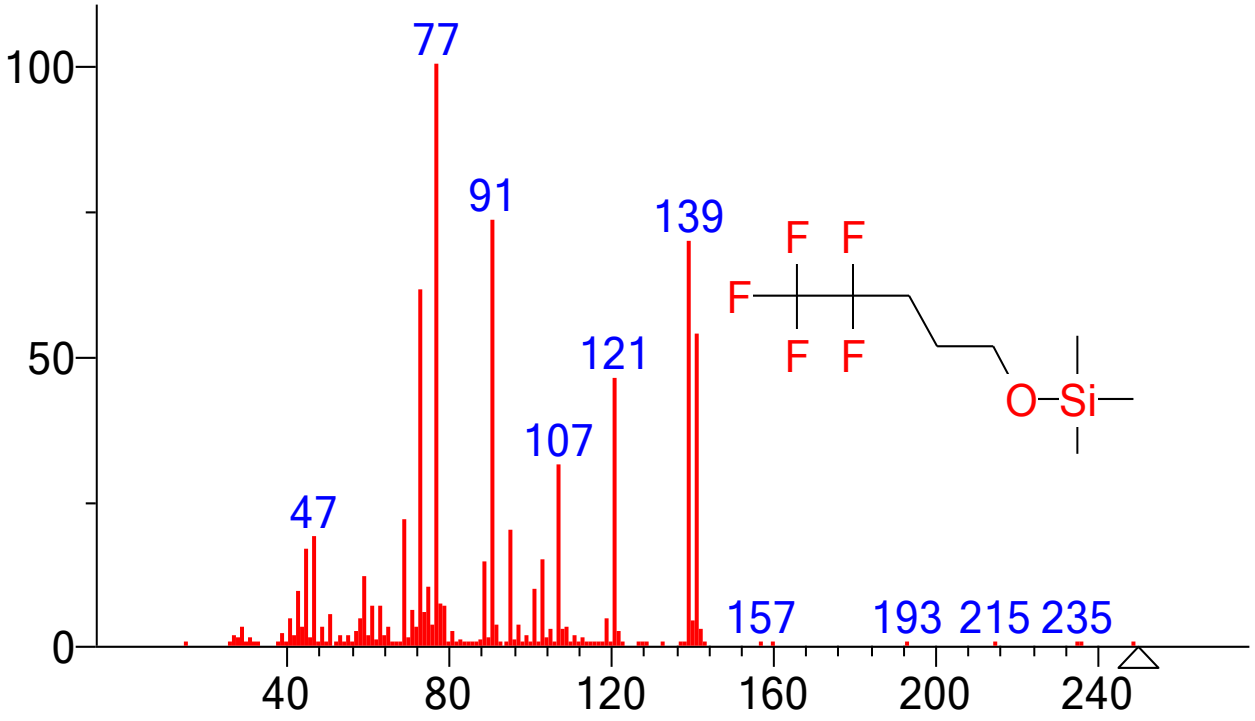
c) Minimum Abundance = 0.094 out of 1
(noise level <0.1, the abundance of ions less than 0.1% will be removed)

d) Fraction Good > 0.90 out of 1
(90% ions in spectrum match the model of the compound)

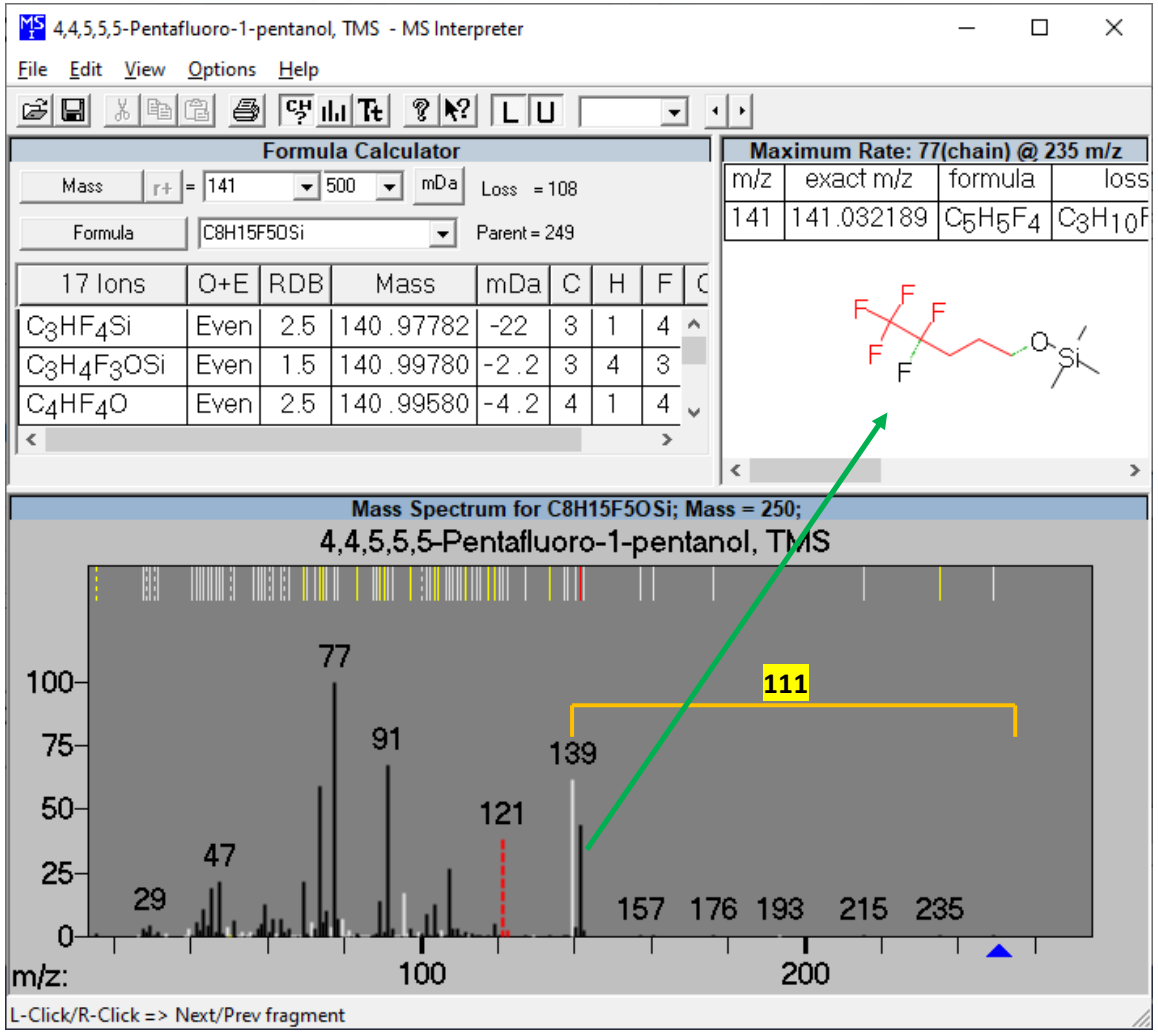
A spectrum extracted by GC deconvolution program

NIST MS Interpreter to Aid Spectrum Evaluation

This program determines the probable origin of peak ions using thermochemical rules

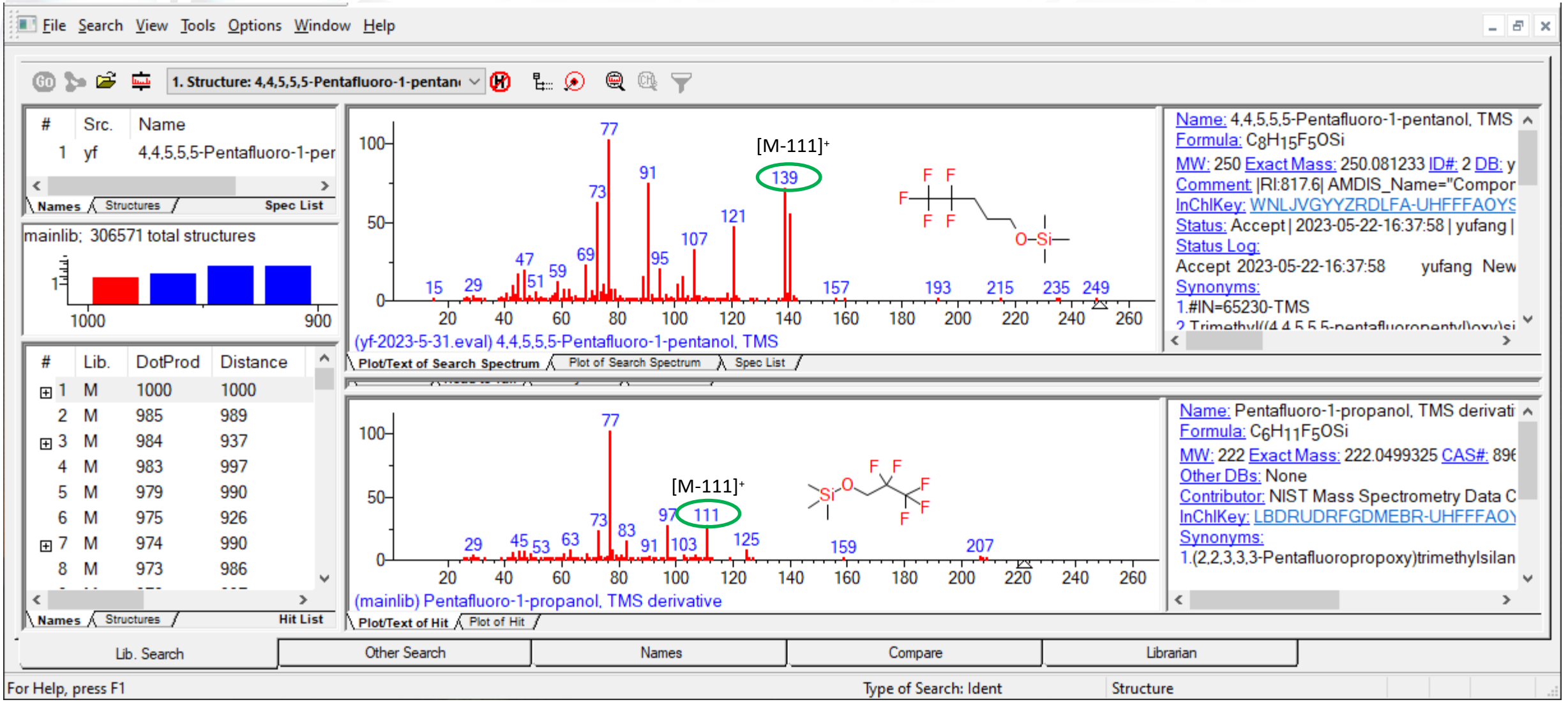


Name: 4,4,5,5,5-Pentafluoro-1-pentanol, TMS
Formula:C8H15F5OSi
MW:250

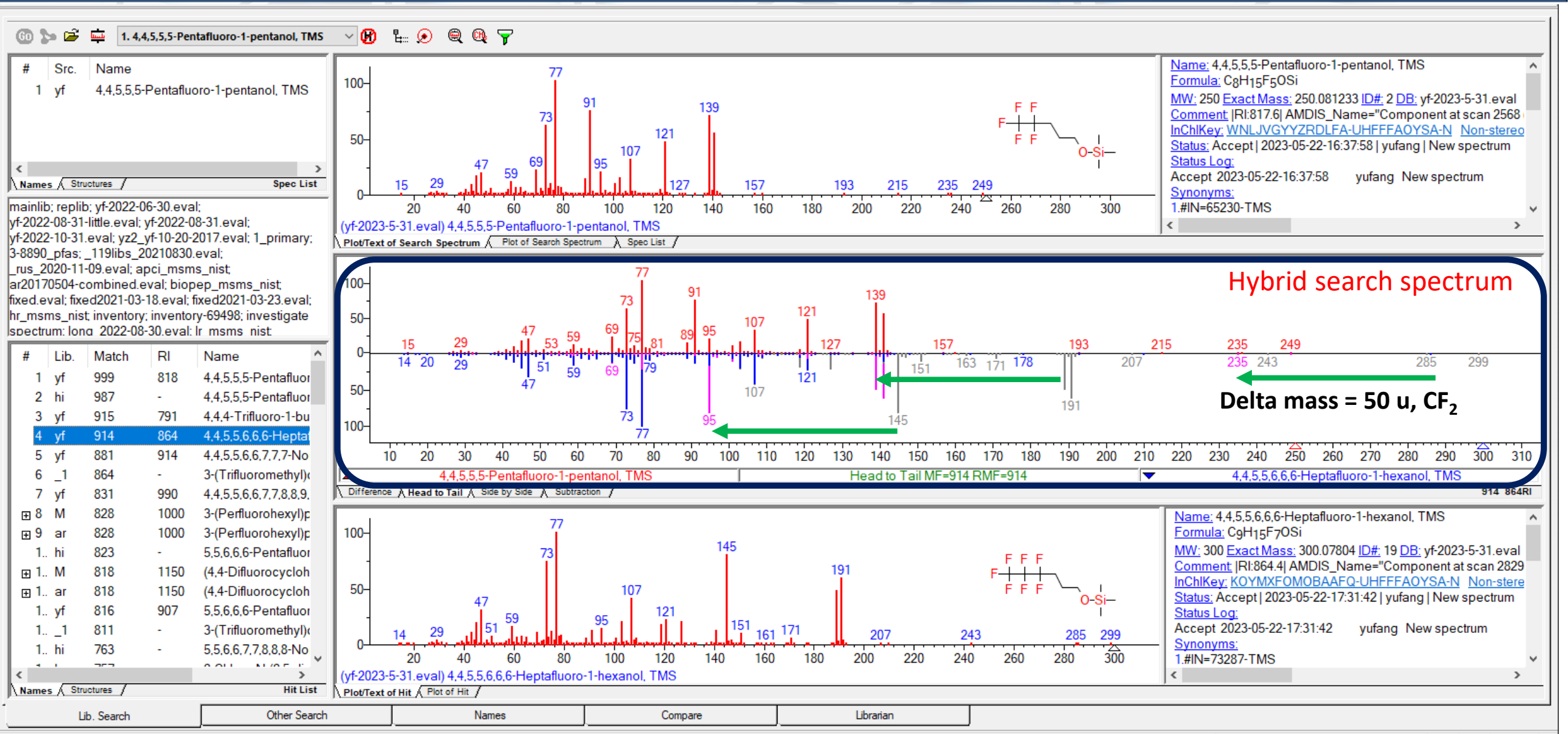


Structure Similarity Search to Aid Spectrum Evaluation

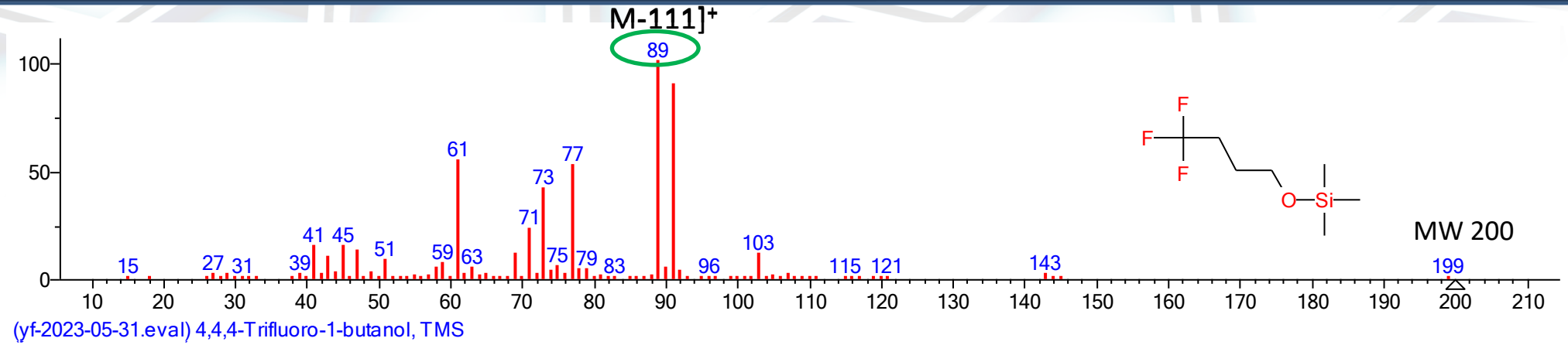
Example: Dealing with unexpected fragment ions of spectrum



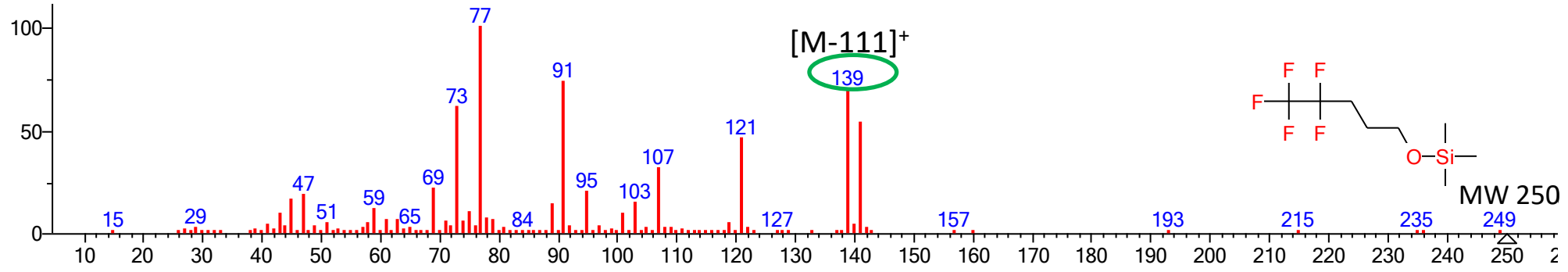
Hybrid Search to Aid Spectrum Evaluation



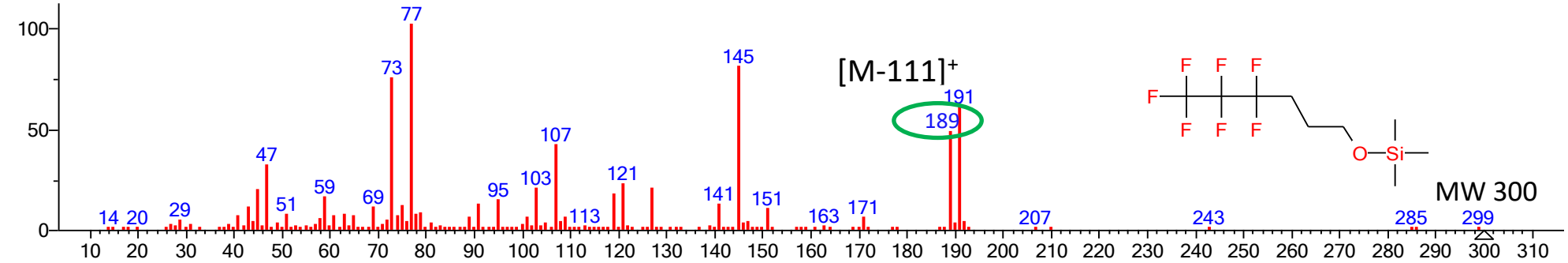
Spectra of PFAS with Different Fluoro- Numbers



(yf-2023-05-31.eval) 4,4,4-Trifluoro-1-butanol, TMS

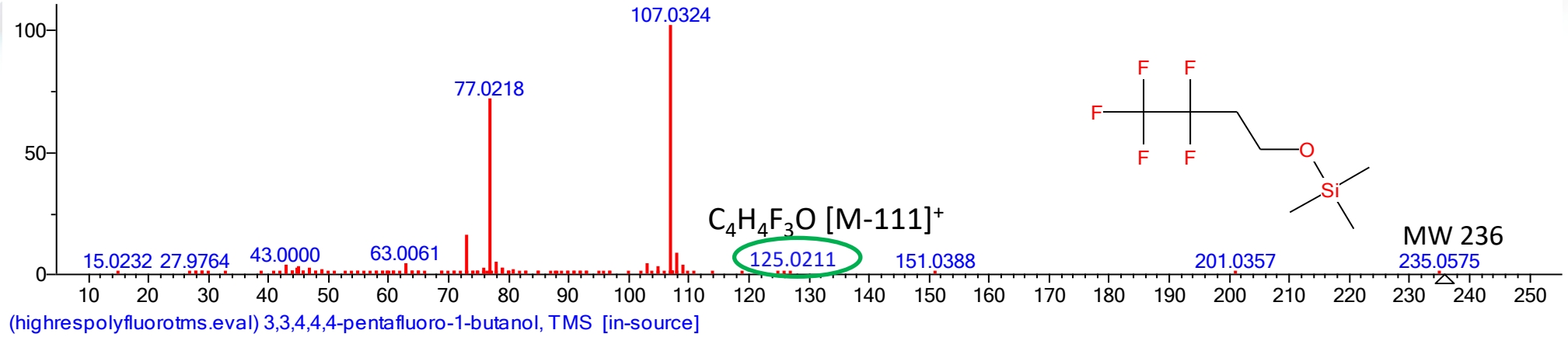


(2-primary_id67525-) 4,4,5,5,5-Pentafluoro-1-pentanol, TMS

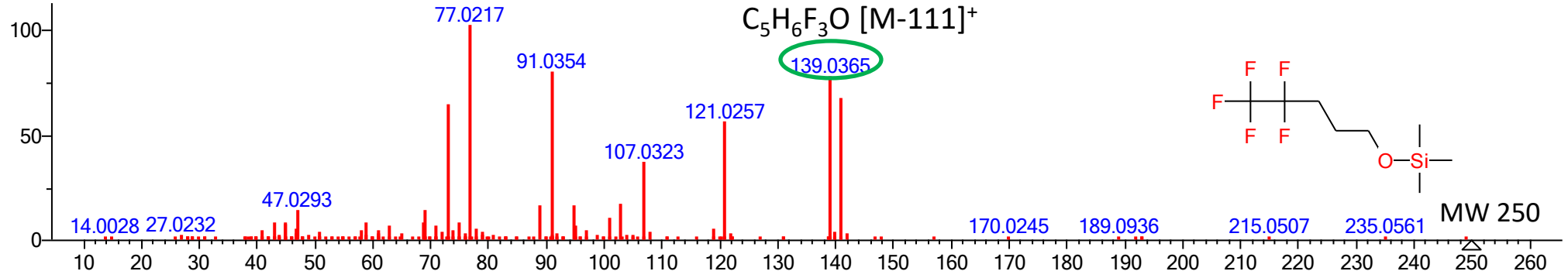


(2-primary_id67525-) 4,4,5,5,6,6,6-heptafluoro-1-hexanol, TMS

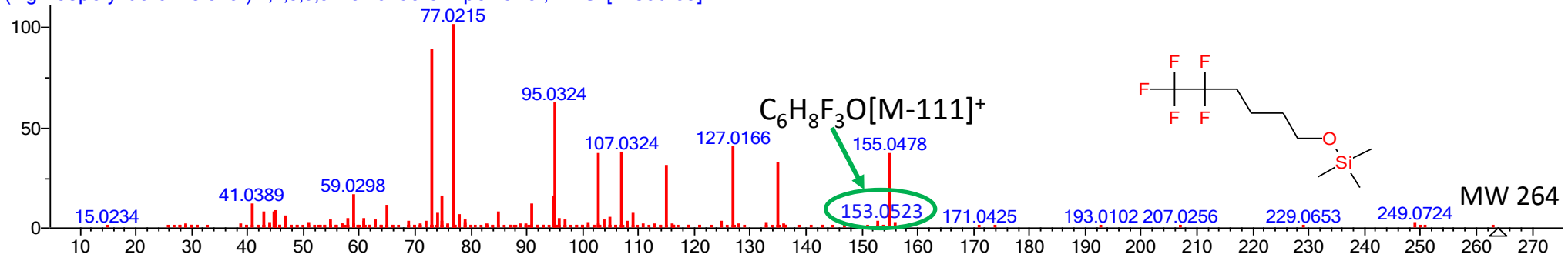
Spectra of PFAS with Similar Structures Acquired by High Resolution GC-MS



(highrespolyfluorotms.eval) 3,3,4,4,4-pentafluoro-1-butanol, TMS [in-source]

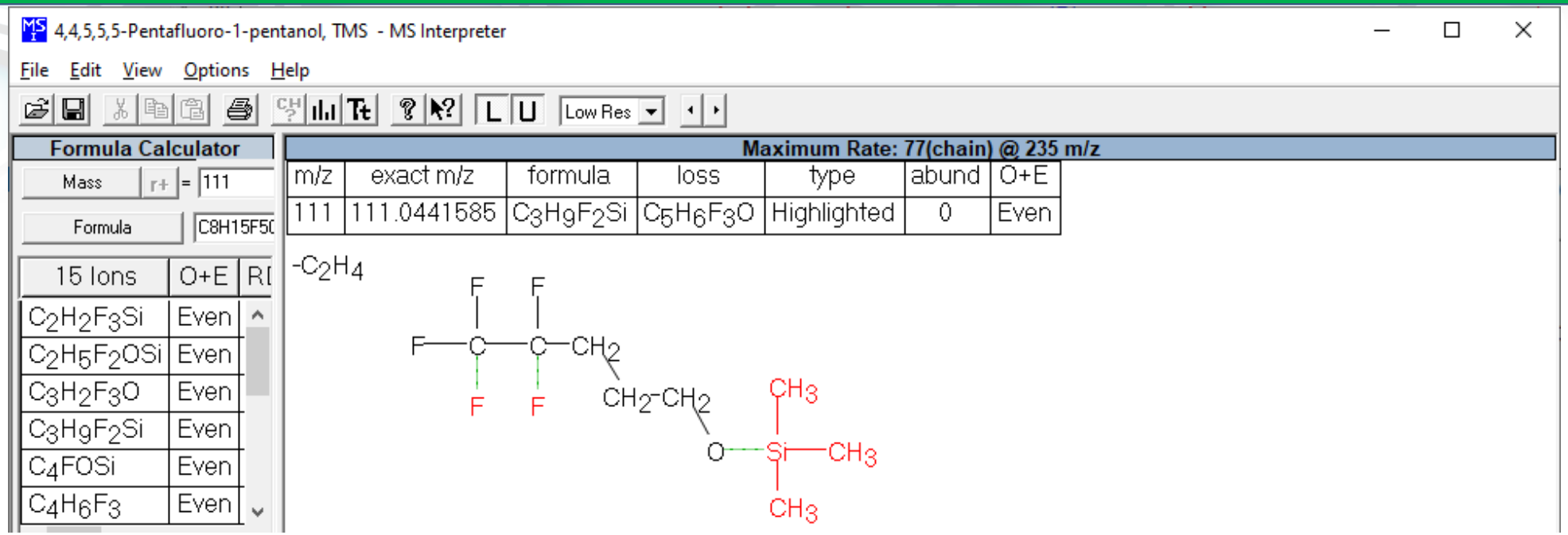


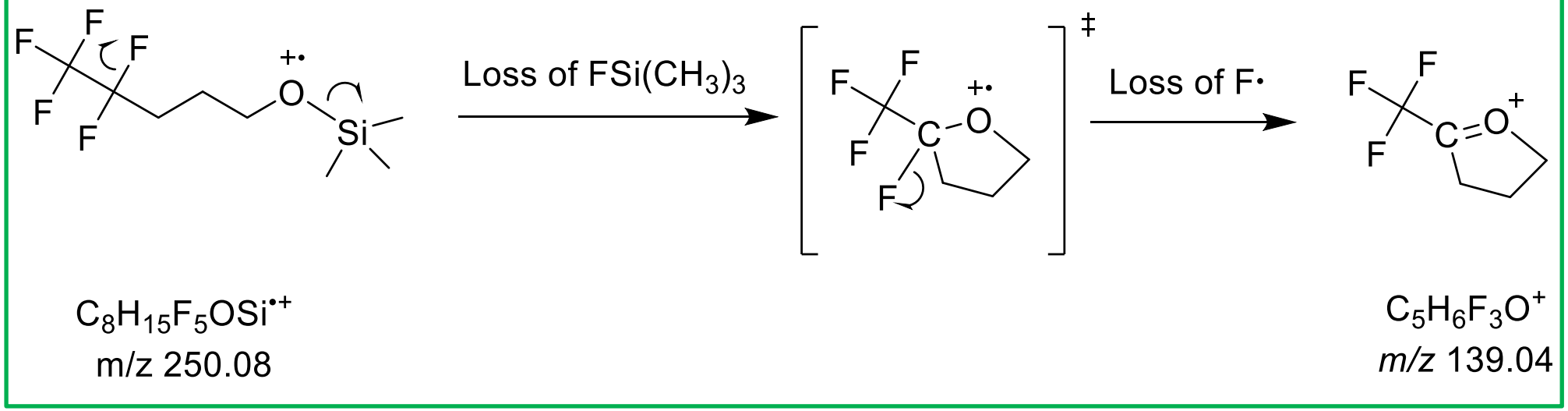
(highrespolyfluorotms.eval) 4,4,5,5,5-Pentafluoro-1-pentanol, TMS [in-source]



(highrespolyfluorotms.eval) 5,5,6,6,6-Pentafluorohexan-1-ol, TMS [in-source]

Proposed Mechanism for Generating the $[M-111]^+$ Ion





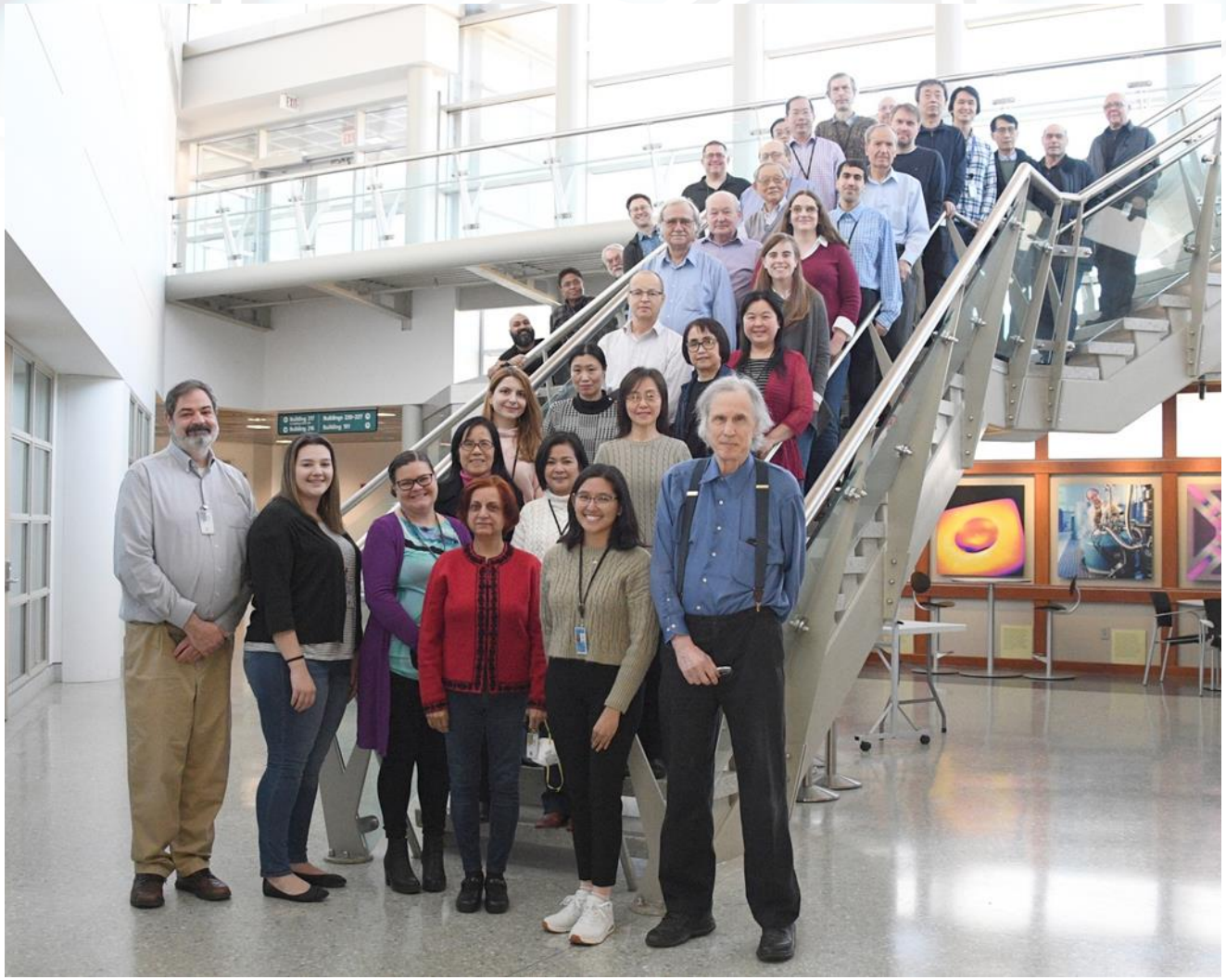
SUMMARY

- A new procedure is presented for expanding coverage of the high-quality PFAS EI spectra in the NIST23 lib.

- A newly developed AI retention index program was utilized to differentiate the right PFAS for Headspace GC-MS analysis. The optimal Headspace injection method was developed for these highly volatile PFAS with RI ranged from 300-850.

- Each spectrum was extracted from the total ion chromatogram using the NIST AMDIS program. Confirmation of identity was aided with NIST developed MS Interpreter, Structure Similarity Search and Hybrid Search algorithm, making it much easier to interpret most of fragmentation ions.

ACKNOWLEDGEMENTS



MS Data Center

Edward Erisman
Quanlong Pu
Weihua Ji
Tytus Mak
Lewis Y. Geer
Stephen Stein
William Wallace

Thank you for your attention!