

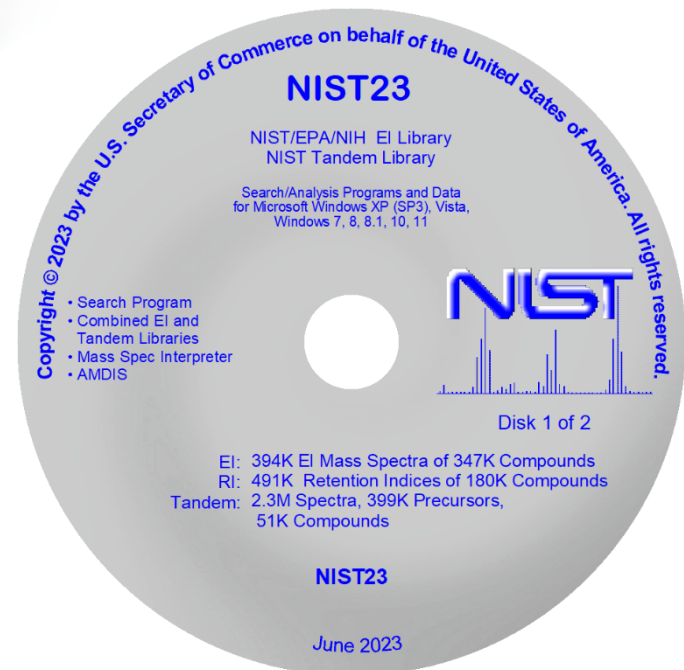
Enhancing the Coverage and Quality of Spectra of Per- and Polyfluoroalkyl Substances in a Comprehensive Electron Ionization Mass Spectral Library

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ASMS 2023

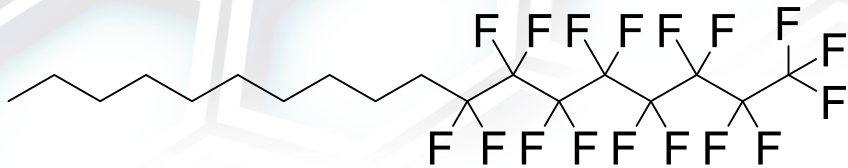


INTRODUCTION

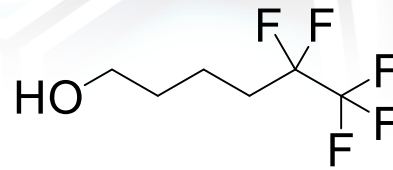
- The NIST/EPA/NIH EI MS Library is a world's most widely used and trusted mass spectral reference library.
- The 2023 release EI library includes 394,000 carefully-evaluated spectra of 347,100 unique compounds. 40,200 compounds were added to the NIST 2020.
- It includes a GC retention index library (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.



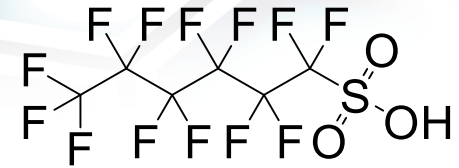
Overview



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



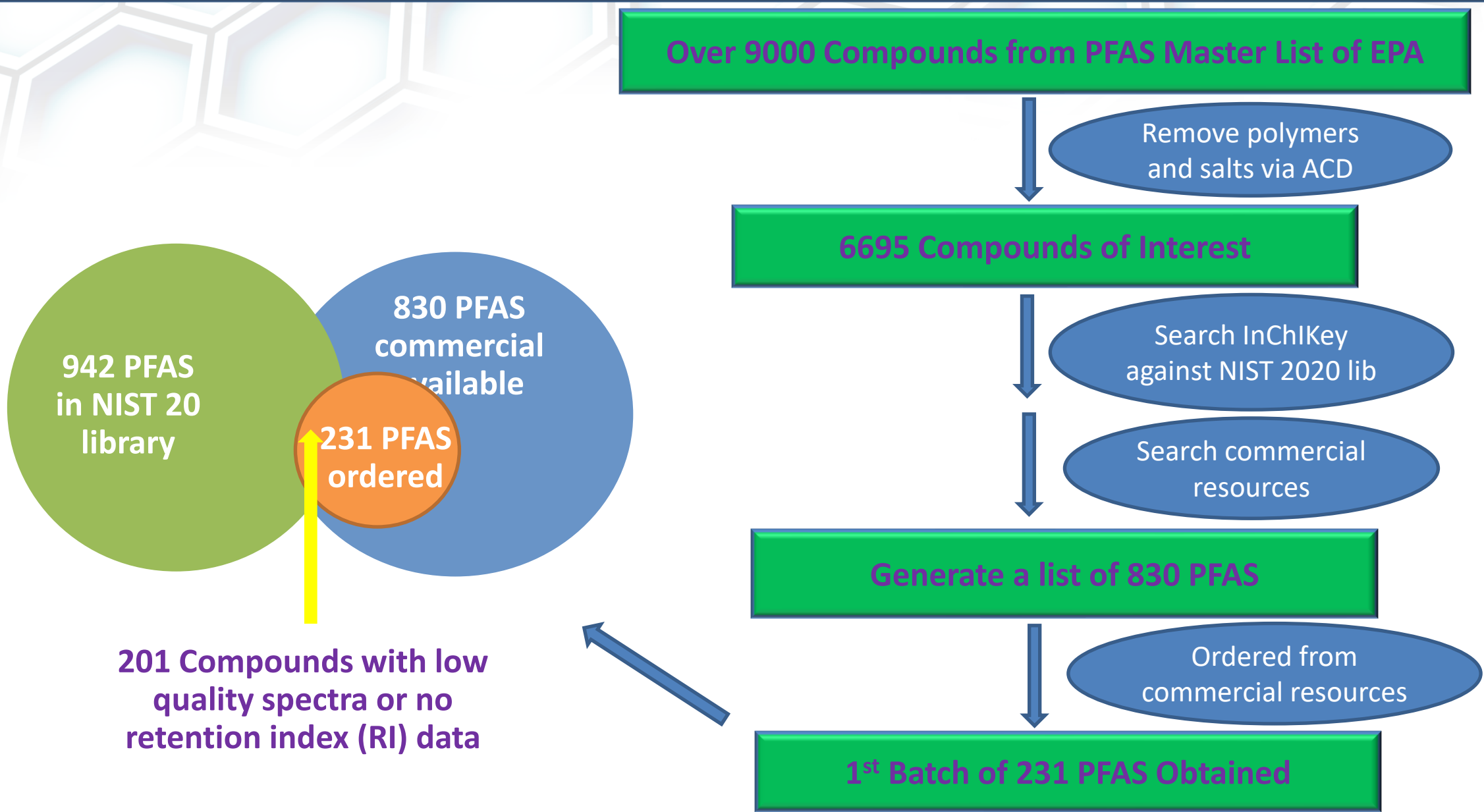
5,5,6,6,6-pentafluorohexan-1-ol



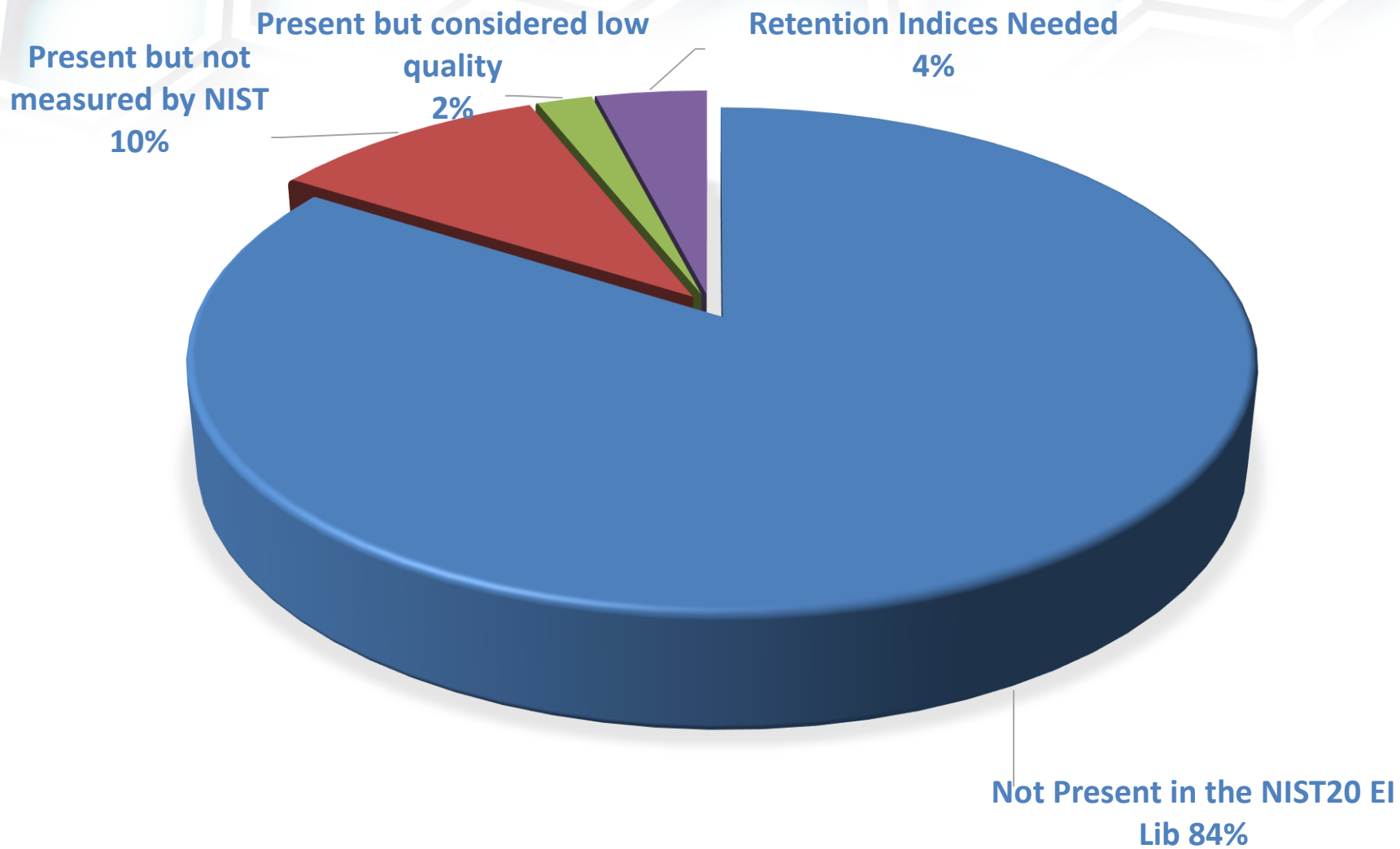
1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexane-1-sulfonic acid

- 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



Distribution of 231 PFAS



Replacement with an high quality spectrum with RI

1. Structure: Perfluorooctanonitrile

Src. Name
1 5_ Perfluorooctanonit

mainlib: 306571 total structures

(5_combined pfas-01-2023.eval) Perfluorooctanonitrile

Plot/Text of Search Spectrum / Plot of Search Spectrum / Spec List

Perfluorooctanonitrile Head to Tail MF=888 RMF=967 Perfluorooctanonitrile

Difference / Head to Tail / Side by Side / Subtraction

(mainlib) Perfluorooctanonitrile

Plot/Text of Hit / Plot of Hit

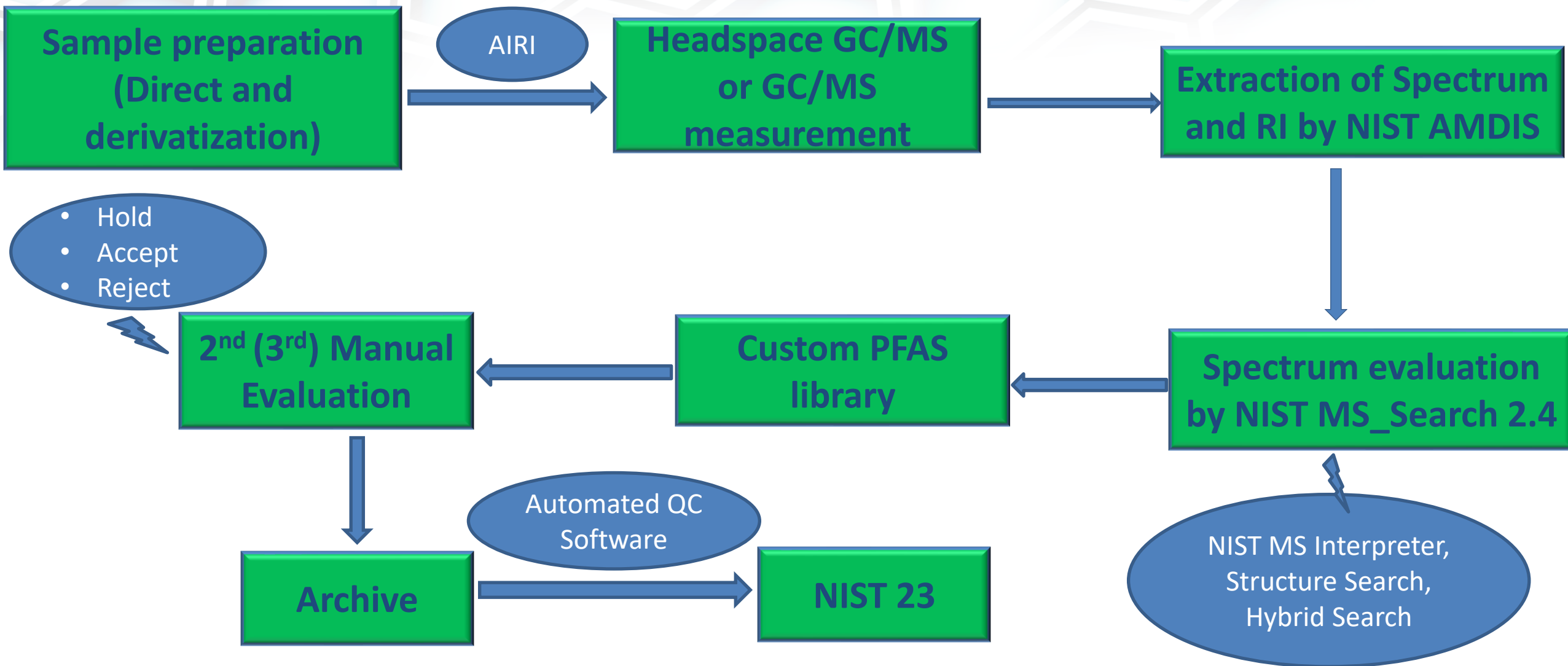
Lib. Search Other Search Names Compare Librarian

Type of Search: Hybrid Structure

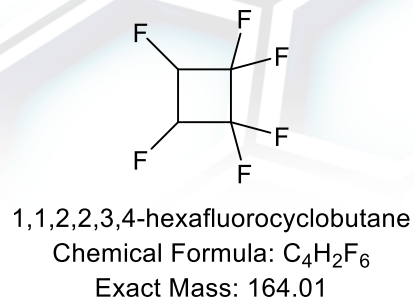
Name: Perfluorooctanonitrile
Formula: C₈F₁₅N
MW: 395 **Exact Mass:** 394.979122 **CAS#:** 647-12-1 **ID#:** 377
Other DBs: None
Comment: AMDIS_Name="Component at scan 604 (4.095 r
InChIKey: FULLNJNBFUCVES-UHFFFAOYSA-N **Non-ste**
Status: Accept | 2023-05-11-11:14:38 | yufang | updated chem
Status Log:
Accept 2023-05-11-11:14:38 yufang updated chemica
76 m/z Values and Intensities:
26 2 | 31 45 | 32 1 | 38 1 | 50 20 |
51 1 | 55 1 | 57 5 | 62 3 | 68 2 |
69 999 | 70 13 | 74 5 | 76 200 | 77 5 |

Name: Perfluorooctanonitrile
Formula: C₈F₁₅N
MW: 395 **Exact Mass:** 394.979122 **CAS#:** 647-12-1 **NIST#:** 14
Other DBs: Fine, EINECS
Contributor: ASES Database, Dalian Institute, P.R. China
InChIKey: FULLNJNBFUCVES-UHFFFAOYSA-N **Non-ste**
15 m/z Values and Intensities:
31 99 | 69 999 | 76 200 | 93 29 | 100 179 |
119 400 | 126 49 | 131 231 | 169 250 | 181 90 |
219 89 | 231 59 | 269 69 | 319 50 | 395 39 |
Synonyms:

Workflow for Expanding PFAS EI Library



Artificial Intelligence prediction of Retention Indices to Aid in Experiment Design



Predicts RI of 231 PFAS using AIRI Program

RI < 850

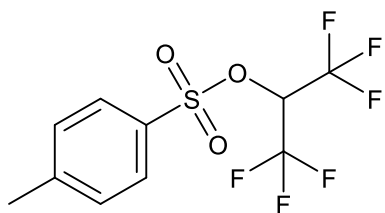
RI > 850

35% of PFAS measured on
Headspace GC/MS method

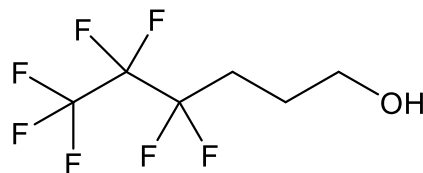
65% of PFAS measured on
GC/MS by liquid injection

Functional Group

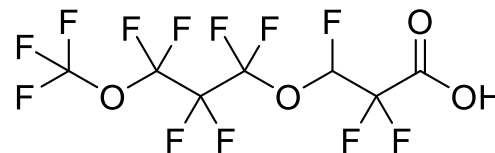
(sulfonates, alcohols, acids, and sulfur acid)



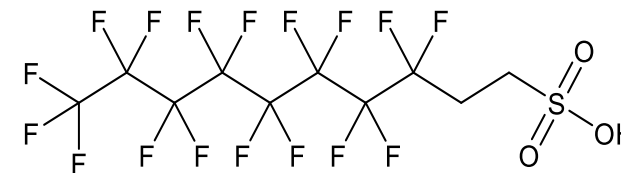
EI direct Analysis



EI direct, Silylation, Acetylation
and Methylation



EI direct, Silylation,
and Methylation

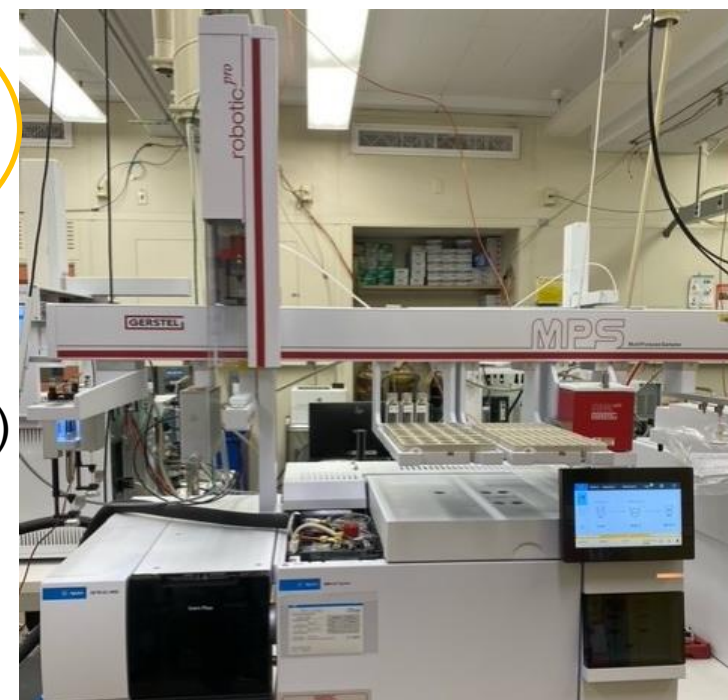


ESI MS analysis

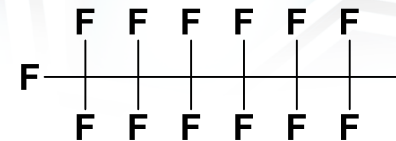
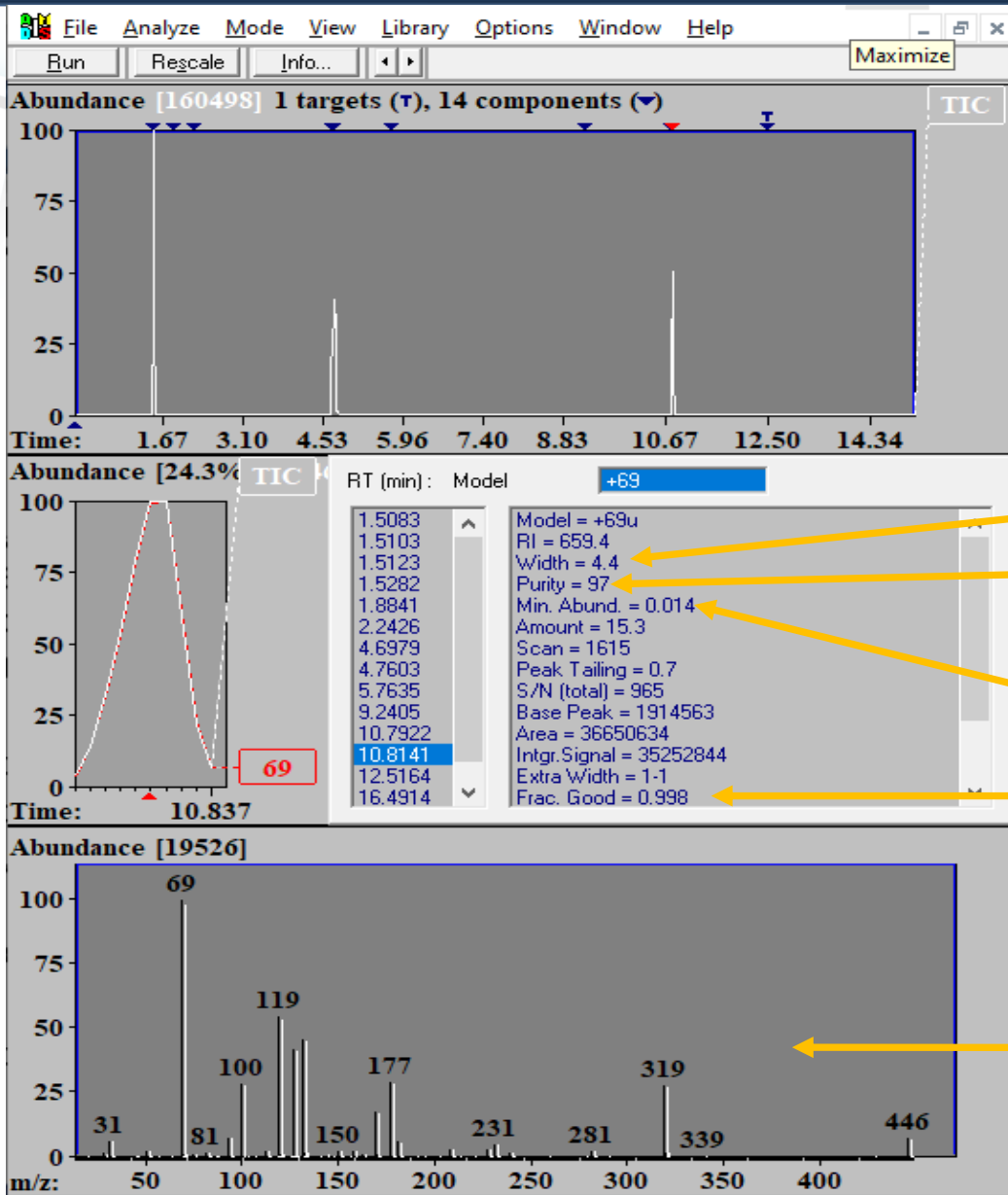
Headspace GC-MS Method

- **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
- **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.

One single run is
completed in 15 mins



Spectrum Quality Control by NIST AMDIS



Perfluorohexyl iodide

Chemical Formula: $\text{C}_6\text{F}_{13}\text{I}$

Exact Mass: 445.88

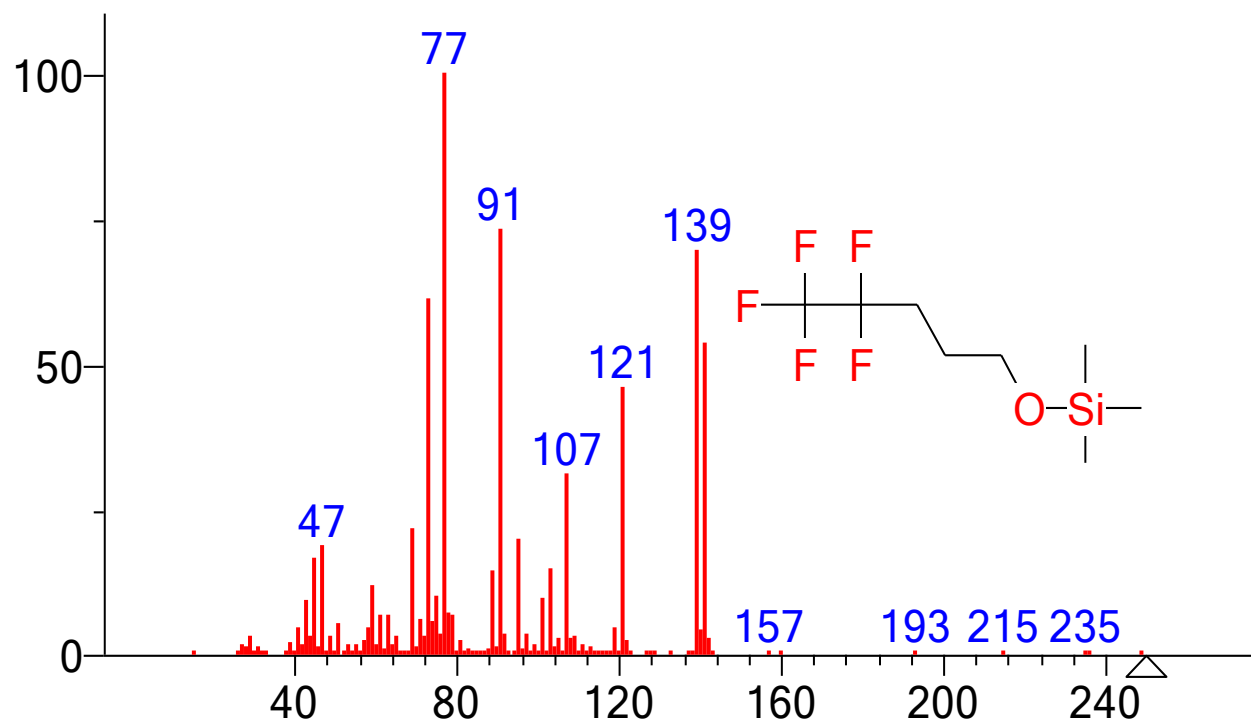
Chromatographic peak meets the following requirements:

- 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

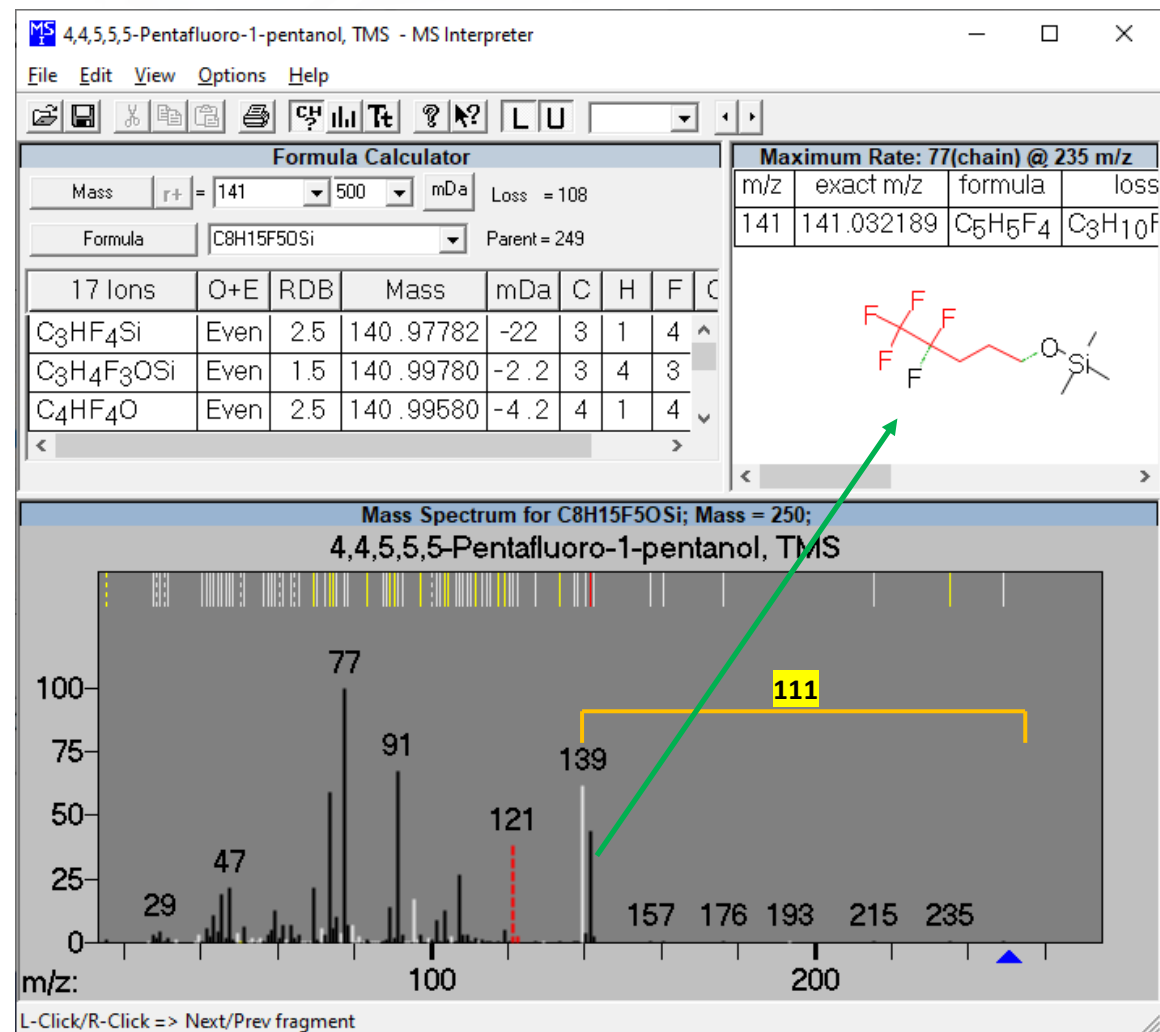
This program determines the probable origin of peak ions using thermochemical rules



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

File Search View Tools Options Window Help

1. Structure: 4,4,5,5,5-Pentafluoro-1-pentanol

#	Src.	Name
1	yf	4,4,5,5,5-Pentafluoro-1-per

mainlib: 306571 total structures

#	Lib.	DotProd	Distance
1	M	1000	1000
2	M	985	989
3	M	984	937
4	M	983	997
5	M	979	990
6	M	975	926
7	M	974	990
8	M	973	986

Plot/Text of Search Spectrum

(yf-2023-5-31.eval) 4,4,5,5,5-Pentafluoro-1-pentanol, TMS

Plot of Search Spectrum

Spec List

Name: 4,4,5,5,5-Pentafluoro-1-pentanol, TMS
Formula: C₈H₁₅F₅O_{Si}
MW: 250 Exact Mass: 250.081233 ID# 2 DB: y
Comment [RI:817.6] AMDIS_Name="Compor
InChIKey: WNLJVGYYZRDLEA-UHFFFAOYS
Status: Accept | 2023-05-22-16:37:58 | yufang |
Status Log:
Accept 2023-05-22-16:37:58 yufang New
Synonyms:
1.#IN=65230-TMS
2 Trimethyl(4,4,5,5,5-pentafluoropentyl)oxysilane

Plot/Text of Hit

(mainlib) Pentafluoro-1-propanol, TMS derivative

Plot of Hit

Name: Pentafluoro-1-propanol, TMS derivati
Formula: C₆H₁₁F₅O_{Si}
MW: 222 Exact Mass: 222.0499325 CAS#: 896
Other DBs: None
Contributor: NIST Mass Spectrometry Data C
InChIKey: LBDRUDRFGDMEBR-UHFFFAOY
Synonyms:
1.(2,2,3,3,3-Pentafluoropropoxy)trimethylsilan

Lib. Search Other Search Names Compare Librarian

For Help, press F1 Type of Search: Ident Structure

Hybrid Search to Aid Spectrum Evaluation

1. 4,4,5,5,5-Pentafluoro-1-pentanol, TMS

#	Src.	Name
1	yf	4,4,5,5,5-Pentafluoro-1-pentanol, TMS

Name: 4,4,5,5,5-Pentafluoro-1-pentanol, TMS
Formula: C₈H₁₅F₅OSi
MW: 250 **Exact Mass:** 250.081233 **ID#:** 2 **DB:** yf-2023-5-31.eval
Comment: [RI:817.6] AMDIS_Name="Component at scan 2568"
InChIKey: WNLJVGYYZRDLFA-UHFFFAOYSA-N **Non-stereo**
Status: Accept | 2023-05-22-16:37:58 | yufang | New spectrum
Status Log:
Accept 2023-05-22-16:37:58 yufang New spectrum
Synonyms:
1.#IN=65230-TMS

Hybrid search spectrum

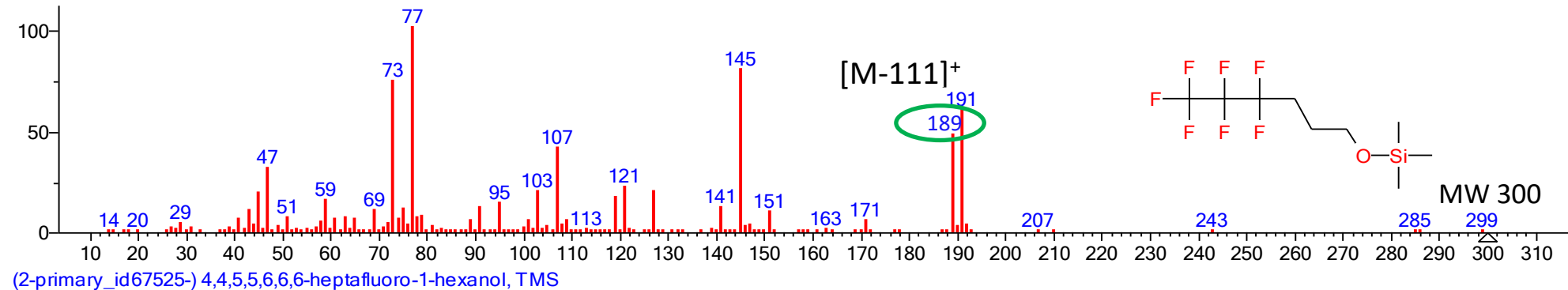
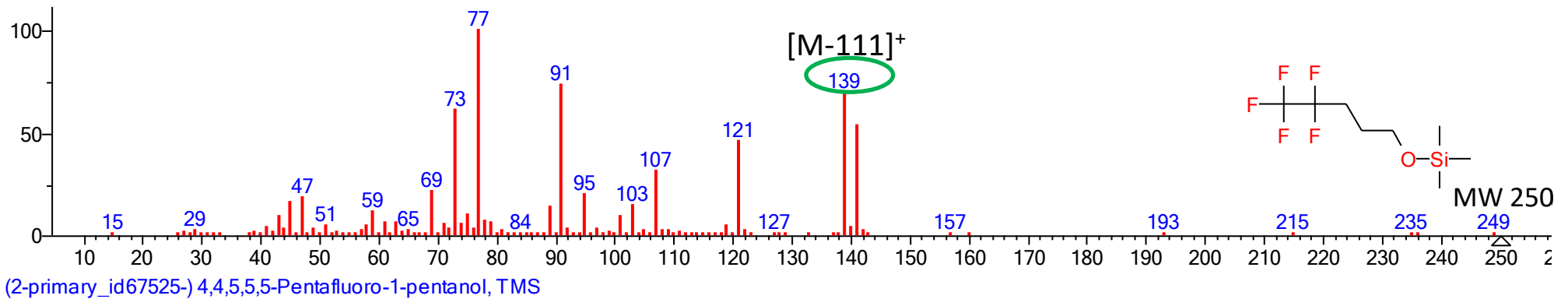
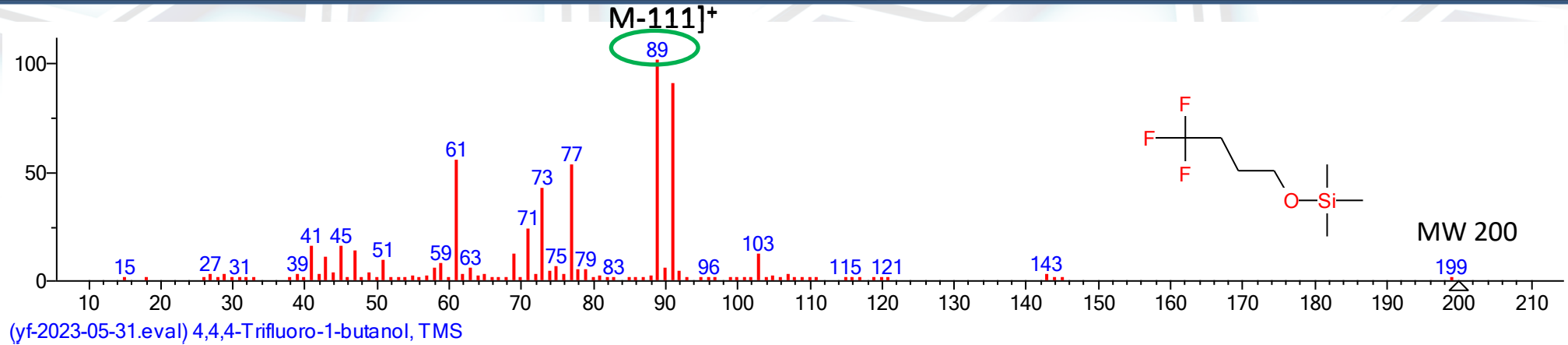
Name: 4,4,5,5,6,6,6-Heptafluoro-1-hexanol, TMS
Formula: C₉H₁₅F₇OSi
MW: 300 **Exact Mass:** 300.07804 **ID#:** 19 **DB:** yf-2023-5-31.eval
Comment: [RI:864.4] AMDIS_Name="Component at scan 2829"
InChIKey: KOYMXFOMOBAAFQ-UHFFFAOYSA-N **Non-stereo**
Status: Accept | 2023-05-22-17:31:42 | yufang | New spectrum
Status Log:
Accept 2023-05-22-17:31:42 yufang New spectrum
Synonyms:
1.#IN=73287-TMS

#	Lib.	Match	RI	Name
1	yf	999	818	4,4,5,5,5-Pentafluoro-1-pentanol, TMS
2	hi	987	-	4,4,5,5,5-Pentafluoro-1-pentanol, TMS
3	yf	915	791	4,4,4-Trifluoro-1-butanol, TMS
4	yf	914	864	4,4,5,5,6,6,6-Heptafluoro-1-hexanol, TMS
5	yf	881	914	4,4,5,5,6,6,7,7,7-Nonafluoro-1-heptanol, TMS
6	_1	864	-	3-(Trifluoromethyl)propan-1-ol, TMS
7	yf	831	990	4,4,5,5,6,6,7,7,8,8,9,9-Nonafluoro-1-decanol, TMS
8	M	828	1000	3-(Perfluorohexyl)propan-1-ol, TMS
9	ar	828	1000	3-(Perfluorohexyl)propan-1-ol, TMS
1..	hi	823	-	5,5,6,6,6-Pentafluoro-1-hexanol, TMS
1..	M	818	1150	(4,4-Difluorocyclohexyl)methanol, TMS
1..	ar	818	1150	(4,4-Difluorocyclohexyl)methanol, TMS
1..	yf	816	907	5,5,6,6,6-Pentafluoro-1-hexanol, TMS
1..	_1	811	-	3-(Trifluoromethyl)propan-1-ol, TMS
1..	hi	763	-	5,5,6,6,7,7,8,8,8-Nonafluoro-1-octanol, TMS

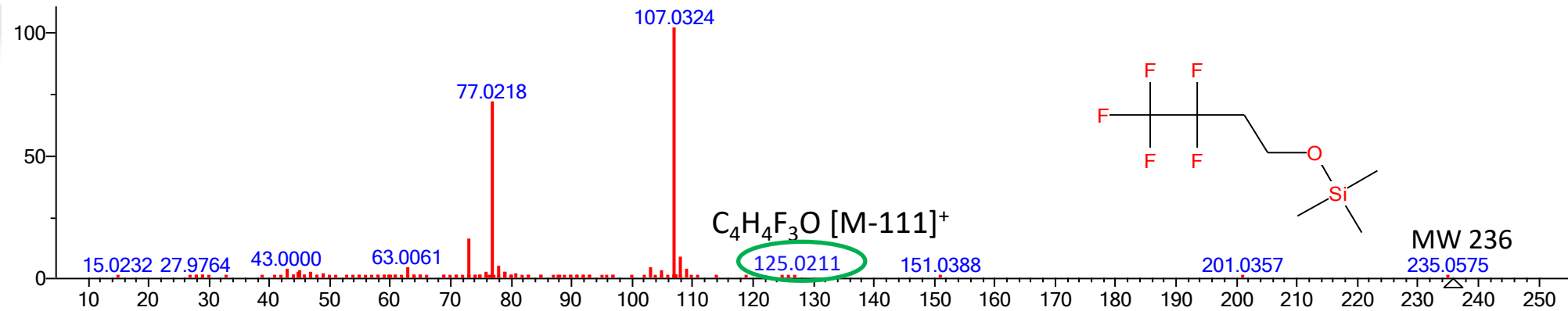
Lib. Search Other Search Names Compare Librarian

Type of Search: Hybrid Displayed: Hybrid 250

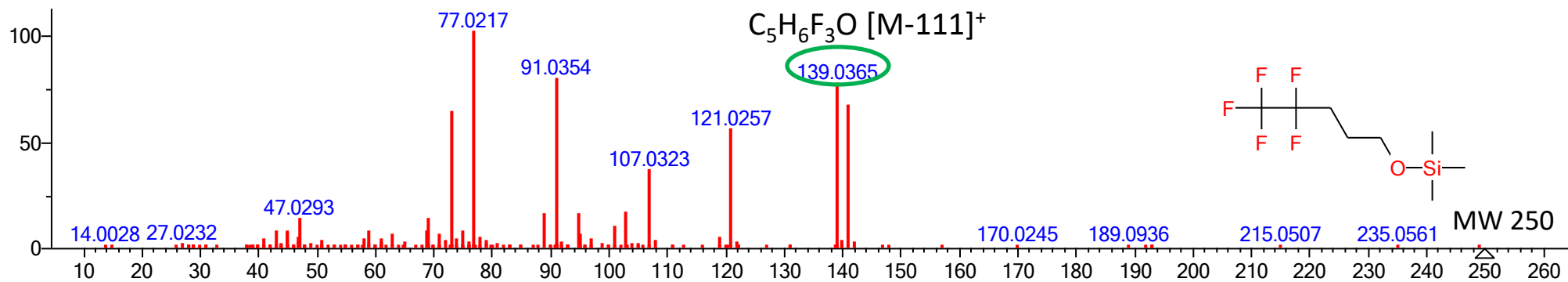
Spectra of PFAS with Different Fluoro- Numbers



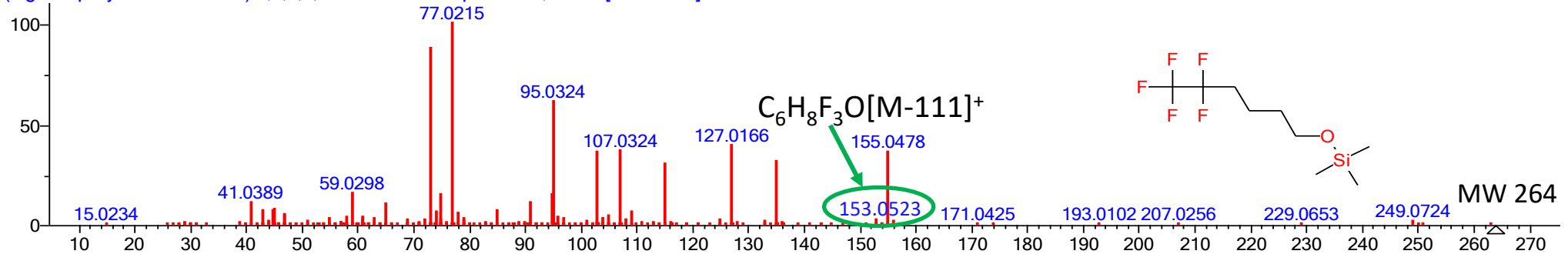
Spectra of PFAS with Similar Structures Acquired by High Resolution GC-MS



(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

MS 4,4,5,5,5-Pentafluoro-1-pentanol, TMS - MS Interpreter

File Edit View Options Help

CH₃ | | T₁ | ? | ? | L | U | Low Res

Formula Calculator

Mass r+ = 111

Formula C₈H₁₅F₅O₂Si

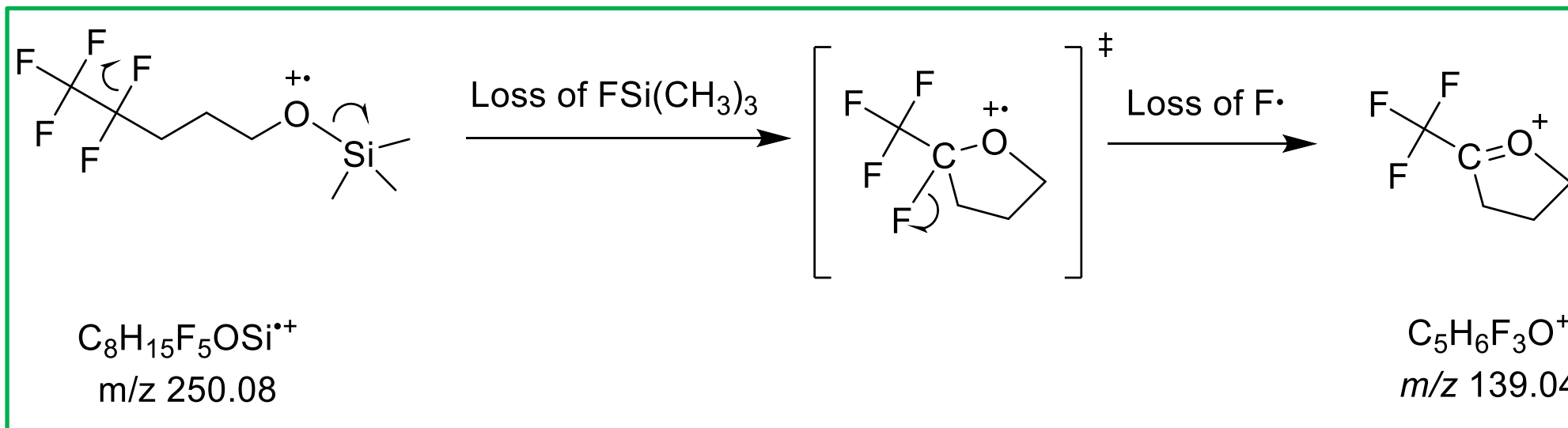
15 Ions O+E RI

C ₂ H ₂ F ₃ Si	Even	^
C ₂ H ₅ F ₂ O ₂ Si	Even	
C ₃ H ₂ F ₃ O	Even	
C ₃ H ₉ F ₂ Si	Even	
C ₄ FOSi	Even	
C ₄ H ₆ F ₃	Even	∨

Maximum Rate: 77(chain) @ 235 m/z

m/z	exact m/z	formula	loss	type	abund	O+E
111	111.0441585	C ₃ H ₉ F ₂ Si	C ₅ H ₆ F ₃ O	Highlighted	0	Even

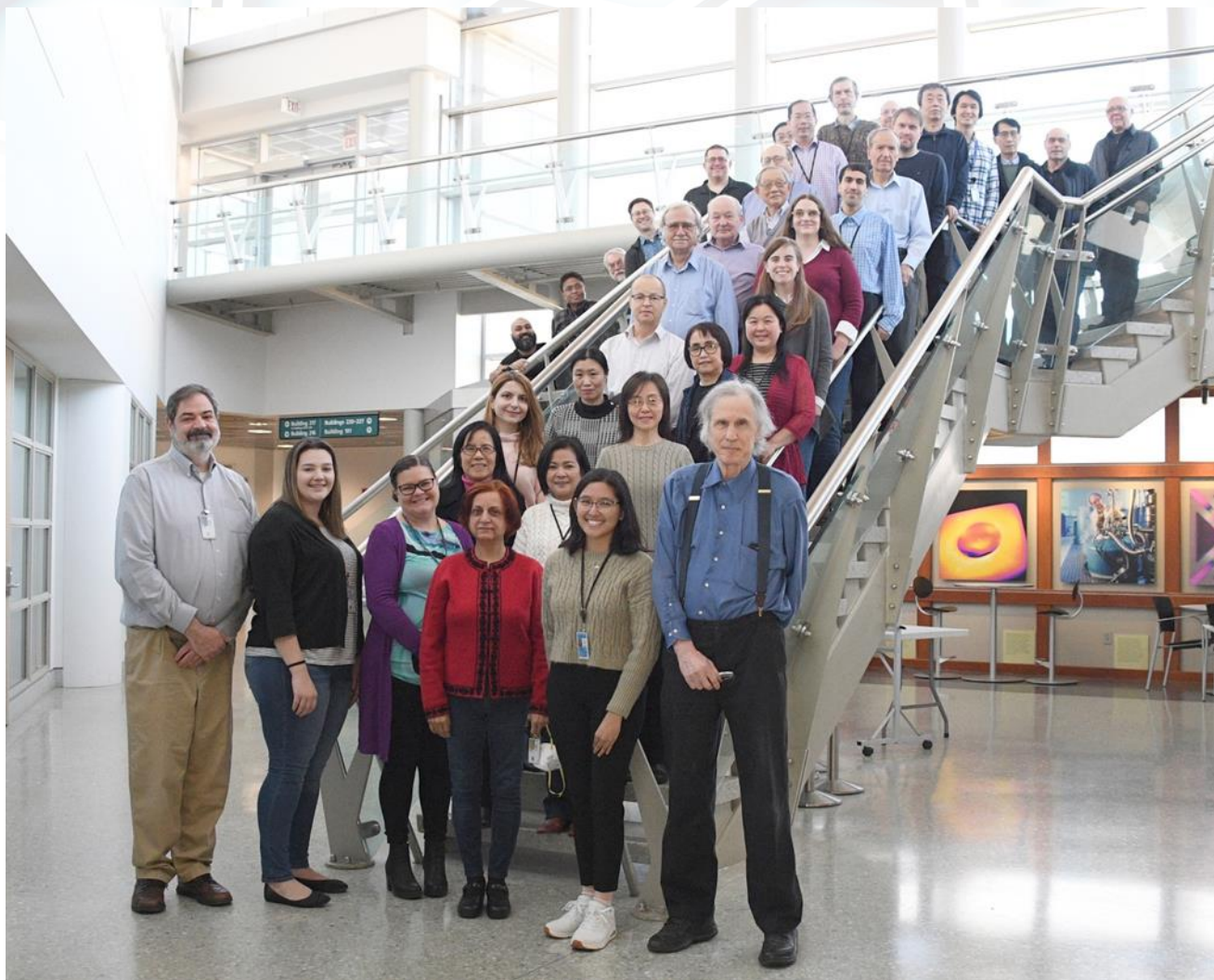
-C₂H₄



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



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William Wallace

Thank you for your attention!