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High Resolution Mass Spectrometry (HRMS) Techniques for Screening of PFAS in Environmental Samples

Kari Organtini, Ph.D
Principal Scientist

Per- and Polyfluoroalkyl Substances (PFAS)

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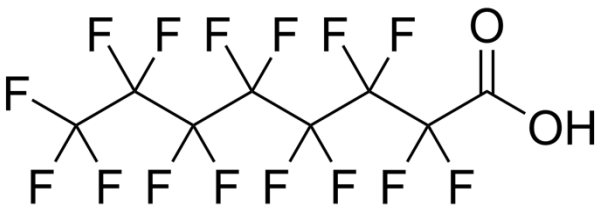
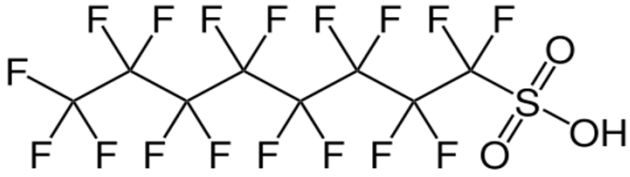
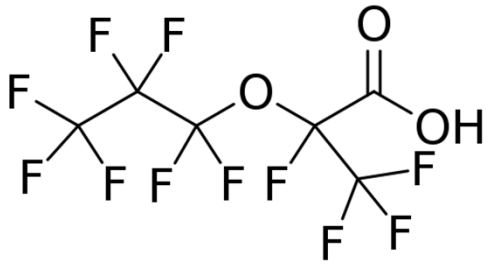


PFOA



PFOS



GenX (HFPO-DA)

Why is High Resolution Screening Helpful for PFAS?

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- Estimated 4000-6000+ PFAS have been created/used
- Targeted techniques only cover a tiny portion of that number
- Toxicity
- Novel and replacement PFAS are typically unknown
- Source apportionment and forensics

Method	# PFAS
EPA 537.1	18
EPA 533	25
EPA 8327	24
ISO 21675	30
EU DWD	20

Advantages of accurate mass screening?

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- Over recent years high resolution mass spectrometry has gained in popularity as a screening tool
  - ✓ **Ability to perform non-targeted analysis**
    - The freedom to measure compounds without prior compound specific tuning
  - ✓ **Ability to perform historical data review**
    - The capability of performing structural elucidations of unknowns or suspect compounds
  - ✓ **Ability to perform full spectral analysis**
    - Providing greater insight into the composition of a complex sample
  - ✓ **Ability to screen for larger number of compounds and adducts**
    - Compared to QqQ based screening

Power of High-Resolution MS

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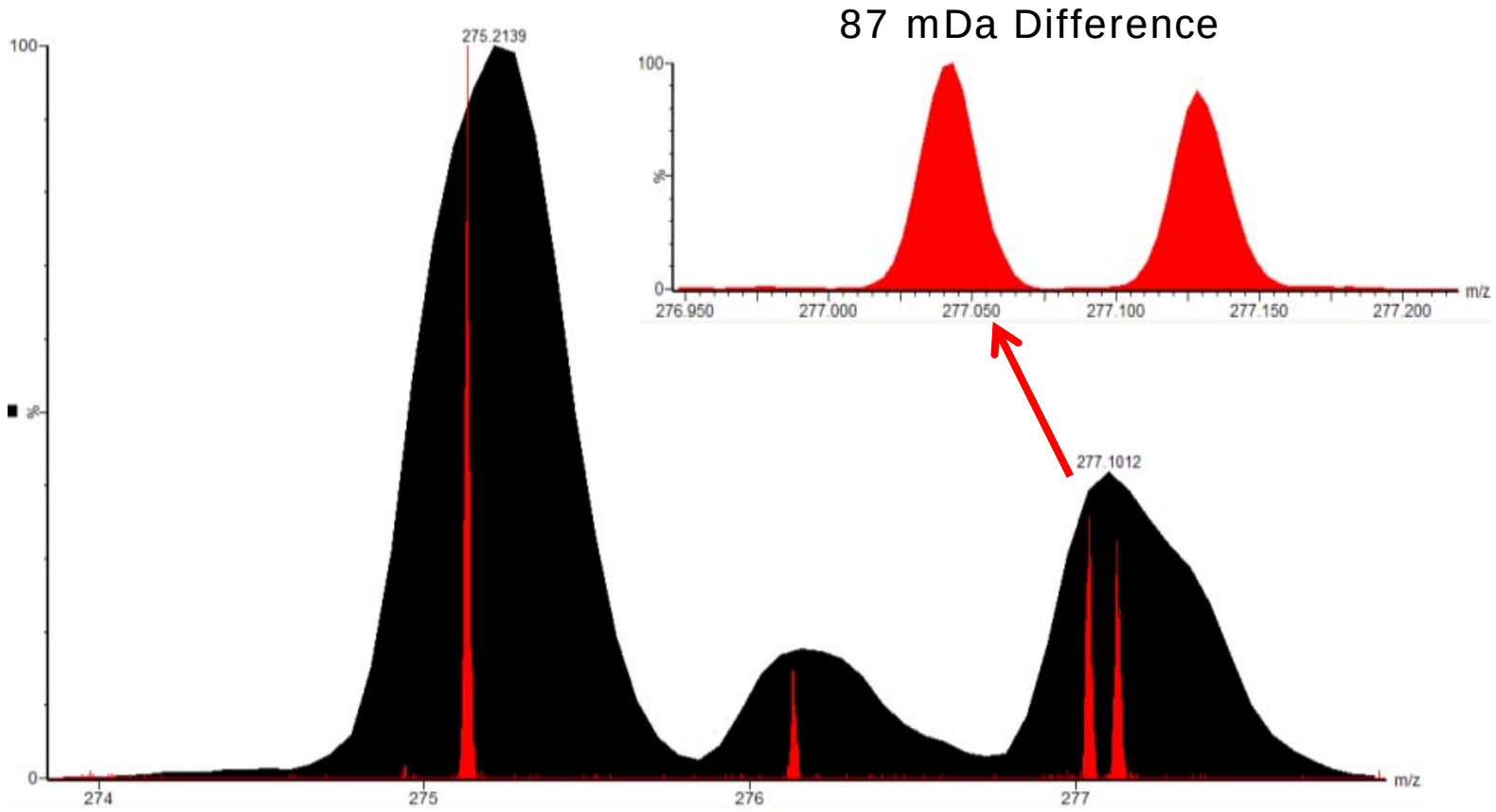

Power of High-Resolution MS Analysis of PFPeA: MRM Vs. HRMS

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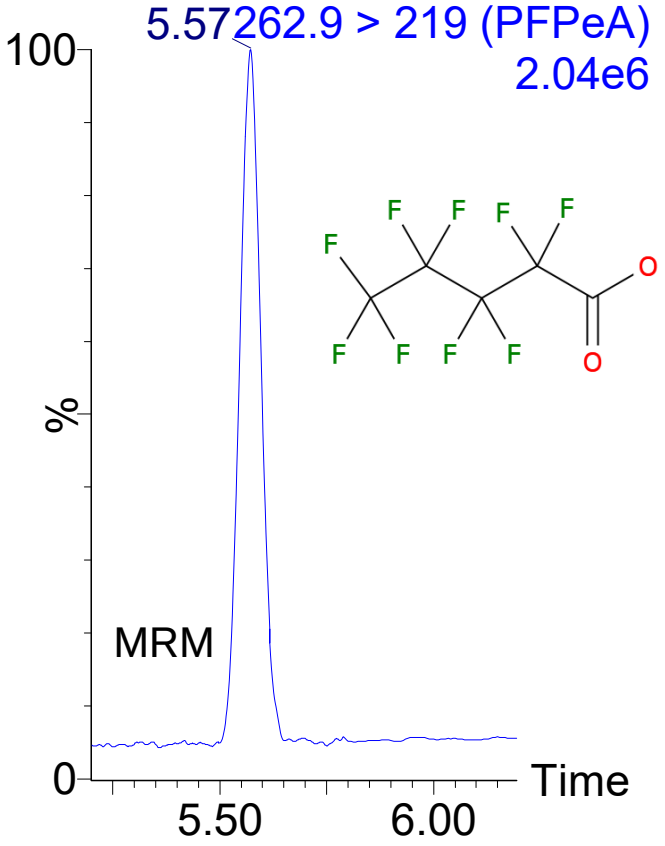

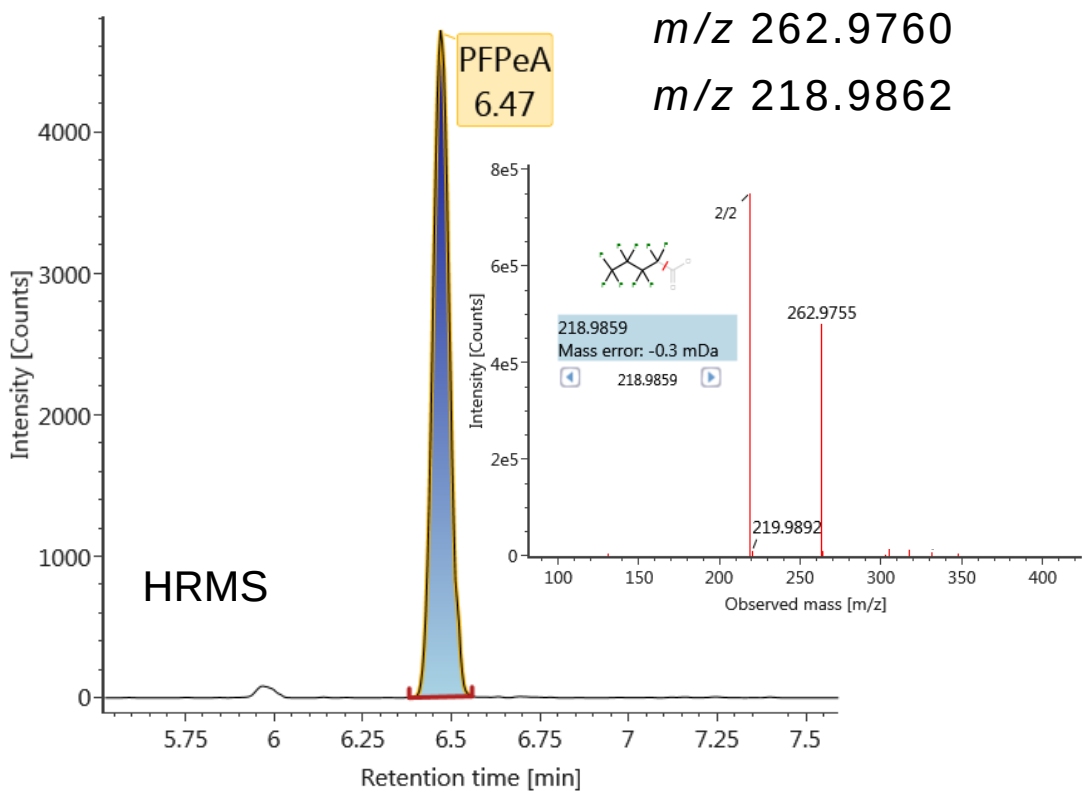

Four Fundamental Questions

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Are these compounds in my sample?

Targeted analysis

How much is in my sample?

Quantitation

What else is in my sample?

Non-Targeted Analysis

What are the differences between samples?

Comparison

Collecting a Comprehensive Profile

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UltraPerformance Separation

Universal Ion Sources

Xevo G2-XS QTof

Scientific Information System

UNIFI

LC modifications for PFAS analysis

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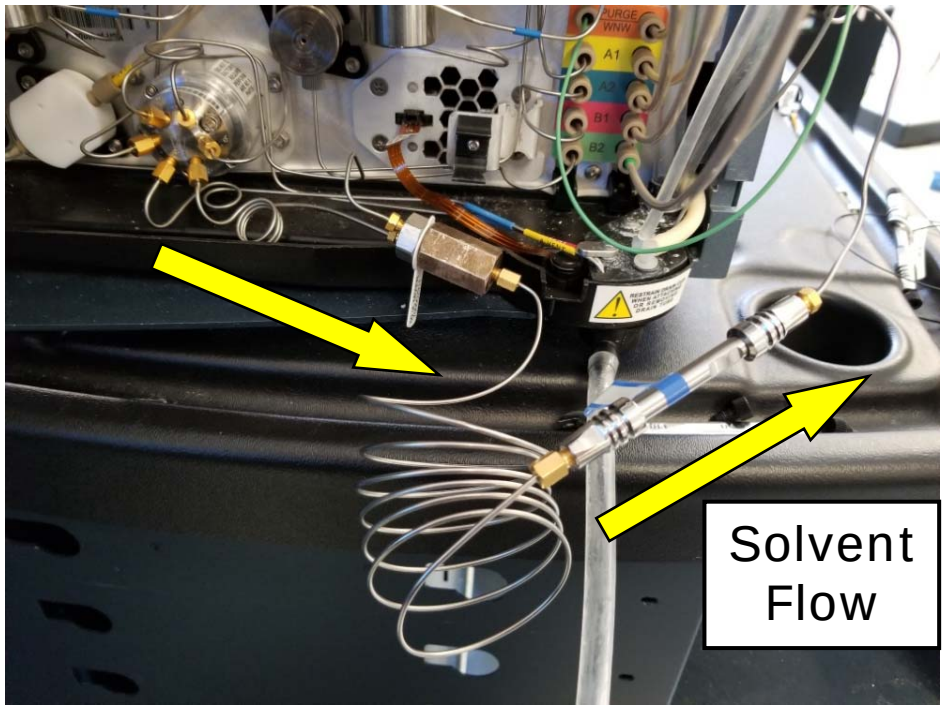
- Care must be taken when analyzing samples for PFAS compounds to avoid procedural and instrument contamination.
- System contamination can be reduced by taking the appropriate steps.
- PFAS Kit must be installed on the UPLC system prior to use for PFAS analysis.
- The kit is comprised of PFAS-free components and an isolator column.



Separation, Detection and Identification Workflow

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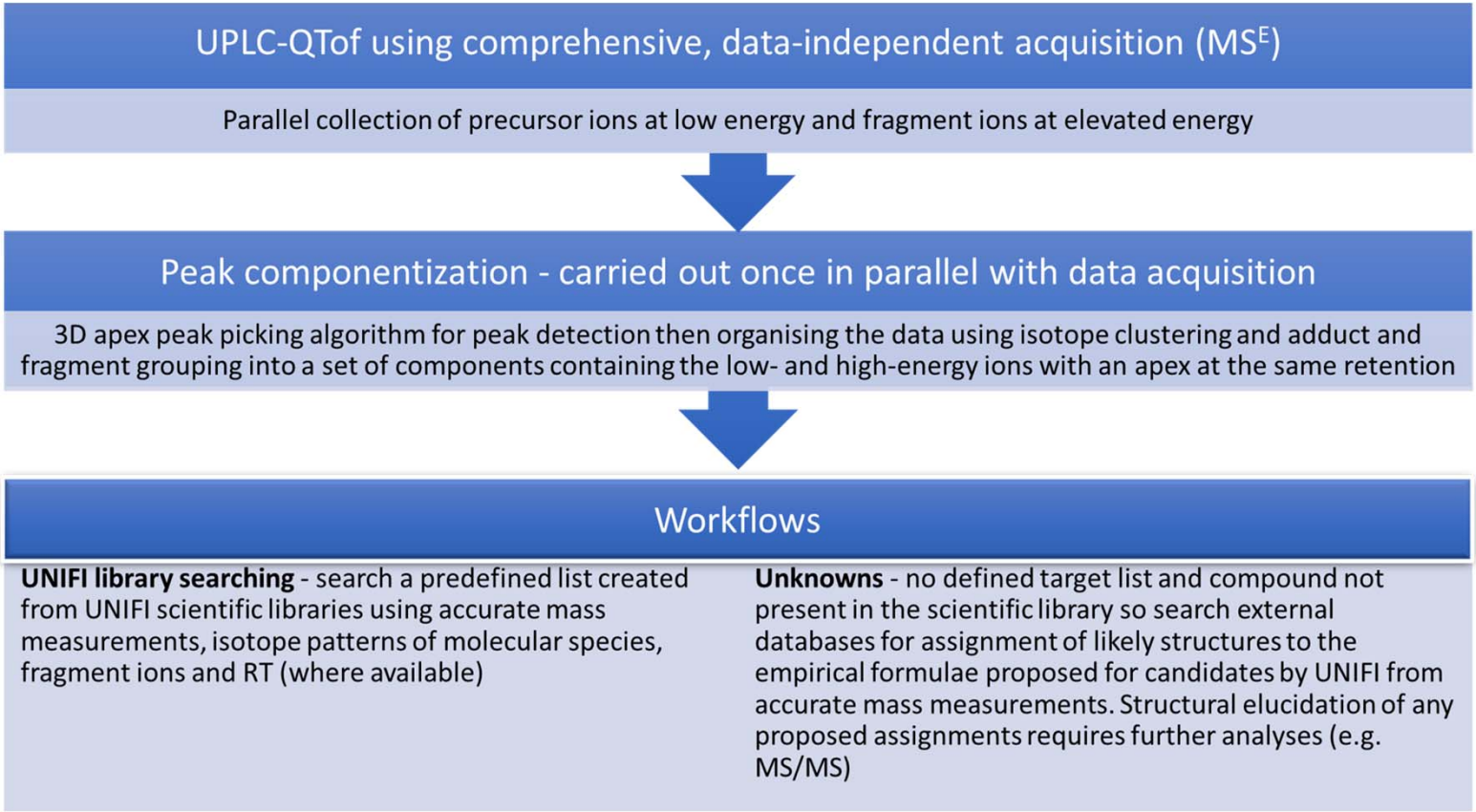
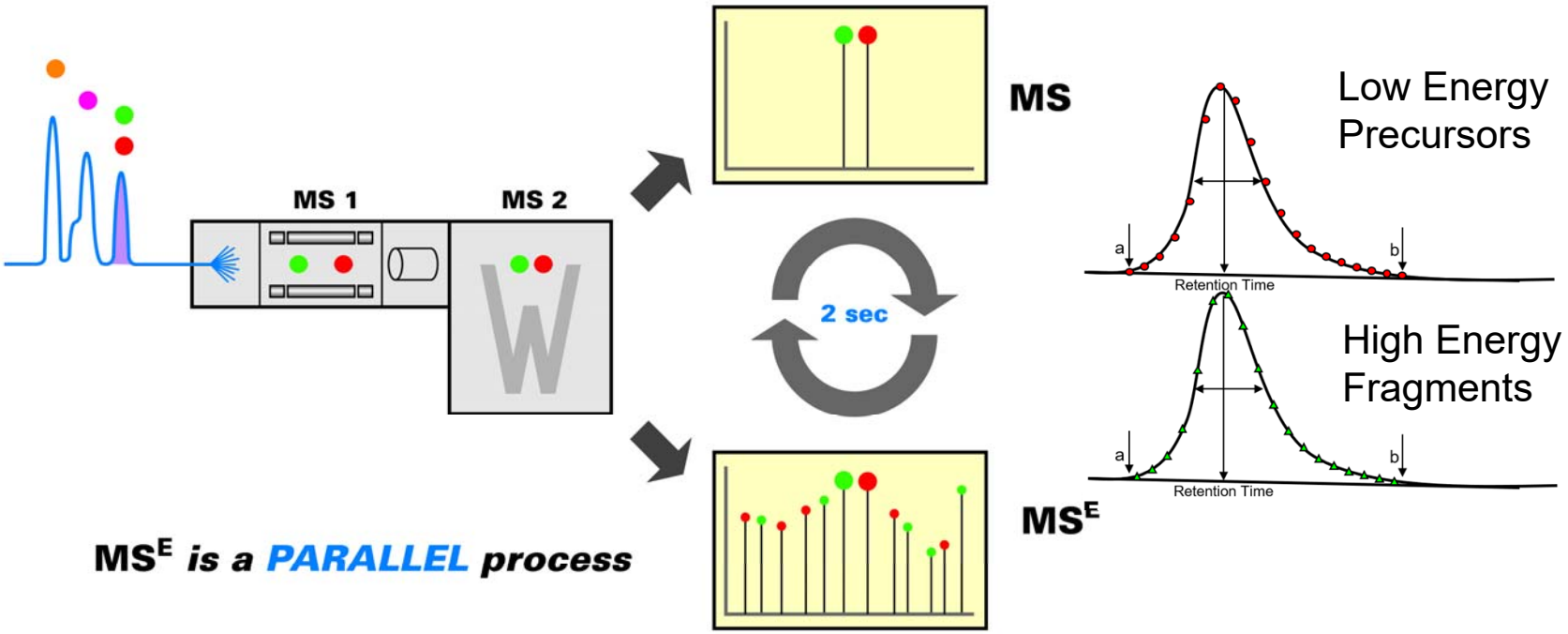


MS^E: Data Independent Acquisition



Sample Preparation

WATER

5 mL sample,
Spike surrogate,
Dilute

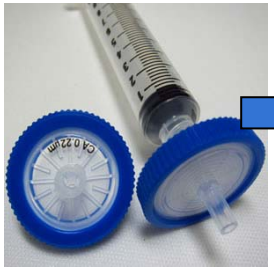
SOIL

2 g sample,
Spike surrogate,
Add Solvent

Centrifuge

Water
Surface
Ground
Influent
Effluent

Soils
Sand
Silt
Lean Clay
Fat Clay



Syringe filter entire sample

Acidify and transfer to polypropylene vial

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Targeted Analysis

UNIFI Library Generation

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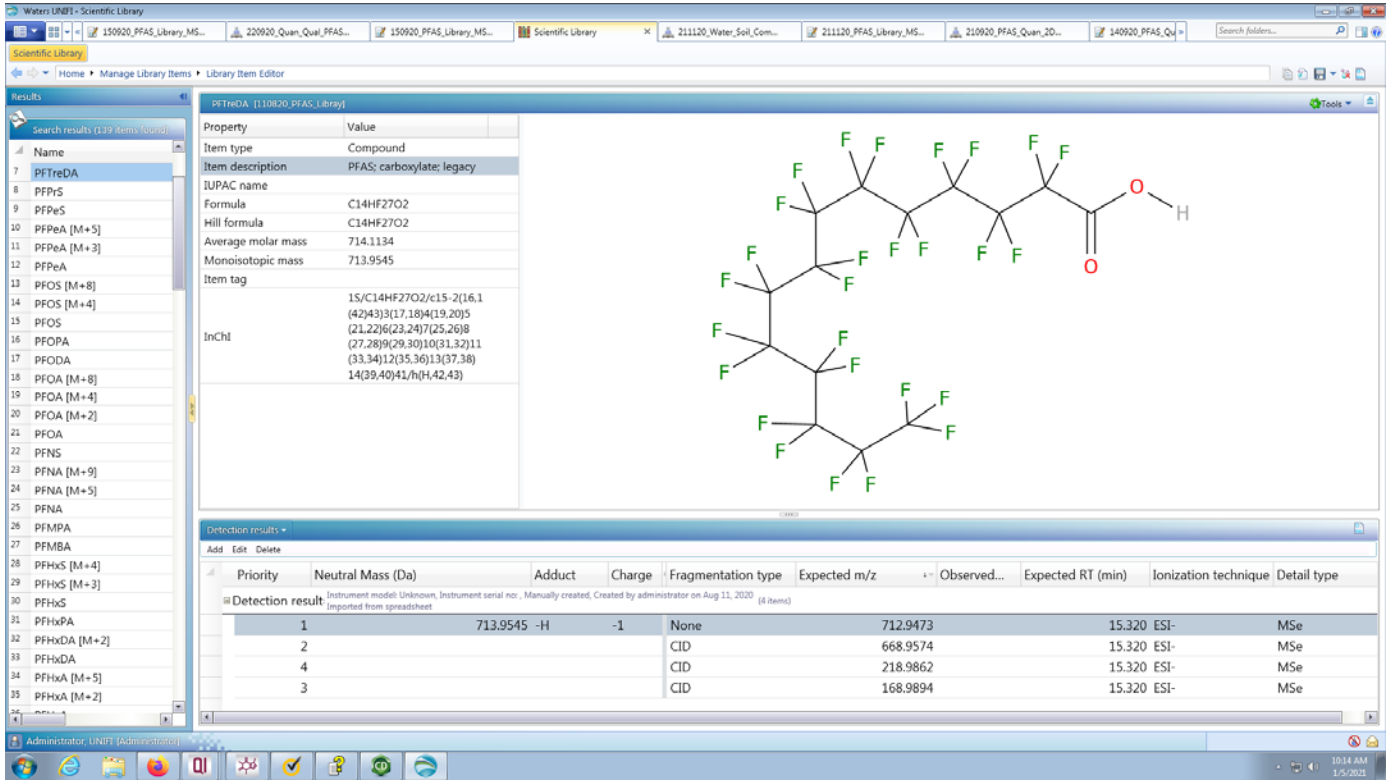
- Gather structures (mol files) → UNIFI automatically determines exact mass
- Inject standards for RTs and fragments



Library Generation Based on Authentic Standards

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Assessing Identified Components

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View Filters for Efficient Data Review

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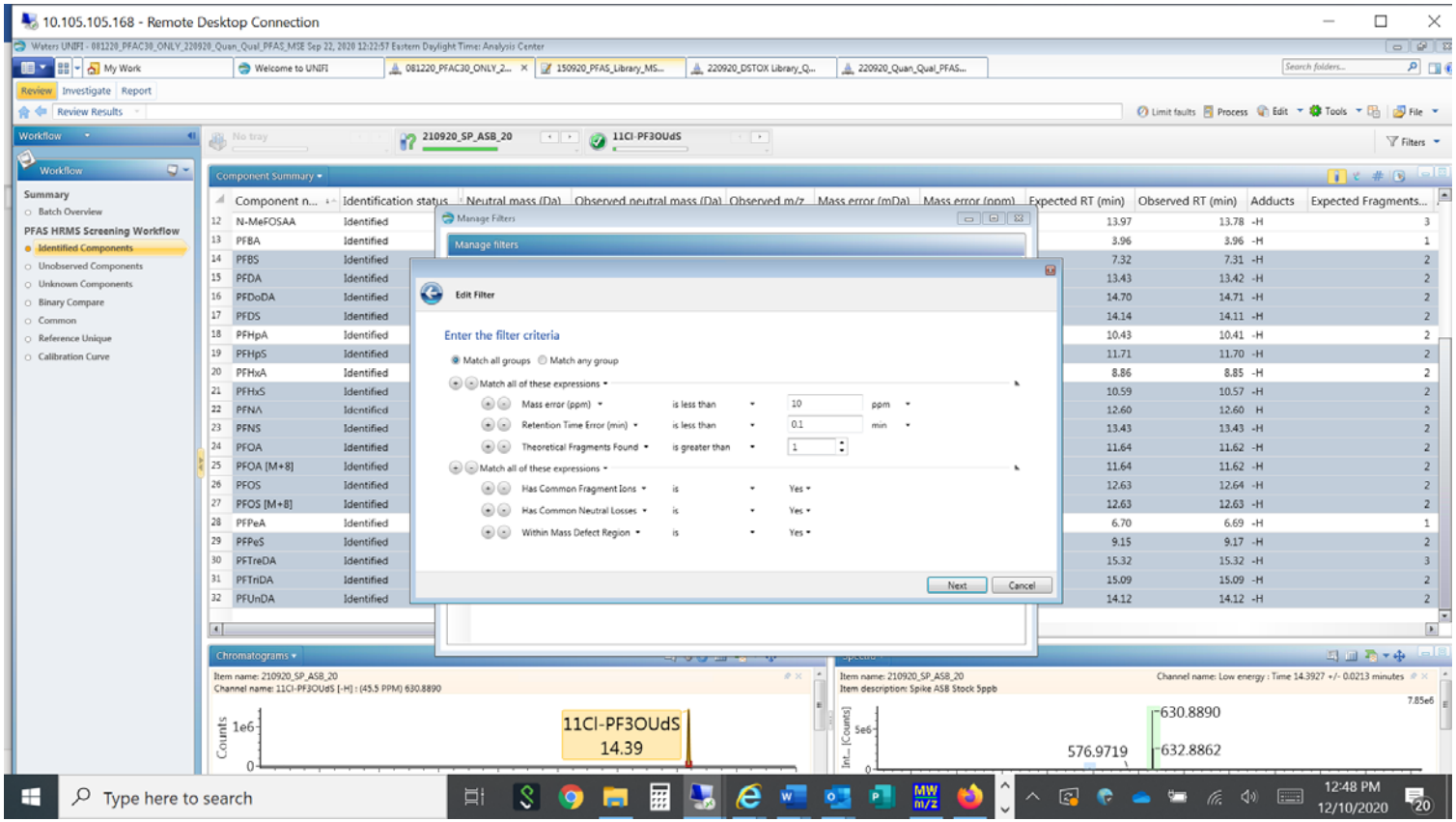

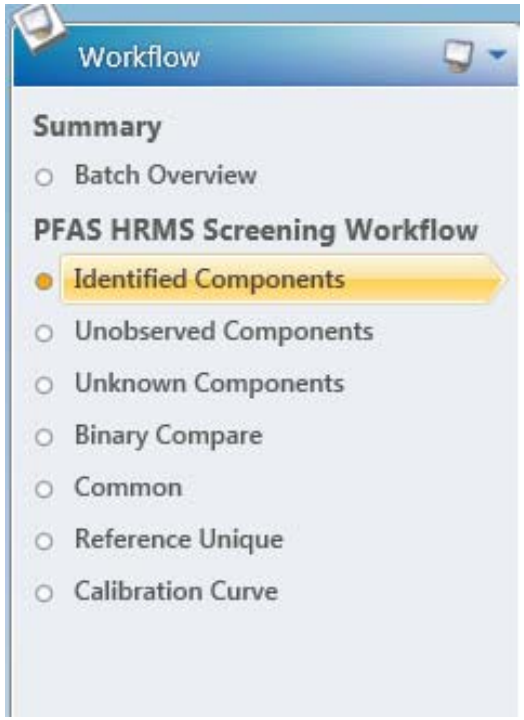

Identification of PFAS in Soil Samples

Identification of PFAS in a Soil Sample

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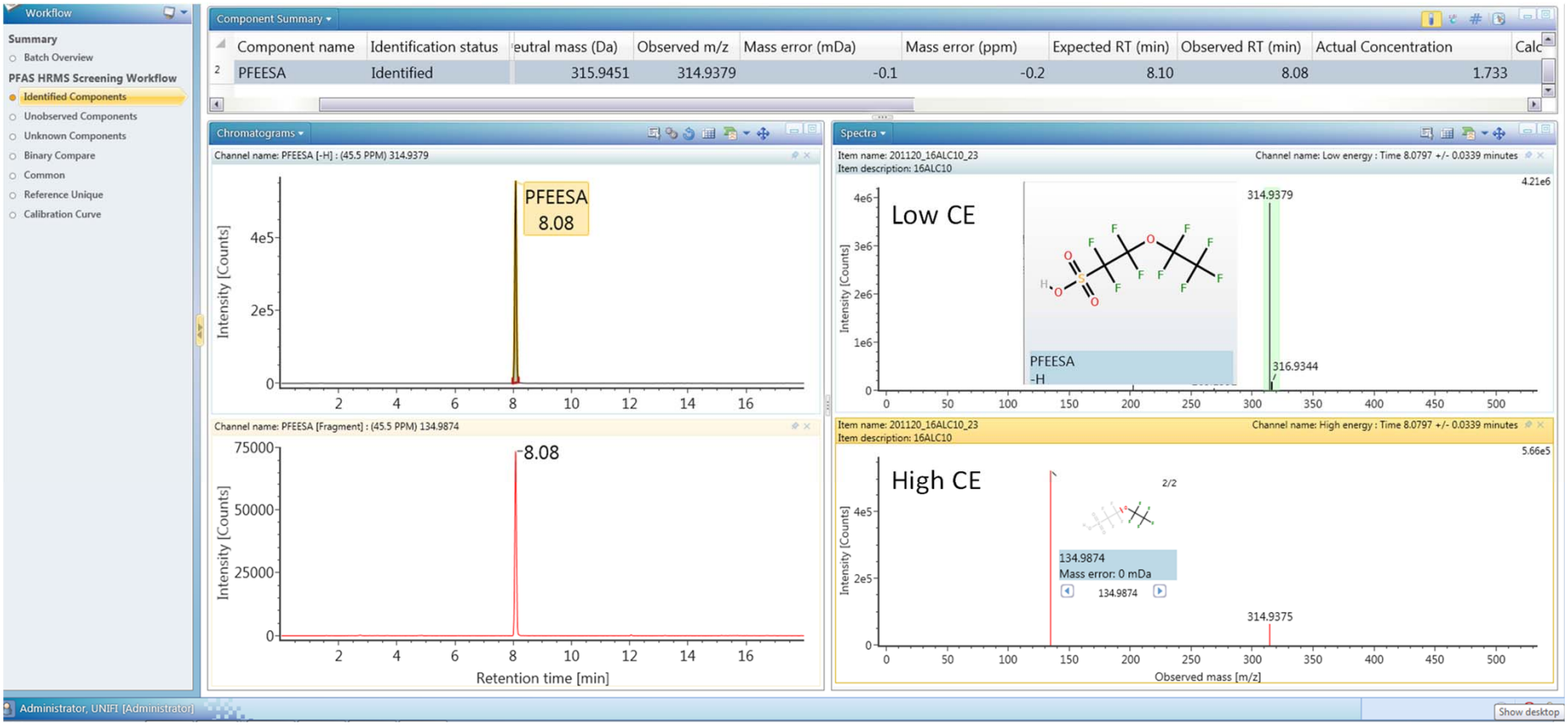
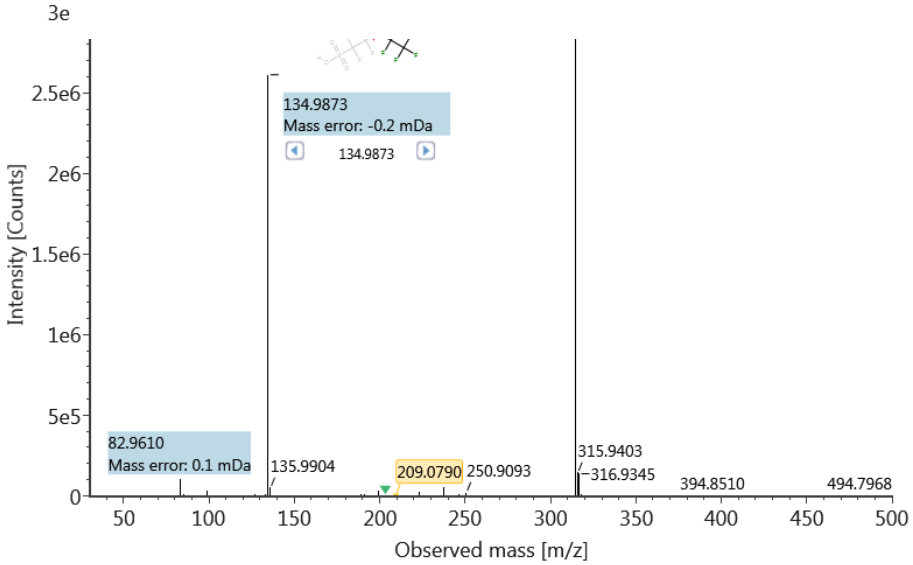


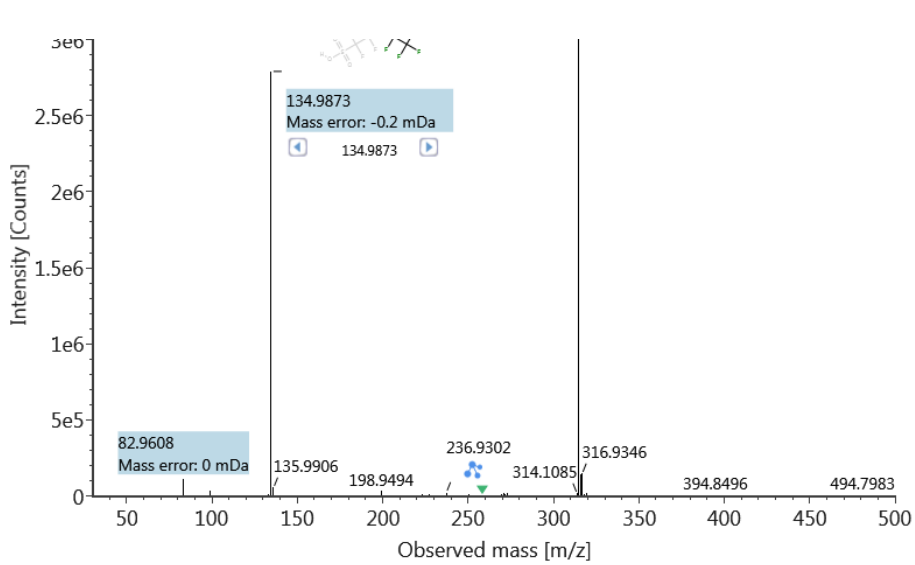
Confirmatory Targeted MS/MS

Item name
Item descri

Authentic standard
MS/MS spectrum for *m/z* 314.9379 at t_R 8.12



Lean Clay extract
MS/MS spectrum for *m/z* 314.9379 at t_R 8.12



Quantitation of PFEESA in a Soil Sample

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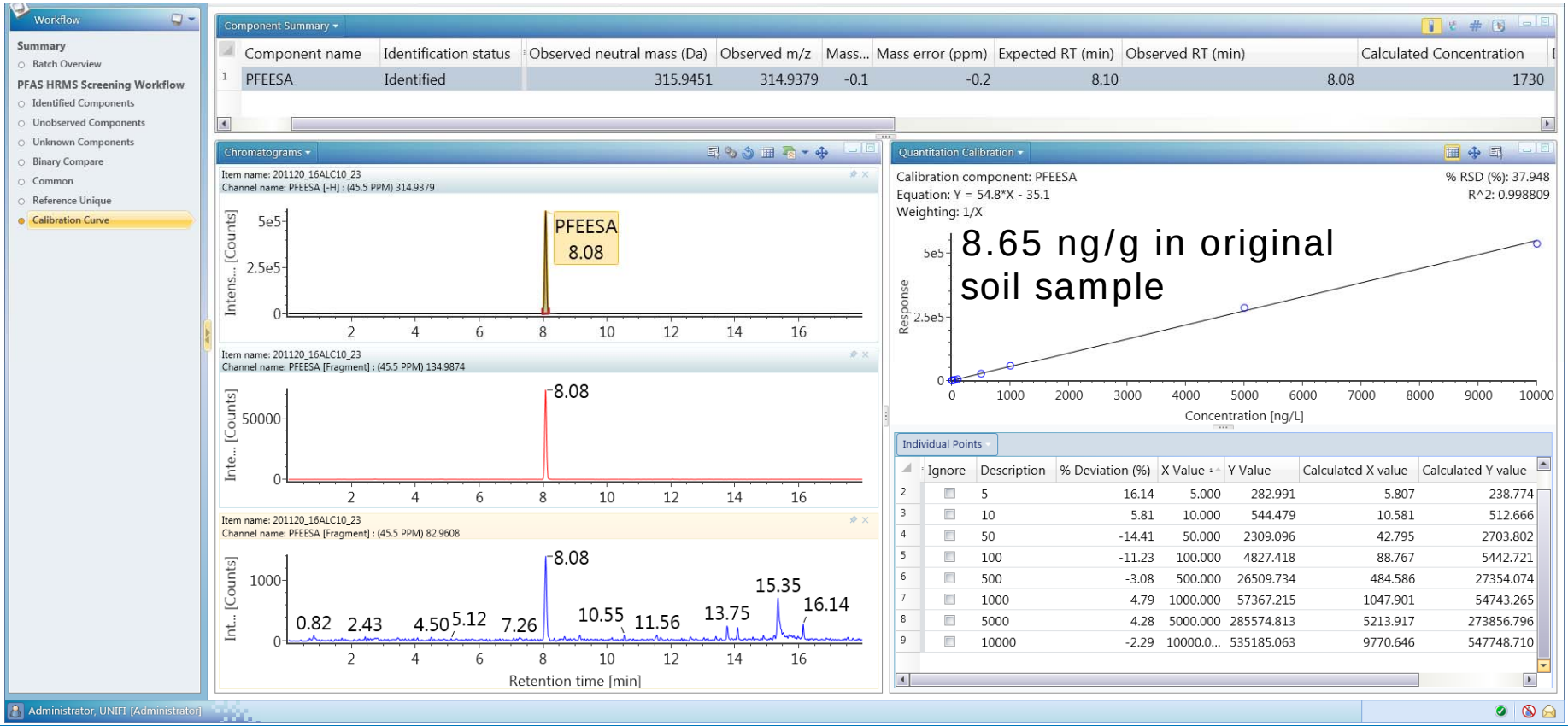

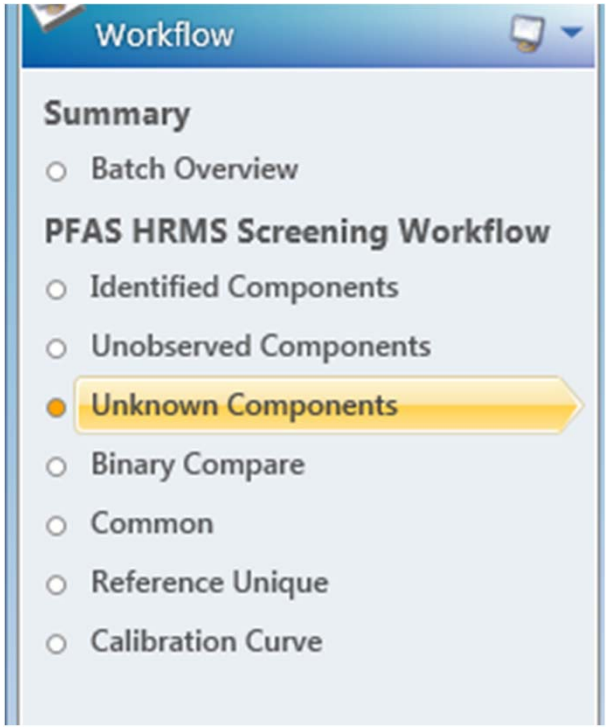

Non-Targeted Analysis

Structural Elucidation Tools-Common Fragments

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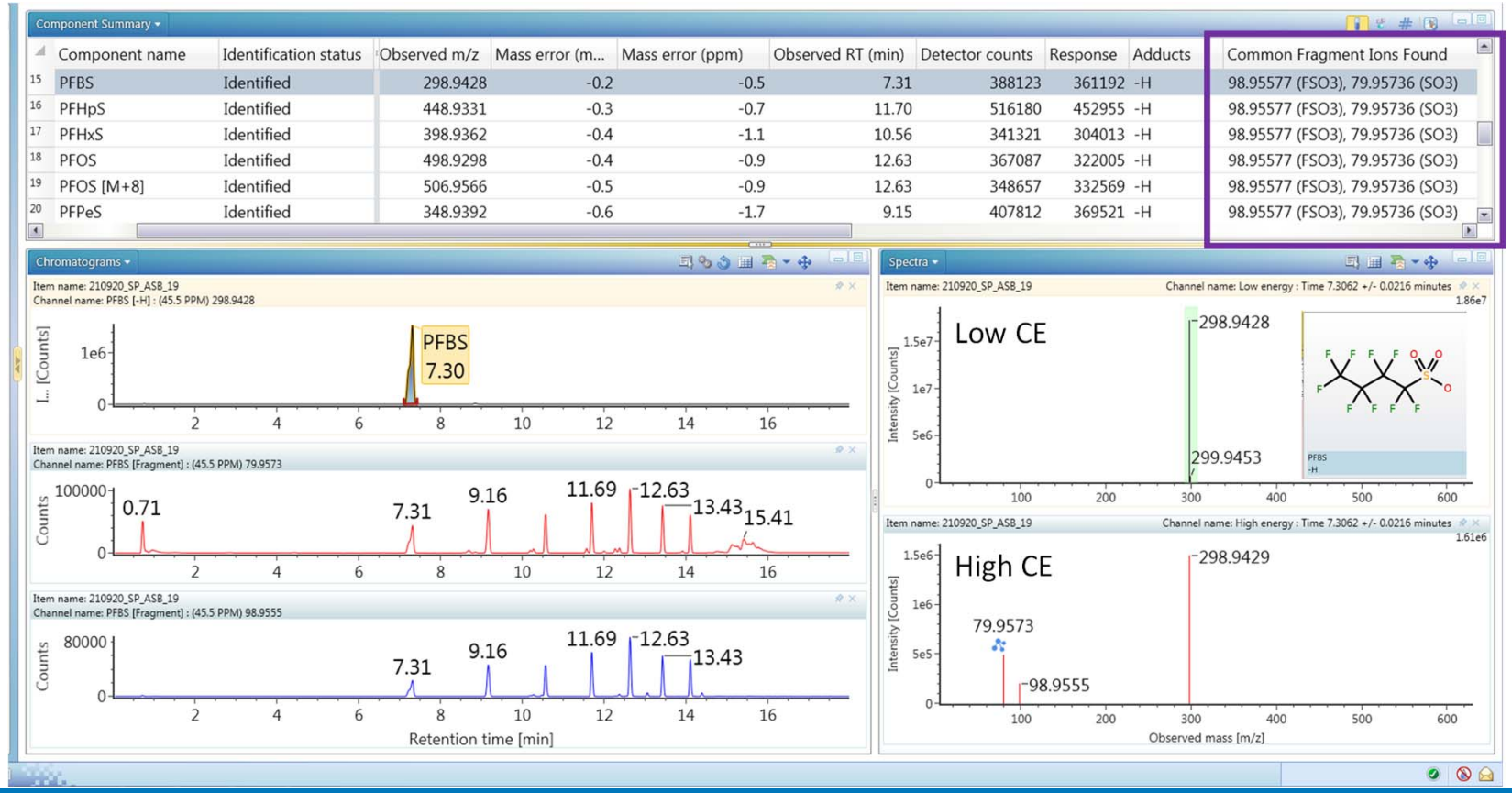
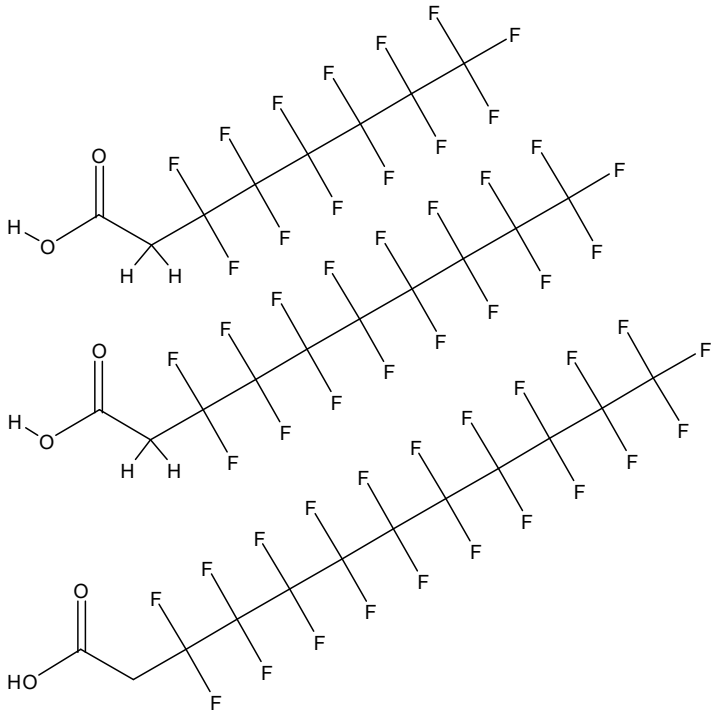


Structural Elucidation Tools-Neutral Loss

FHEA
$C_8H_3F_{13}O_2$

FOEA
$C_{10}H_3F_{17}O_2$

FDEA
$C_{12}H_3F_{21}O_2$



Structural Elucidation Tools-Neutral Loss

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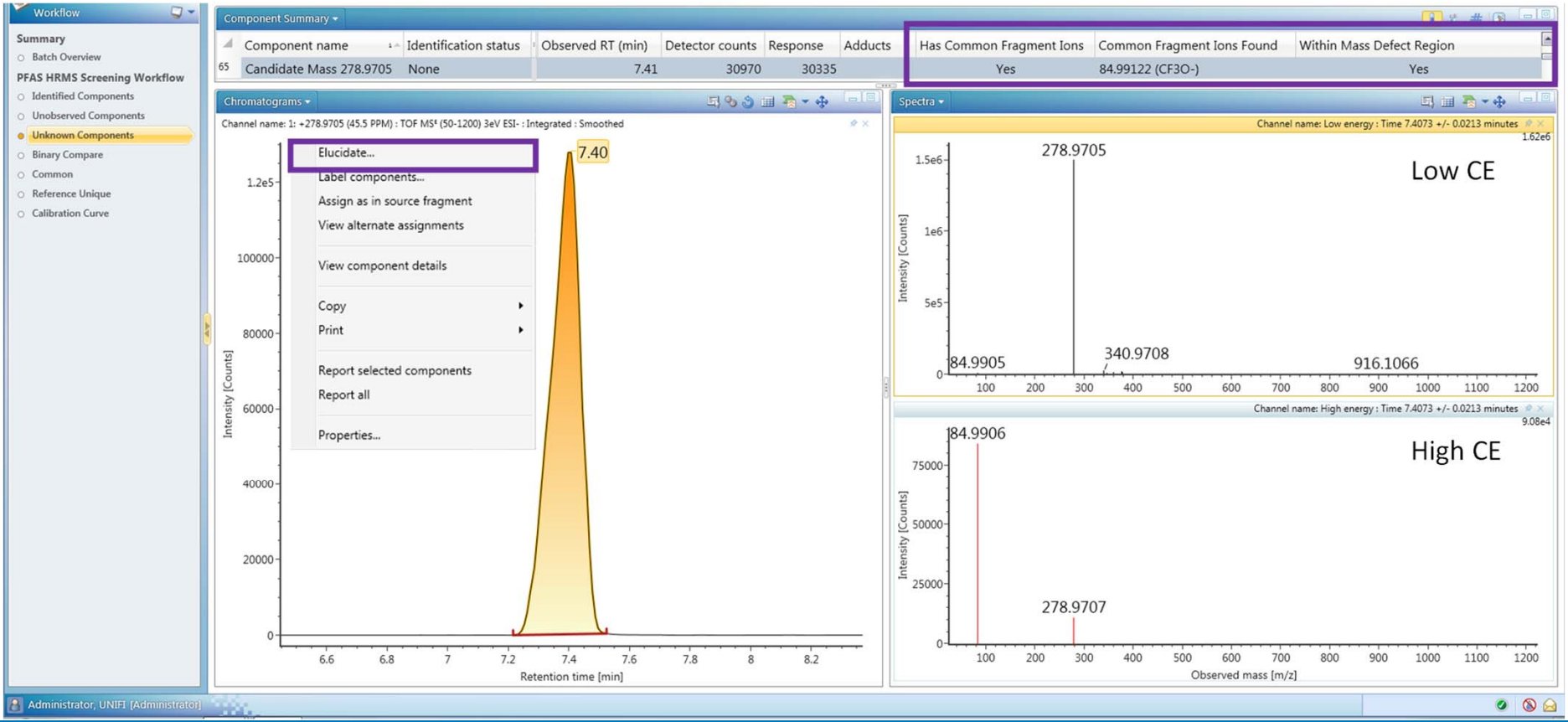
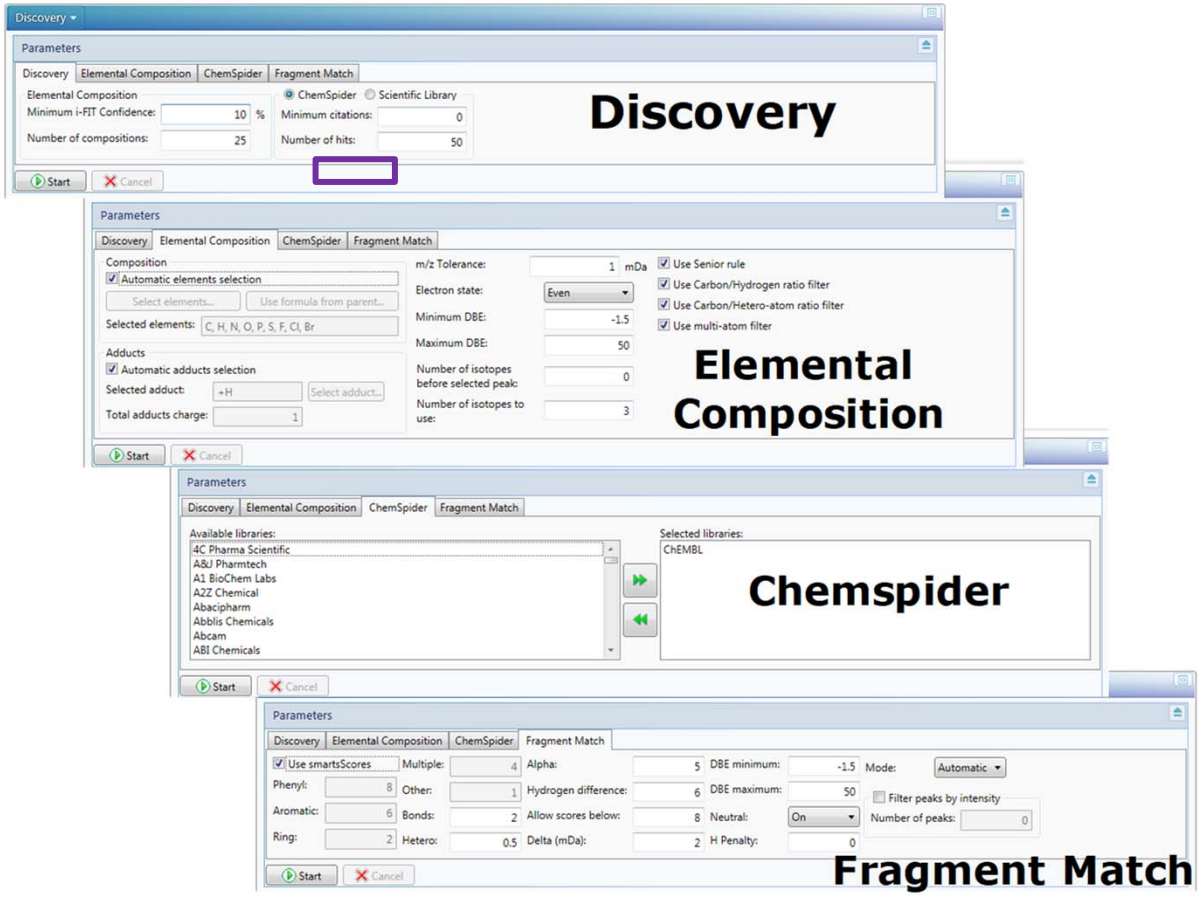
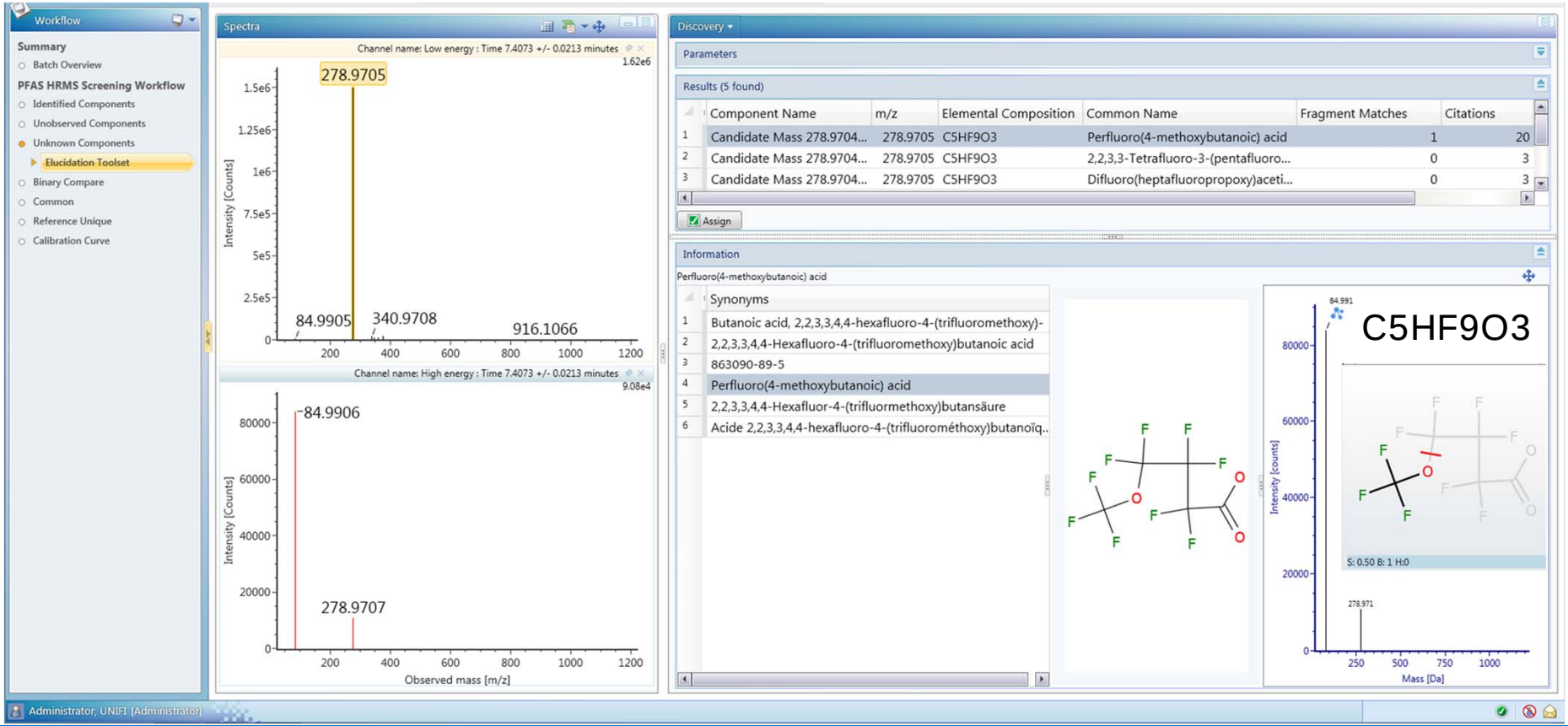
Elucidation of a Suspect Component



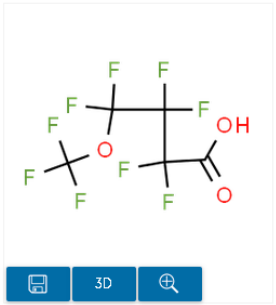
Discovery Tool



Discovery Tool



ChemSpider Review



Perfluoro(4-methoxybutanoic) acid

Molecular Formula	$C_5HF_9O_3$
Average mass	280.045 Da
Monoisotopic mass	279.978210 Da
ChemSpider ID	23955753

More details:

This record has not been tagged. + TAG

Names | Properties | Searches | Spectra | Vendors | Articles | More

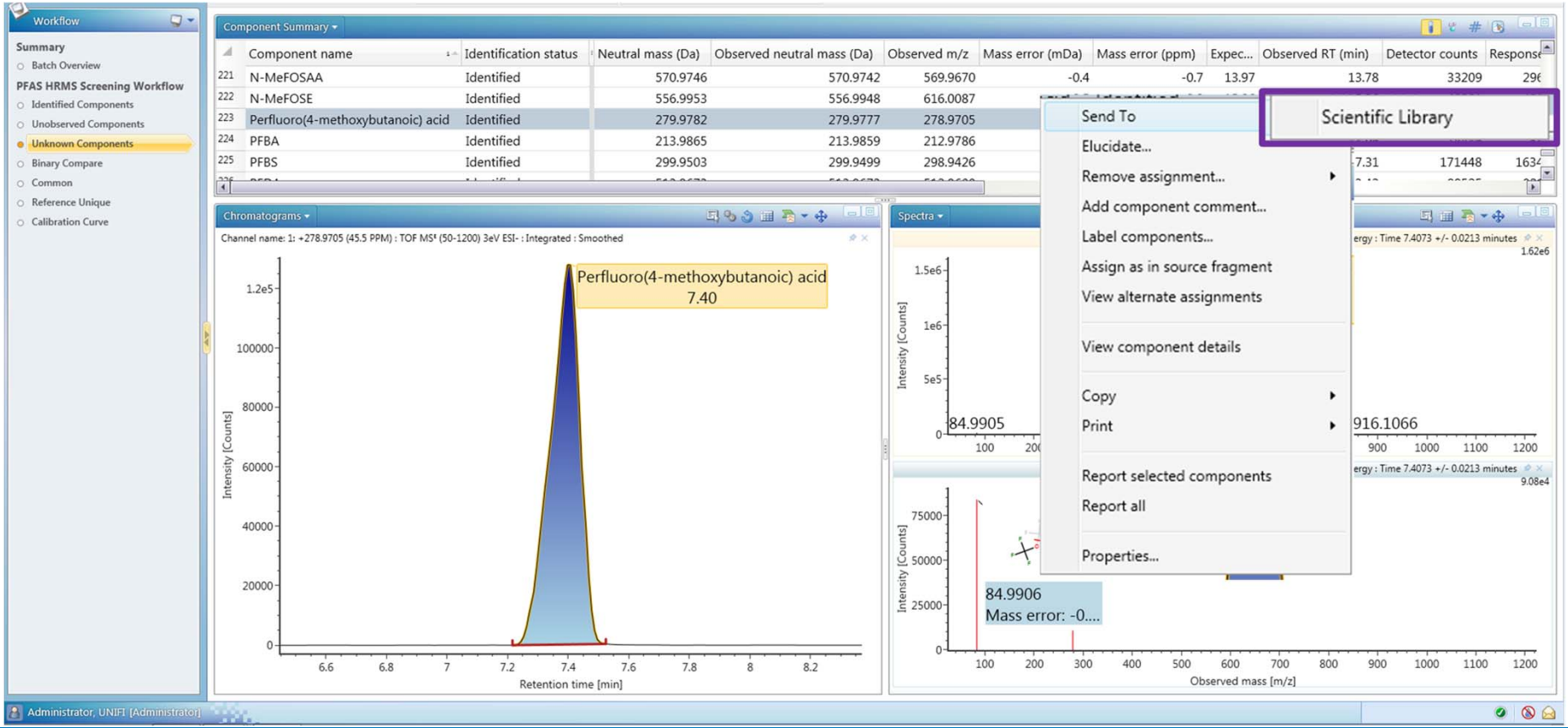
Names and Synonyms

Validated by Experts, Validated by Users, Non-Validated, ~~Removed by Users~~

EDIT

2,2,3,3,4,4-Hexafluor-4-(trifluormethoxy)butansäure *[German] [ACD/IUPAC Name]*
2,2,3,3,4,4-Hexafluoro-4-(trifluoromethoxy)butanoic acid *[ACD/IUPAC Name]*
863090-89-5 *[RN]*
Acide 2,2,3,3,4,4-hexafluoro-4-(trifluorométhoxy)butanoïque *[French] [ACD/IUPAC Name]*
Butanoic acid, 2,2,3,3,4,4-hexafluoro-4-(trifluoromethoxy)- *[ACD/Index Name]*
Perfluoro(4-methoxybutanoic) acid
MFCD07784238 *[MDL number]*
Perfluoro-4-methoxybutanoic acid
Perfluoro-4-methoxybutanoic acid (PFMOBA)

Sending Identified Compounds to the Library



Summary

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- HRMS screening allows for more thorough characterization of environmental samples
- MSe data collection allows for comprehensive data collection in one injection that can be processed and queried in many different ways without needing to re-inject
- A custom library greatly aided in the assignment of the PFAS compounds detected in the wastewater and soil samples.
- The UNIFI software provides a set of tools to aid in the identification of potential unknown PFAS not present in the library, using common fragments, neutral loss, and mass defect searching

Acknowledgements

- UMass Amherst
  - Aarthi Mohan
- Waters
  - **Marian Twohig, Ph.D.**
  - Gordon Fujimoto, Ph.D.
  - Sarah Dowd, Ph.D.
  - Ken Rosnack
  - Simon Hird, Ph.D.

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Thank you!