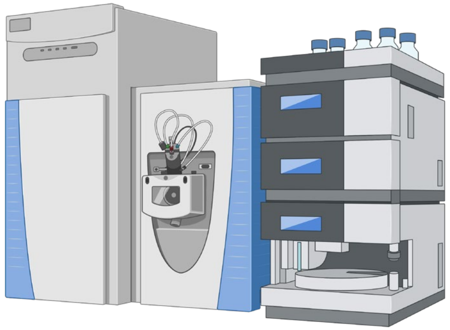
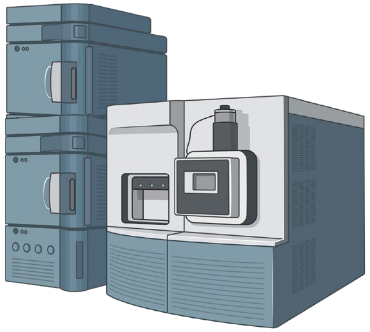
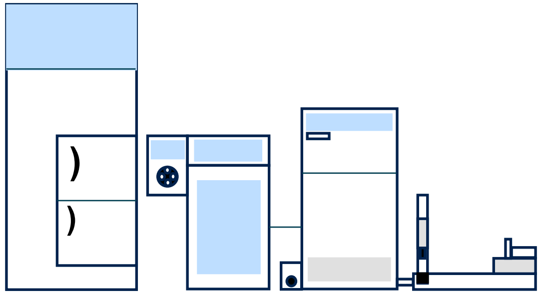
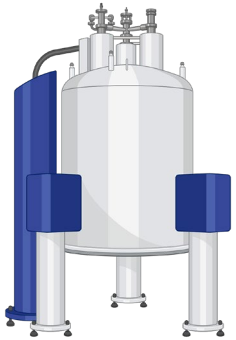
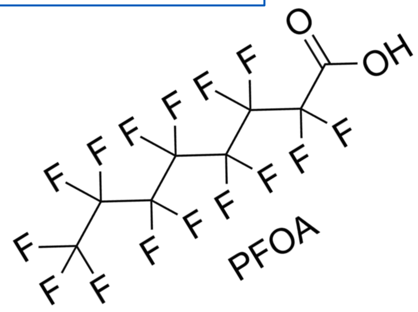
“Complementary tools for the identification and quantification of total and specific PFAS: LC-HRMS, SFC, CIC and ^{19}F-NMR”

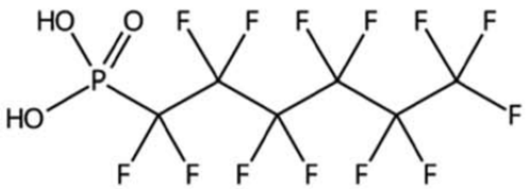





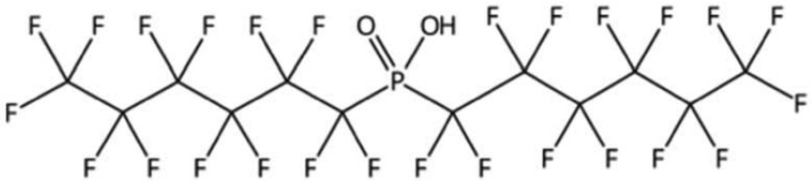
Dr. Diana S. Aga
October 6, 2023
dianaaga@buffalo.edu
Department of Chemistry, University at Buffalo
RENEW Institute, University at Buffalo

Analytical Challenges:
Per- and Polyfluoroalkyl Substances (PFAS)

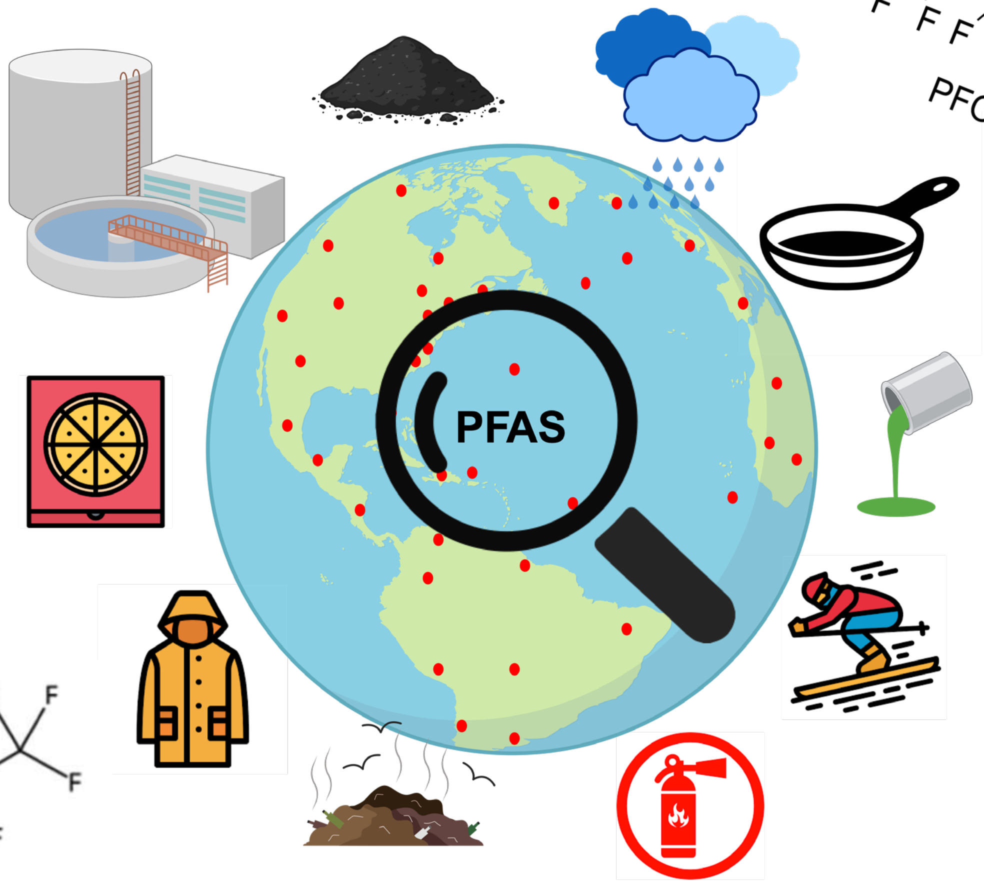
Diverse chemicals

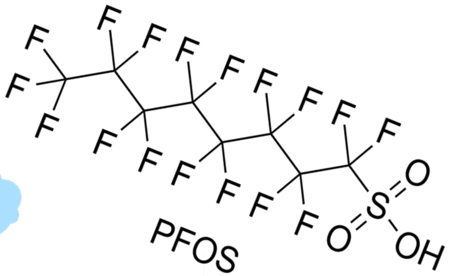




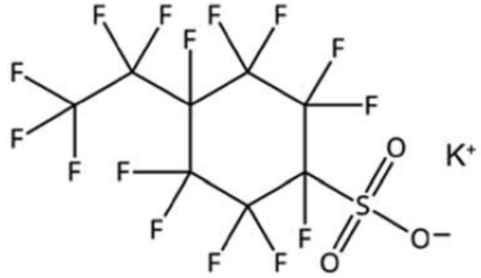


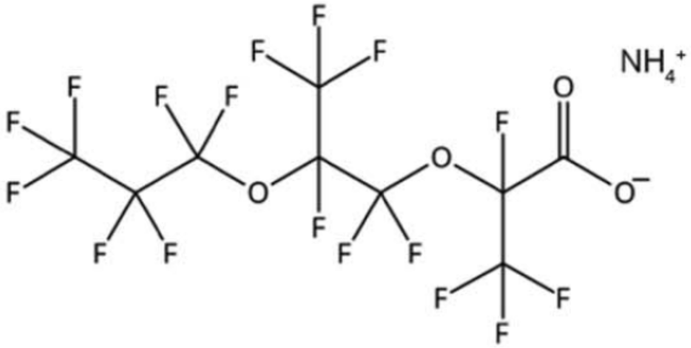
Matrix effects





Lack of Reference Standards





Having the right tools is key to PFAS Analysis

Chromatography with Mass spectrometry (ion-trap, triple quad, Q-ToF, Orbitrap)

LC/MS/MS and GC/MS/MS



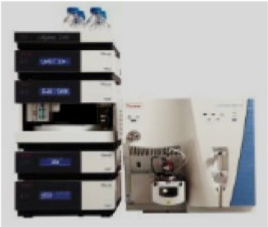




Target and Non-target Analysis

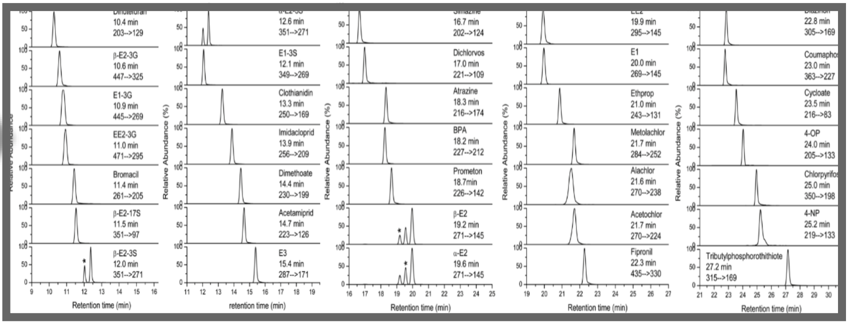
Targeted Analysis ...Trace analysis of priority compounds

Triple Quad LC-MS/MS System



Thermo TSQ Quantum Ultra

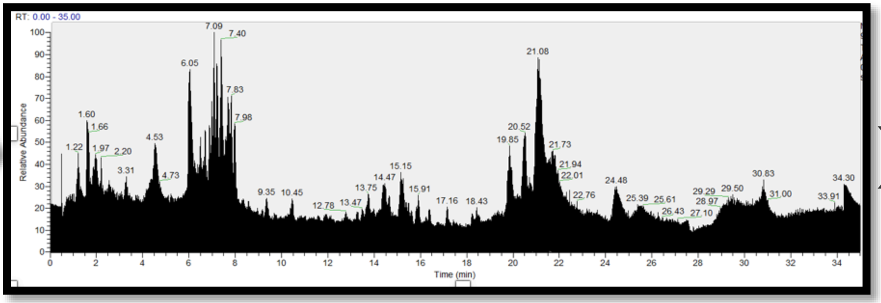
- 60 Antibiotics
- 55 Pesticides
- 40 PFAS



Non-targeted Analysis ...What else could be present?

Orbitrap-LC/MS System

Q Exactive™ Focus Hybrid Quadropole Orbitrap™

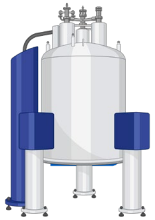


Database screening

TraceFinder™

m/z CLOUD

EPA Toxi Chemspider



^{19}F-NMR for PFAS analysis

Contents lists available at ScienceDirect
Journal of Hazardous Materials Letters
journal homepage: www.elsevier.com/locate/hazl

Total and class-specific analysis of per- and polyfluoroalkyl substances in environmental samples using nuclear magnetic resonance spectroscopy

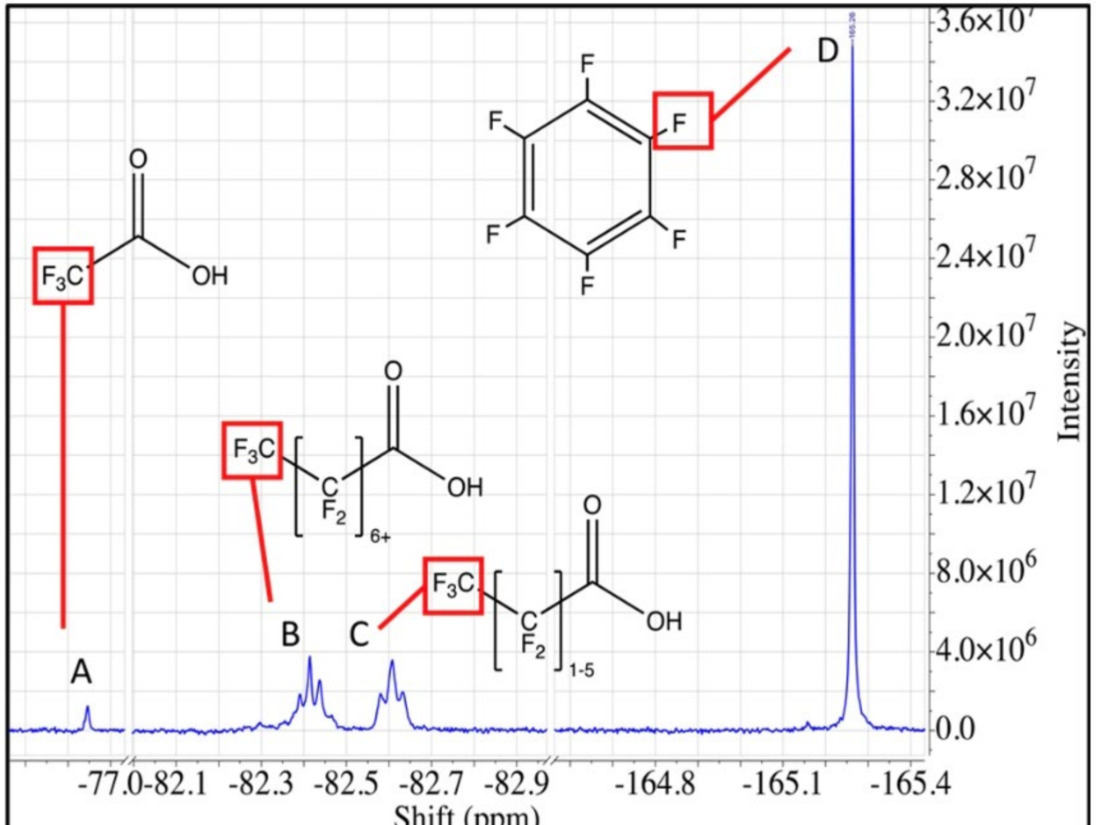
Dino Camdzic, Rebecca A. Dickman, Diana S. Aga *
Chemistry Department, University at Buffalo, The State University of New York, Buffalo, NY 14260, United States

analytical chemistry
pubs.acs.org/ac
Letter

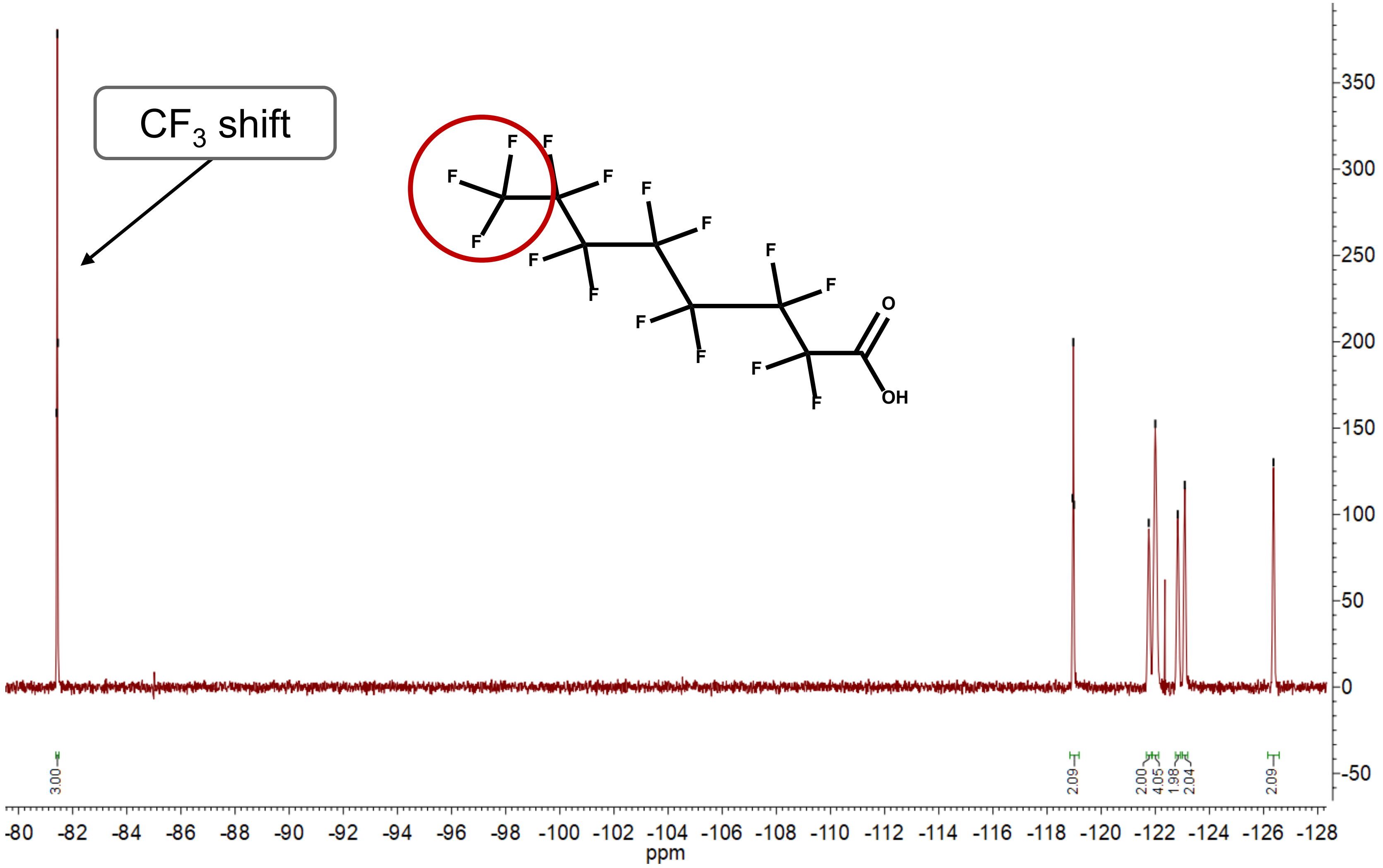
Quantitation of Total PFAS Including Trifluoroacetic Acid with Fluorine Nuclear Magnetic Resonance Spectroscopy

Dino Camdzic,[‡] Rebecca A. Dickman,[‡] Abigail S. Joyce, Joshua S. Wallace, P. Lee Ferguson, and Diana S. Aga*

- ^{19}F-NMR can be used to characterize and quantify PFAS with minimal background signal interferences at the chemical shifts expected for PFAS.
- Intensity of the terminal -CF_3 signal can be used to determine the total PFAS regardless of headgroup.

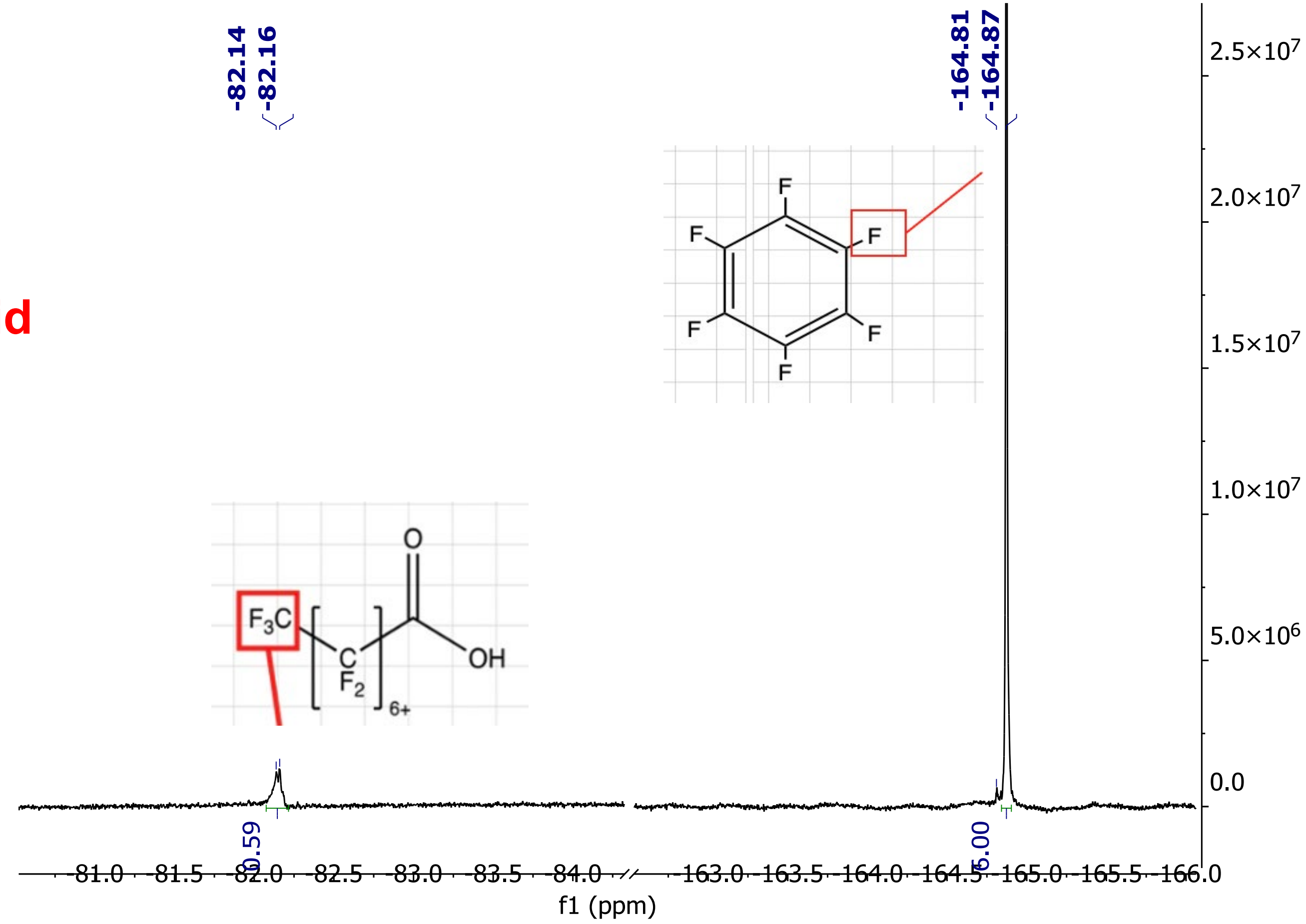


∑ PFAS ^{19}F-NMR


CF$_3$ shift
F
F
F
F
F
F
F
F
F
F
F
F
F
F
F
O
OH
3.00
2.09
2.00
4.05
1.98
2.04
2.09
-80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128
ppm
350
300
250
200
150
100
50
0
-50

Analysis of PFAS in Biosolids using ^{19}F-NMR

15.4 nmol $–CF_3$/g biosolid

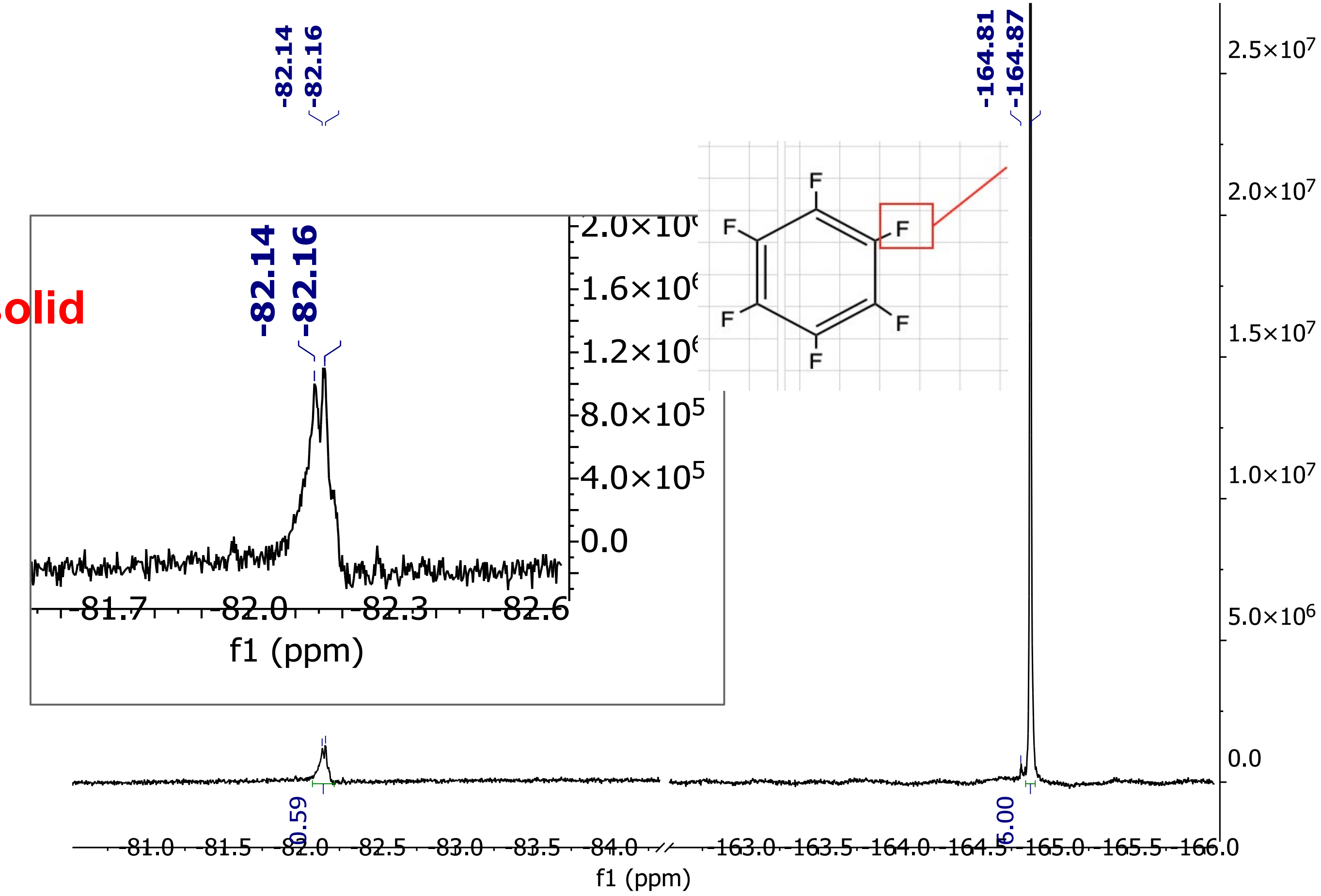


1. Camdzic et al., *Analytical Chemistry*. 2023.

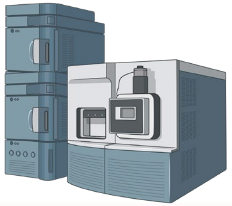
7

Total PFAS – ^{19}F-NMR

15.4 nmol –CF_3/g biosolid



1. Camdzic et al., *Analytical Chemistry*. 2023.



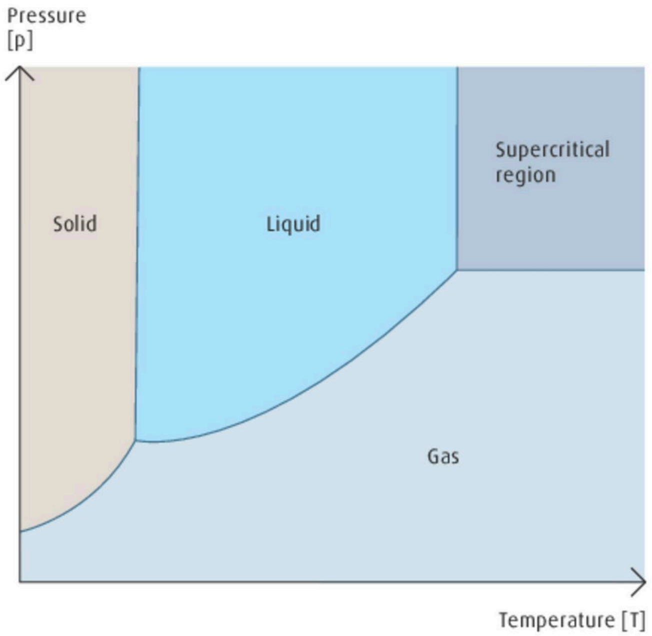
Supercritical Fluid Chromatography (SFC)

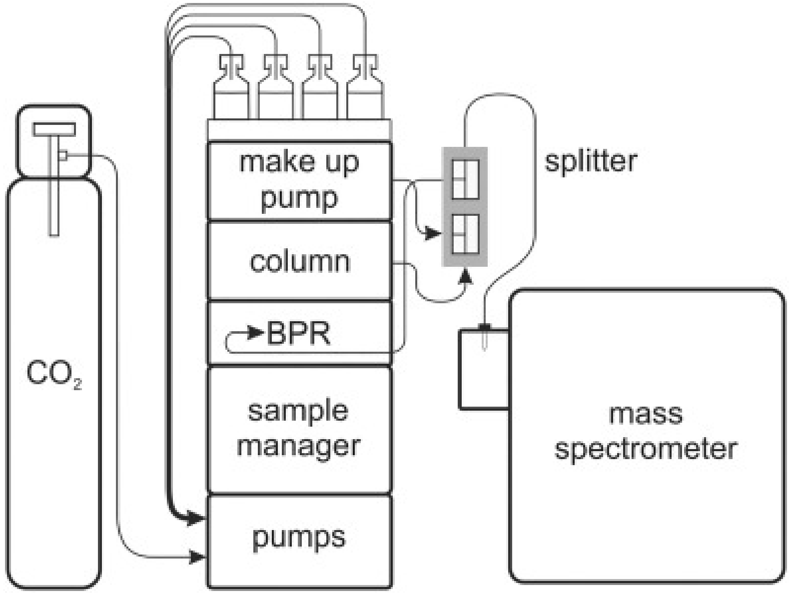
Utilizes supercritical fluids as the mobile phase

- Combines properties of both gas and liquid chromatography
- Supercritical fluids have viscosities similar to those of gases
- Supercritical fluids have densities much closer to that of a liquid

Advantages of SFC

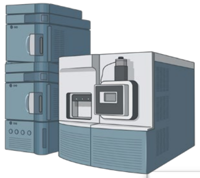
- Enhanced isomer separation
- Shorter analysis time
- Environmentally friendly
- Reduced matrix effects



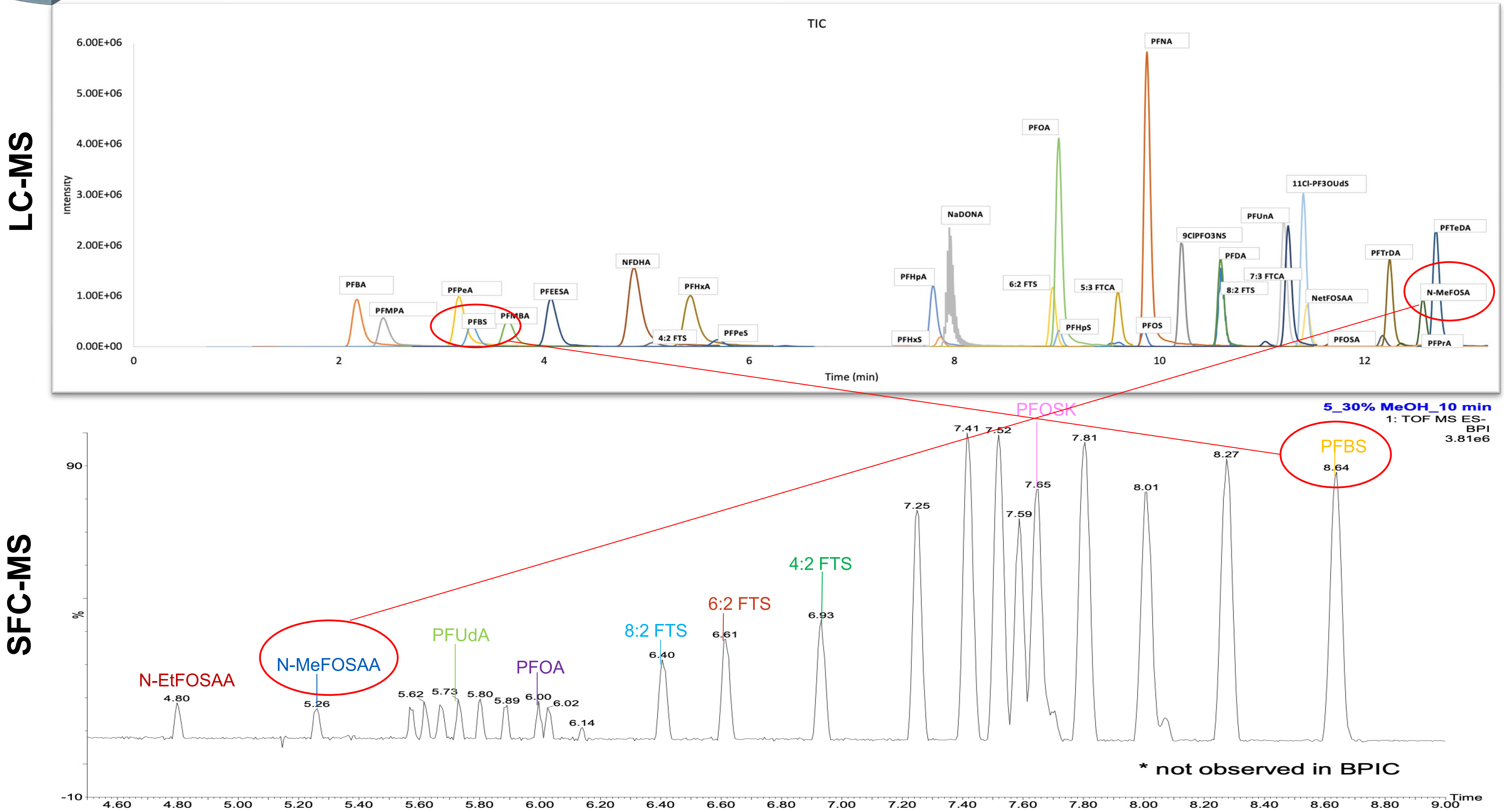


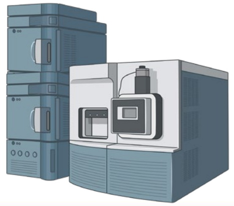
Compound	Critical Temperature (°C)	Critical Pressure (atm)
carbon dioxide	31.3	72.9
ethane	32.4	48.3
nitrous oxide	36.5	71.4
ammonia	132.3	111.3
diethyl ether	193.6	36.3
isopropanol	235.3	47.0
methanol	240.5	78.9
ethanol	243.4	63.0
water	374.4	226.8

Laboureur, L., et al. *International Journal of Molecular Sciences* (2015).

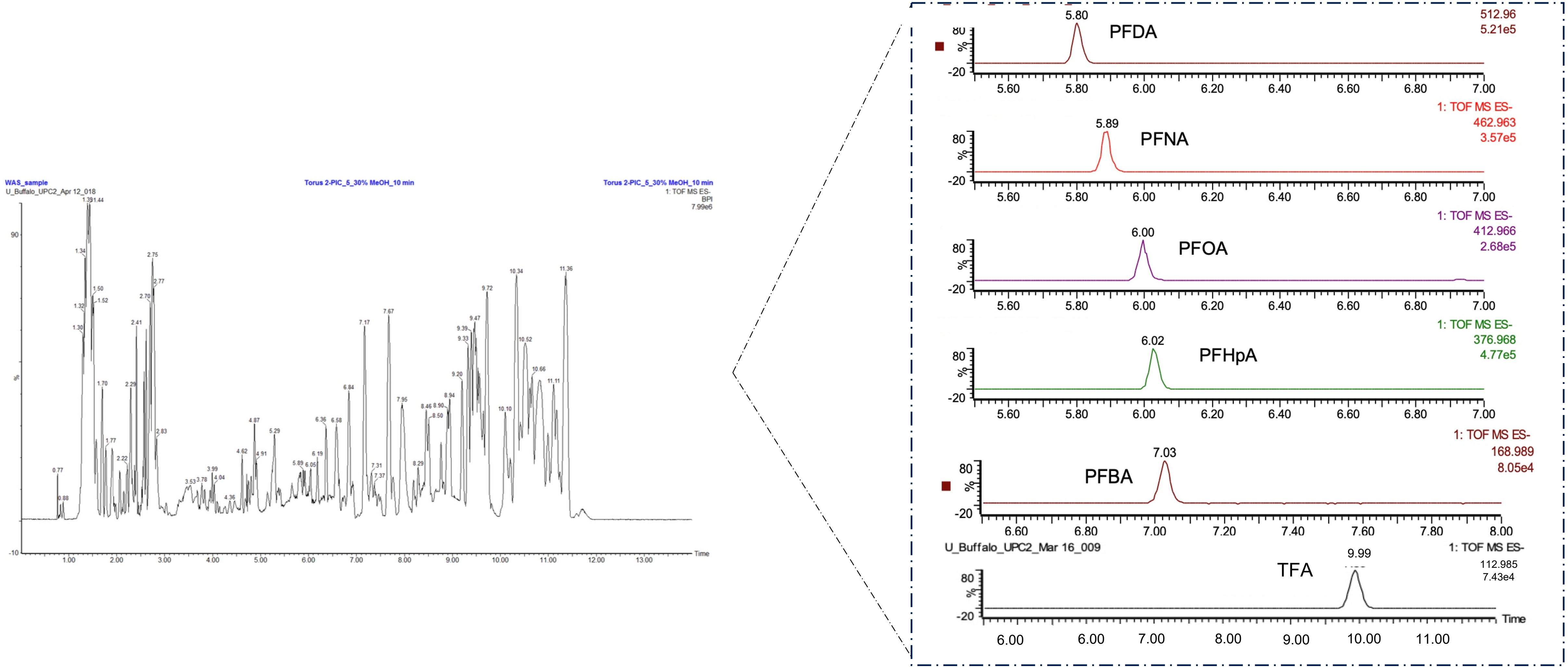


PFAS chromatograms: SFC-MS vs. LC-MS

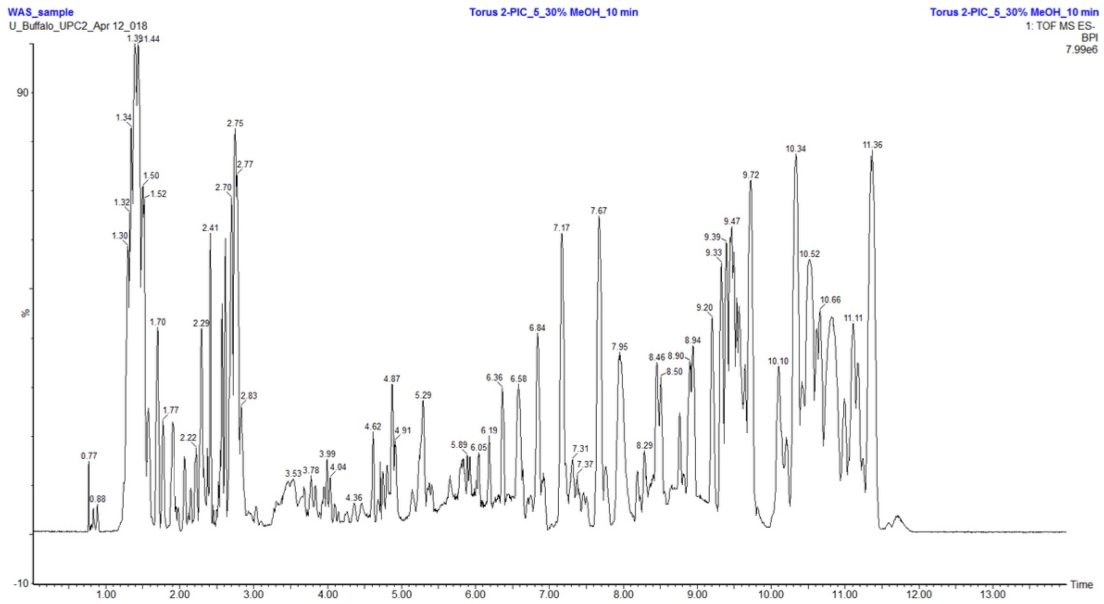


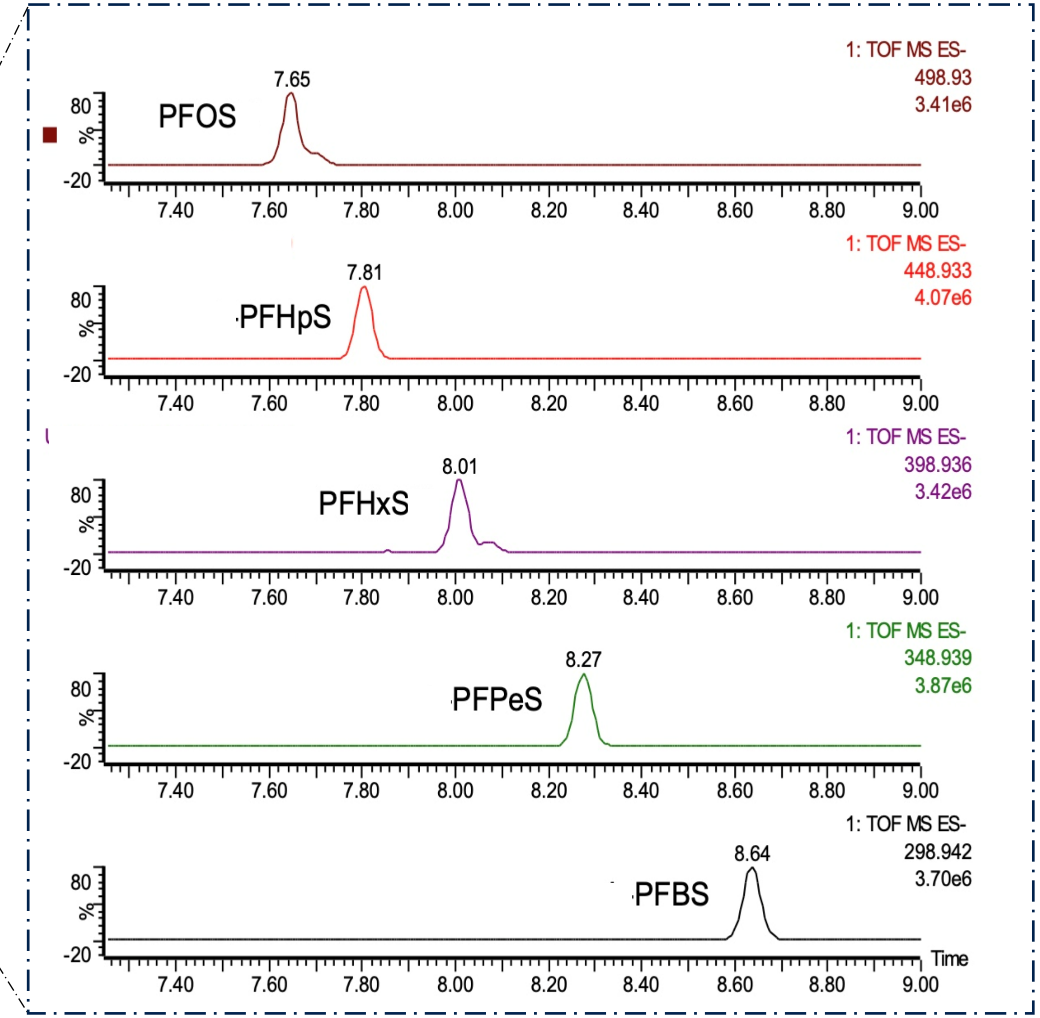


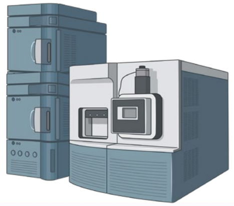
PFCAs detected in Wastewater Activated Sludge (WAS)



PFSAs detected in Wastewater Activated Sludge (WAS)





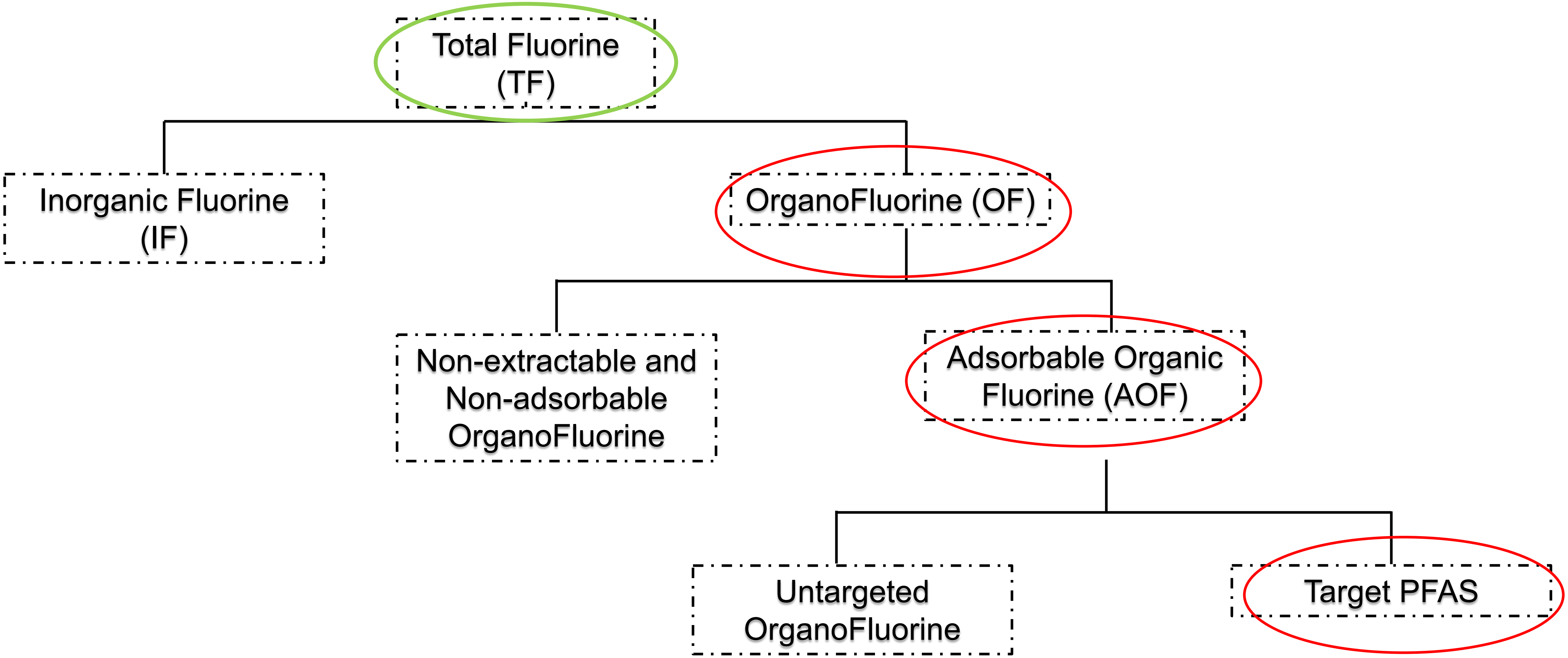


Estimated PFAS concentrations detected in WAS sample

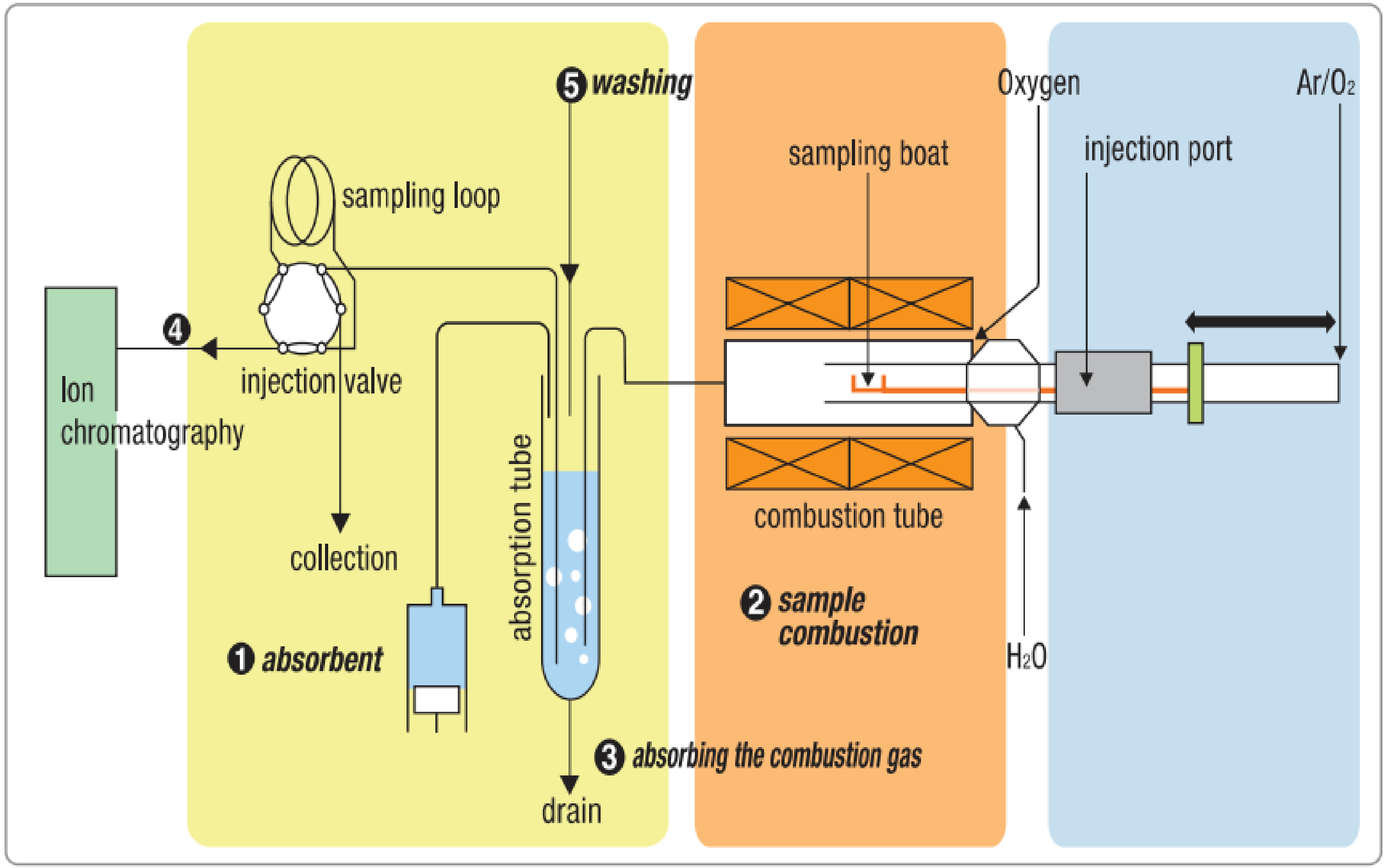
Concentrations calculated by external calibration curve

PFAS name			Concentration (ppb)
Perfluorinated carboxylates (PFCAs)	Trifluoroacetic acid	TFA	**0.21**
	Perfluorobutanoic acid	PFBA	0.10
	Perfluoropentanoic acid	PFPeA	0.19
	Perfluorooctanoic acid	PFOA	**0.21**
	Perfluorodecanoic acid	PFDA	0.016
Perfluoroalkyl sulfonates (PFSAs)	Perfluorobutane sulfonate	PFBS	0.017
	Perfluorohexane sulfonate	PFHxS	0.088
	Perfluorooctane sulfonate	PFOS	**0.19**

Combustion Ion Chromatography (CIC)

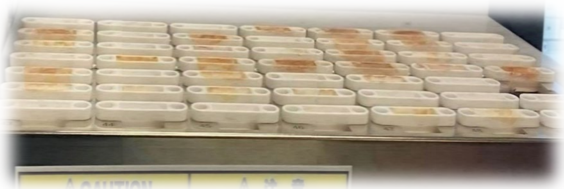


CIC instrument



Schematic diagram of a combustion ion chromatography[1]

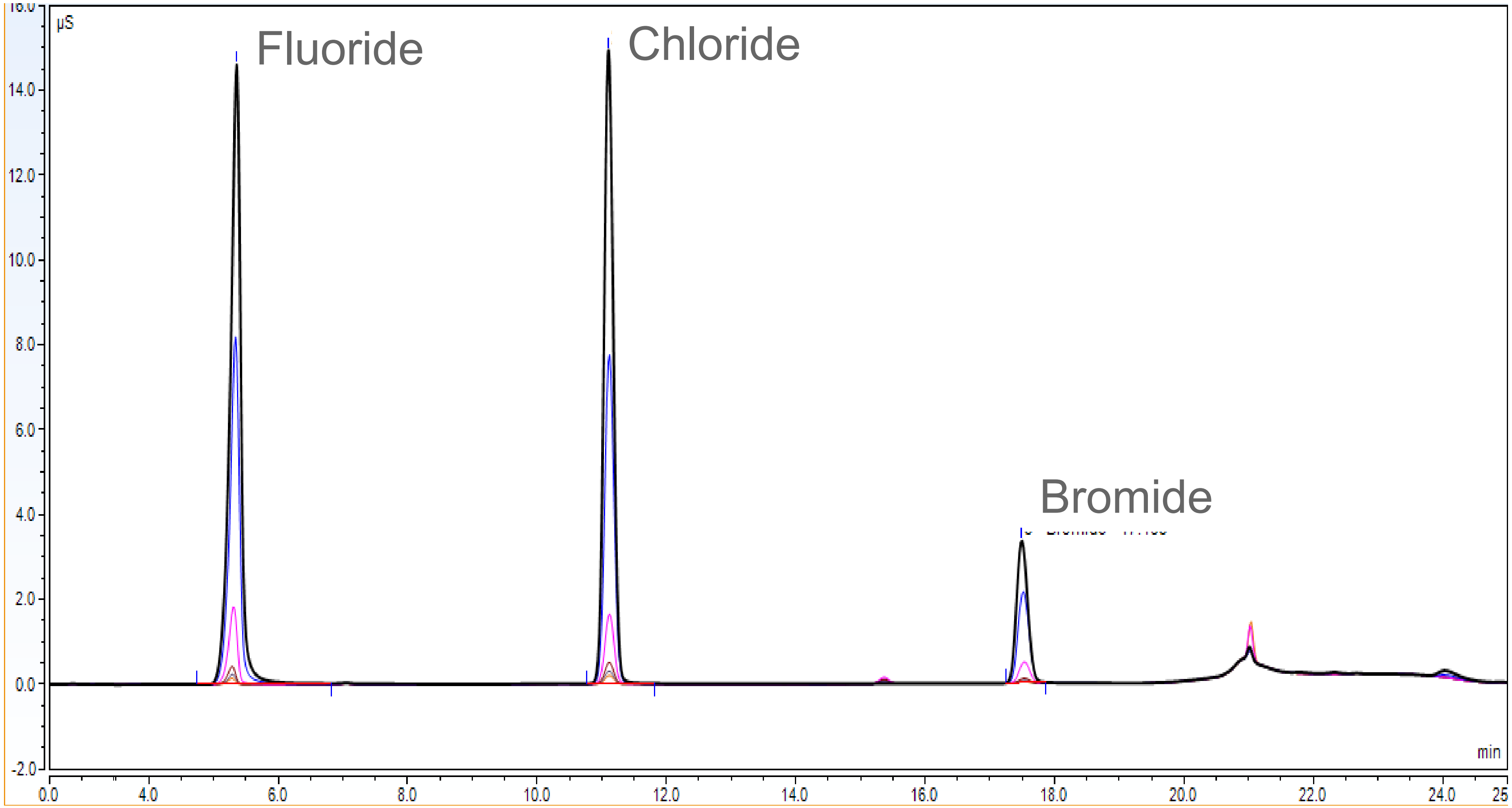
Sample



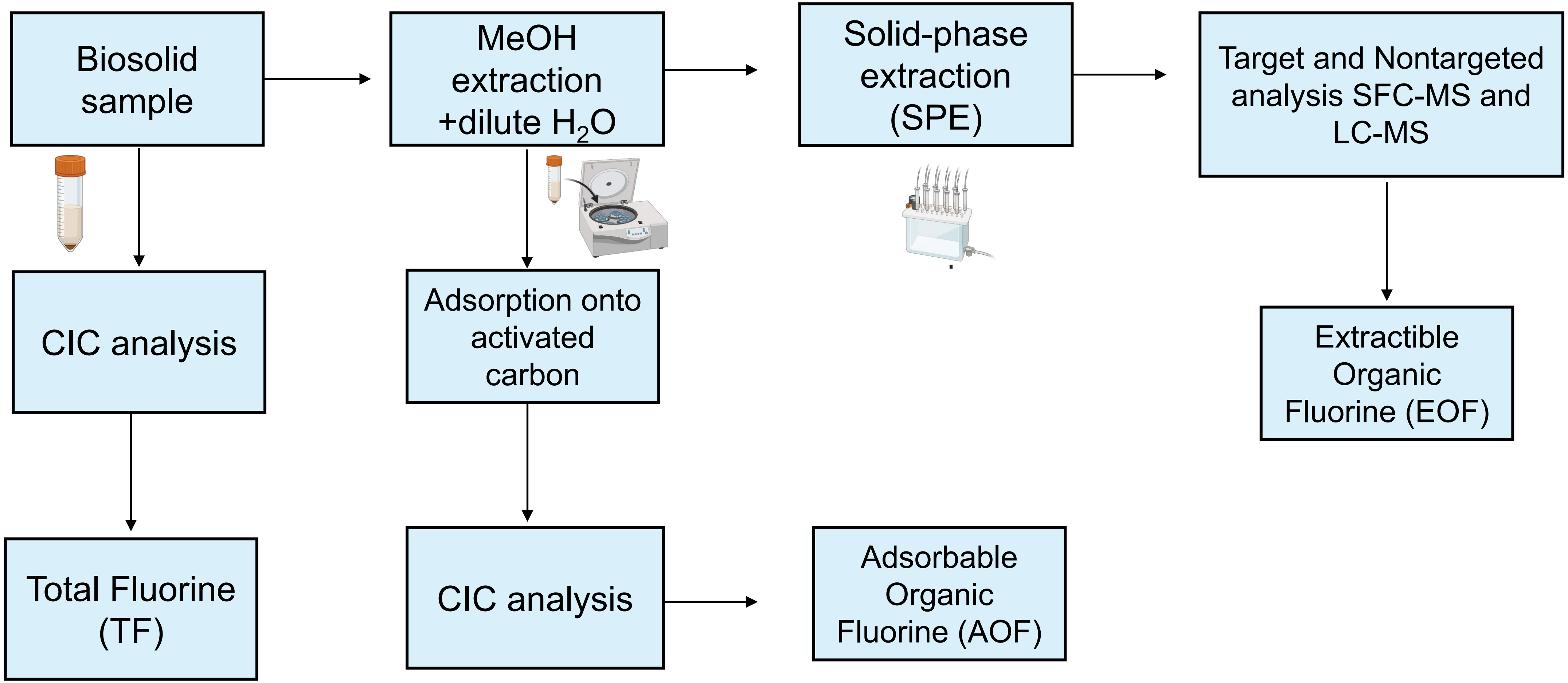
Autosampler boats

1. ThermoFisher Scientific. Combustion IC system, 2022

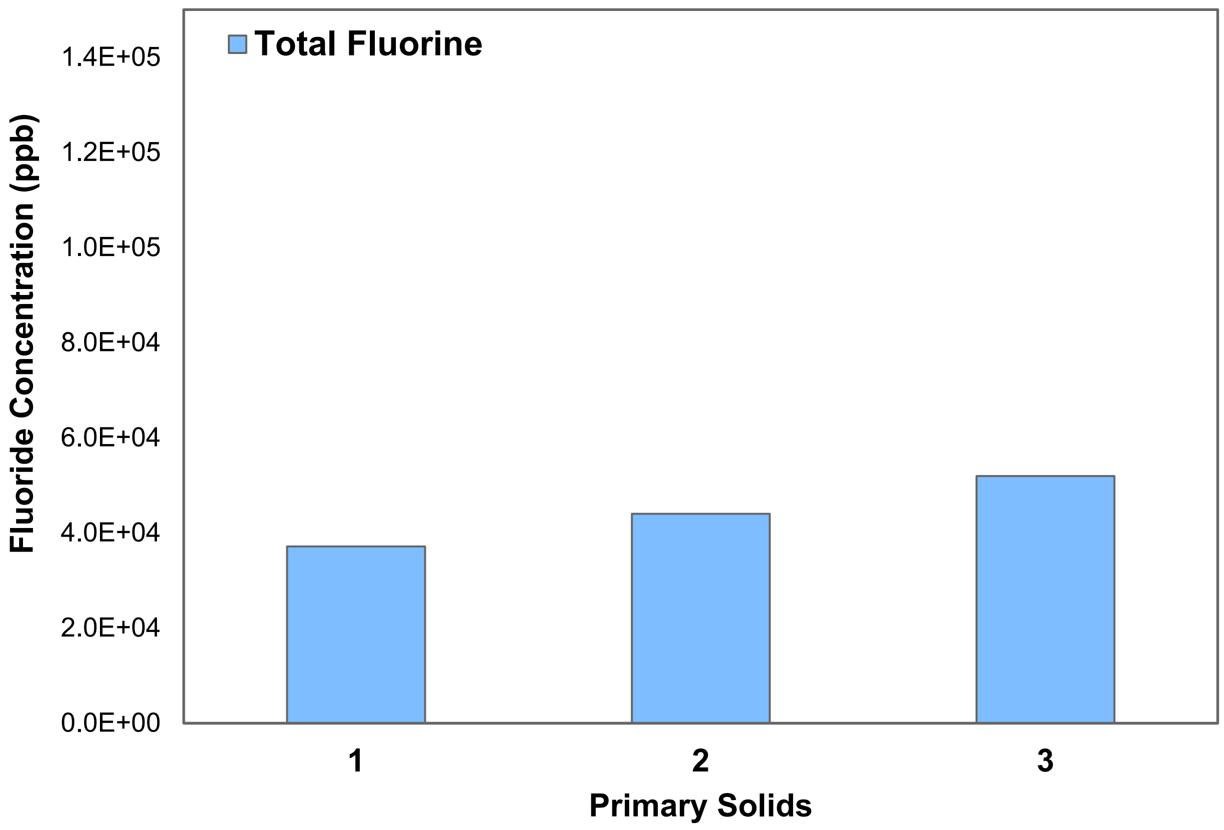
Sample Ion Chromatogram

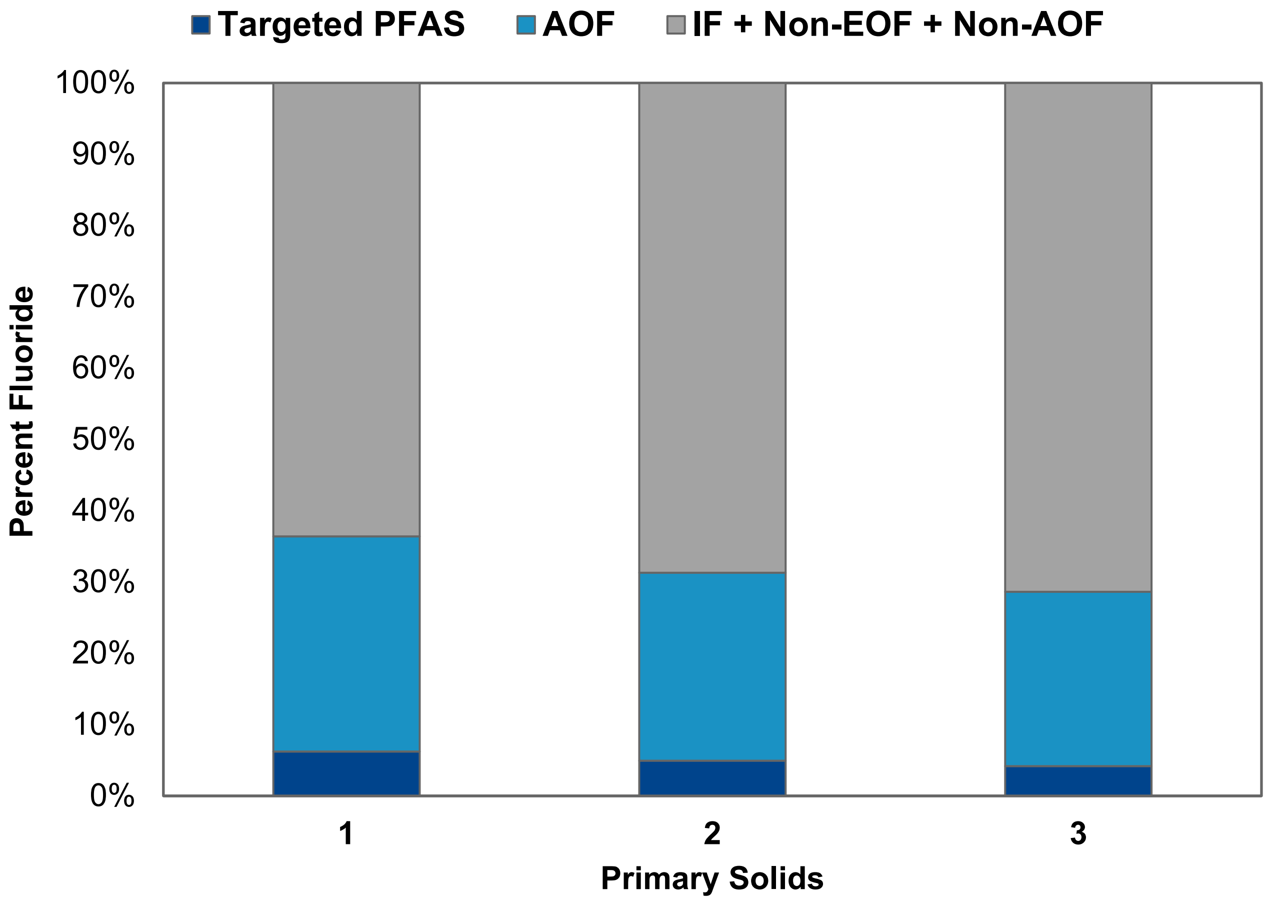


Workflow for Biosolids analysis



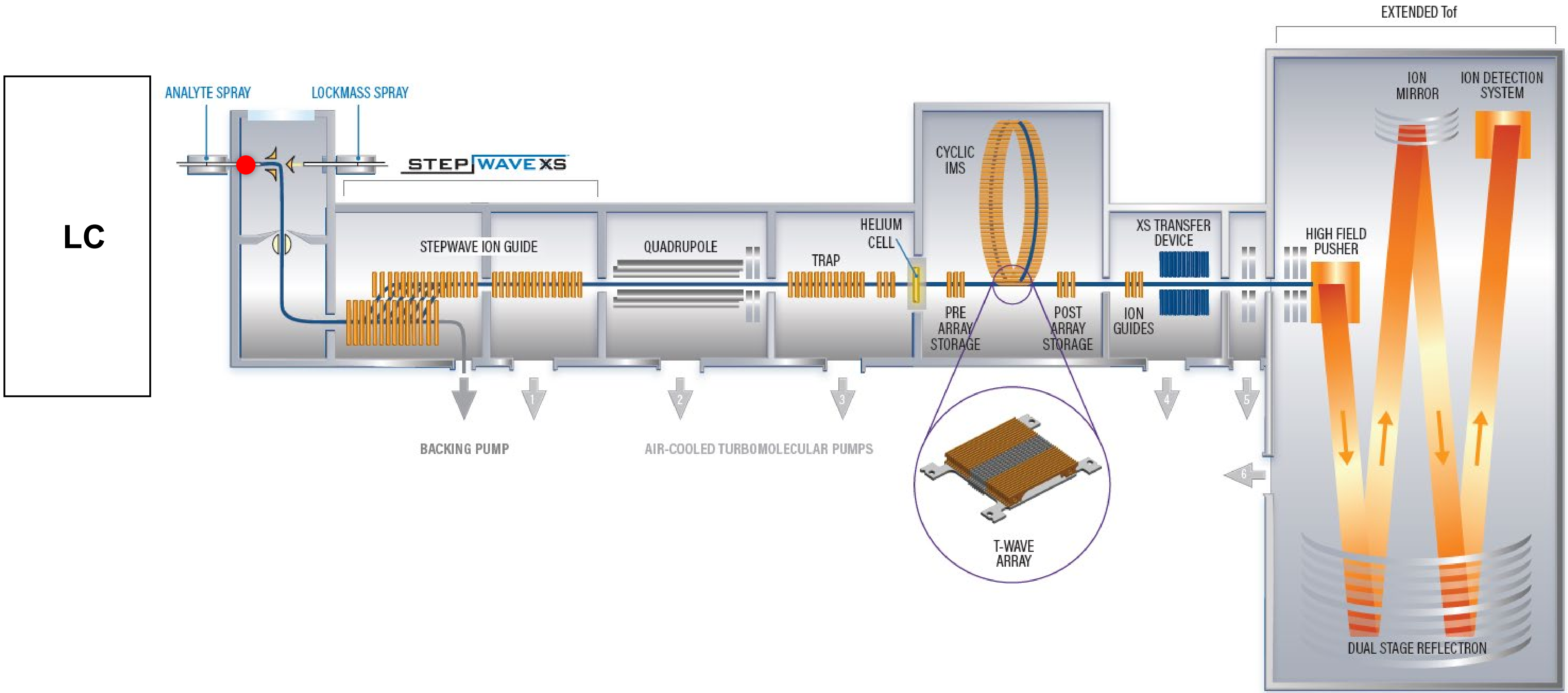
Biosolids Analysis by Combustion Ion Chromatography (CIC)





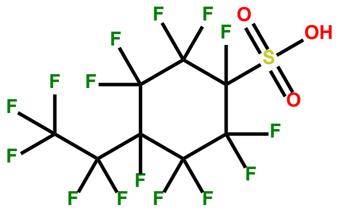
LC-IMS-QTOF-MS

Liquid Chromatography-Ion Mobility Spectrometry- Quadrupole Time of Flight-Mass Spectrometry

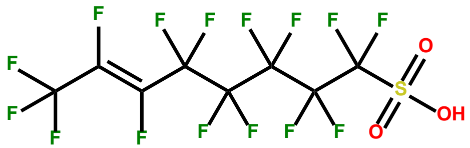


Cyclic Ion Mobility

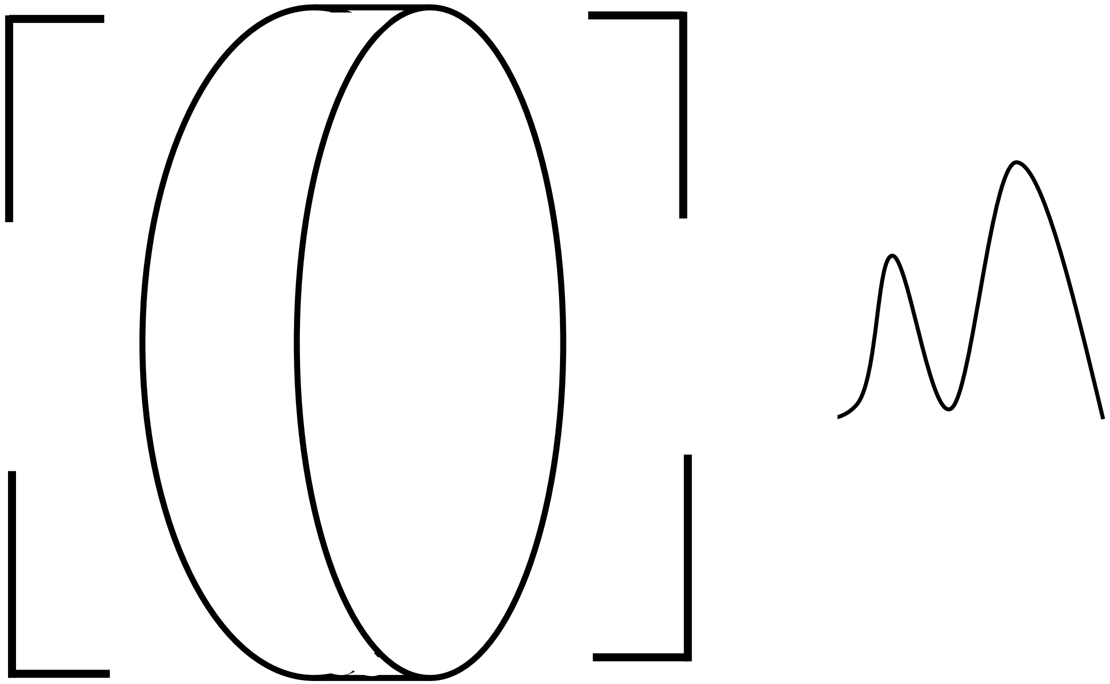
- Utilizes a circular ion mobility cell to trap and manipulate ions in a continuous circular path, allowing for improved separation based on the collision cross section (CCS) of a molecule.
- Resolve isomers of small and large molecules using multi pass feature of the Cyclic IMS.



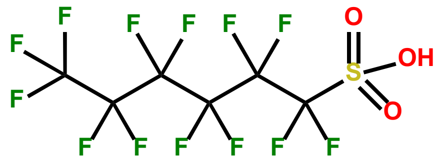
$C_6HF_{12}O_3S$

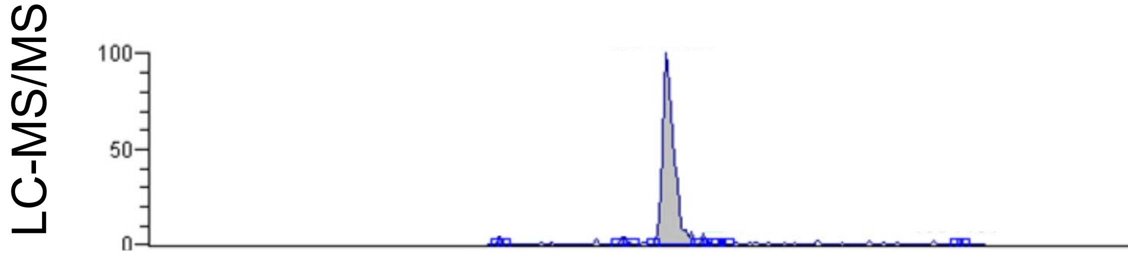


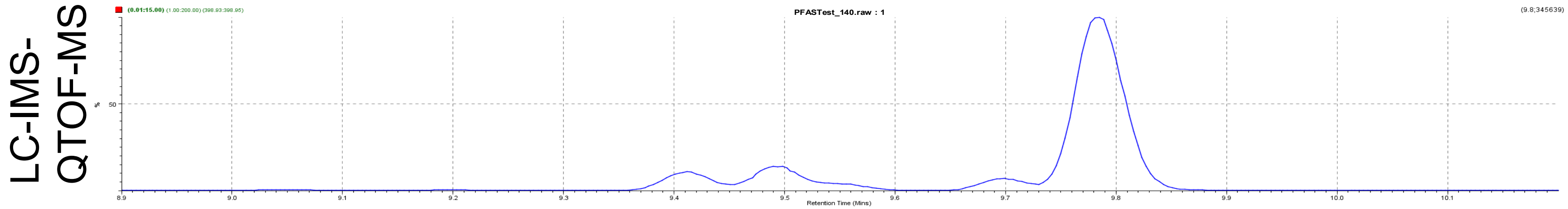
$C_6HF_{12}O_3S$

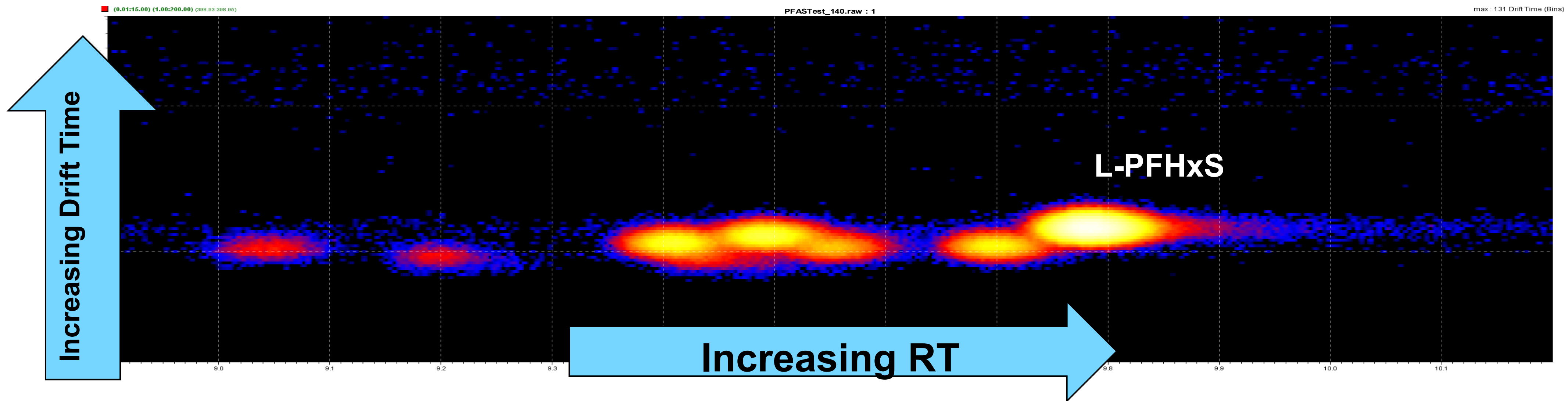


Cyclic Ion Mobility: Isomer separation of perfluorohexane sulfonic acid (PFHxS)

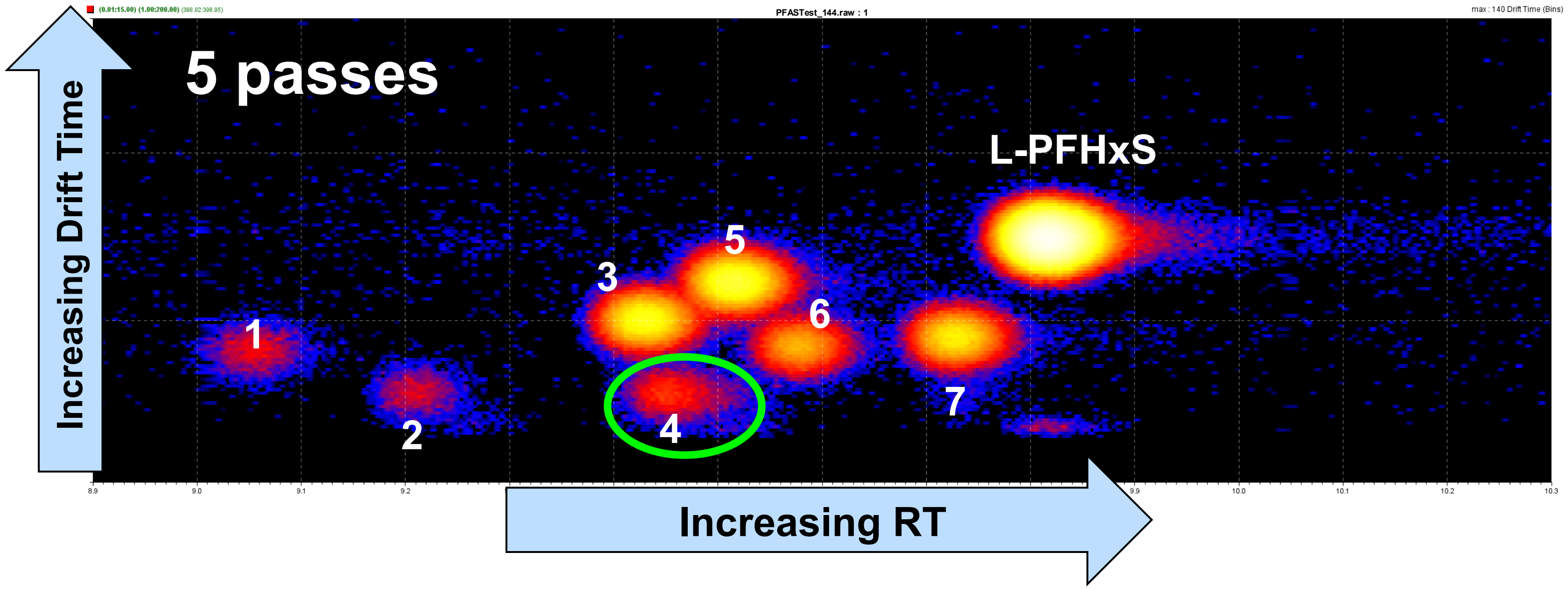


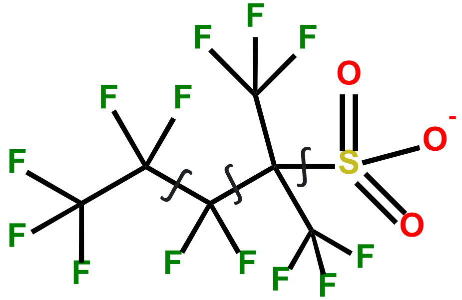




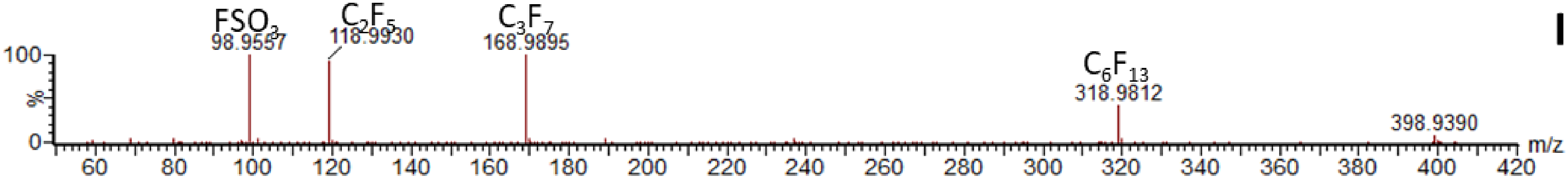


Cyclic Ion Mobility: Isomer separation of perfluorohexane sulfonic acid (PFHxS)- 5 passes

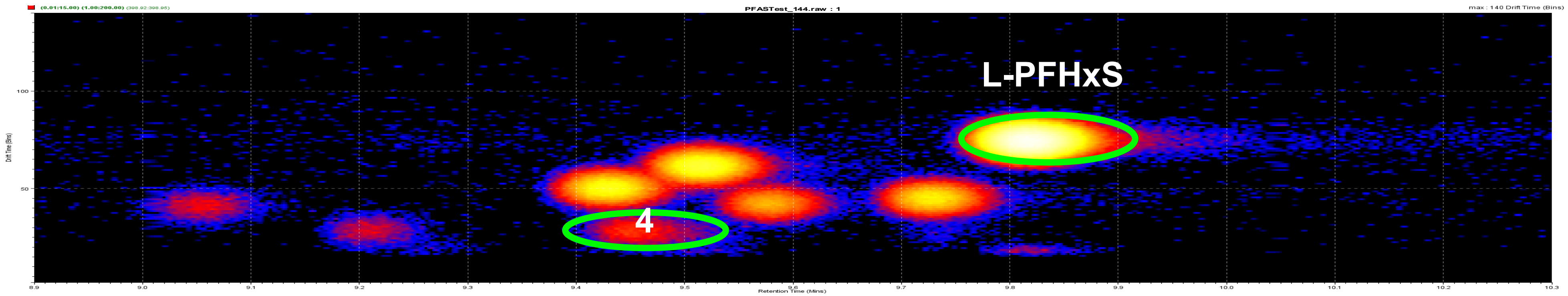


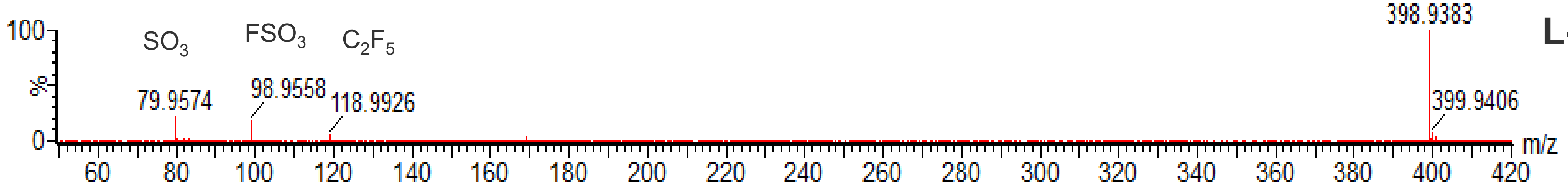


Isomer 4:

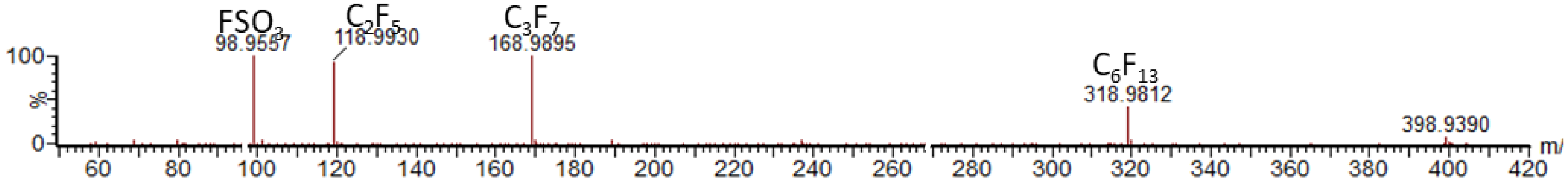


Distinguishing Isomers by IMS and MS fragmentation



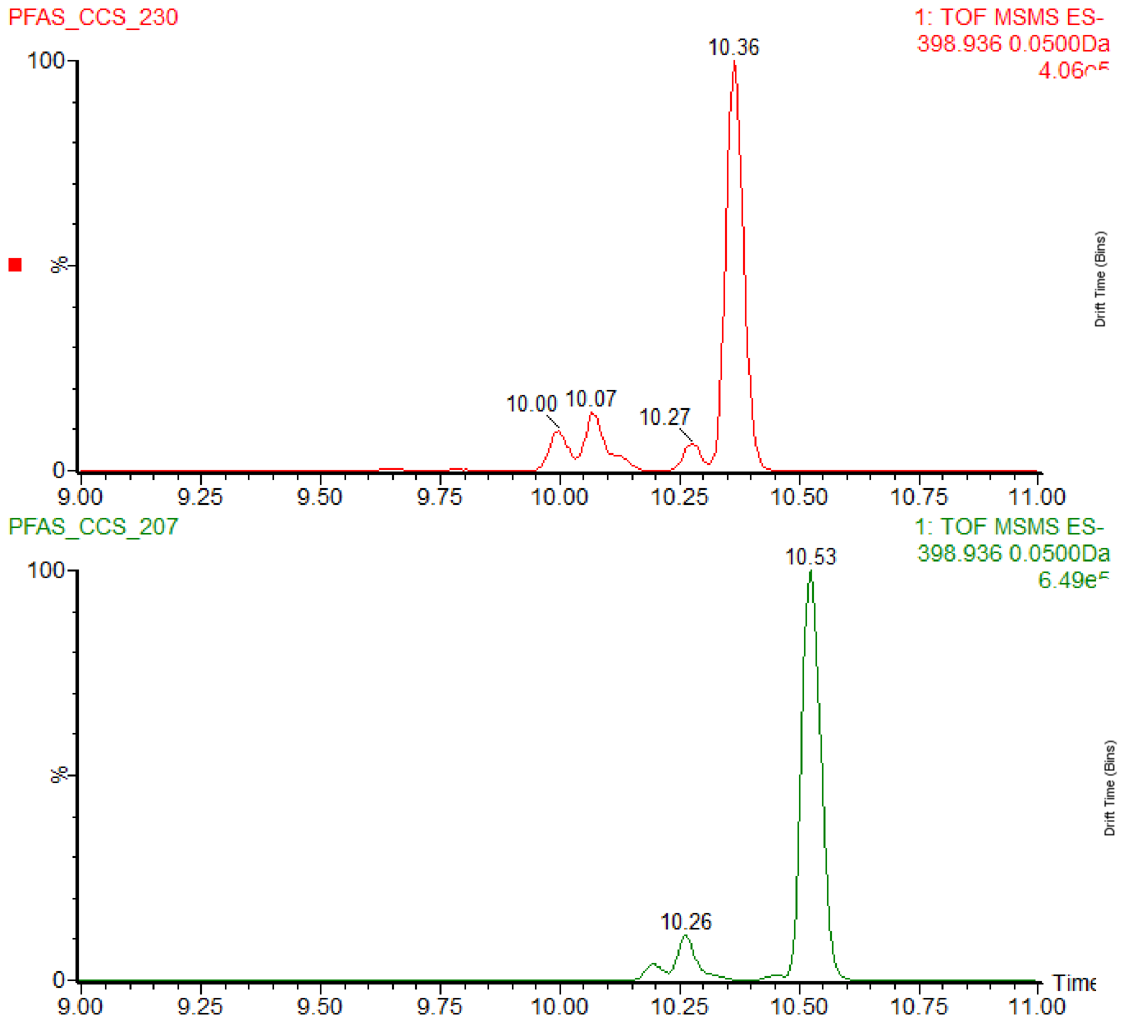


L-PFHxS

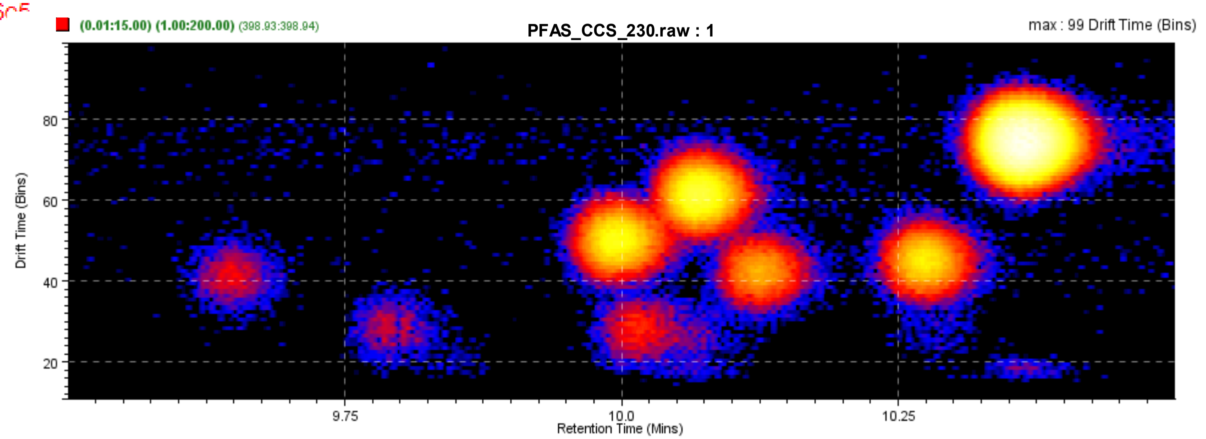


Isomer 4:

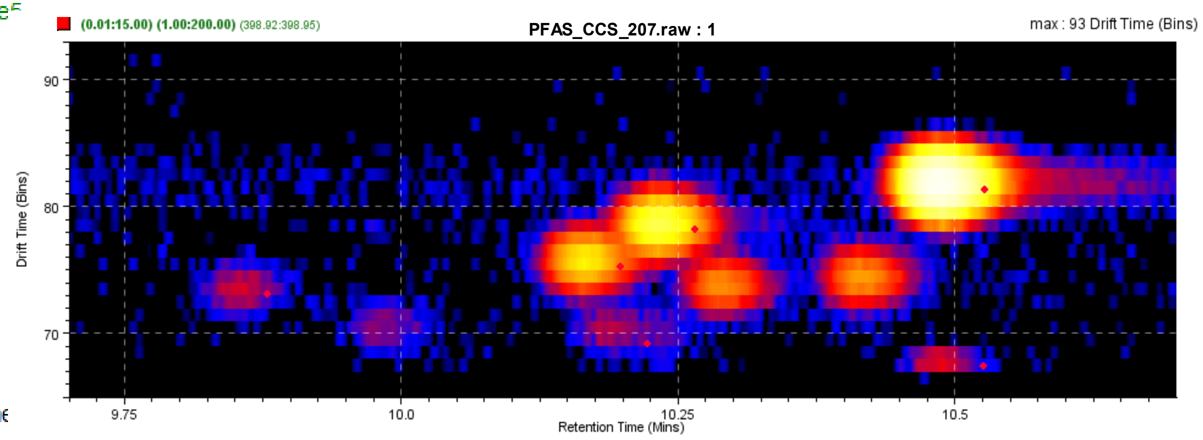
Cyclic Ion Mobility:
PFHxS standard vs. Leachate sample



Leachate Sample



PFHxS Standard



Summary

Techniques	Advantages	Limitations
^{19}F-NMR	• Quantification of PFAS without standards • Not prone to matrix effects • Simple sample preparation	• Very high detection limits • Not suitable for trace analysis
SFC-MS	• Low solvent consumption • Faster analysis time • Retains ultra-short PFAS	• Limited selection of column and mobile phase • Instrument not frequently available
CIC	• Low solvent consumption • Can analyze solid ad liquid samples • Provides total F and adsorbable PFAS	• Lack of structural information
LC-IMS-HRMS	• Separation of multiple isomers • Suitable for non-target (unknown) analysis	• Limited library for CCS values • Instrument not frequently available

Acknowledgements

- Dr. Joshua S. Wallace
- Aga Lab members:
  JM Aguilar
  Jonathan Antle
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  Zach Gernold
  Lahiruni Halwatura
  Paige Montgomery
  Jonathan Navarro Ramos
  Karla Ríos Bonilla
  Mindula Wijayahena

Award # R01ES032717

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