A Forensics Based Approach to Evaluating PFAS Contamination in the Environment

NEMC Environmental Forensics Session

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PFAS Forensic Tools

The tools for PFAS forensics are a developing area of applications. We currently have several tools already in use that can be applied towards forensic investigations;

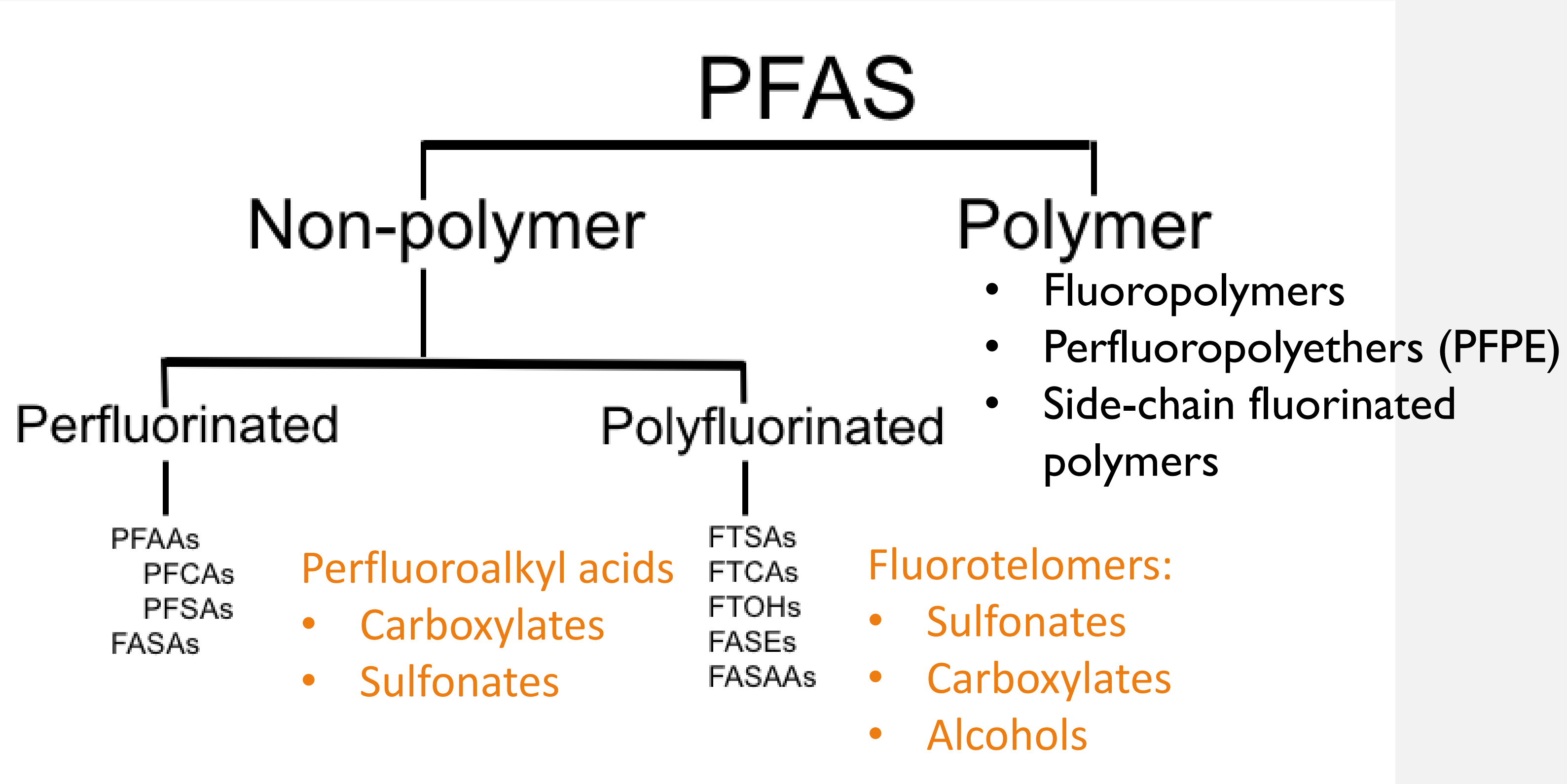
- Chemical Fingerprinting
- Isomer comparison
- Applications of TOP Assay

PFAS Forensic Tools

Additional techniques that are gaining in use and application

- Total Organic Fluorine Analysis
- Non-Target Analysis

The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)



Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet

User-Defined Methods: PUT TO THE TEST!

Complex Matrices

- Biphasic
- Biosolids
- Tissues
- Dispersions
- Activated Carbon
- Cosmetics
- Concrete

Audits & PTs

- NELAC
- DoD ELAP
- Client/Program Specific Audits
- Semiannual PT
- NMI International Round Robin
- DOW Study

3rd Party Validation

- >85% of all PFAS data includes a validation package
- >300,000 sample data validated

Benefits of Isotope Dilution

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What affects the native analyte will equally affect the isotope

Calibration

Most accurate and precise method

Target analytes are quantitated against structurally similar materials, the isotopes themselves

Matrix Mitigation

Expands ability to process a broader range of matrices

Compound Identification

Reduces the potential for false positives

Reduces the potential for error; corrects for retention time shifts

LCMSMS/GCMSMS Analysis

Compounds Included in EPA Draft 1633 (RLs ~2-5ng/L)		Target Compounds Not Part of EPA Draft 1633 (RLs ~2-5ng/L)	
Perfluorobutanoic acid (PFBA)	NEtFOSA	10:2 FTS	EVE Acid
Perfluoropentanoic acid (PFPeA)	NMeFOSA	6:2 FTCA	PFO5DA
Perfluorohexanoic acid (PFHxA)	NMeFOSAA	8:2 FTCA	PMPA
Perfluoroheptanoic acid (PFHpA)	NEtFOSAA	10:2 FTCA	PEPA
Perfluorooctanoic acid (PFOA)	NMeFOSE	6:2 FTUCA	MTP
Perfluorononanoic acid (PFNA)	NEtFOSE	8:2 FTUCA	PS Acid
Perfluorodecanoic acid (PFDA)	4:2 FTS	10:2 FTUCA	Hydro-PS Acid
Perfluoroundecanoic acid (PFUnA)	6:2 FTS	PFECHS	R-PSDA
Perfluorododecanoic acid (PFDoA)	8:2 FTS	PFPrS	Hydrolyzed PSDA
Perfluorotridecanoic acid (PFTriA)	9Cl-PF3ONS	PFPrA	R-PSDCA
Perfluorotetradecanoic acid (PFTeA)	11Cl-PF3OUdS	PFMOAA	6:2 diPAP
Perfluorobutanesulfonic acid (PFBS)	DONA	PFECAG	8:2 diPAP
Perfluoropentanesulfonic acid (PFPeS)	HFPO-DA (GenX)	PFO4DA	6:2/8:2 diPAP
Perfluorohexanesulfonic acid (PFHxS)	3:3 FTCA	PFO3OA	10:2 diPAP
Perfluoroheptanesulfonic Acid (PFHpS)	5:3 FTCA	PFO2HxA	10:2 FTOH (RL=1ug/L)
Perfluorooctanesulfonic acid (PFOS)	7:3 FTCA	R-EVE	8:2 FTOH (RL=1ug/L)
Perfluorononanesulfonic acid (PFNS)	NFDHA	NVHOS	7:2 FTOH (RL=1ug/L)
Perfluorodecanesulfonic acid (PFDS)	PFMBA	Hydro-EVE Acid	6:2 FTOH (RL=1ug/L)
Perfluorododecanesulfonic acid (PFDoS)	PFMPA	Perfluoro-n-octadecanoic acid (PFODA)	4:2 FTOH (RL=1ug/L)
Perfluorooctanesulfonamide (FOSA)	PFEESA	Perfluoro-n-hexadecanoic acid (PFHxDA)	

Additional PFAS Methods

Fluorotelomer Alcohols

- GCMSMS method
- Water and solids
- Instrumental set-up like 8270E and extractions like 3510 and 3540/50
- Current compound list
- Fluorotelomer acrylates and acetates being added

4:2
Fluorotelomer alcohol

6:2
Fluorotelomer alcohol

7:2S
Fluorotelomer alcohol

8:2
Fluorotelomer alcohol

10:2
Fluorotelomer alcohol

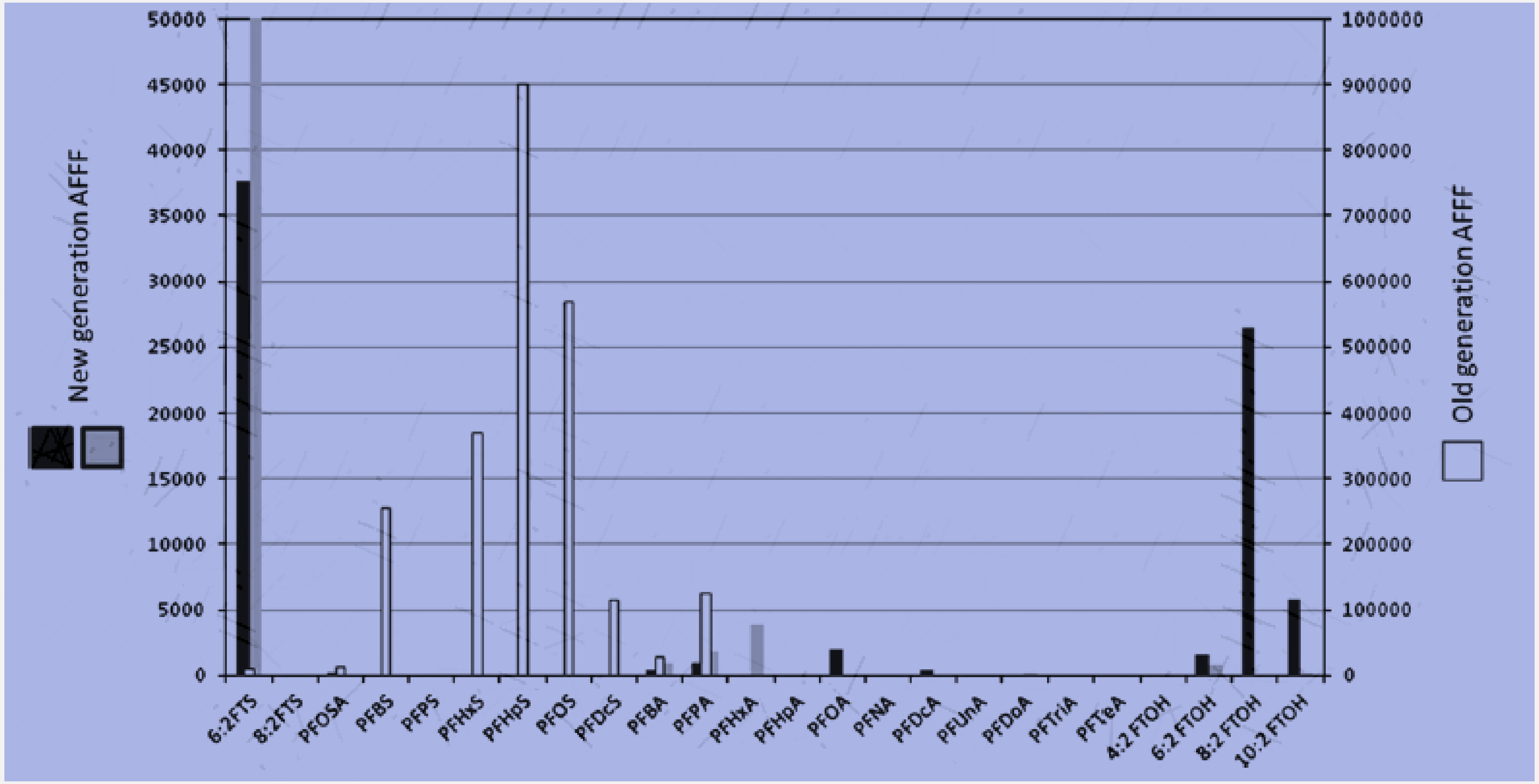
EPA Draft Method In Progress

EPA Draft 1633

- Targeted Analysis of 40 PFAS
- Non-Potable Water, Soil & Tissue
- LCMSMS, WAX SPE, Isotope Dilution
- Multi-Lab Validation Underway

EPA METHODS

Chemical Fingerprinting



Herzke, et al., 2012, Chemosphere, 88, 980-987

Isomer Comparison

$F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$

Linear Perfluorooctane sulfonate (PFOS)

$F_3C\text{-}CF(CF_3)\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$

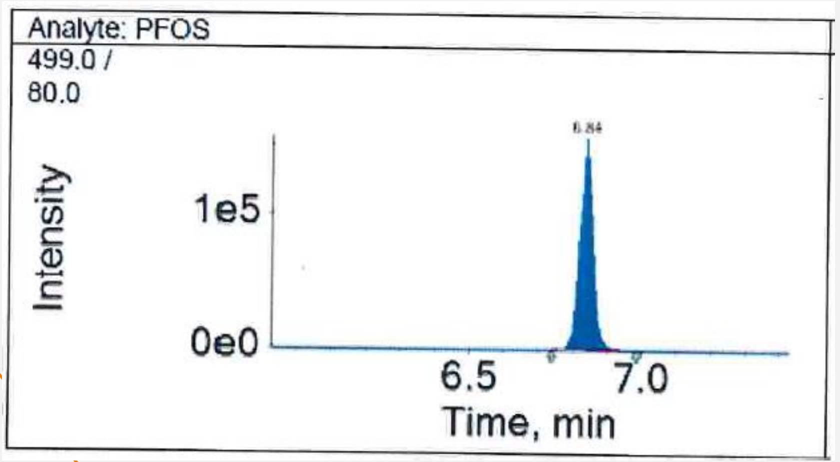
Branched Perfluorooctane sulfonate (PFOS)

Figure 4-1. Linear and one branched isomer of PFOS

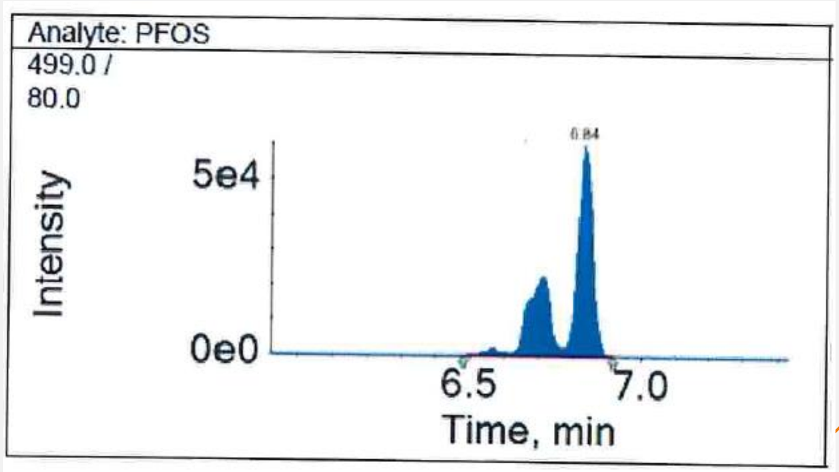
ITRC PFAS Fact Sheet Naming Conventions April 2020

Isomer Comparison

Chromatogram of PFOS Standard of Linear Isomer

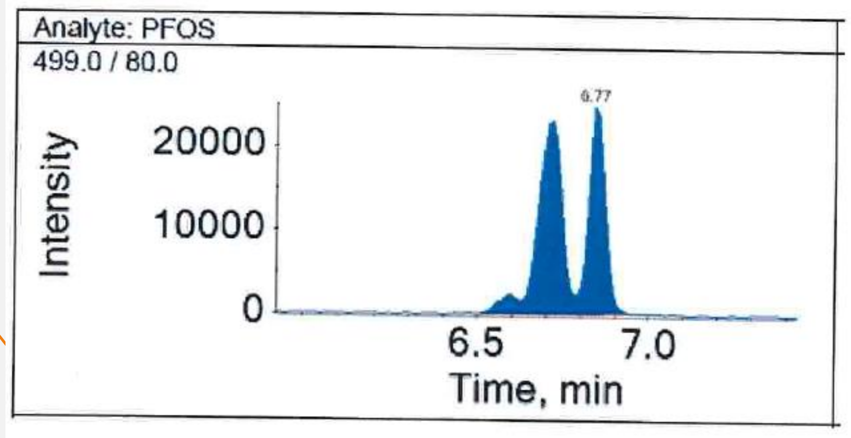


Chromatogram of PFOS Standard of Branched/Linear Mix Typical Ratio

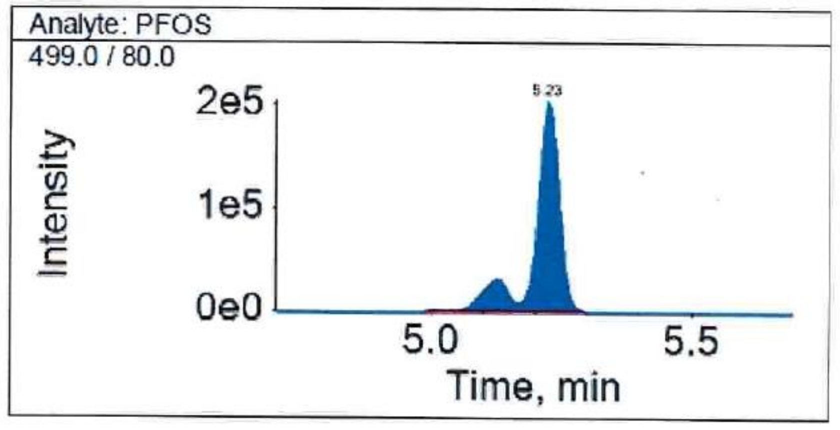


Isomer Comparison

Chromatogram of PFOS Sample with Branched/Linear Mix High Bias Ratio

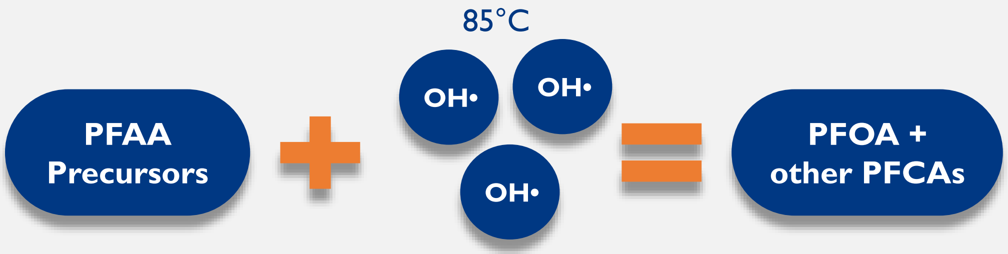


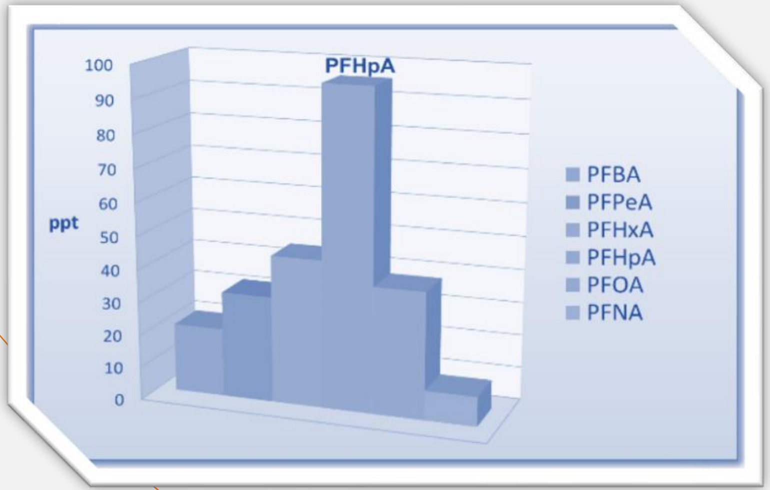
Chromatogram of PFOS Sample with Branched/Linear Mix Low Bias Ratio



Total Oxidizable Precursors

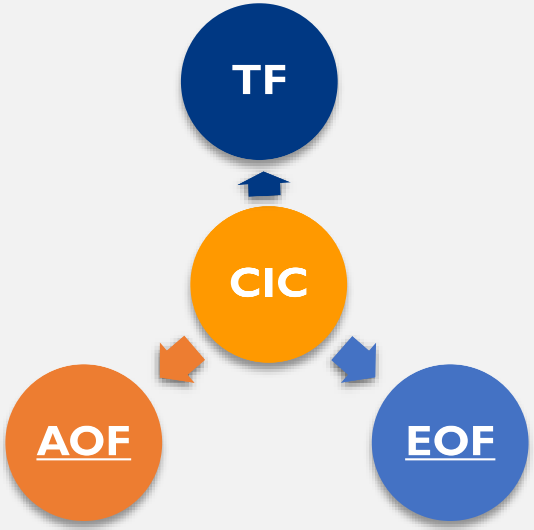
TOP Assay





TOP Conversion of 8:2 FTS

Total Organic Fluorine Analysis



CIC: Combustion Ion Chromatography

Total Oxidizable Precursors - TOP

Environmental Science & Technology

Article

pubs.acs.org/est

Oxidative Conversion as a Means of Detecting Precursors to Perfluoroalkyl Acids in Urban Runoff

Erika F. Houtz and David L. Sedlak*

Department of Civil and Environmental Engineering, University of California at Berkeley, Berkeley, California, 94720-1710

Concept is to analyze a sample for perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA) and any identified precursors . Then subject a second aliquot of the sample to relatively harsh oxidative conditions. Analyze the oxidized sample for the same perfluoroalkyl acids and precursors. Expect to see;

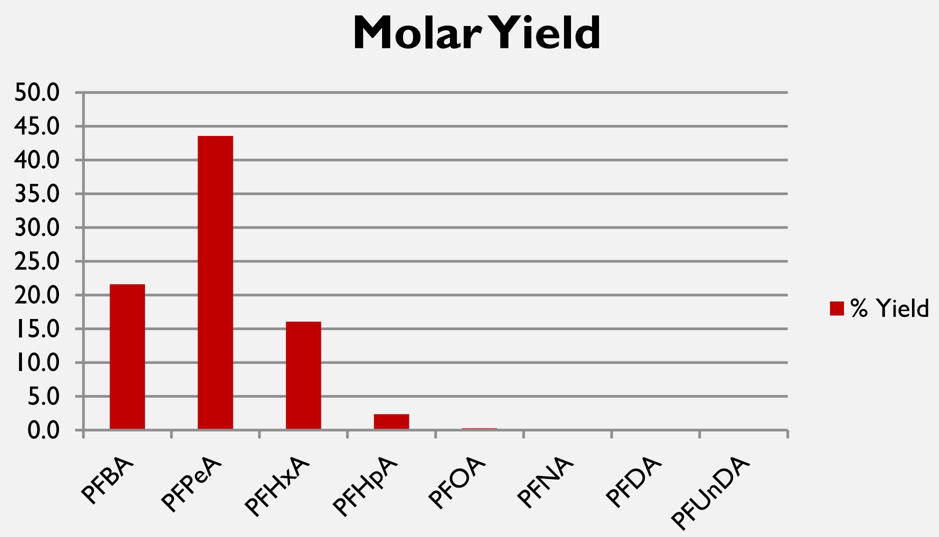
a) Reduction or elimination of the precursors

b) Increase in concentrations of perfluoroalkyl acids

TOP Assay – 6:2 FTS

Results of oxidation of 6:2 Fluorotelomer sulfonate at 250 ng/l

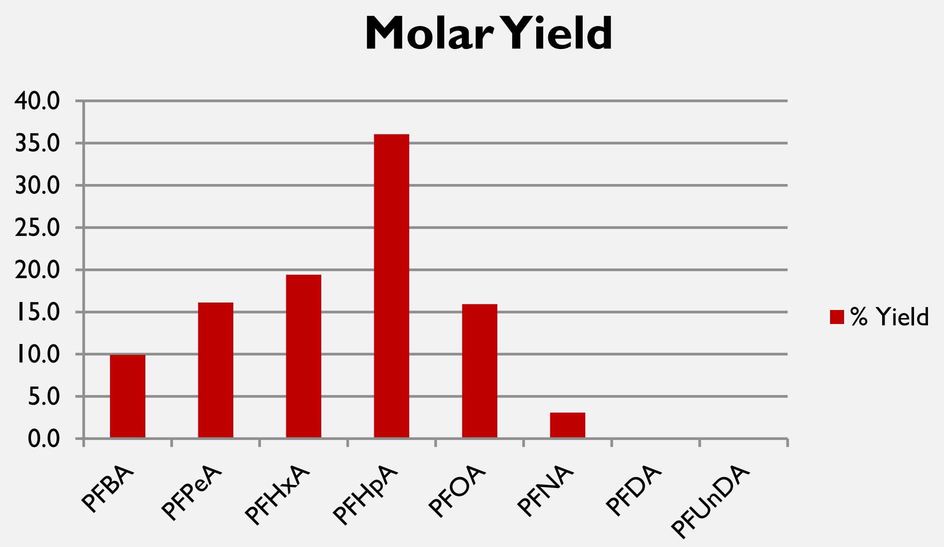
PFCA	ELLE	Houtz
PFBA	21.6	22
PFPeA	43.6	27
PFHxA	16.1	22
PFHpA	2.4	2
PFOA	0.3	0
PFNA	0.0	0
PFDA	0.0	0
PFUnDA	0.0	0



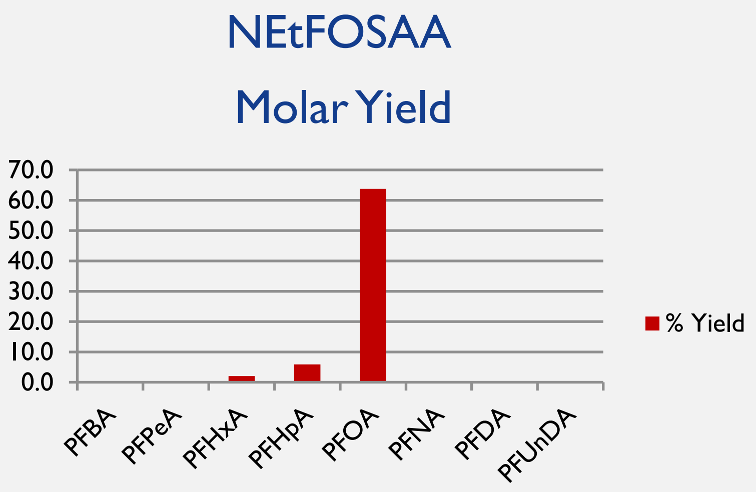
TOP Assay – 8:2 FTS

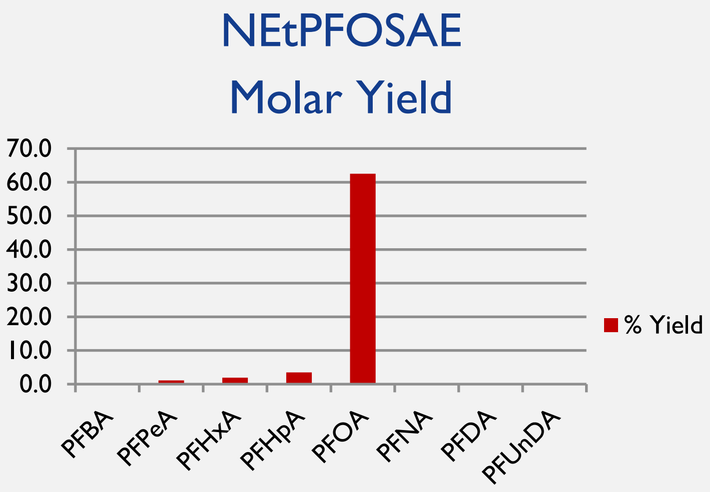
Results of oxidation of 8:2 Fluorotelomer sulfonate at 250 ng/l

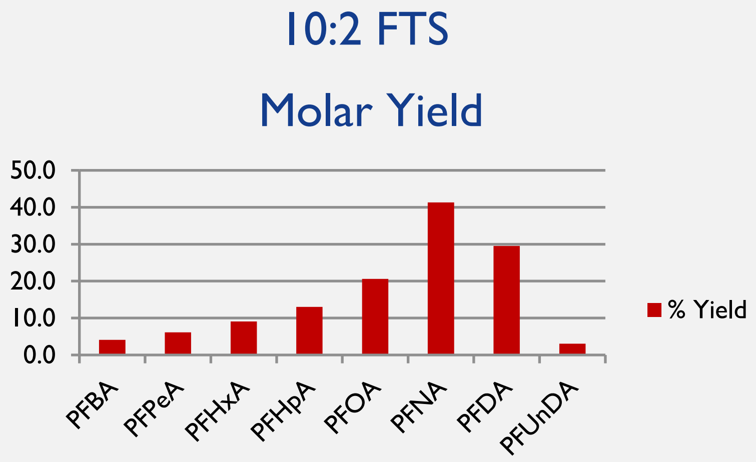
PFCA	ELLE	Houtz
PFBA	9.9	11
PFPeA	16.1	12
PFHxA	19.4	19
PFHpA	36.1	27
PFOA	15.9	21
PFNA	3.1	3
PFDA	0.0	
PFUnDA	0.0	



TOP Assay – Other Precursors







TOP Assay Results

Compound	Pre-Ox	Post-Ox	Difference
PFBA	ND	98 ng/l	98 ng/l
PFPeA	ND	87 ng/l	87 ng/l
PFHxA	5 ng/l	61 ng/l	56 ng/l
6:2 FTS	100 ng/l	ND	- 100 ng/l
PFHpA	11 ng/l	32 ng/l	21 ng/l
PFOA	7 ng/l	26 ng/l	19 ng/l
PFOS	56 ng/l	52 ng/l	- 4 ng/l
8:2 FTS	26 ng/l	ND	- 26 ng/l
PFNA	ND	5 ng/l	5 ng/l

Total Organic Fluorine Analysis

Marriage of TOX and IC

Sample (or treated sample) is combusted in a furnace at 900°C – 1100°C

Effluent collected in buffer and injected into ion chromatograph (IC)

Quantify fluorine (as fluoride) content

Compare ratio of total (or extractable) fluorine to total PFAS

Oxidative pyrohydrolytic combustion

Handling of the sample prior to fluoride determination determines result evaluated

EOF – Extractable Organic Fluorine

AOF – Absorbable Organic Fluorine

Total Organic Fluorine Analysis in Water

Adsorbable Org. F (AOF)

- **Sample Prep**
  - 100mls sample pass thru activated charcoal bed(s)
  - Final wash with nitrate solution to remove inorganic fluoride
- **Combustion of Charcoal into CIC to measure F^- by IC**

Extractable Org. F (EOF)

- **Sample Prep**
  - 100mls sample pass thru weak anion exchange (WAX) SPE
  - Elute PFAS with methanol
  - Concentrate methanol to final 1mL
- **Combustion of extracted sample into CIC to measure F^- by IC**

Total Org. F (TOF)

- **Sample Prep (water samples)**
  - No Sample Prep
- **Direct injection of aqueous sample into CIC system to measure both Inorganic F^- and Organic F^- simultaneously**

Courtesy of Dr. Jayesh Ghandi - Metrohm

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EPA Draft Method In Progress

EPA Draft 1621

- Adsorbable Organic Fluorine (AOF)
- Applicable to waters
- Proxy analysis for ‘Total PFAS’
- Single lab validation complete; multi-lab validation in process

EPA METHODS

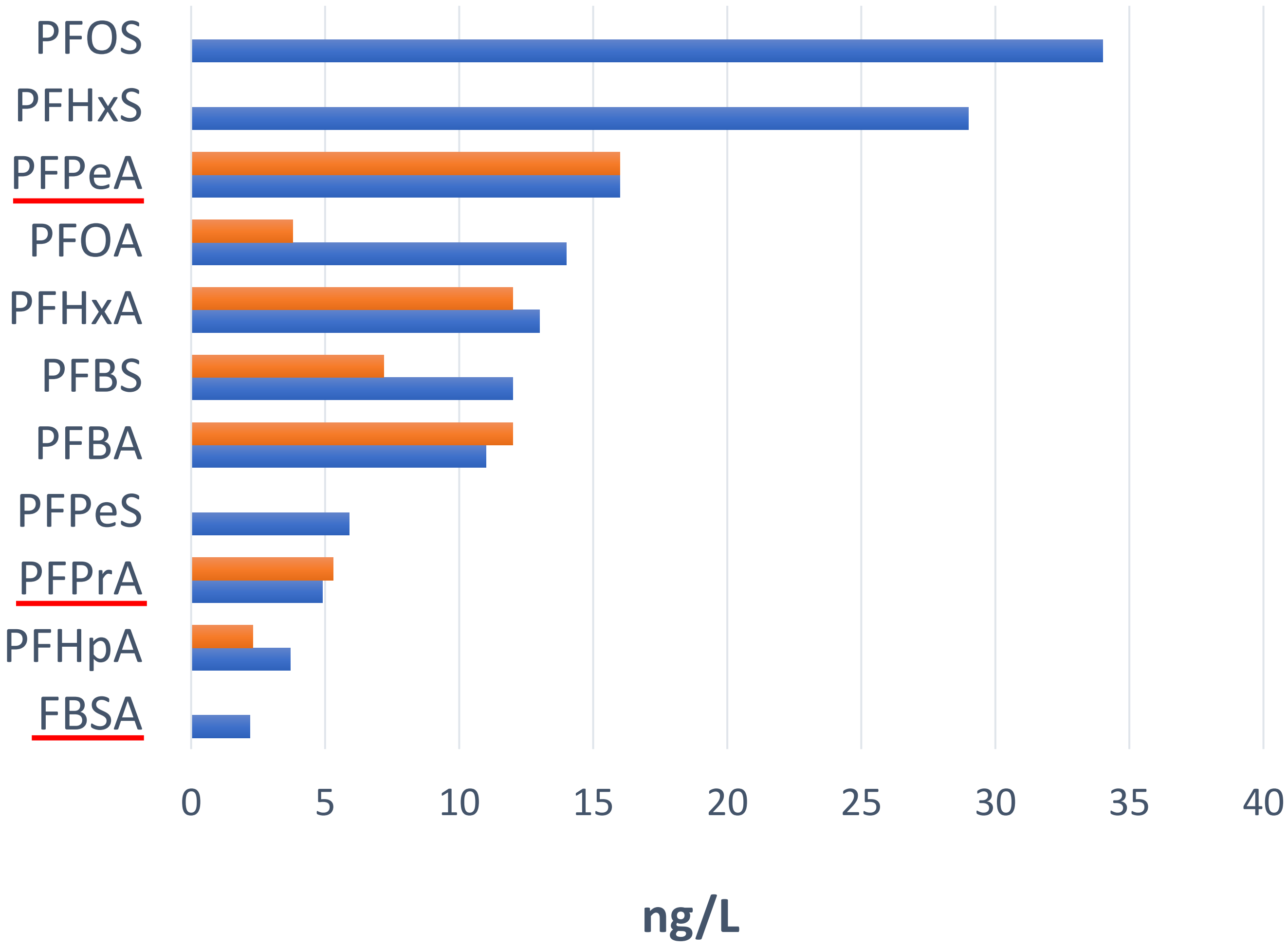
https://www.epa.gov/cwa-methods/cwa-analytical-methods-and-polyfluorinated-alkyl-substances-pfas

Site 1
Private WWTP

Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Influent	1,300	110
Influent Dup	1,300	120
Effluent	1,500	220
Effluent Dup	1,100	230

FTOHs are all non-detect @ 1,000 ng/L

Site 1, Private WWTP Influent & Effluent



∑PFAS 58.6

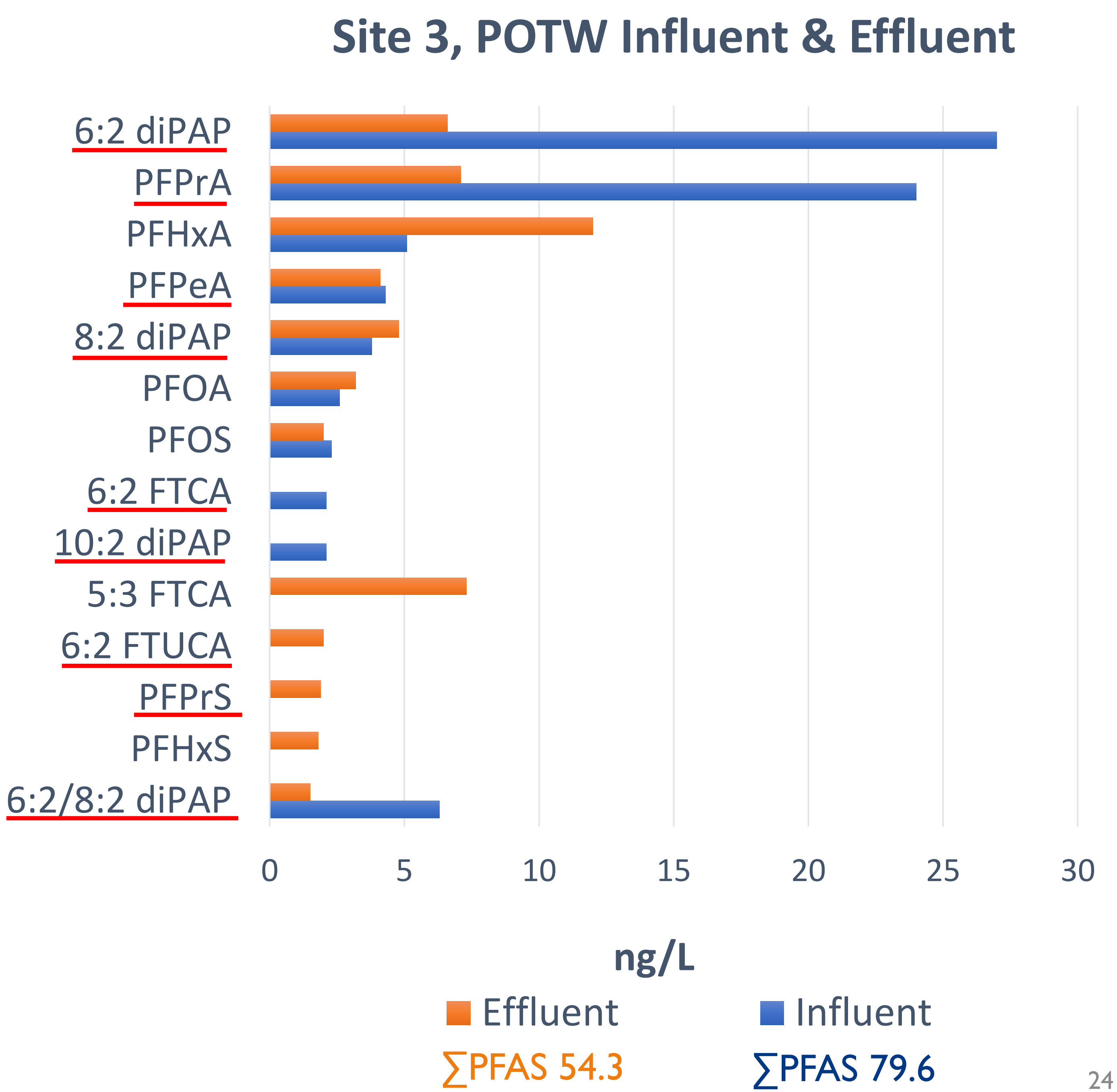
∑PFAS 145.7

AOF Equivalent for these samples is 63%

Site 3 POTW

Sample	AOF (ng/L)	TOP Assay – PFCA Difference (ng/L)
Influent	5,200	170
Influent Dup	4,600	170
Effluent	3,100	94
Effluent Dup	1,800	85

FTOHs are all non-detect @ 1,000 ng/L



Non-Target Analysis

LC-QToF-MS

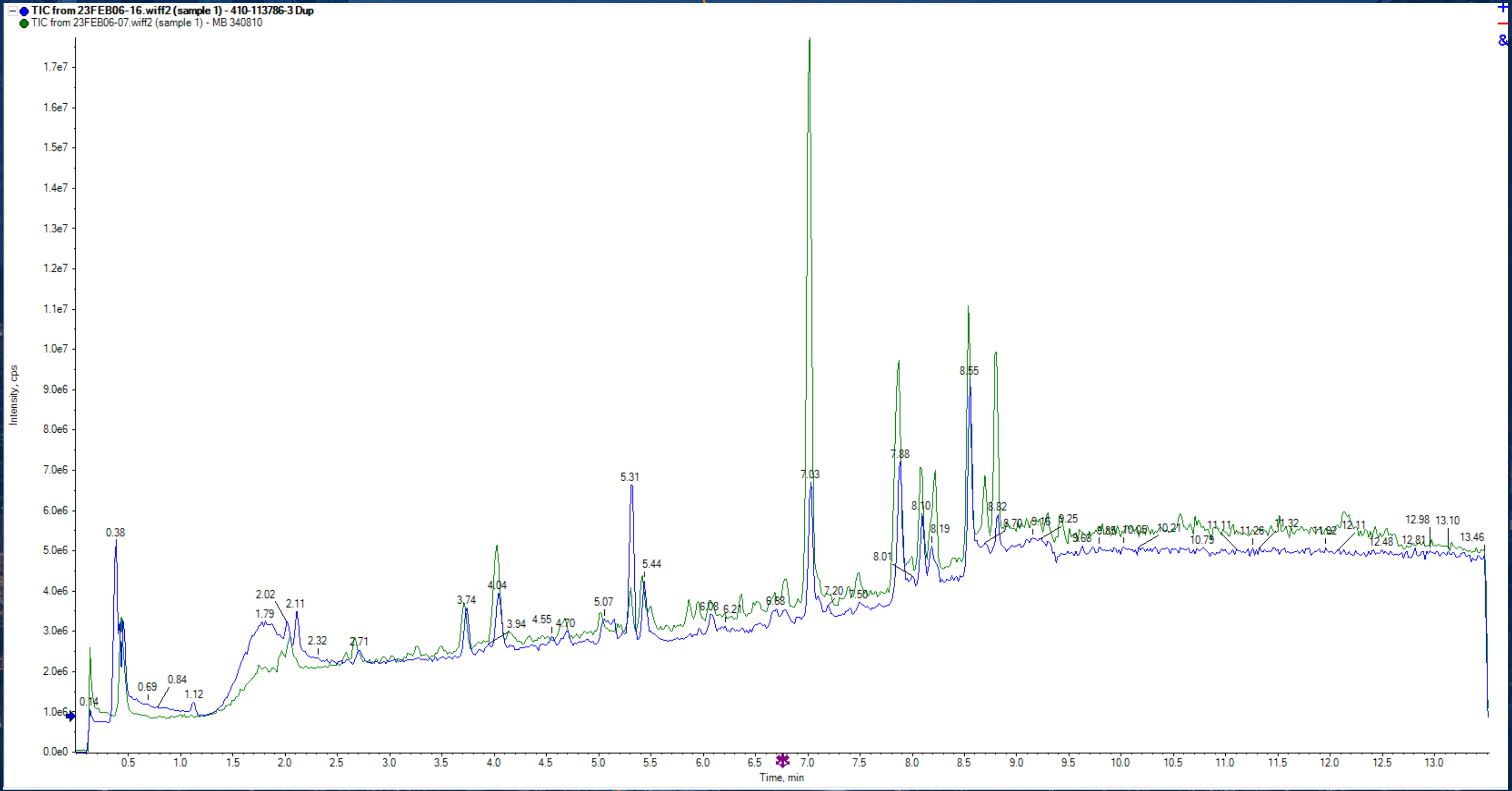
Liquid Chromatography
Quadrupole Time of Flight
Mass Spectrometry

Targeted Analysis

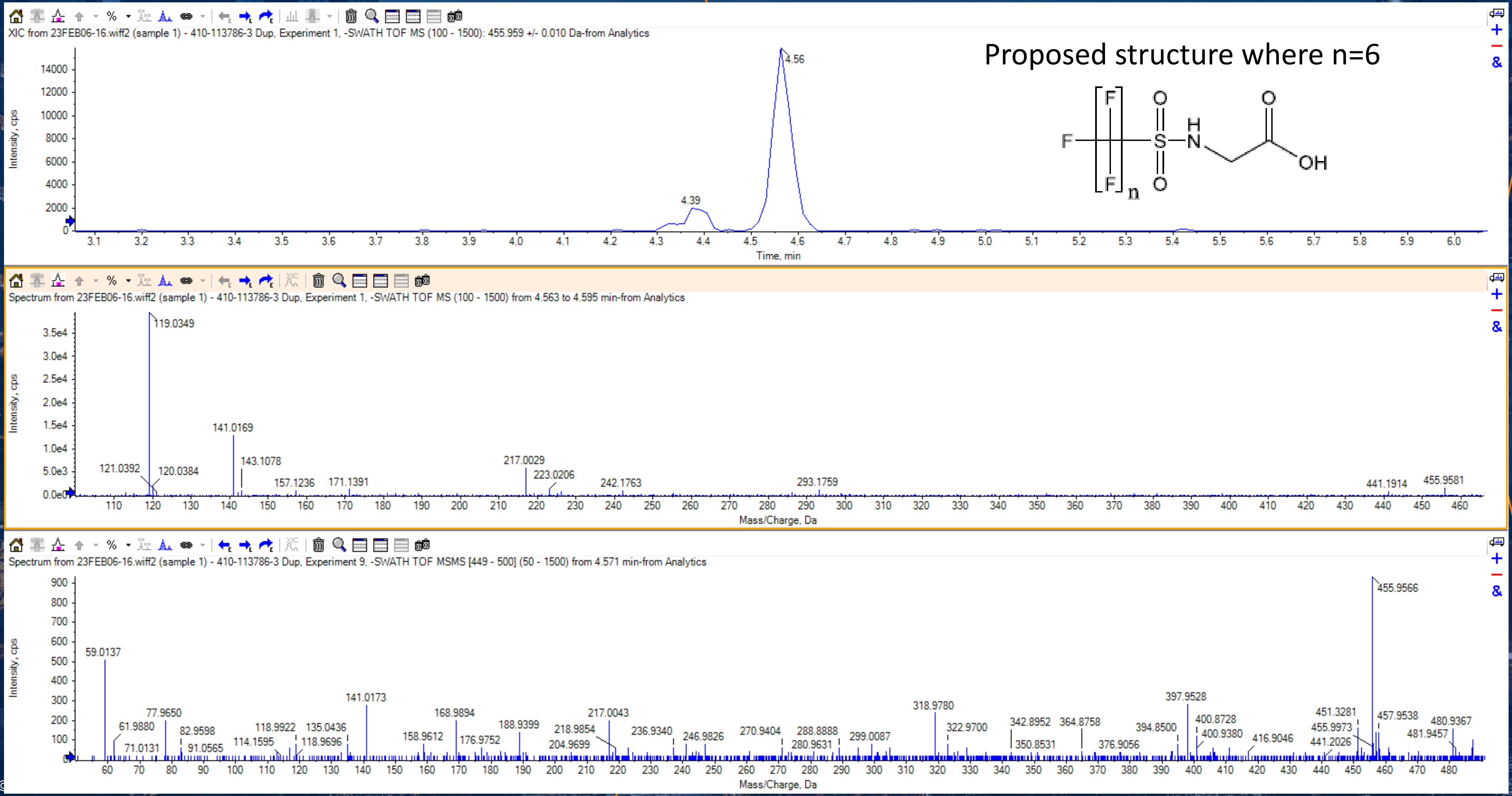
Suspect Screening Analysis

Non-Targeted Analysis

Sample X TIC (blue trace) and extraction blank (green trace).
MB injection volume = 10 ul , sample X injection volume 2 uL . Targeted analysis indicated potential matrix



Sample X spectra at 4.56 min.
Top pane: XIC 455.959 Da, Middle pane: TOF MS (50-470 Da), Bottom pane: TOF MSMS (50 500 Da)
455.9570 Da is referenced in literature with chemical formula C8H3F13NO4S, see inset structure.



Sample X additional spectra at 4.56 min.
Top pane: XIC 640.916 Da, Middle pane: TOF MS (50-660 Da), Bottom pane: TOF MSMS (50 660 Da). Suspected fluorinated spectra with unknown chemical formula. TOF MS ions 640.916 and 642.915 have similar intensity.

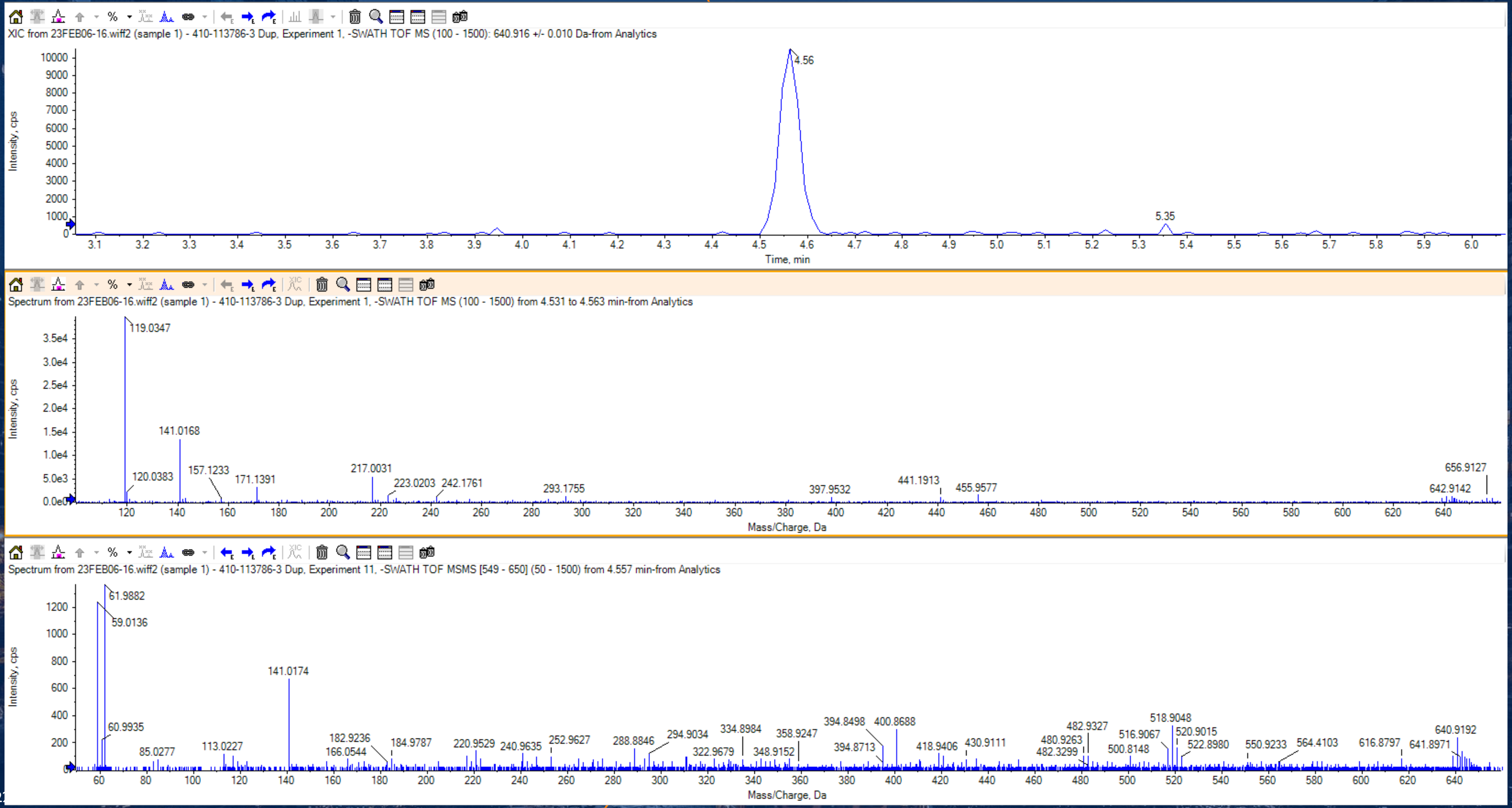


Table 2. Sample X Negative ESI Results

Precursor Mass	Retention Time	Area	Calculated amount (ng/L) using 13C8 PFOA	Calculated Amount (ng/L) using 13C8 PFOS
382.9459	4.29	23695	93.96	83.17
643.8879	4.56	18847	74.74	66.15
642.9146	4.56	30786	122.09	108.05
640.9162	4.56	31474	124.82	110.47
455.9591	4.56	45328	179.76	159.10
519.9572	4.72	25027	99.25	87.84
480.9410	4.82	11983	47.52	42.06
580.9343	5.32	47486	188.32	166.67
1056.9204	5.32	20128	79.82	70.65
501.9306	5.32	25046	99.33	87.91
514.9018	5.44	66940	265.46	234.95
514.9261	5.44	12900	51.16	45.28
623.0533	6.81	33976	134.74	119.25

Non-Target Analysis

Problems?

Accurate mass solves a variety of PFAS problems

No More Limitations

Precursors without TOP Assay

No LIMS constraints

Want to know all byproducts?

Byproducts?

SWATH uses a moving small mass window for non-target MS/MS spectra; can capture all byproducts

QTOF exact mass analysis for > 40 PFAS analytes

Exact mass confirmation of 'suspect' positive results

Mitigation of matrix effects for short chain analytes

Application for PFAS lacking standards and unknowns (NTAs)

Targeted PFAS

All Matrices – Up to 80 Compounds

Strengths: Selectivity, Sensitivity at ~1-5ppt

Can be used for risk assessment

Weaknesses: Limited list of compounds

TOP Assay

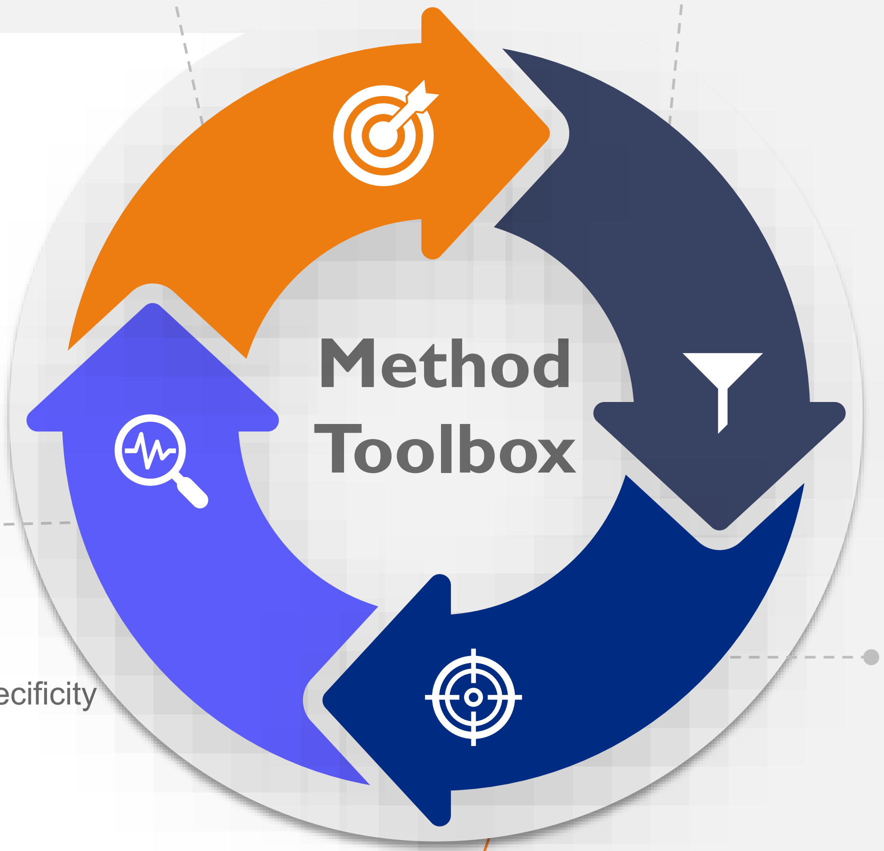
All Matrices – Oxidizable Precursors

Strengths: Sensitivity at ~1-5ppt

Specific to ‘unknowns’ with potential to convert to risk drivers

Weaknesses: Not specific

Does not complete a mass balance



Non-Target Analysis

All Matrices – Unknowns

Strengths: Ability to identify ‘unknowns’ with specificity

Ability to conduct novel compound identification

Weaknesses: Limited to current libraries

Limited quantitation

Total Organic Fluorine

All Matrices – Organic Fluorine

Strengths: Closest to a mass balance

Weaknesses: Sensitivity at ~1ppb

No selectivity

QUESTIONS?

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THANK YOU

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