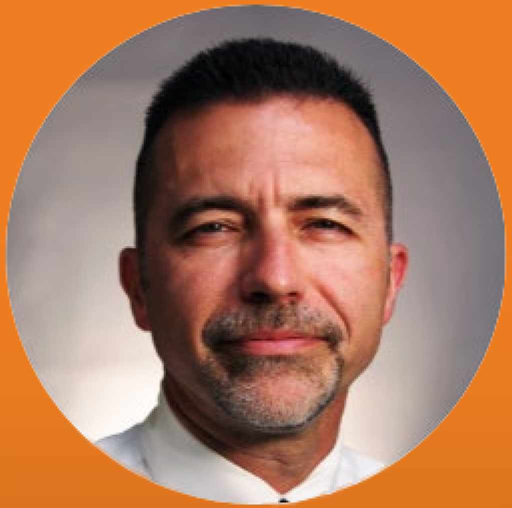
The Analysis for PFAS: A Review of Methodologies, Pros/Cons and Liabilities



Midwest Section A&WMA Environmental Technical Conference
May 2, 2023

Charles Neslund

Scientific Officer and PFAS Practice Leader

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

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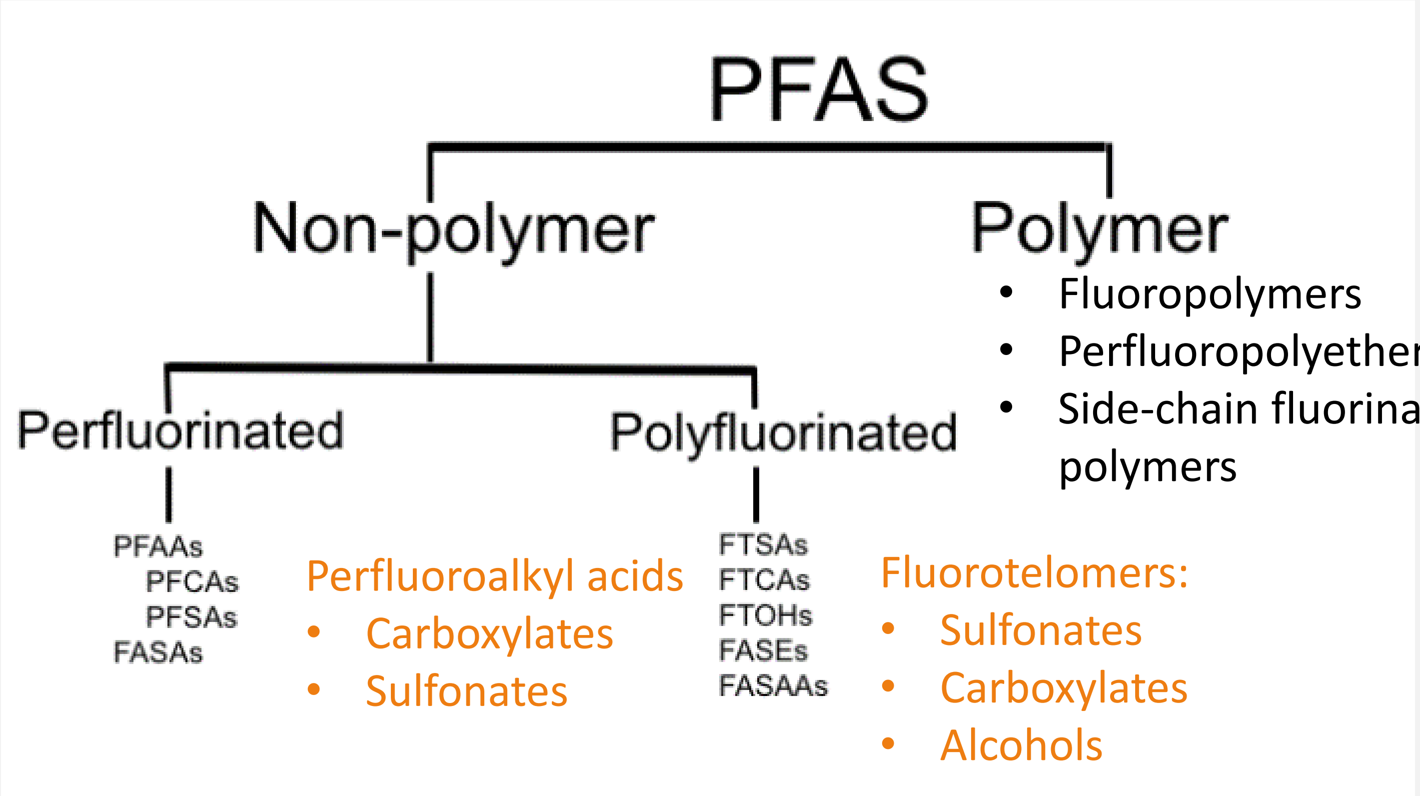

Polymer
- Fluoropolymers
- Perfluoropolyethers (PFPE)
- Side-chain fluorinated polymers

Perfluoroalkyl acids
- Carboxylates
- Sulfonates

Fluorotelomers:
- Sulfonates
- Carboxylates
- Alcohols

Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet

What Are The Data Being Used For?

QUALITY DRIVERS

Preliminary Investigation

Site characterization, screening, estimates, modeling all appropriate

Remedial Investigation

Both screening and regulatory data could be appropriate, might be mitigating risk associated with unknowns

Compliance or Litigation

Defensible data that can withstand legal scrutiny

Treatment

Measure the efficacy of the process, regulatory and technology driven

EPA DRINKING WATER METHODS

EPA 537.1
EPA 533

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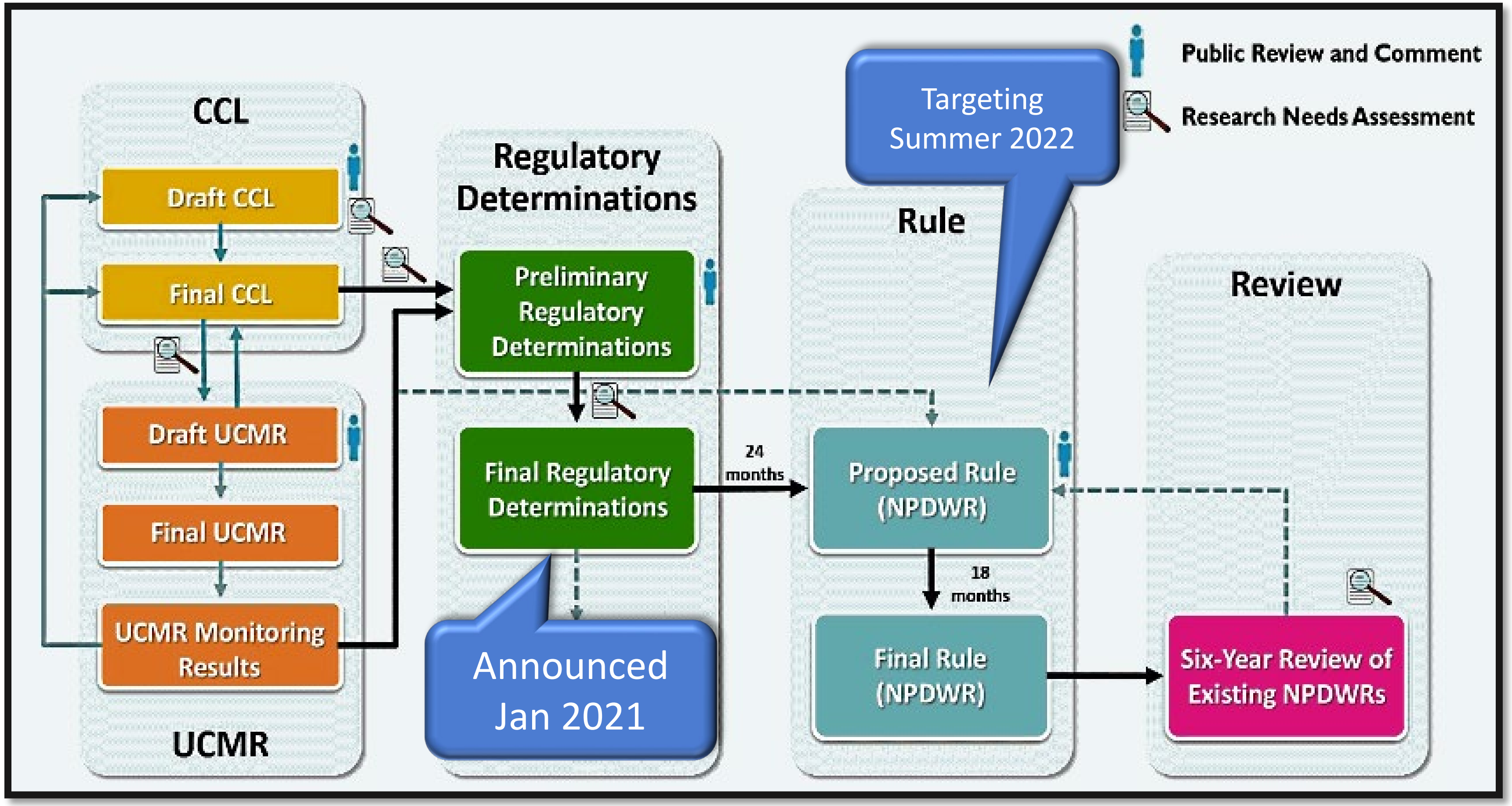
PFAS Maximum Contaminant Levels (MCLs)

DRINKING WATER



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DRINKING WATER

SDWA: UCMR 5

Unregulated Contaminant Monitoring Rule

Rule Adopted

Final Rule Adopted, Dec 2021

UCMR 5 period spans 2022–2026

Analytes

29 PFAS Analytes

Includes all analytes from 537.1 & 533

Monitoring

Will occur 2023 - 2025

PWS serving >10,000

PWS serving 3,300-10,000

Small systems serving < 3,300

https://www.epa.gov/newsreleases/epa-announces-nationwide-monitoring-effort-better-understand-extent-pfas-drinking

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SDWA: UCMR 5

PFAS Analyte List

DRINKING WATER

537.1 Analytes		
PFBS	PFUnA	DONA
PFHxA	PFDoA	HFPO-DA
PFHxS	PFTA	
PFHpA	PFTrDA	
PFOA	NMeFOSAA	
PFOS	NEtFOSAA	
PFNA	11Cl-PF3OUdS	
PFDA	9Cl-PF3ONS	

533 Analytes
NFDHA
PFBA
PFEESA
PFHpS
PFMPA
PFMBA
PFPeA
PFPeS
4:2 FTS
6:2 FTS
8:2 FTS

https://www.epa.gov/dwucmr/fifth-unregulated-contaminant-monitoring-rule

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EPA PFAS Methods

Drinking Water

533	537.1
Drinking Water	Drinking Water
Branched/Linear Isomers -YES	Branched/Linear Isomers -YES
14 of the same and 15 unique compounds	14 of the same and 4 unique compounds
SPE WAX	SPE SDVB
Hold Time: 28/28 days	Hold Time: 14/28 days
LCMSMS with confirmation ion	LCMSMS - no confirmation ion
Isotope Dilution	Internal standard
Recovery Correction - YES	Recovery Correction – NO
RLs: Not defined	RLs: 2ppt - 40ppt

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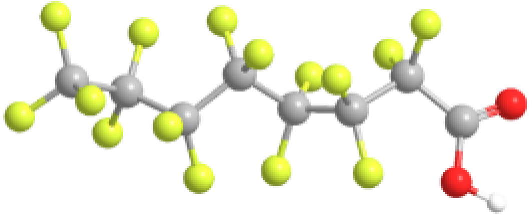
Isotope Dilution

Labeled Analogues

The Parr Family = Native PFOS

+  =

The Incredible Family = Labeled PFOS



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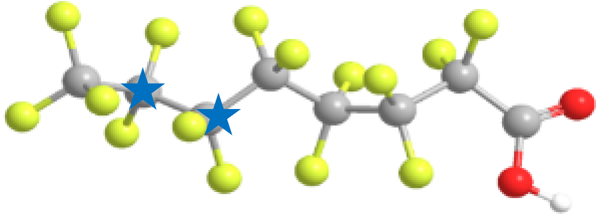

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Benefits of Isotope Dilution

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

NON-POTABLE WATER & SOLIDS

User-Defined Isotope Dilution Method
EPA Draft 1633 Method

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Comprehensive PFAS Testing

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

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)	

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

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

EPA *Draft* 1633 for Non-Potable Water & Solids

SIMILARITIES

- Applicable to a variety of solids and aqueous matrices
- Solid Phase Extraction using WAX
- Isotope Dilution Quantitation using all available isotopes
- Ion Transitions, monitoring ratios
- *Using non-Extracted Internal Standards (NEIS) for quantitation of extracted internal standards (EIS)
- **Use of carbon cleanup

*QSM 5.3 dropped it, but they are bringing it back with B-24

**User-defined methods use stacked carbon vs. loose carbon

Compared to:
User-Defined Methods
and
DoD QSM Table B-15

DIFFERENCES

- Soil/Tissue Prep: concentration step
- S/N Ratio
- Waters Oasis WAX SPE Cartridge with loose carbon cleanup
- TDCA Check: 60 sec window specification
- Includes frozen storage option
- Complex dilution scheme with 10X dilution limitation
- Mass transitions vary for some

EMERGING TECHNOLOGIES

PFAS in Air/Stack Emissions
TOP Assay
Total Organic Fluorine (TOF)
Non-Target Analysis (NTA)

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Source Air

EPA OTM 45

Application: Semivolatile and particulate-bound PFAS from Source Air Emissions

Sample Collection: Based off of EPA Method 0010

Sample Preparation: Based off of 3542

Analysis: LCMSMS with Isotope Dilution based off of EPA Method 533

Ambient Air

Modified TO-13A / LCMSMS

Application: Semivolatile and particle-bound PFAS in Ambient Air

Sample Collection: PUF/XAD Cartridge based off of EPA Method TO-13A

Sample Preparation: Methanol Extraction based off of User-defined method

Analysis: User-defined method for PFAS by LCMSMS with Isotope Dilution

Vapor

Modified TO-17 / GCMSMS

Application: Volatile PFAS in Indoor Air and Soil Vapor

Sample Collection: Thermal Desorption Tube based off of EPA Method TO-17

Sample Preparation: Thermal Desorption based off of EPA Method TO-17

Analysis: User-defined method for PFAS by GCMSMS

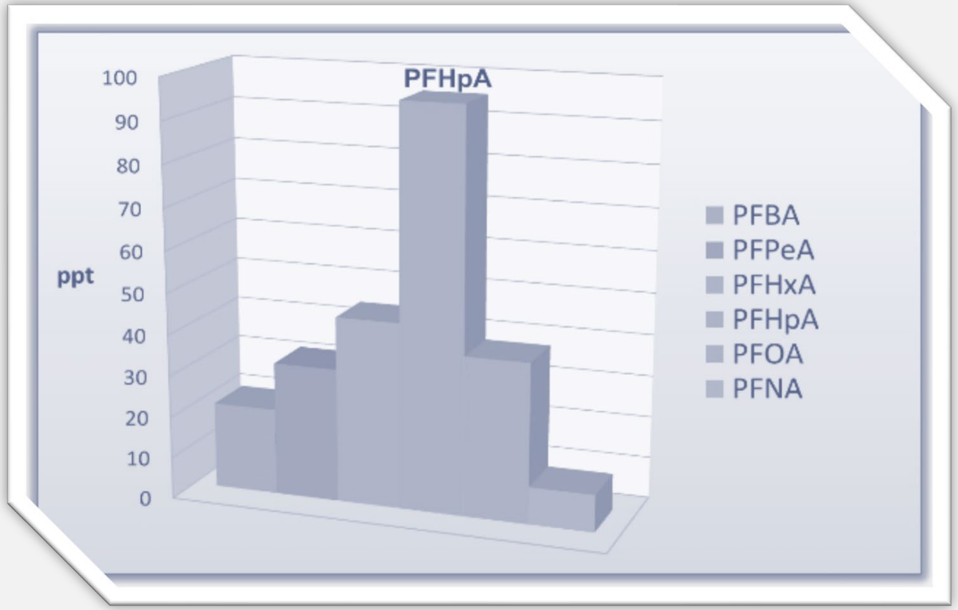
https://www.epa.gov/sites/production/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

Total Oxidizable Precursors

TOP Assay

85°C

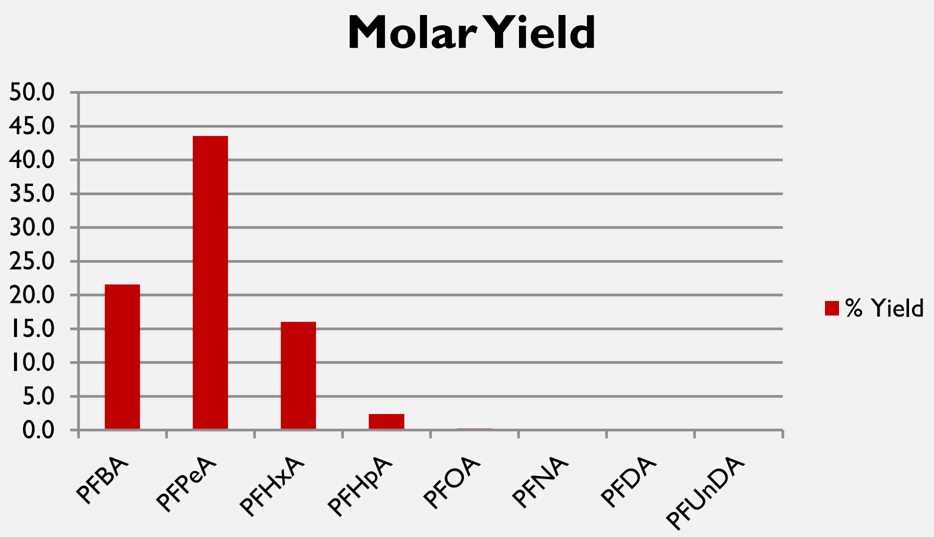
PFAA Precursors + OH• OH• OH• = PFOA + other PFCAs



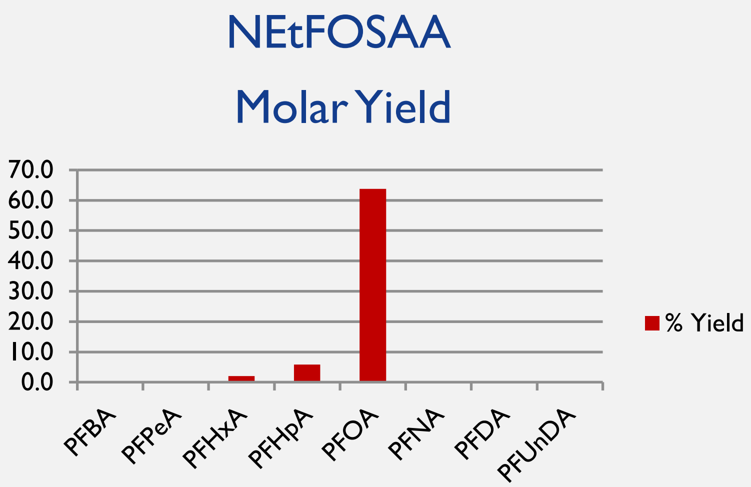
TOP Assay – 6:2 FTS

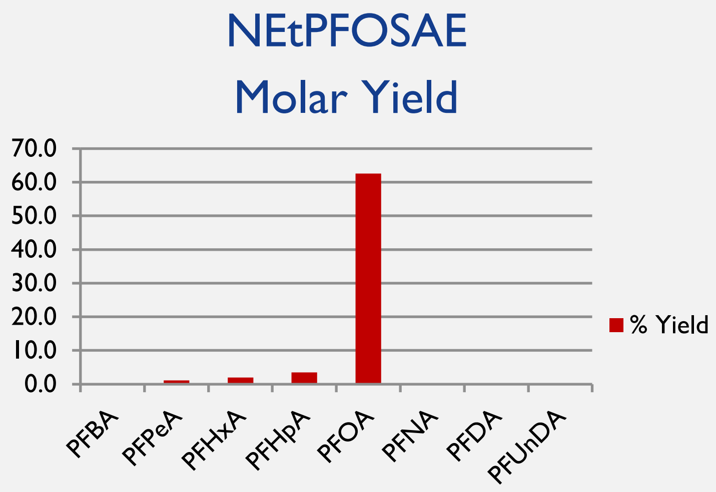
Results of oxidation of 6:2 Fluorotelomer sulfonate at 250 ng/l

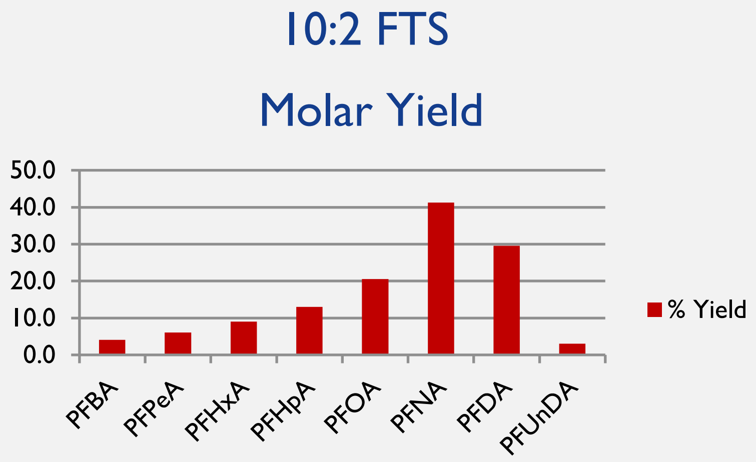
PFCA	ELLE	Houtz
PFBA	21.6	22
PFPeA	43.6	27
PFHxA	16.1	22
PFHpA	2.4	2
PFOA	0.3	0
PFNA	0.0	0
PFDA	0.0	0
PFUnDA	0.0	0



TOP Assay – 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

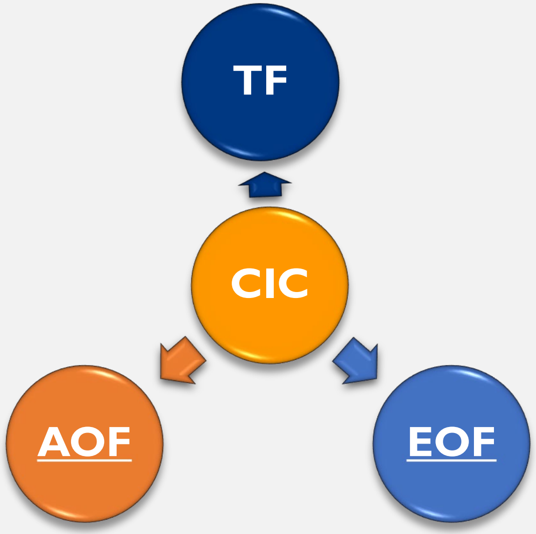
Compare ratio of total (or extractable) fluorine to total PFAS

Oxidative pyrohydrolytic combustion

Handling of the sample prior to fluoride determination determines result evaluated

EOF – Extractable Organic Fluorine

AOF – Absorbable Organic Fluorine



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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

EPA Draft Method In Progress

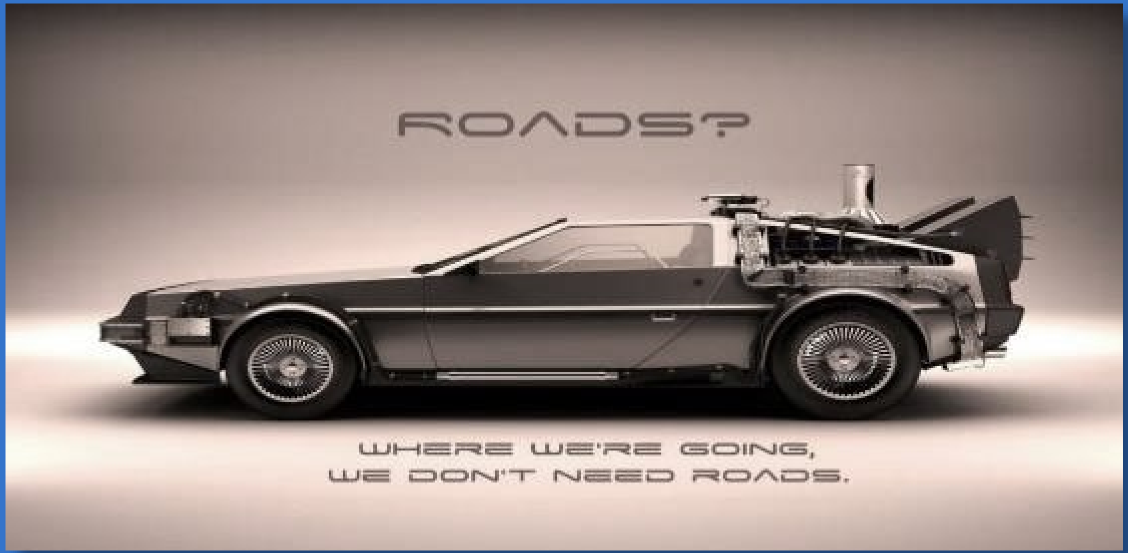
EPA METHODS

EPA Draft 1621

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

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

Non-Target Analysis



LC-QToF-MS

Liquid Chromatography
Quadrupole Time of Flight
Mass Spectrometry

Targeted Analysis

Suspect Screening Analysis

Non-Targeted Analysis

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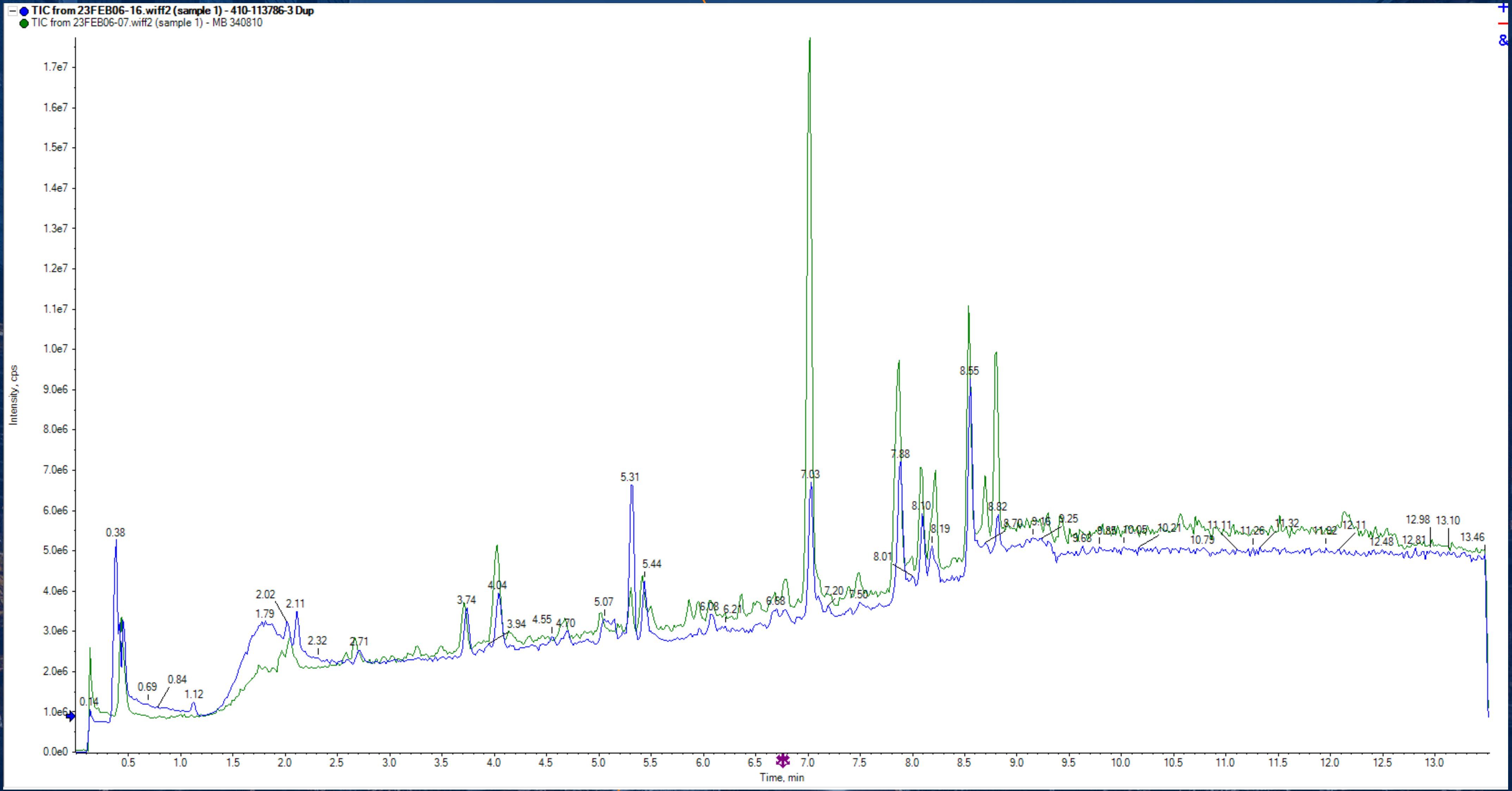
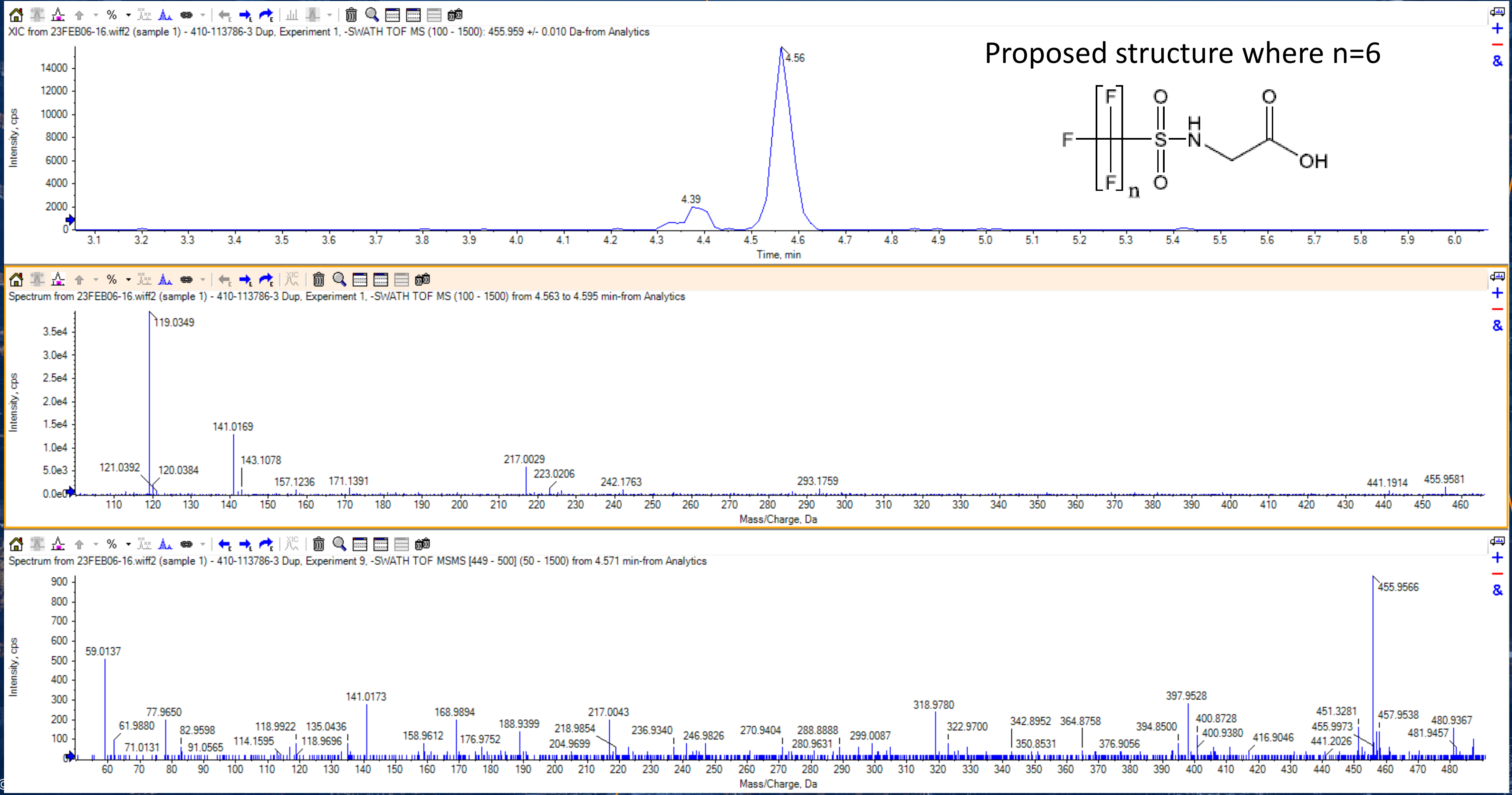
Sample X TIC (blue trace) and extraction blank (green trace).

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.



Proposed structure where n=6

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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

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

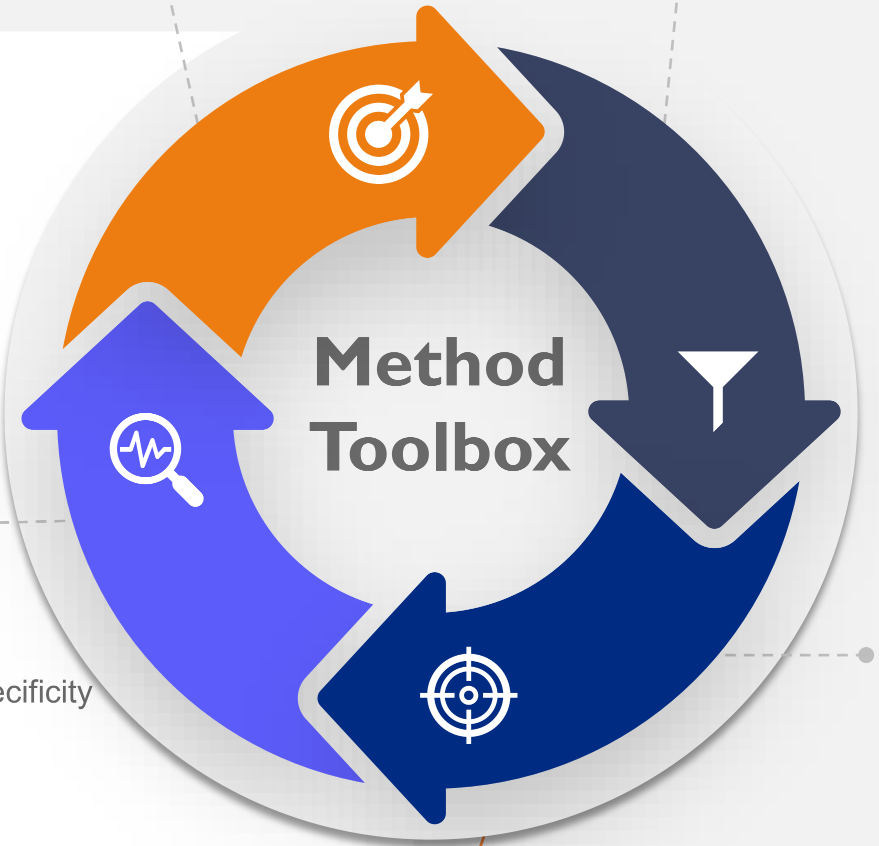
All Matrices – Oxidizable Precursors

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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