## Presentation for: PFAS: Forensic Tools, TOF, TOP Assay and Non-Target Analysis, Part 4

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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





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#### **PFAS Forensic Tools**

Additional techniques that are gaining in use and application

- Total Organic Fluorine Analysis
- Non-Target Analysis



#### **Benefits of Isotope Dilution**

#### What affects the native analyte will equally affect the isotope





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### **User-Defined Methods: PUT TO THE TEST!**







Biphasic
Biosolids
Tissues
Dispersions
Activated Carbon
Cosmetics

Concrete

NELAC
DoD ELAP
Client/Program
Specific Audits
Semiannual PT

NMI International Round Robin

DOW Study



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



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#### **TARGETED PFAS**

Perfluorobutanoic acid (PFBA)	Perfluoro-1-nonanesulfonate (PFNS)	NFDHA	PFO4DA
Perfluoropentanoic acid (PFPeA)	Perfluorododecanesulfonic acid (PFDoS)	PFEESA	PFO3OA
Perfluorohexanoic acid (PFHxA)	Perfluoro-n-hexadecanoic acid (PFHxDA)	PFMPA	PFO2HxA
Perfluoroheptanoic acid (PFHpA)	Perfluoro-n-octadecanoic acid (PFODA)	PFMBA	PFO5DA
Perfluorooctanoic acid (PFOA)	NMeFOSAA	3:3 FTCA	R-EVE
Perfluorononanoic acid (PFNA)	NEtFOSAA	5:3 FTCA	NVHOS
Perfluorodecanoic acid (PFDA)	NEtFOSA	7:3 FTCA	Hydro-EVE Acid
Perfluoroundecanoic acid (PFUnA)	NMeFOSA	6:2 FTCA	EVE Acid
Perfluorododecanoic acid (PFDoA)	NMeFOSE	8:2 FTCA	R-PSDA
Perfluorotridecanoic Acid (PFTriA)	NEtFOSE	10:2 FTCA	Hydrolyzed PSDA
Perfluorotetradecanoic acid (PFTeA)	4:2FTS	6:2 FTUCA	R-PSDCA
Perfluorobutanesulfonic acid (PFBS)	6:2FTS	8:2 FTUCA	PS Acid
Perfluorohexanesulfonic acid (PFHxS)	8:2FTS	10:2 FTUCA	Hydro-PS Acid
Perfluoroheptanesulfonic Acid (PFHpS)	10:2FTS	PFECHS	4:2 FTOH
Perfluorooctanesulfonic acid (PFOS)	DONA	PFPrS	6:2 FTOH
Perfluorodecanesulfonic acid (PFDS)	HFPO-DA (GenX)	PFMOAA	7:2S FTOH
Perfluorooctane Sulfonamide (FOSA)	11Cl-PF3OUdS	PFECA G	8:2 FTOH
Perfluoro-1-pentanesulfonate (PFPeS)	9CI-PF3ONS	МТР	10:2 FTOH
PFPrA	PMPA	PEPA	

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### **Additional PFAS Methods**

## **Fluorotelomer Alcohols**

- GCMSMS method
- Water and solids

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- Instrumental set-up like 8270E and extractions like 3510 and 3540/50
- Current compound list

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4:2 Fluorotelomer alcohol 6:2 Fluorotelomer alcohol 7:25 Fluorotelomer alcohol 8:2 Fluorotelomer alcohol 10:2 Fluorotelomer alcohol

#### **Chemical Fingerprinting**



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

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#### **Isomer Comparison**

 $F_{3}C-CF_{2}-CF_{2}-CF_{2}-CF_{2}-CF_{2}-CF_{2}-CF_{2}-CF_{2}-SO_{3}^{-1}$ 

Linear Perfluorooctane sulfonate (PFOS)

F<sub>3</sub>C-CF-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-SO<sub>3</sub><sup>-</sup> Branched Perfluorooctane sulfonate (PFOS)

CF<sub>3</sub>

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

ITRC PFAS Fact Sheet Naming Conventions April 2020

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#### **Isomer Comparison**



## Chromatogram of PFOS Standard of Linear Isomer



#### Chromatogram of PFOS Standard of Branched/Linear Mix Typical Ratio



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#### **Isomer Comparison**



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



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



181 PP

#### **Total Oxidizable Precursors - TOP**



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# 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		

#### Molar Yield







# 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	

Molar Yield



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#### **TOP Assay – Other Precursors**





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10:2 FTS





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#### **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

St. Party

#### **Total Organic Fluorine Analysis**



Marriage of TOX and IC

Sample (or treated sample) is combusted in a furnace at  $900^{\circ}C - 1100^{\circ}C$ 

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<sup>-</sup> 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<sup>-</sup> 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<sup>-</sup> and Organic F<sup>-</sup> simultaneously

Courtesy of Dr. Jayesh Ghandi - Metrohm



## Non-Target Analysis



## LC-QToF-MS

Liquid Chromatography Quadrupole Time of Flight Mass Spectrometry







#### **Non-Target Results**

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#	Analyte Peak Name	Precursor Mass	Found At Mass	Library Hit	Library Score	Formula Finder Results	Formula Finder Score	Combined Score
47	207.1384 / 9.59	207.140	207.1386	Ser-Cys (NIST)	86.3	C13H20O2	77.080	81.702
75	205.1582 / 10.62	205.159	205.1591	Met-Gly (NIST)	82.3	C8H23N4P	83.194	82.724
93	271.2263 / 11.21	271.227	271.2271	DLbetaHydroxypalmitic acid (NIST)	81.8	C16H32O3	68.518	75.154
119	265.1468 / 12.04	265.148	265.1472	Dodecyl sulfate (NIST)	99.3	C8H24N6P2	78.457	88.862
127	199.1699 / 12.08	199.171	199.1699	Dodecanoic acid (NIST)	93.5	C12H24O2	81.919	87.725
128	297.1516 / 12.16	297.153	297.1520	Ricinoleic acid (NIST)	97.5	C8H21F2N8P	89.209	93.349
129	205.1591 / 12.22	205.160	205.1592	2,6-Di-tert-butylphenol (NIST)	100.0	C8H23N4P	82.310	91.155
130	297.2424 / 12.22	297.243	297.2428	Ricinoleic acid (NIST)	97.5	C18H34O3	71.444	84.466
146	514.9789 / 12.55	514.980	514.9792	CI-PFOS (chloro-perfluorooctane sulfonate) (neg)	89.8	C8H13FN6O15S2	98.473	4.123
152	309.1728 / 12.64	309.174	309.1733	Ethylene glycol dodecyl ether sulfate (NIST)	100.0	C14H30O5S	73.122	86.561
168	531.0069 / 12.94 M- H-	531.008	531.0081	CI-PFENS neg	81.5	Too many formula	0.000	40.743
171	353.1999 / 12.94	353.201	353.1996	Diethylene glycol dodecyl ether sulfate (NIST)	99.6	C15H29F3N4S	91.220	95.397
176	241.2162 / 13.06	241.217	241.2165	N2-Trifluoroacetyl-L-glutamine (NIST)	89.3	No formula found	0.000	44.666
192	293.1788 / 13.45	293.180	293.1784	Myristyl sulfate (NIST)	97.8	C14H30O4S	73.162	85.459
216	253.2158 / 14.02	253.217	253.2168	cis-7-Hexadecenoic acid (NIST)	97.8	C16H30O2	77.687	87.726
220	339.1986 / 14.08	339.200	339.1991	Tridecylbenzenesulfonic acid (NIST)	80.2	C13H33N4O2PS	89.239	84.697
260	281.2480 / 14.90	281.249	281.2479	1,4-D-Xylobiose (NIST)	100.0	C18H34O2	73.760	86.880
300	407.2938 / 15.97	407.295	407.2942	.gammaMuricholic acid (NIST)	96.5	C21H37FN6O	95.929	96.220
327	311.2943 / 17.36	311.295	311.2943	Benzenesulfonic acid, 4-undecyl- (NIST)	76.3	C16H36N6	53.227	64.777
434	265.1465 / 26.87	265.148	265.1470	Dodecyl sulfate (NIST)	84.6	C13H27FS2	84.840	84.720

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#### **Non-Target Results**



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#### **Non-Target Analysis**

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#### 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

#### **Non-Target Analysis**

#### All Matrices – Unknowns

Strengths: Ability to identify 'unknowns' with specificityAbility to conduct novel compound identificationWeaknesses: Limited to current librariesLimited quantitation



#### • 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

#### **Total Organic Fluorine**

All Matrices – Organic Fluorine

**Strengths:** Closest to a mass balance **Weaknesses:** Sensitivity at ~1ppb No selectivity



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## QUESTIONS?

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## THANK YOU



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