



Environment Testing America

Development of a Forensics Based Approach to Evaluating Impacts of PFAS Contamination in the Environment



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Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet



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

- Chemical Fingerprinting
- Isomer comparison
- AFFF Forensics
- Applications of TOP Assay

Chemical Fingerprinting – PFAS by Isotope Dilution



- Matrices
 - Potable water
 - Nonpotable water
 - Soil/sediment
 - Tissue/biota

- Dust wipes
- Landfill leachate
 - AFFF Formulations

- 36 Compounds
- Solid Phase Extraction/Cleanup using weak anion exchange
- Isotope Dilution quantitation
 - 25 isotopically labeled internal standards
- Injection Standards for monitoring instrument vs extraction performance
- Advantages
 - Isotope Dilution offers the highest degree of quantitative accuracy and precision
 - Broadest list of compounds and widest range of matrices
 - Lowest reporting limits across matrices
 - Used for TOP Assay

Per- and Polyfluorinated Compounds



Perfluorobutanoic acid Perfluoropentanoic acid Perfluorohexanoic acid Perfluoroheptanoic acid Perfluorooctanoic acid Perfluorononanoic acid Perfluorodecanoic acid Perfluoroundecanoic acid Perfluorododecanoic acid Perfluorotridecanoic acid Perfluorotetradecanoic acid Perfluorohexadecanoic acid Perfluorooctadecanoic acid N-methylperfluoro-1-octanesulfonamidoacetic acid N-ethylperfluoro-1-octanesulfonamidoacetic acid 2-(N-methylperfluoro-1-octanesulfamido)-ethanol 2-(N-ethylperfluoro-1-octanesulfamido)-ethanol

Perfluorobutanesulfonate Perfluoropentanesulfonate Perfluorohexanesulfonate Perfluoroheptanesulfonate Perfluorooctanesulfonate Perfluorononanesulfonate Perfluorodecanesulfonate Perfluorododecanesulfonate Perfluorooctanesulfonamide Methylperfluoro-1-octanesulfonamide Ethylperfluoro-1-octanesulfonamide 4:2 Fluorotelomer sulfonate 6.2 Fluorotelomer sulfonate 8:2 Fluorotelomer sulfonate 10:2 Fluorotelomer sulfonate HFPO-DA (GenX) **ADONA** F53b (major and minor)

EPA 537.1 list

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
 - 4:2 Fluorotelomer alcohol
 - 6:2 Fluorotelomer alcohol
 - 7:2S Fluorotelomer alcohol
- 8:2 Fluorotelomer alcohol
- 10:2 Fluorotelomer alcohol



Chemical Fingerprinting





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







CF₃ F₃C-CF-CF₂-CF₂-CF₂-CF₂-SO₃⁻

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



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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



AFFF Forensics



PFAS ¹	Development Time Period								
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s	
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics				
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS ²)	
PFOA		Initial Production	Pr Co	otective batings					
PFNA					Initial Production	Architectural	Resins		
Fluoro- telomers					Initial Production	Firefighting F	oams	Predominant form of firefighting foam	
Dominant Process ³		Electrochemical Fluorination (ECF) telomerization (shorter chain ECF)							
Pre-Invent	Pre-Invention of Chemistry / Initial Chemical Synthesis / Commercial Products I and Used					Introduced			
Notes: 1. This tab PFOS, F 2. Refer to 3. The dor both been	le includes PFOA, and I Section 3.4 ninant man , and contir	fluoropolyme PFNA (perfluo 4. ufacturing pro nue to be, use	ers, PFAAs, a prononanoic pocess is show ed for the pro	nd fluorotelon acid) are PFA vn in the table duction of se	ners. PTFE (po As. e; note, howev lect PFAS.	olytetrafluoroet	hylene) is nd fluorote	a fluoropolymer. elomerization have	

Table 2-1. Discovery and manufacturing history of select PFAS

ITRC PFAS Fact Sheet History and Use April 2020



AFFF Forensics



Legacy PFOS AFFF

- PFOS and ECF Sulfonamides
- PFOS and other PFSAs

Legacy Fluorotelomer AFFF

- Fluorotelomer Precursors with C6 and C8 carbon chains
- 6:2 and 8:2 fluorotelomers
- PFOA and long chain acids

Modern Fluorotelomer AFFF

- Fluorotelomer Precursors with C6 carbon chains
- 6:2 Fluorotelomers and short chain acids



Total Oxidizable Precursors - TOP





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

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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



TOP Assay – other precursors



NEtPFOSAE

Molar Yield

NEtFOSAA





Environment Testing America Newer Techniques being Developed



Total Organic Fluorine (TOF) - Combustion Ion Chromatography (CIC)

- 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



Newer Techniques – Non Targeted Analysis



	Targeted	Screening	Discovery
Chemical Target	Selected Chemicals	100s-100,000s per library	Any Chemical
Method of Analysis	Focused Method	Non-Targeted Method	Non-Targeted Method(s)
Chemical Structure	Known	Known in Library	Unknown
Reference Data	Available	Some	Some, maybe simulated
Standards	Available	Maybe, for common compounds	Unlikely

Adapted from McCord, ACECNC, April 23, 2019



Newer Techniques – Non Targeted Analysis



Technique utilizes LC/MS-qTOF (quadrapole time of flight mass spectrometry)

- Technique allows for determination of accurate mass (0.0001 amu)
- Initial differentiation based on extraction of sample
- Then analysis of targeted compounds (knowns) to remove those from "background"
- Compare remaining peaks to limited mass spectral libraries to identify the known/unknowns
- Remaining peaks are unknowns and would rely on regression of accurate mass determinations for possible identification



Newer Techniques – Non Targeted Analysis





Eurofins Capacity – New Space





Questions





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