PFAS Forensic Tools: TOF, TOP Assay and Non-Target Analysis

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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)

PFAS

Non-polymer

Perfluorinated

PFAAs
PFCAs
PFSAs
FASAs

Perfluoroalkyl acids
- Carboxylates
- Sulfonates

Polyfluorinated

FTSAs
FTCAs
FTOHs
FASEs
FASAAs

Fluorotelomers:
- Sulfonates
- Carboxylates
- Alcohols

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

Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet

Chemical Fingerprinting – PFAS by Isotope Dilution



Matrices

- Potable water
- Nonpotable water
- Soil/sediment
- Tissue/biota
- Dust wipes
- Landfill leachate
- AFFF Formulations

70 Compounds

Solid Phase Extraction/Cleanup using weak anion exchange

Isotope Dilution quantitation

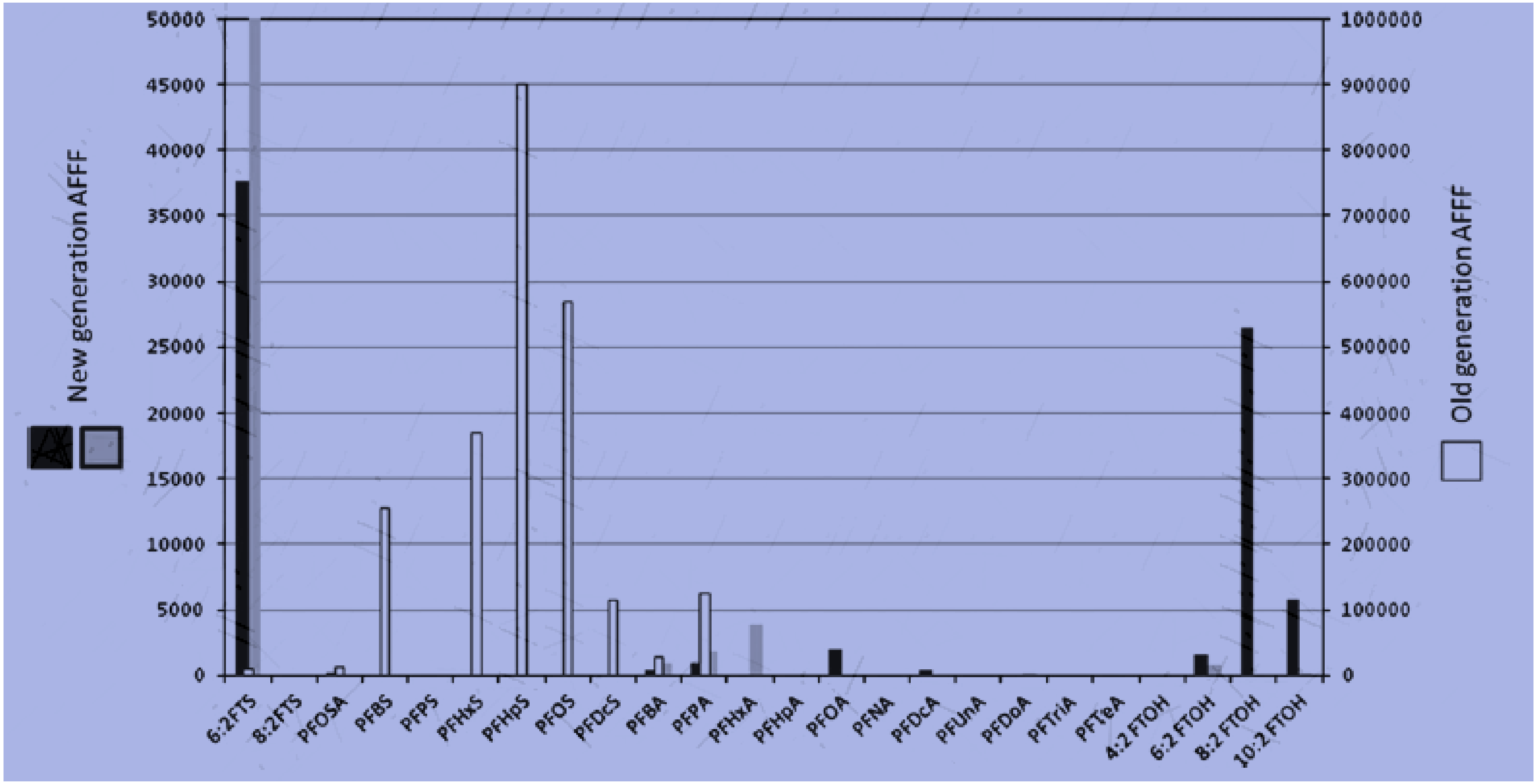
- 25+ isotopically labeled internal standards

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

Chemical Fingerprinting



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

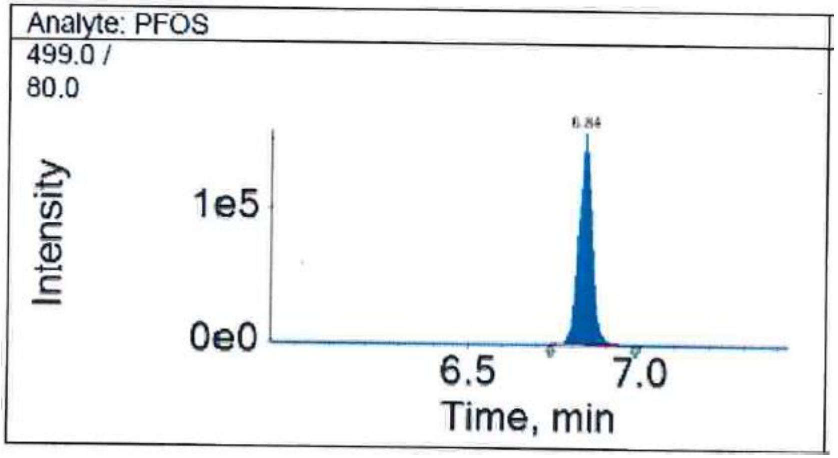
Isomer Comparison

Linear Perfluorooctane sulfonate (PFOS) **Branched Perfluorooctane sulfonate (PFOS)**

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

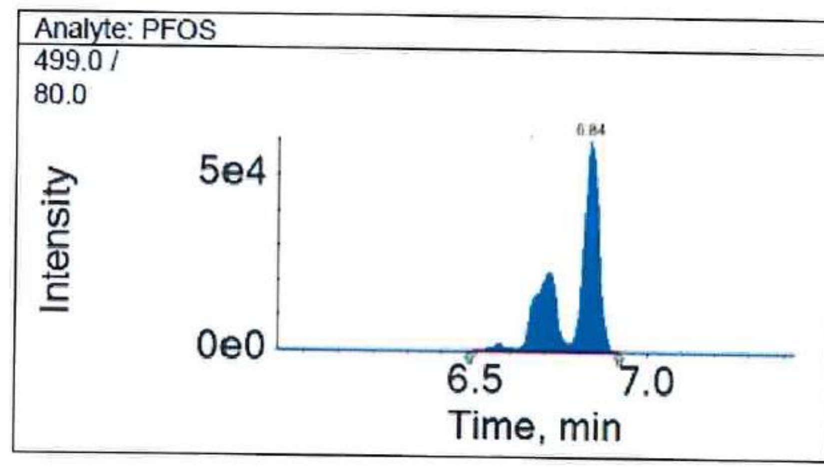
ITRC PFAS Fact Sheet Naming Conventions April 2020

Isomer Comparison

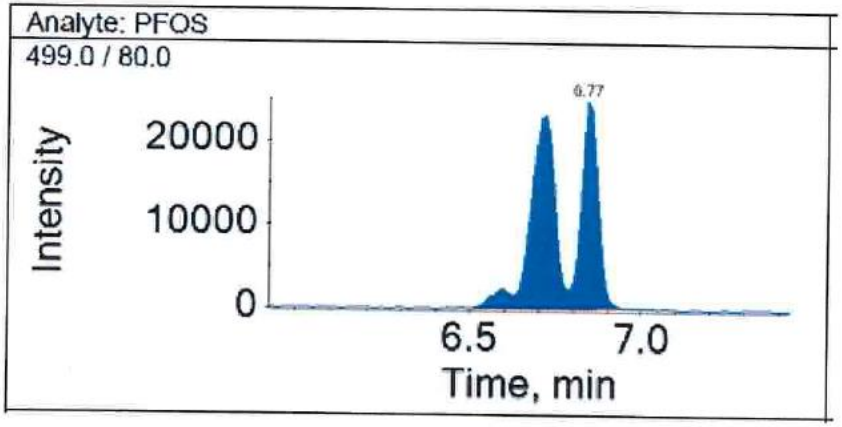


Chromatogram of PFOS Standard of Linear Isomer

Chromatogram of PFOS Standard of Branched/Linear Mix Typical Ratio

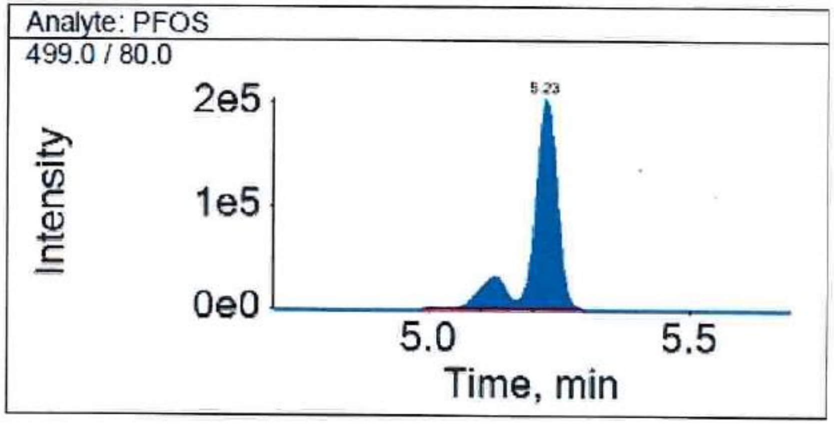


Isomer Comparison



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



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

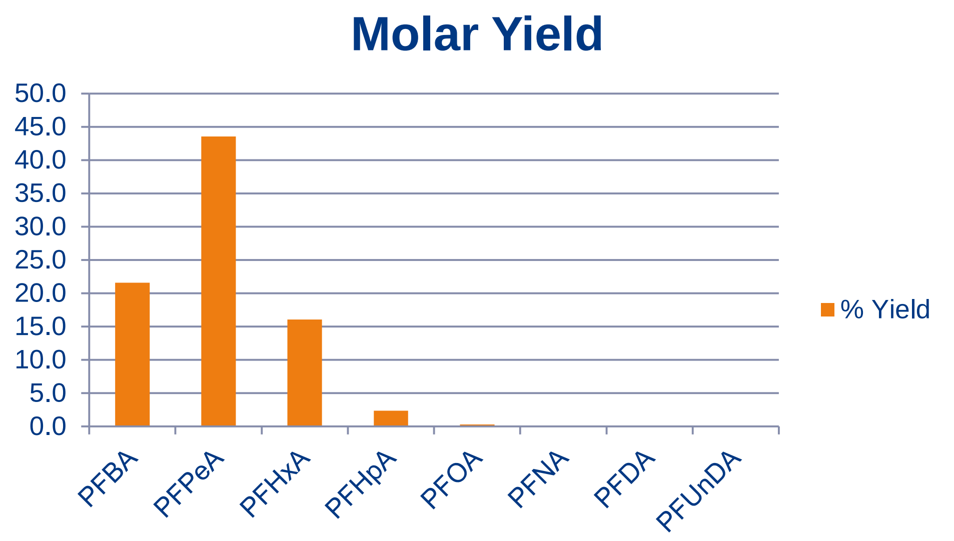
Concept is to analyze a sample for perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA) and any identified precursors . Then subject a second aliquot of the sample to relatively harsh oxidative conditions. Analyze the oxidized sample for the same perfluoroalkyl acids and precursors.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

a. Reduction or elimination of the precursors
b. Increase in concentrations of perfluoroalkyl acids

TOP Assay – 6:2 FTS

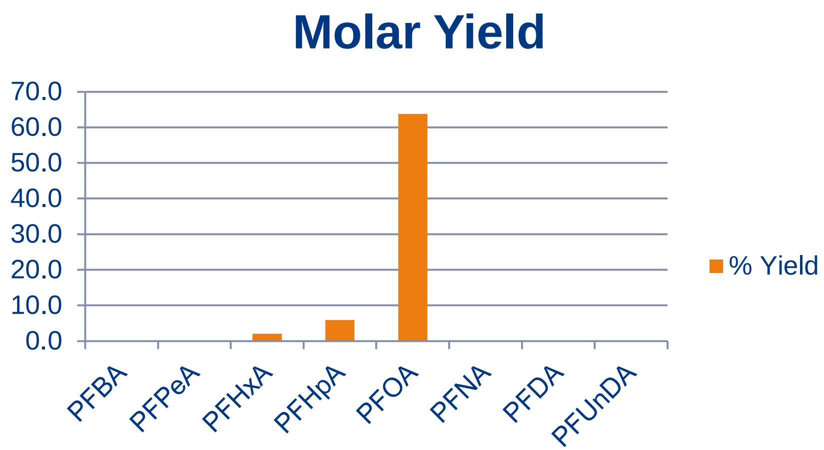
Results of oxidation of 6:2 Fluorotelomer sulfonate at 250 ng/l

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

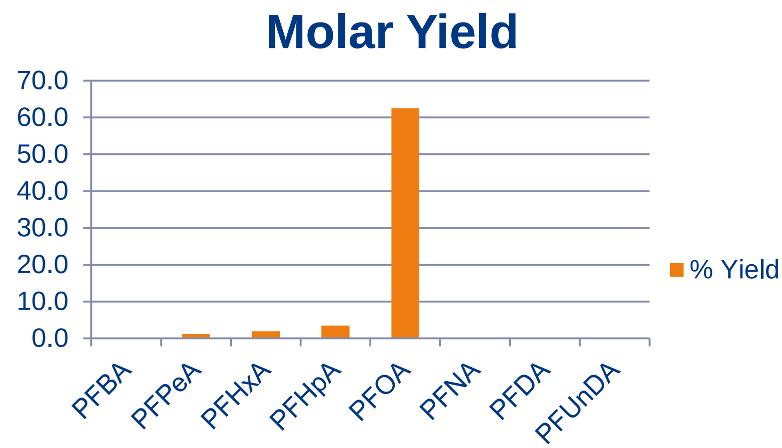


TOP Assay – other precursors

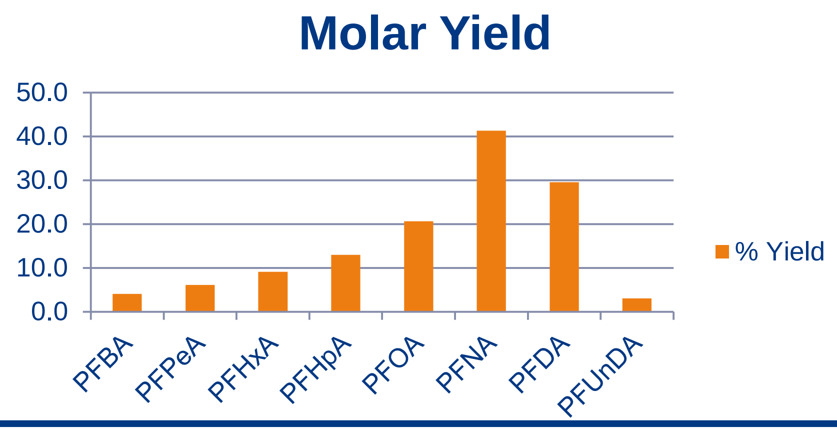
NEtFOSAA



NEtPFOSAE



10:2 FTS



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 (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

Total Organic Fluorine Analysis

Oxidative pyrohydrolytic combustion

Handling of the sample prior to fluoride determination determines result evaluated

EOF – Extractable Organic Fluorine

AOF – Absorbable Organic Fluorine

Example for Solids Analysis

Total Organic Fluorine (TOF)	410 mg F/kg
Extractable Organic Fluorine (EOF)	390 mg F/kg
LC-MS/MS ΣPFAS (n=28)	120 mg/kg

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**

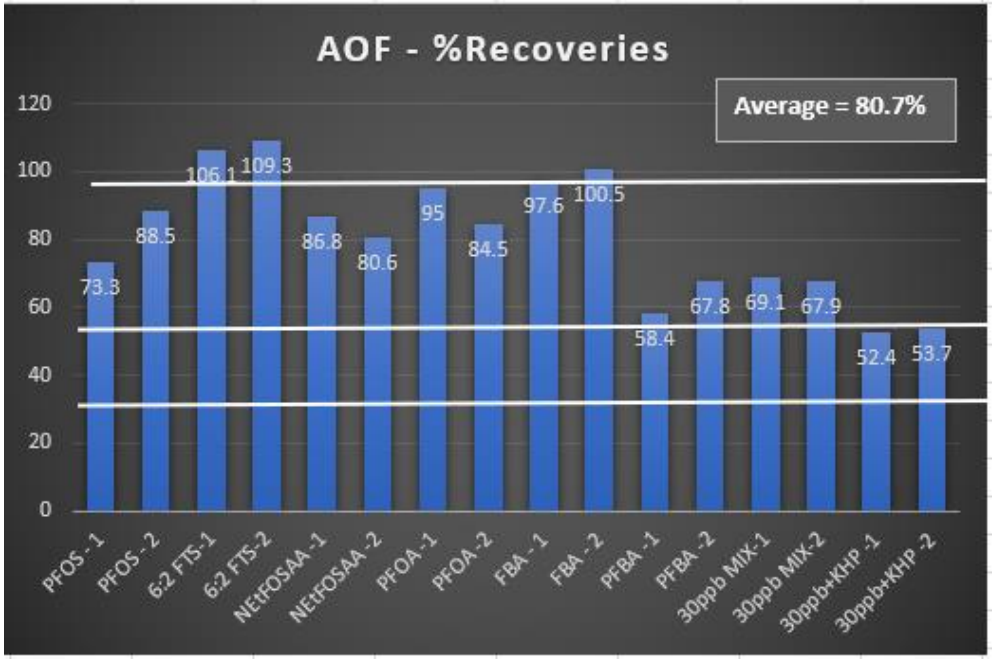
Total Org. F (TOF)

- **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

AOF Data using 50 mls of Water

Sample ID	% recovery, AOF
PFOS - 1	73.3
PFOS - 2	88.5
6:2 FTS-1	106.1
6:2 FTS-2	109.3
NEtFOSAA -1	86.8
NEtFOSAA -2	80.6
PFOA -1	95
PFOA -2	84.5
FBA - 1	97.6
FBA - 2	100.5
PFBA -1	58.4
PFBA -2	67.8
30ppb MIX-1	69.1
30ppb MIX-2	67.9
30ppb+KHP -1	52.4
30ppb+KHP -2	53.7
Average	**80.7**



Note: When High TOC value samples were subjected to 6 carbon beds in series, PFAS recovery is ~79%

Courtesy of Dr. Jayesh Ghandi - Metrohm

Non-Target Analysis

Targeted Analysis

Suspect Screening Analysis

Non-Targeted Analysis

Quadrupole
Time of Flight (qToF)

Newer Techniques – Non Targeted Analysis

Technique utilizes LC/MS-qTOF (quadrupole 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

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)

Non-Target Results

#	Formula	Precursor Mass	Library Hit	Library Score	Combined Score	Formula Finder Results	Formula Finder Score
30	{220.18451}	219.178	PFPeA in-source fragment (perfluoro-n-pentanoic acid) (neg)	87.3	87.976	C12H25FO2	89.039
661	{399.94691}	398.940	PFHxS (perfluorohexane sulfonate) (neg)	100.0	97.841	C9H3F11OS2	94.602
829	{427.97642}	426.970	6:2 FTS (6:2 fluorotelomer sulfonate) (neg)	87.0	91.802	C12H3F10N2O2P	99.064
842	{487.05667}	486.050	4:2 FHxThPA-MePS (4:2 tridecafluorohexyl thiapropanoamido-methylpropyl sulfonate) (neg,pos)	84.0	82.515	C11H27FIN5O3S2	80.349
867	{603.04586}	602.039	6:2 fluorotelomer sulfinyl ethyl amide trimethyl sulfonic acid 1,1-dimethyl ethyl sul.. (neg,pos)	99.9	59.920	Too many formula	0.000
950	{499.94181}	498.935	PFOS (perfluorooctane sulfonate) (neg)	63.9	71.200	C12H16F3IN2O2S3	82.093
1127	{499.93963}	498.933	PFOS (perfluorooctane sulfonate) (neg)	98.3	97.935	C14H6F5IN4O3	97.337
1212	{570.03056}	569.024	PFDoA in-source fragment (perfluoro-n-dodecanoic acid) (neg)	46.4	27.862	Too many formula	0.000
1285	{587.05056}	586.044	6:2 FOThPA-MePS (6:2 tridecafluorooctyl thiapropanoamido-methylpropyl sulfonate) (neg,pos)	98.5	59.089	Too many formula	0.000
1293	{587.06852}	586.062	6:2 FOThPA-MePS (6:2 tridecafluorooctyl thiapropanoamido-methylpropyl sulfonate) (neg,pos)	98.5	59.089	Too many formula	0.000
1296	{498.95760}	497.951	FOSA (perfluorooctane sulfonamide) (neg)	100.0	60.000	Too many formula	0.000
1559	{687.05070}	686.044	8:2 FDThPA-MePS (8:2 tridecafluorodecyl thiaproanoamido-methylpropyl sulfonate) (neg,pos)	95.8	57.495	Too many formula	0.000
2086	{420.31006}	419.303	PFNA in-source fragment (perfluoro-n-nonanoic acid) (neg)	20.1	44.785	C16H40N10OS	81.771

Thank You

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