

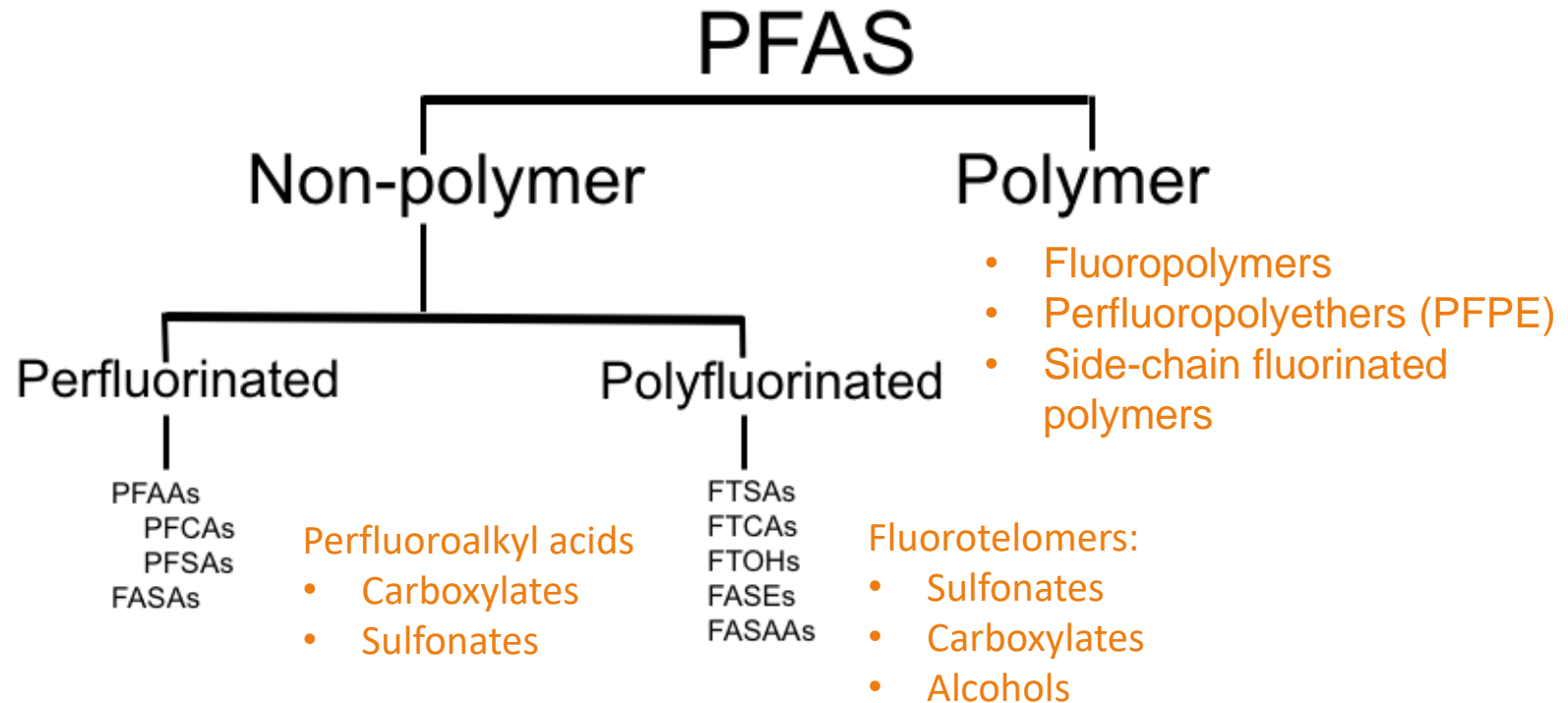


Updates on the Use of TOF for PFAS Investigations – Where does it fit in?

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



Source: ITRC Naming Conventions and Physical Chemical Properties fact sheet

Current Analysis Climate



- Current methods for LCMSMS
 - USEPA 533
 - USEPA 537.1
 - ASTM D7979
 - SW846 method 8327
 - Individual laboratory “537 Mod”/Isotope Dilution
- Largest of these options are method(s) that are limited to only 40+ compounds
- Might add in analysis for fluorotelomer alcohols

Current Analysis Climate



- Need for screening method – For total Fluoride
 - Better risk assessment tool for true “impact” in the environment
 - Screening method for narrowing focus of target compound approach
- What are the options?
 - TOP Assay
 - PIGE (particle induced gamma-ray emission spectroscopy)
 - XPS (x-ray photoelectron spectroscopy)
 - TOF (total organic fluorine)



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

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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 Results



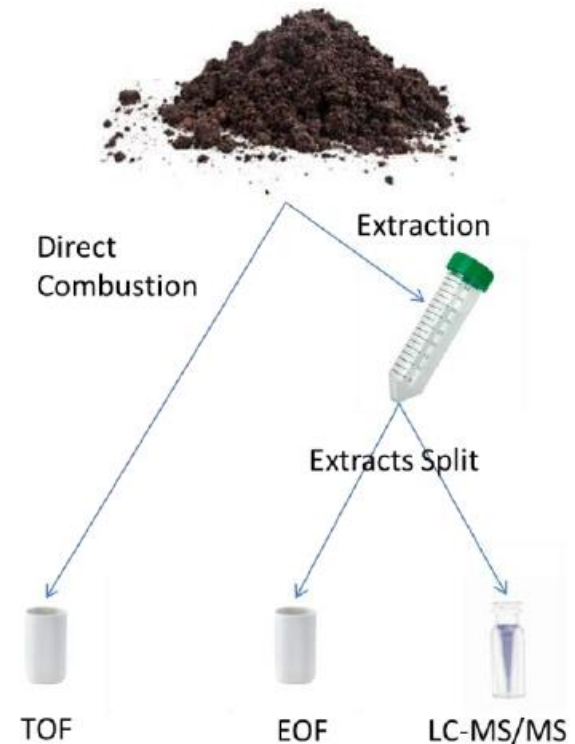
Compound	Pre-Ox	Post-Ox	Difference
PFBA	ND	98 ng/l	98 ng/l
PFPeA	ND	87 ng/l	87 ng/l
PFHxA	5 ng/l	61 ng/l	56 ng/l
6:2 FTS	100 ng/l	ND	- 100 ng/l
PFHpA	11 ng/l	32 ng/l	21 ng/l
PFOA	7 ng/l	26 ng/l	19 ng/l
PFOS	56 ng/l	52 ng/l	- 4 ng/l
8:2 FTS	26 ng/l	ND	- 26 ng/l
PFNA	ND	5 ng/l	5 ng/l

Total Organic Fluorine



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 in Water



Methods available or being proposed

- DIN EN ISO 9562:2004
Water quality — Determination of adsorbable organically bound halogens (AOX)
- ASTM D19.06 – WK68866
Determination of Adsorbable Organic Fluorine in Waters and Waste Waters by adsorption on Activated Carbon followed by Combustion Ion Chromatography
- Definitions
 - Adsorbable Organic Fluoride – AOF (Activated Charcoal method)
 - Extractable Organic Fluoride – EOF (WAX SPE sample preparation method)

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)

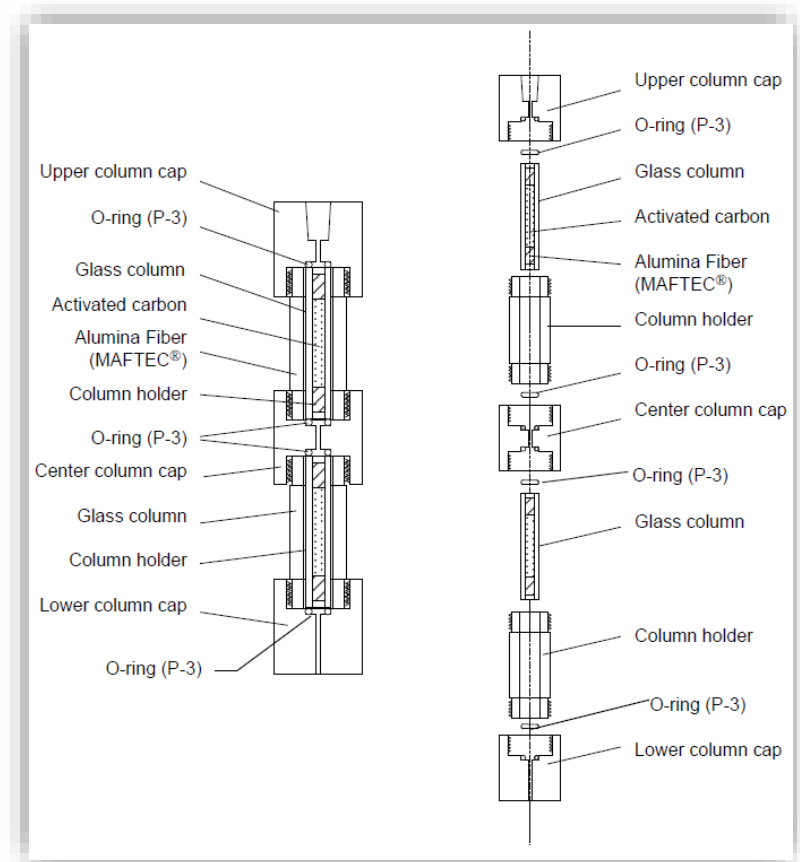
- **Sample Prep (water samples)**
 - No Sample Prep
- **Direct injection of aqueous sample into CIC system to measure both Inorganic F⁻ and Organic F⁻ simultaneously**

Courtesy of Dr. Jayesh Ghandi - Metrohm

Adsorbable Organic Fluoride (AOF)



- Currently Proposed ASTM Method (WK 68866)
- Currently Proposed DIN committee NA 119-01-03-01-12
- Basics of method
 - 100mls of water sample is passed through vertically aligned two carbon cartridges
 - Organic compounds (PFAS) are adsorbed on carbon bed
 - Final rinsing is performed with Potassium Nitrate to remove inorganic Fluoride (interference)
 - Carbon is then combusted with CIC

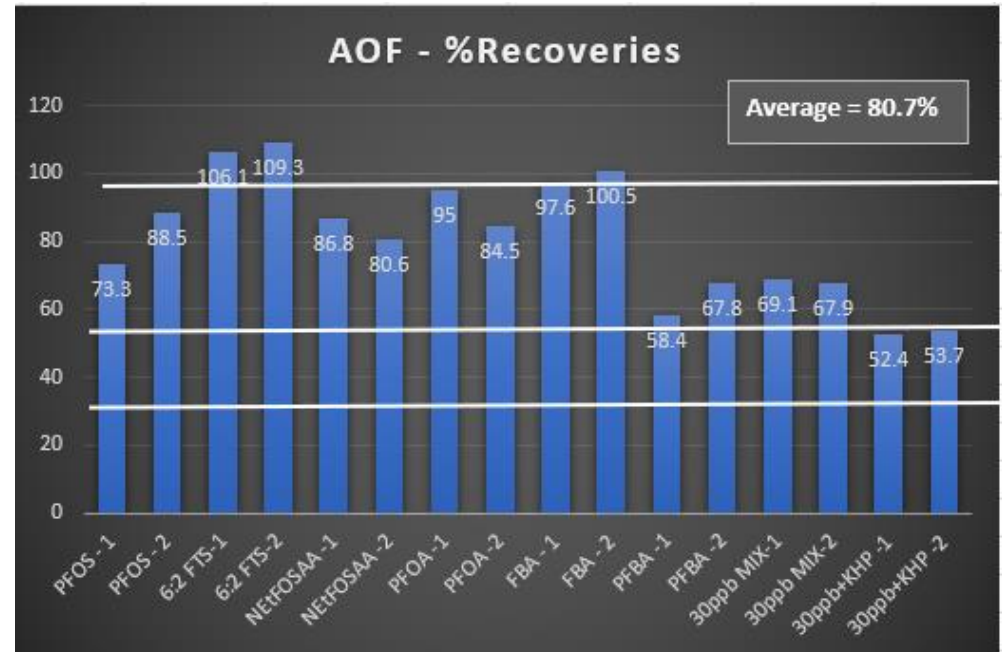


Courtesy of Dr. Jayesh Ghandi - Metrohm

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

Total Organic Fluorine Analysis of Solids



Extractable Org. F (EOF)

- **Sample Prep**
 - Extract solid sample with a methanolic solution
 - Concentrate methanol to final 1mL or less
- **Combustion of extracted sample into CIC to measure F⁻ by IC**

Total Org. F (TOF)

- **Sample Prep**
 - For non-soil solids, grind or pulverize sample
 - For soil, evaluate granularity
- **Direct combustion of solid sample into CIC system to measure both Inorganic F⁻ and Organic F⁻ simultaneously**

Total Organic Fluorine Analysis



Oxidative pyrohydrolytic combustion

Handling of the sample prior to fluoride determination determines result evaluated

EOF – Extractable Organic Fluorine

AOF – Adsorbable 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



PFAS Percent Fluorine



Compound	Fluorinated Alkane Carbon Chain Length	Chemical Abstracts Service (CAS) No.	Molecular Weight	Weight of Fluorine	Percent Fluorine
Perfluoroalkylcarboxylic acids (PFCAs)					
PFBA	C4	375-22-4	214.04	132.99	62.13%
PFPeA	C5	2706-90-3	264.05	170.99	64.76%
PFHxA	C6	307-24-4	314.05	208.98	66.54%
PFHpA	C7	375-85-9	364.06	246.98	67.84%
PFOA	C8	335-67-1	414.07	284.98	68.82%
PFNA	C9	375-95-1	464.08	322.97	69.59%
PFDA	C10	335-76-2	514.08	360.97	70.22%
PFUnDA	C11	2058-94-8	564.09	398.97	70.73%
PFDoDA	C12	307-55-1	614.1	436.96	71.16%
PFTTrDA	C13	72629-94-8	664.11	474.96	71.52%
PFTeDA	C14	376-06-7	714.11	512.96	71.83%
PFHxDA	C16	67905-19-5	814.13	588.95	72.34%
PFODA	C18	16517-11-6	914.14	664.94	72.74%
Perfluorinated sulfonic acids (PFSAs)					
PFBS	C4	375-73-5	300.1	170.99	56.98%
PFPeS	C5	2706-91-4	350.11	208.98	59.69%
PFHxS	C6	355-46-4	400.11	246.98	61.73%
PFHpS	C7	375-92-8	450.12	284.98	63.31%
PFOS	C8	1763-23-1	500.13	322.97	64.58%
PFNS	C9	474-511-07-4	550.13	360.97	65.62%
PFDS	C10	335-77-3	600.14	398.97	66.48%
PFDoS	C12	79780-39-5	700.16	474.96	67.84%

PFAS Percent Fluorine



Compound	Fluorinated Alkane Carbon Chain Length	Chemical Abstracts Service (CAS) No.	Molecular Weight	Weight of Fluorine	Percent Fluorine
Perfluorooctane Sulfonamide and Derivatives					
PFOSA	C8	754-91-6	499.14	322.97	64.71%
NEtPFOSAE	C8	1691-99-2	571.25	322.97	56.54%
NMEPFOSAE	C8	24448-09-7	577.22	322.97	55.95%
NEtPFOSA	C8	4151-50-2	527.2	322.97	61.26%
NMEPFOSA	C8	31506-32-8	513.17	322.97	62.94%
NMeFOSAA	C8	2355-31-9	571.21	322.97	56.54%
NEtFOSAA	C8	2991-50-6	585.23	322.97	55.19%
Fluorotelomer sulfonates (FTS)					
4:2-FTS	C4	757124-72-4	328.15	170.99	52.11%
6:2-FTS	C6	27619-97-2	428.17	246.98	57.68%
8:2-FTS	C8	39108-34-4	528.17	322.97	61.15%
10:2-FTS	C10	120226-60-0	628.2	398.97	63.51%
Perfluoroalkyl ether carboxylic acids (PFECA)					
HFPO-DA	C6	13252-13-6	330.05	208.98	63.32%
ADONA	C9	919005-14-4	378.04	227.98	60.31%
Polyfluoroalkyl Ether Sulfonic Acids (PFESAs)					
9Cl-PF3ONSA	C9	756426-58-1	532.58	303.97	57.08%
11Cl-PF3OUdS	C11	763051-92-9	632.62	379.97	60.06%



Summary

- Many things to be learned about the application of CIC
 - How is inorganic fluoride being managed? Or is it?
 - What “selectivity” does the sample preparation apply to the fluoride determination
 - Are multiple fluoride determinations needed to differentiate inorganic vs organic
- Need to agree on definition of AOF vs EOF and relationship to TOF and TF



Thank You

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