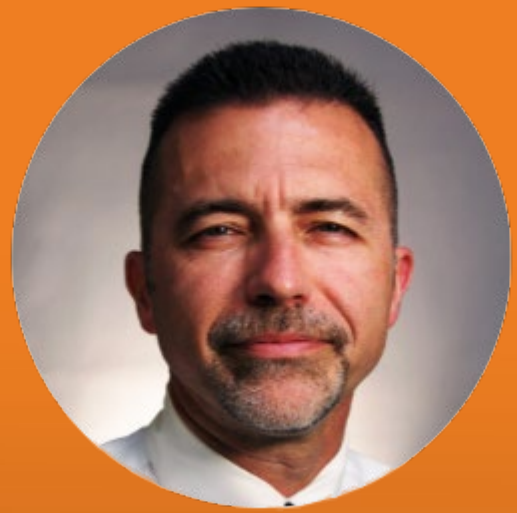
Presentation for:

A Method for the Determination of Total Organic Fluorine and Its Correlation with PFAS Analysis



Charles Neslund

Scientific Officer and PFAS Practice Leader

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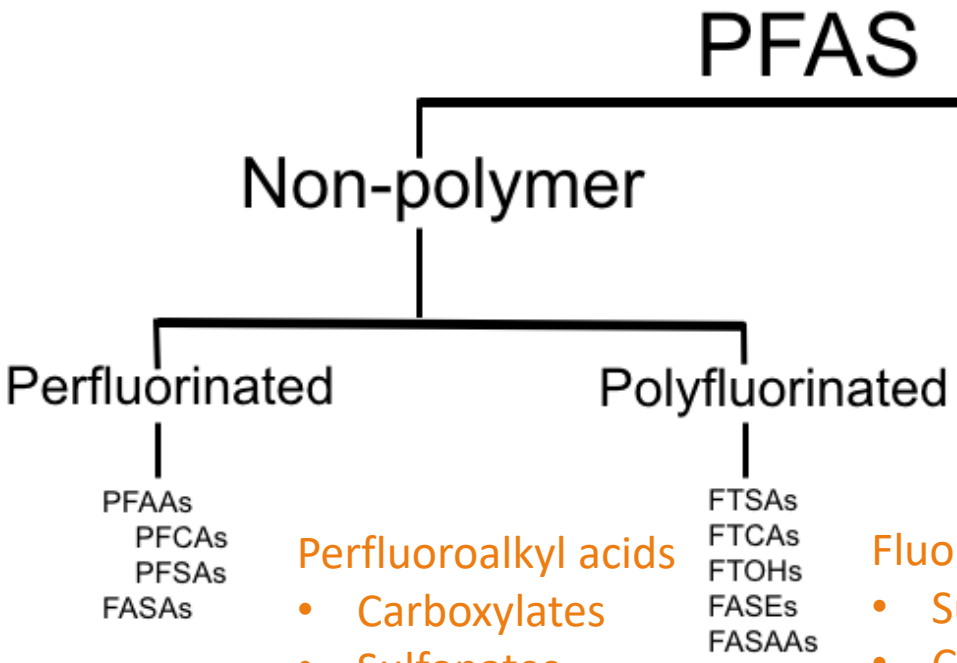
The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)



- 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

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

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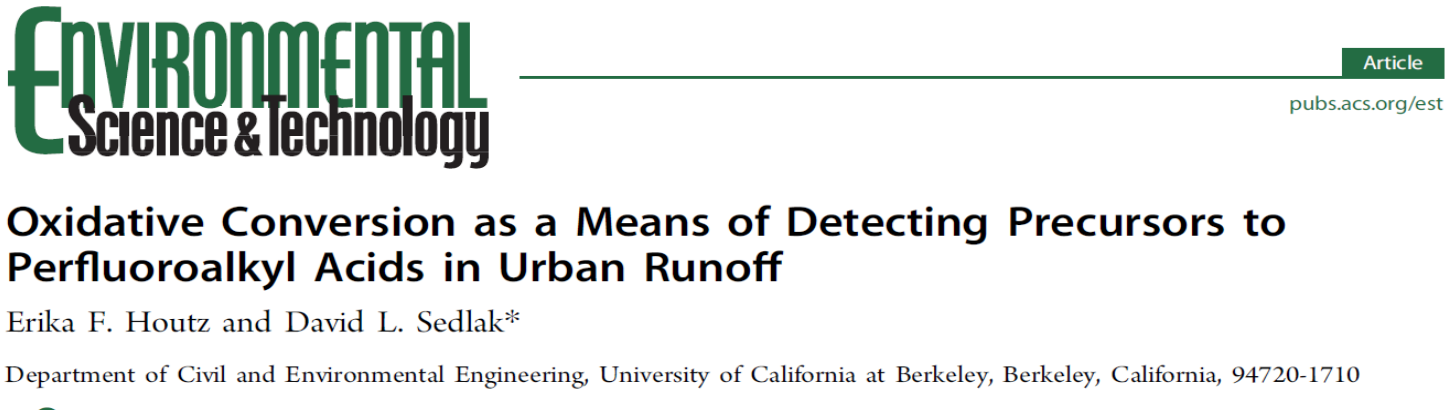
Current Analysis Climate

- 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)

Total Oxidizable Precursors - TOP



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Article

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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

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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

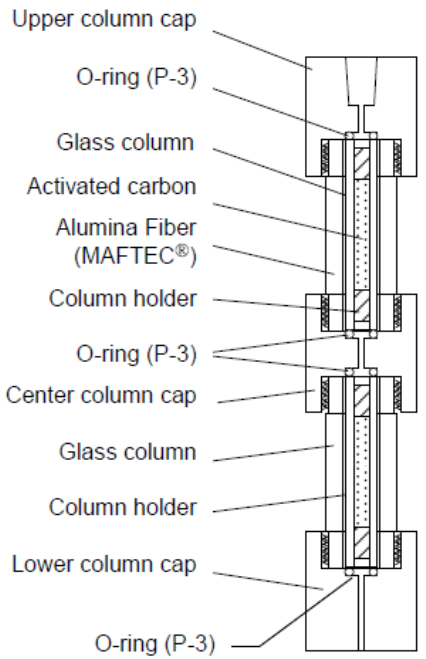
Handling of the sample prior to fluoride determination determines result evaluated

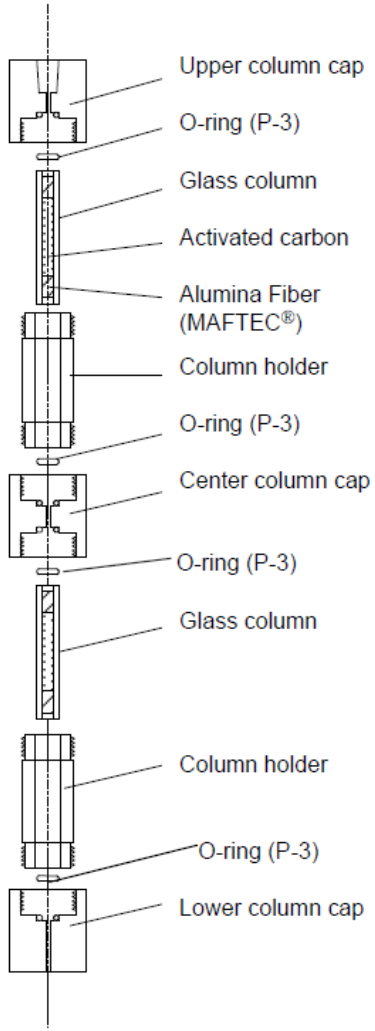
EOF – Extractable Organic Fluorine

AOF – Absorbable Organic Fluorine

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

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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**

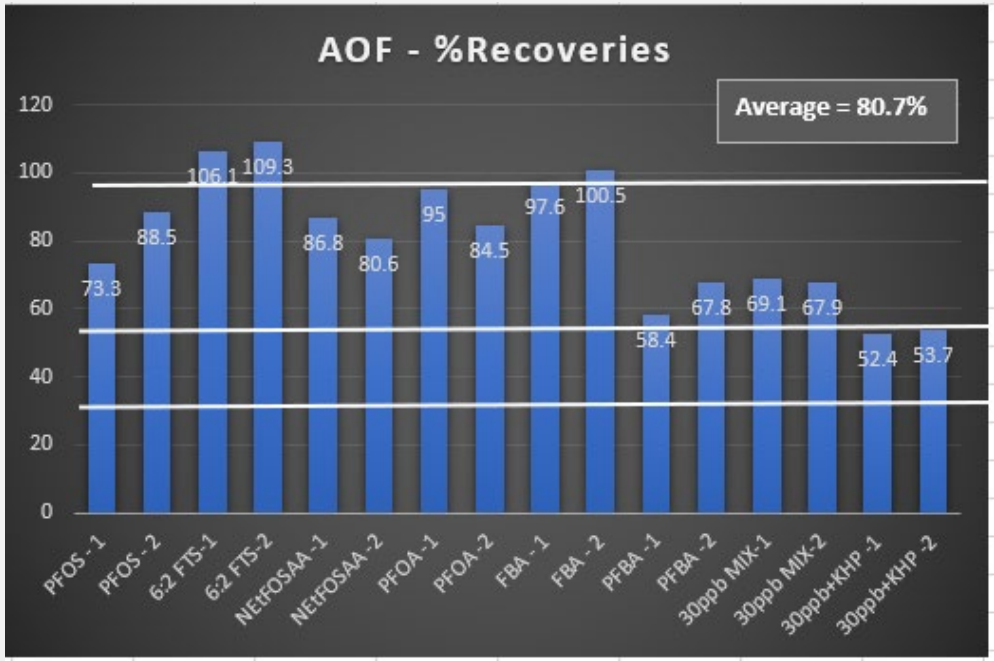
Total Org. F (TOF)

- **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

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

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

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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**

Strengths & Weaknesses

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Strengths & Utility

AOF/EOF:

- Proxy for entire class of PFAS
- Mass balance applications

TOP Assay:

- Insight specific to current risk drivers
- Sensitivity at single digit ppt

Weaknesses

AOF/EOF:

- 1ppb reporting limit
- Subject to certain interferences

TOP Assay:

- Oxidizable precursors only
- Does not complete a mass balance

Fluorine Content

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%
PFTrDA	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%

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Fluorine Content

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%

Application Examples

Wastewaters

Sample A

AOF = 1900 ugF/l
Targeted Analysis = 0.943 ugF/l

Sample B

Inorganic Fluoride = < 250 ugF/l
AOF = 2100 ugF/l
Targeted Analysis = 10,710 ugF/l

Solids

Sample A

EOF = 8300 ngF/g
Targeted Analysis = 201.8 ngF/g
13 PFAS detected

Sample B

EOF = 55,000 ngF/g
Targeted Analysis = 302.3 ngF/g
2 PFAS Detected

Total Organic Fluorine Analysis

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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?
  - Are we separately defining polymeric vs non-polymeric TOF?
- Need to agree on definition of AOF vs EOF and relationship to TOF and TF

QUESTIONS?

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THANK YOU

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