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

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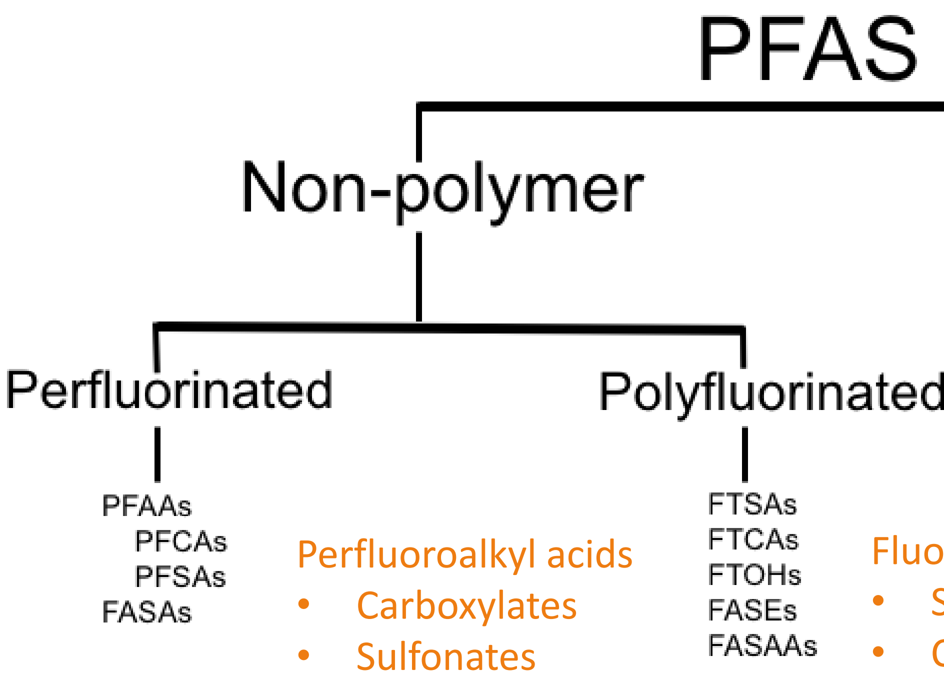
The General Classes of Per- and Polyfluoroalkyl Substances (PFAS)



Polymer:
- 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

PFAS Forensics



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

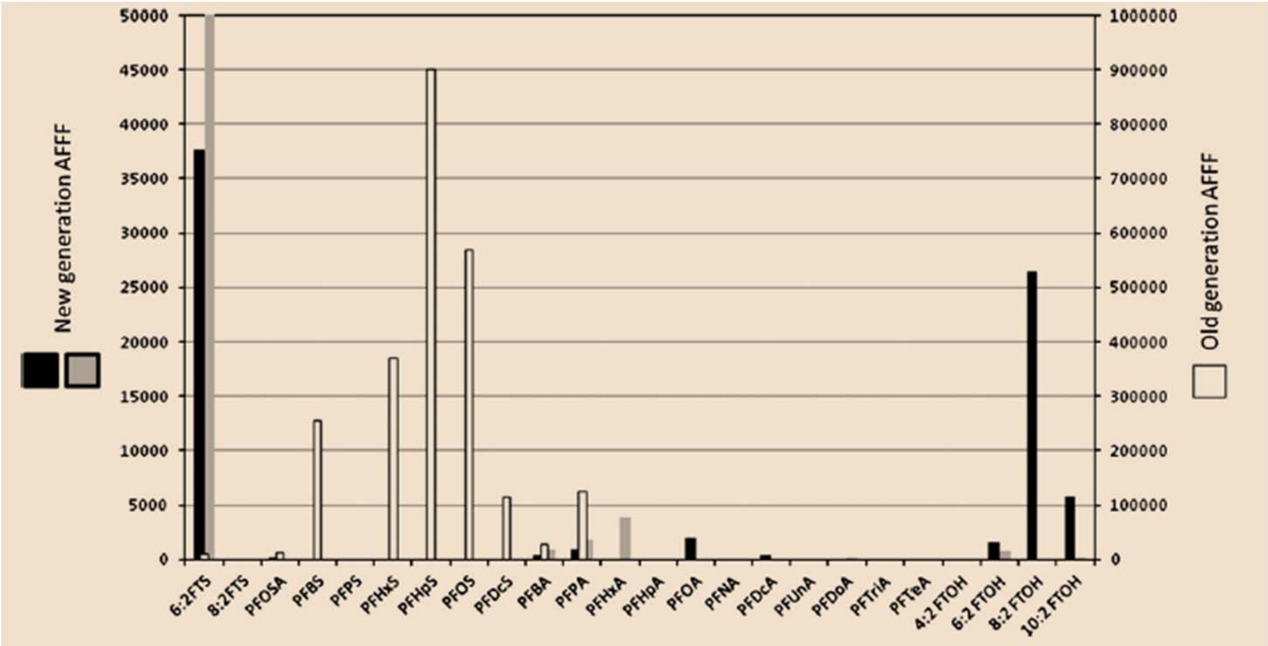
Perfluorobutanesulfonate
Perfluoropentanesulfonate
Perfluorohexanesulfonate
Perfluoroheptanesulfonate
Perfluorooctanesulfonate
Perfluorononanesulfonate
Perfluorodecanesulfonate
Perfluorododecanesulfonate
Perfluorooctanesulfonamide
Methylperfluoro-1-octanesulfonamide
Ethylperfluoro-1-octanesulfonamide
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

- <u>Fluorotelomer Alcohols</u>
  - 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

Isomer Comparison

$F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^-$

Linear Perfluorooctane sulfonate (PFOS)

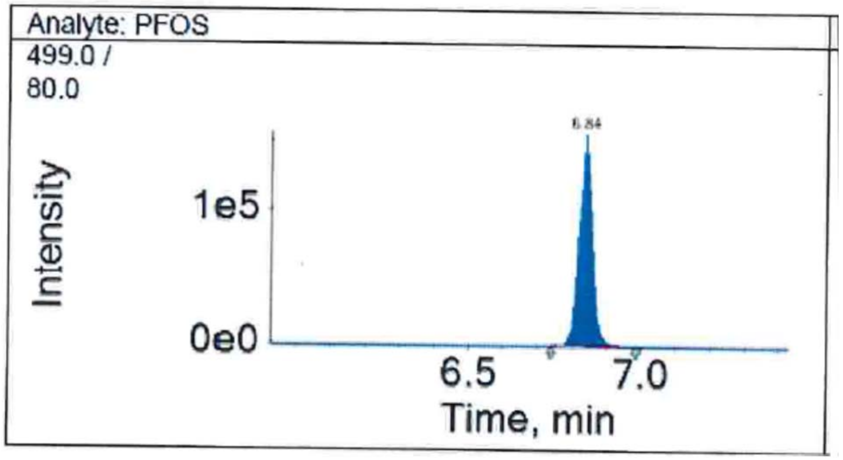
$$\begin{array}{l} \quad\;\; CF_3 \\ \quad\;\; | \\ F_3C\text{-}CF\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}SO_3^- \end{array}$$

Branched Perfluorooctane sulfonate (PFOS)

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

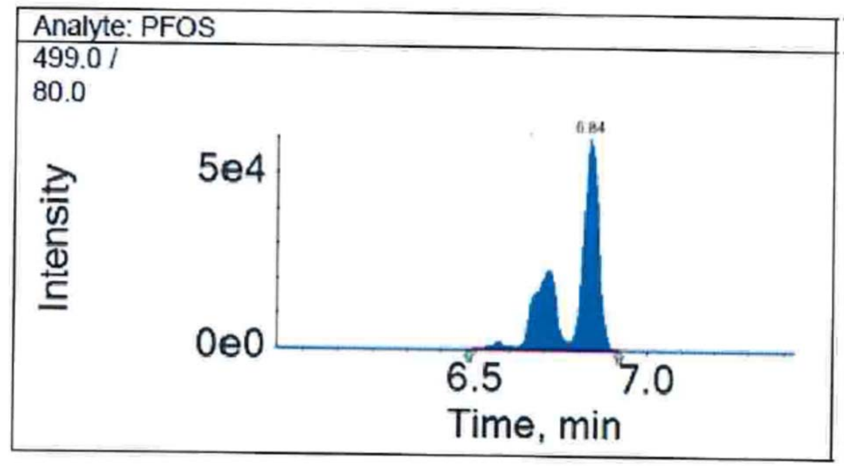
ITRC PFAS Fact Sheet Naming Conventions April 2020

Isomer Comparison

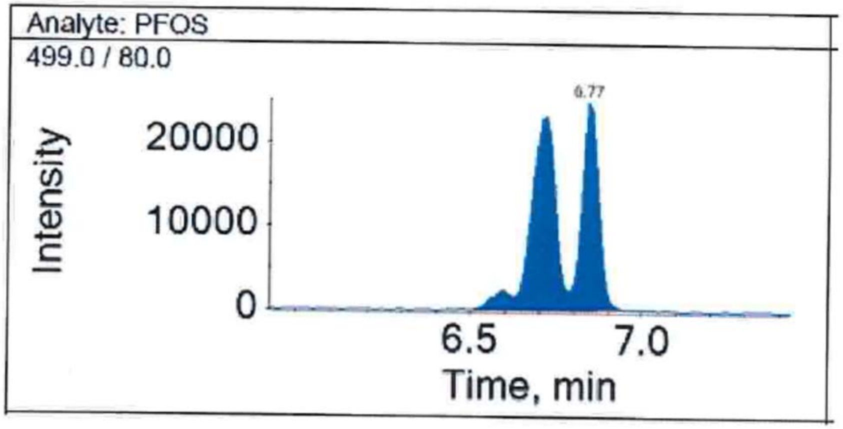


Chromatogram of PFOS Standard of Linear Isomer

Chromatogram of PFOS Standard of Branched/Linear Mix Typical Ratio

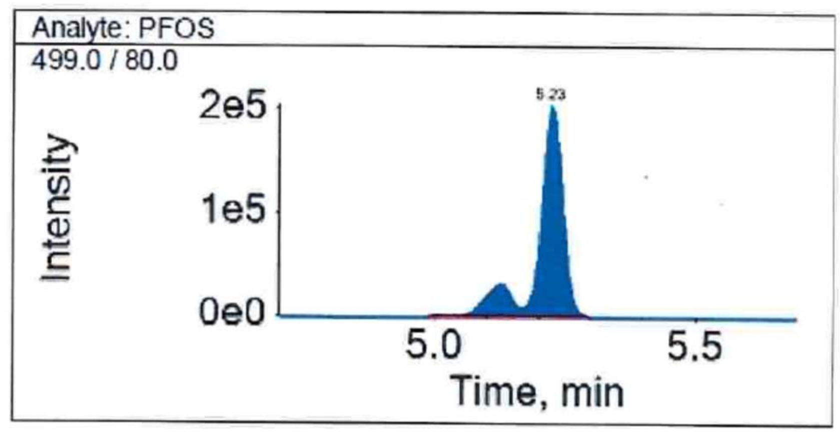


Isomer Comparison



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

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



AFFF Forensics

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

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	Protective Coatings					
PFNA					Initial Production	Architectural Resins		
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam
Dominant Process[3]		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used		

Notes:
1. This table includes fluoropolymers, PFAAs, and fluorotelomers. PTFE (polytetrafluoroethylene) is a fluoropolymer. PFOS, PFOA, and PFNA (perfluorononanoic acid) are PFAAs.
2. Refer to Section 3.4.
3. The dominant manufacturing process is shown in the table; note, however, that ECF and fluorotelomerization have both been, and continue to be, used for the production of select PFAS.

Sources: Prevedouros et al. 2006; Concawe 2016; Chemours 2017; Gore-Tex 2017; US Naval Research Academy 2017

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

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

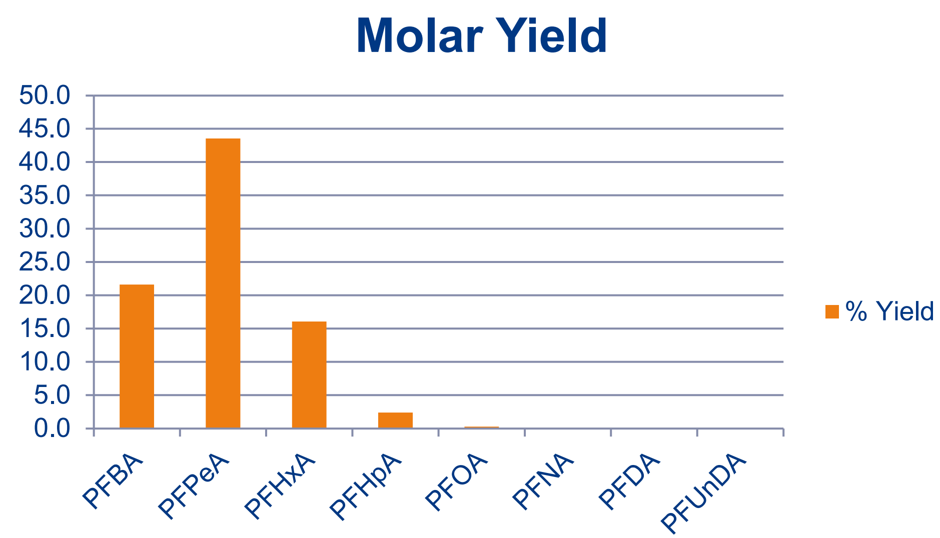
Concept is to analyze a sample for perfluoroalkyl carboxylic acids (PFCA) and perfluoroalkyl sulfonic acids (PFSA) and any identified precursors . Then subject a second aliquot of the sample to relatively harsh oxidative conditions. Analyze the oxidized sample for the same perfluoroalkyl acids and precursors.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

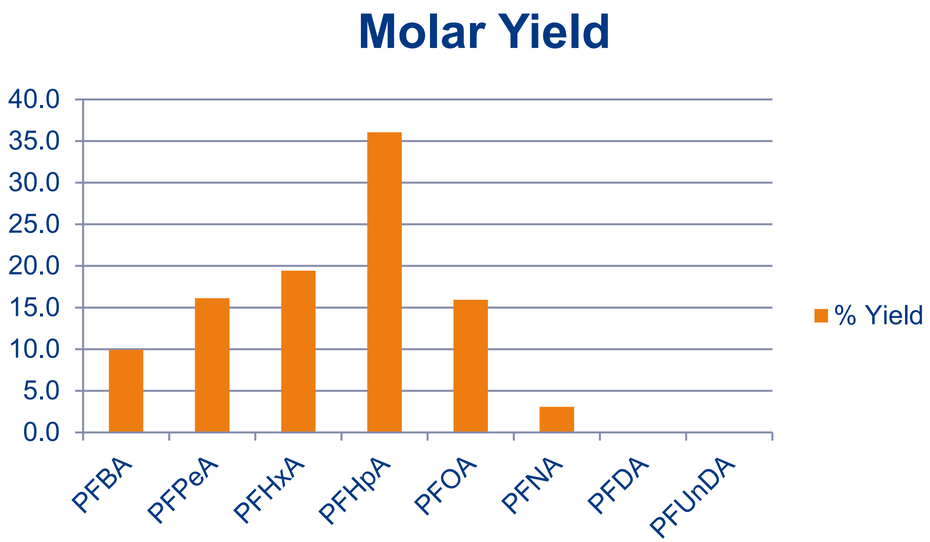
PFCA	ELLE	Houtz
PFBA	21.6	22
PFPeA	43.6	27
PFHxA	16.1	22
PFHpA	2.4	2
PFOA	0.3	0
PFNA	0.0	0
PFDA	0.0	0
PFUnDA	0.0	0



TOP Assay – 8:2 FTS

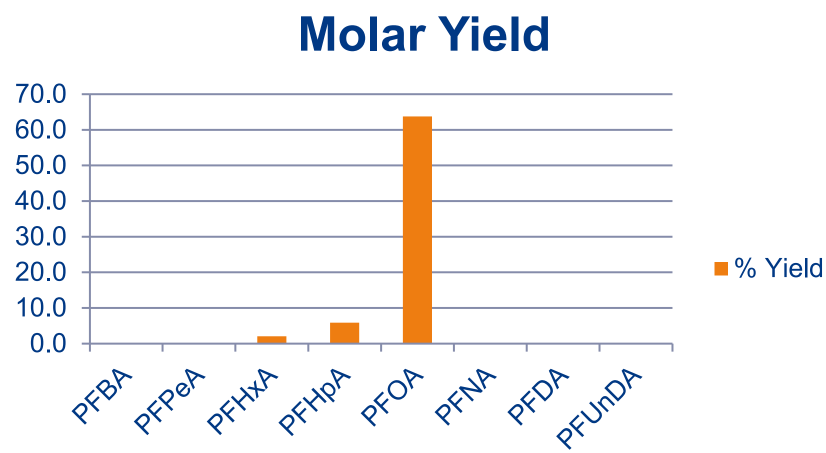
Results of oxidation of 8:2 Fluorotelomer sulfonate at 250 ng/l

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	

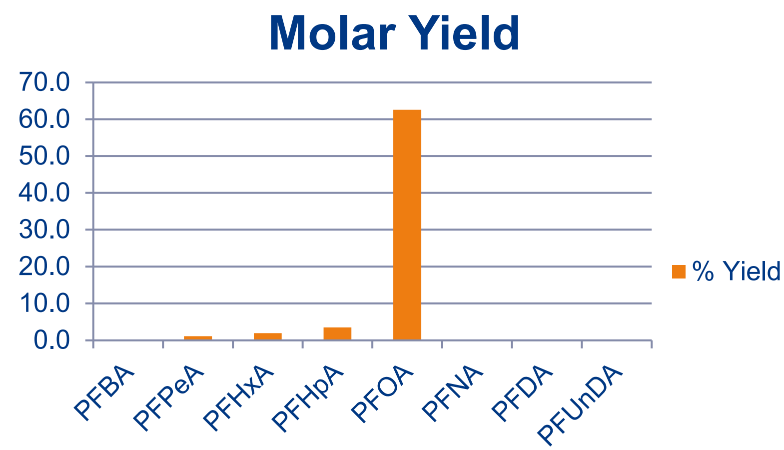


TOP Assay – other precursors

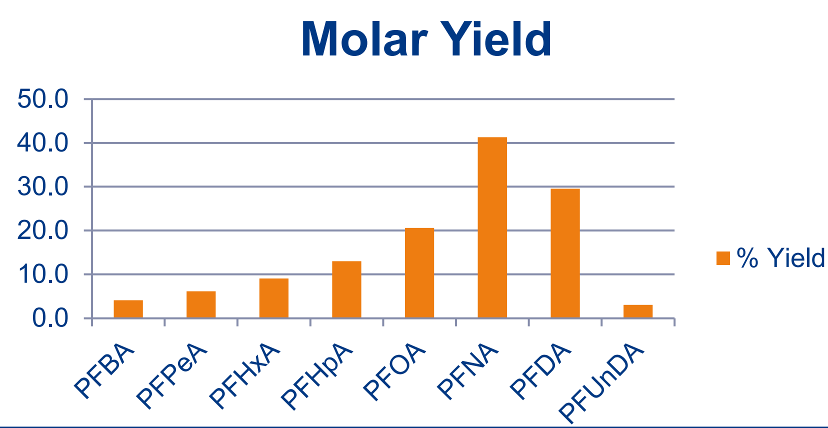
NEtFOSAA



NEtPFOSAE



10:2 FTS



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

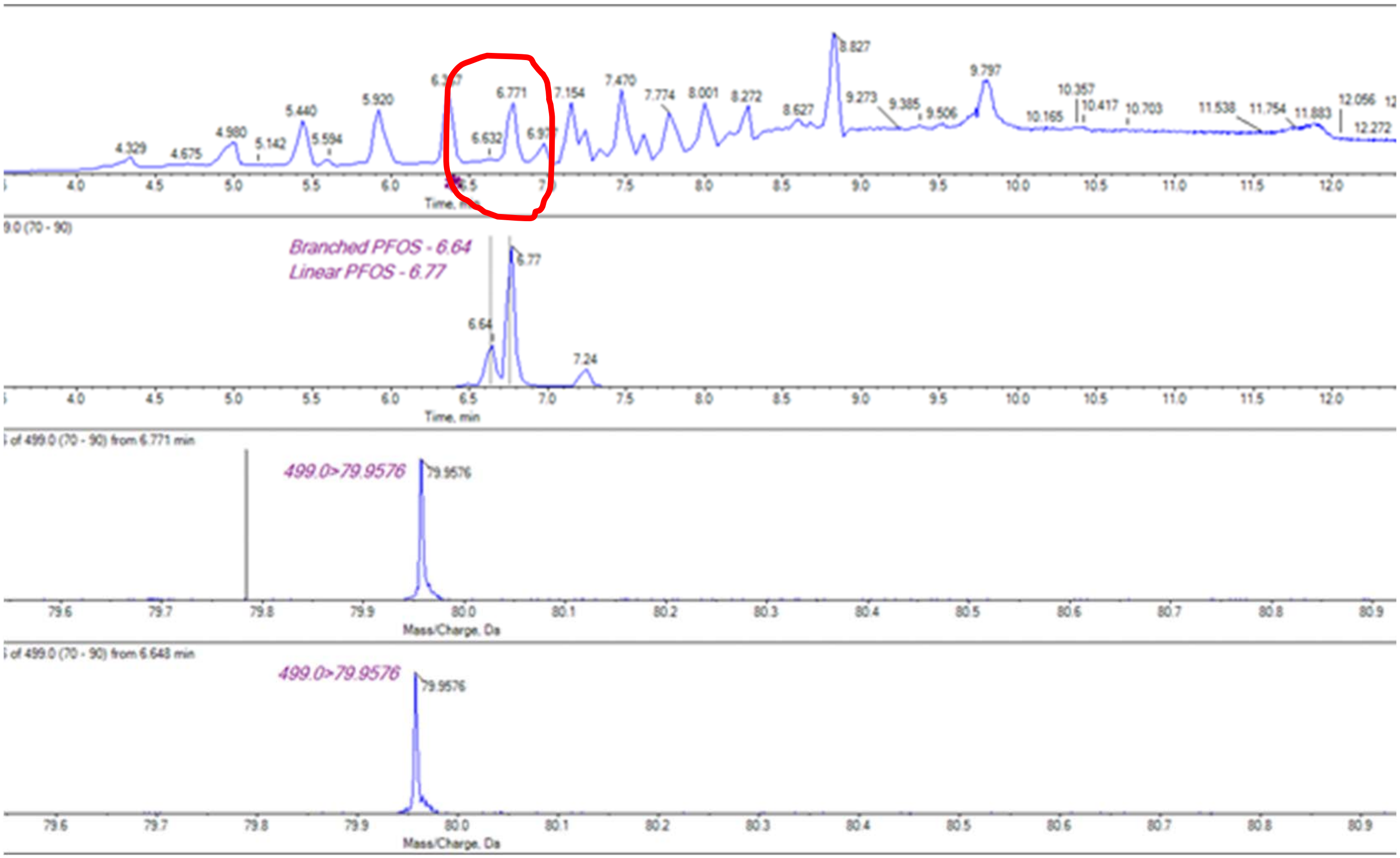
Newer Techniques – Non Targeted Analysis



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



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Eurofins Capacity – New Space

Questions

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