Forensics analysis of PFAS using advanced analytical techniques

Session: Environmental Forensics

Tuesday, August 6, 2024

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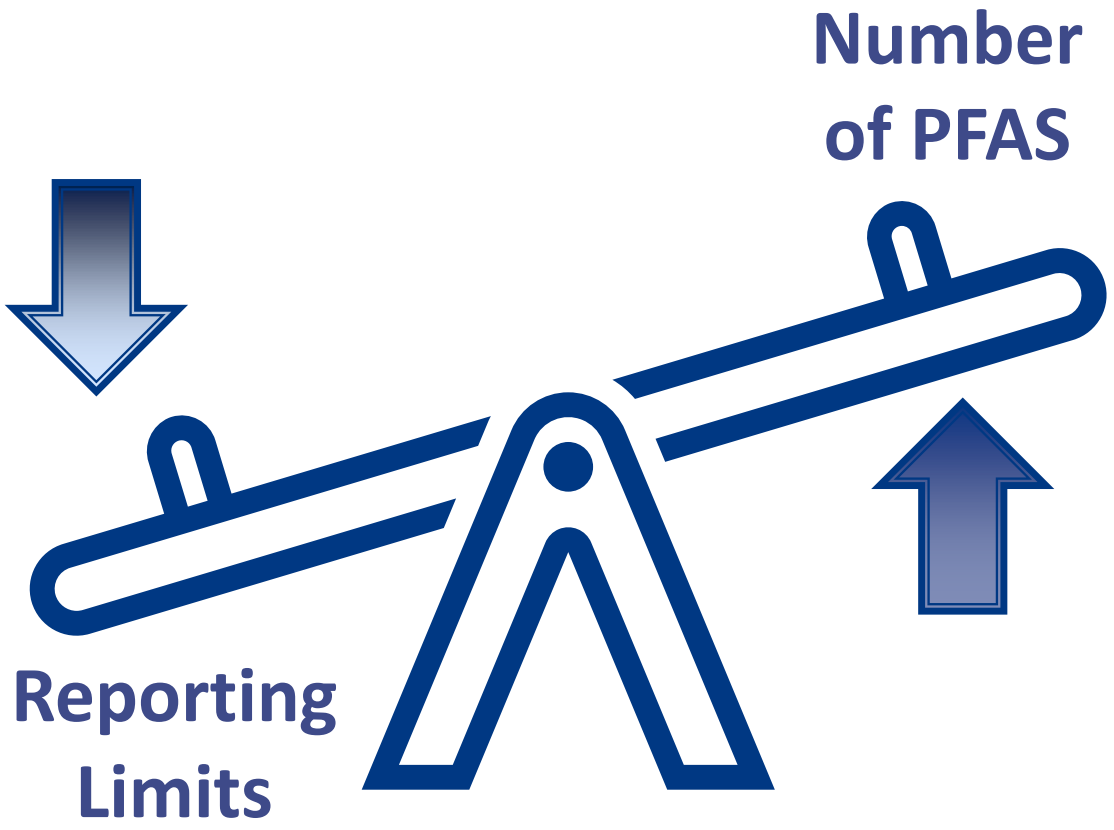
Evolution of the Science: PFAS

- Improvements in instrumentation
- Understanding of PFAS chemistry



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Method Selection

Pre-Planning
Quality, Regulatory, & Laboratory Drivers
Sample Collection Procedures

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Drinking Water

EPA Method 533
25 PFAS

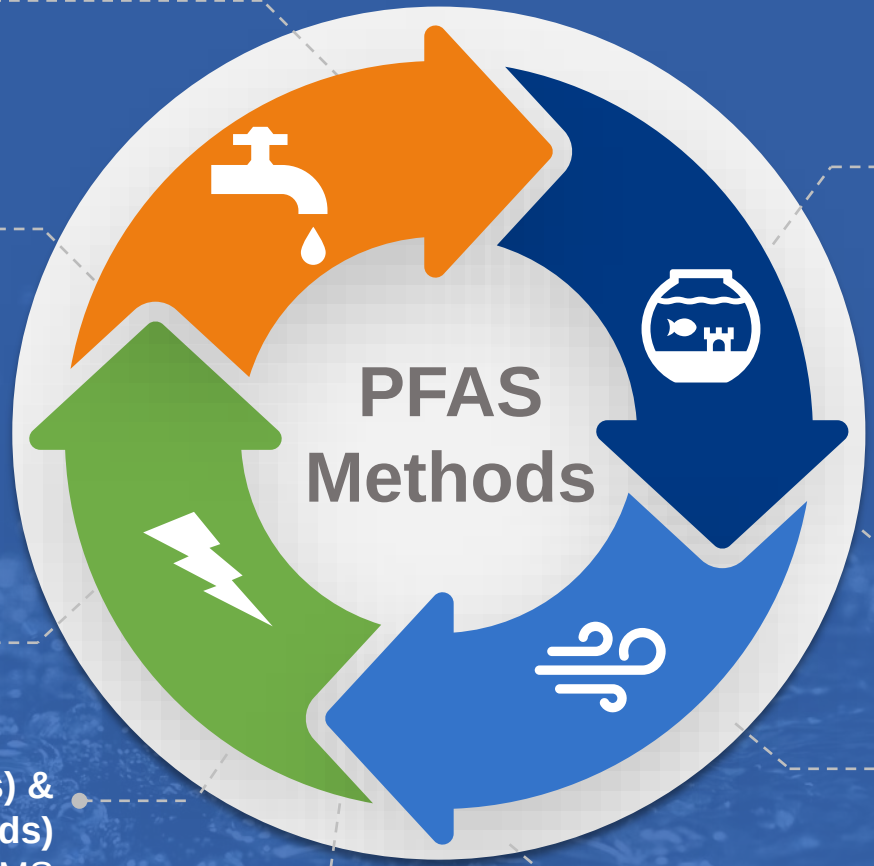
EPA Method 537.1
18 PFAS

Screening

EPA Method 1621
Adsorbable Organic Fluorine (AOF) by CIC

ASTM Methods D8421 (Aqueous) & D7968 (Solids)
External Calibration by LC-MS/MS

EPA Method 8327 (Aqueous)
External Calibration by LC-MS/MS



Non-Potable Water, Solid, & Tissue

EPA Method 1633
40 PFAS

Air

OTM 45- Air Emissions
50 PFAS

OTM 50- Air Emissions
30 PFAS

Modified TO-13A/10A/17 – Ambient Air

https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research

Drinking Water

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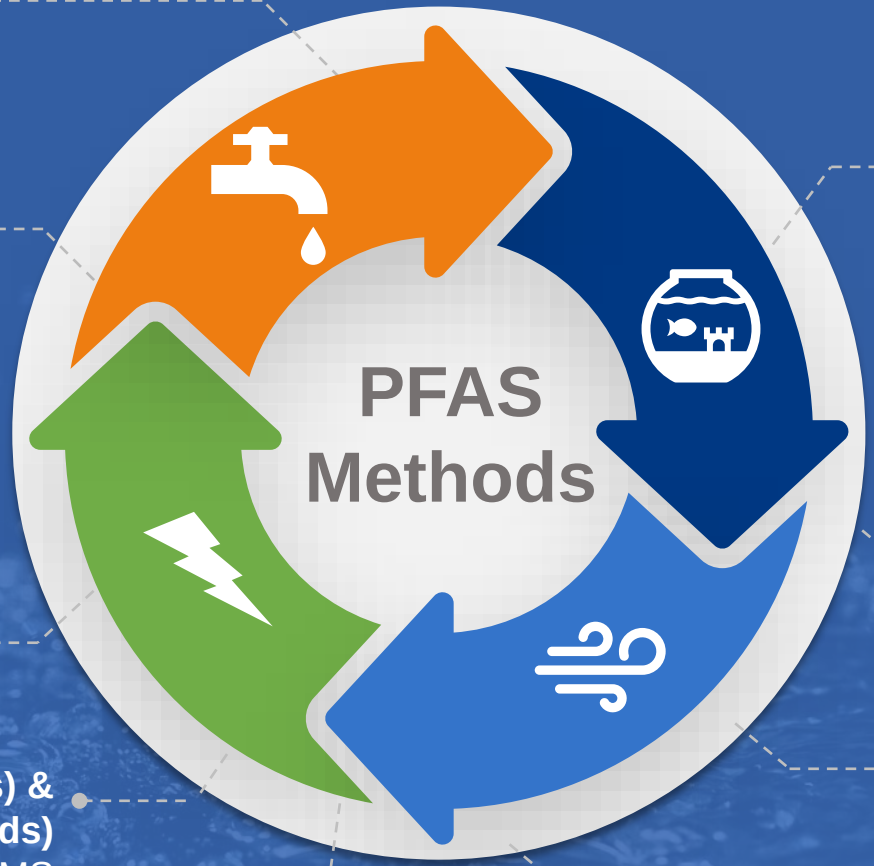

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queous) &
(Solids)
C-MS/MS

Modified TO-13A/10A/17 – Ambient Air

8327 (Aqueous)
ion by LC-MS/MS

- **TOP Assay**
- **EOF**
- **Branched/Linear**
- **Non-Targeted Analysis & Suspect Screening**

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Why are samples collected?

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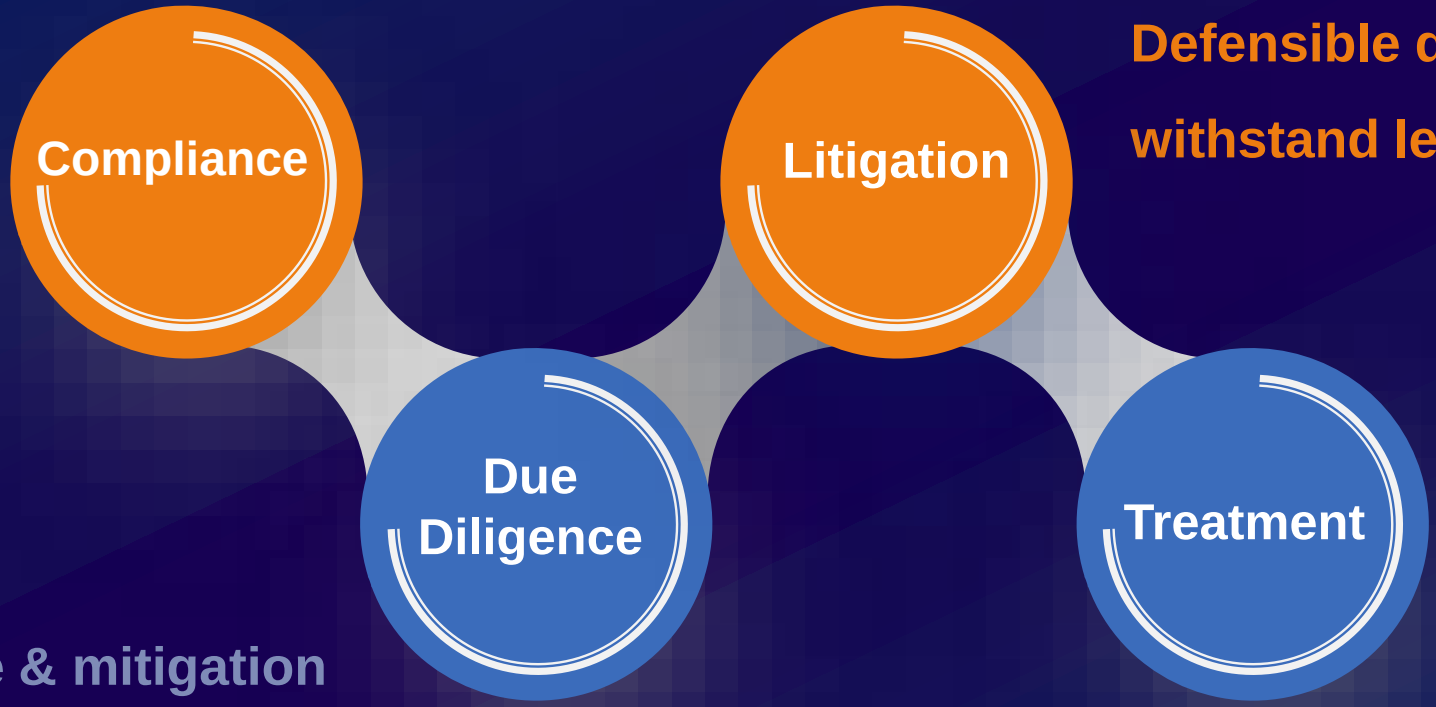
QUALITY DRIVERS



Where to begin?

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WHAT WILL THE DATA BE USED FOR?

Developing a Conceptual Site Model?

Determining the extent of contamination?

Investigating sources of contamination?

Assessing human health impacts?

Implementing a remediation plan?

Analyzing for PFAS? We've got options

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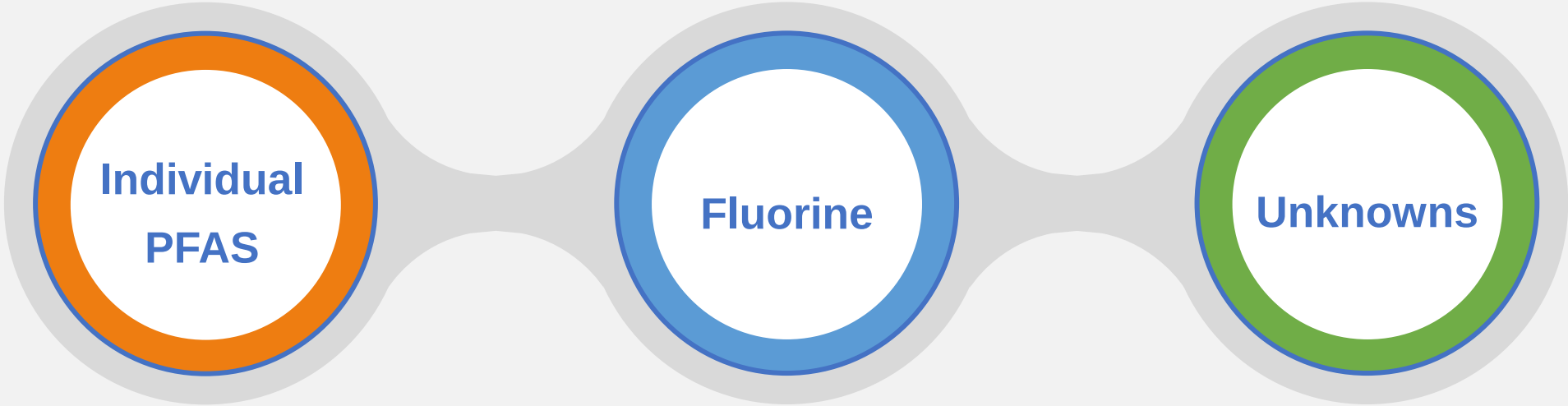

Targeted PFAS by LC/MS/MS

EPA Methods 533, 537.1, 1633

Up to 70+ monomer PFAS

Screening Methods available

(ASTM 8421)

Total or Organic Fluorine by CIC

"TOF-CIC"

Total Fluorine (inorganic + organic)

Total Organic Fluorine (TOF)

(may include polymers)

Adsorbable Organic Fluorine

Non-Target Analysis by LC/QTOF

Total Oxidizable Precursor

Unknown PFAS present at unknown concentrations may be detectable and identifiable

Developments in Targeted & Definitive Methods

NPW, Solids & Tissue: EPA Method 1633

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NPW & Solids Methods for PFAS

EPA Method 1633
NPW, Solids & Tissues
Branched/Linear Isomers –YES
40 Analytes
SPE WAX
Hold Time: 28/28 days (90 for solids & tissues)
LC-MS/MS with confirmation ion
Isotope Dilution
Recovery Correction – YES
RLs: range

Advances and Lessons in EPA Methods 1633

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Additional Analytes (RSL)

- TFSI/HQ-115
- PFPrA
- PFHxA (CA)
- PFODA

Lower limits

- Tap Water
  - HFPO-DA: 1.5 ng/L
  - PFOA: 0.0027 ng/L
  - PFOS: 2.0 ng/L
- Residential Soil
  - PFOA: 0.019 µg/kg
  - PFOS: 6.3 µg/kg

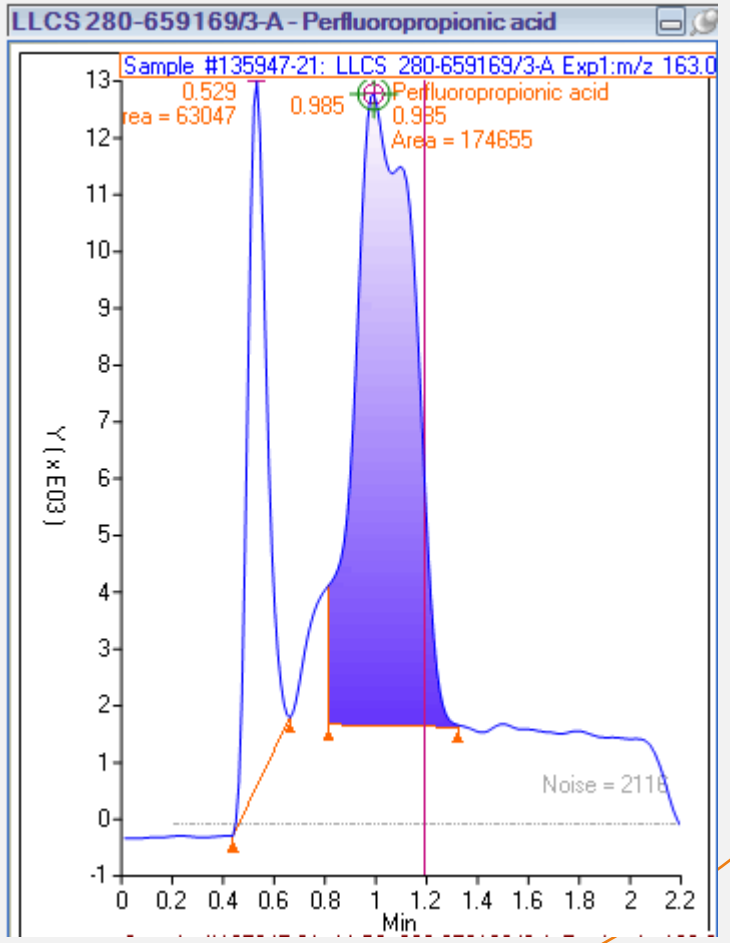
Advances and Lessons in EPA Methods 1633

Additional Analytes (RSL)

- TFSI/HQ-115
- **PFPrA**
- PFHxA (CA)
- PFODA

If no changes to EPA 1633:

- Peak splitting
- Unstable RT for Ultra Long chains



Advances and Lessons in EPA Methods 1633

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TSS Matters:

- >50 mg TSS/sample bottle

Procedural Options:

- Subsample
- Spike, Centrifuge, Decant

Let isotopes (EIS) do the work

Advances and Lessons in EPA Methods 1633

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Isotope Dilution: Quantitation method uses ^{13}C- or deuterated stable isotopes for internal standardization

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Matrix + Target

Isotope Dilution: Quantitation method uses ^{13}C- or deuterated stable isotopes for internal standardization

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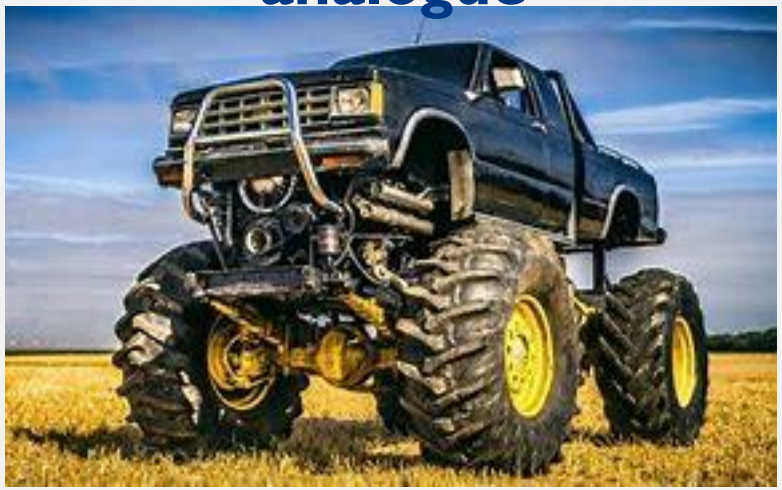
Matrix + Target

+

+ ^{13}C or d-labeled analogue



Isotope Dilution: Quantitation method uses ^{13}C- or deuterated stable isotopes for internal standardization

Matrix + Target

+ ^{13}C or d-labeled analogue

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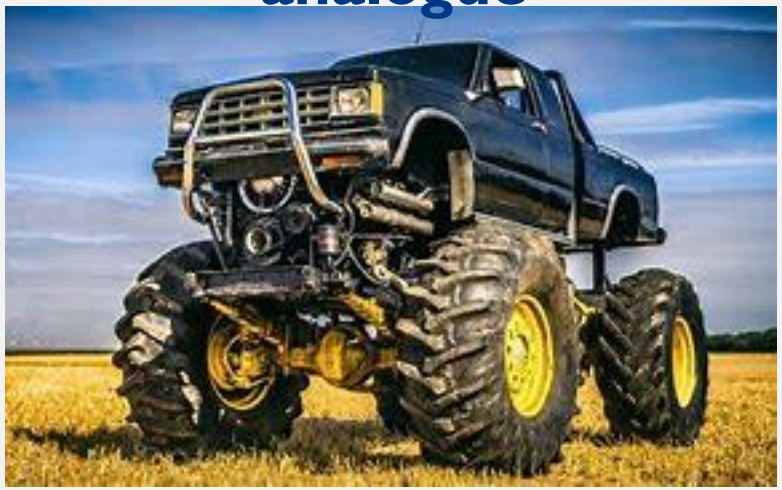

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- **Most accurate & precise quantitation method**
- **Broader range of matrices**
- **Reduces potential of false positives & error**

Emerging Technologies

TOP Assay
Total Organic Florine (TOF)
Non-Targeted Analysis (NTA)

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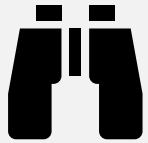
Screening Methods for PFAS

Rapid Screening

EPA Method 8327

ASTM D8421 (aq.)

ASTM D7968 (solid)



Non-Target Screening

TOP Assay

AOF/EOF

Non-Targeted Analysis

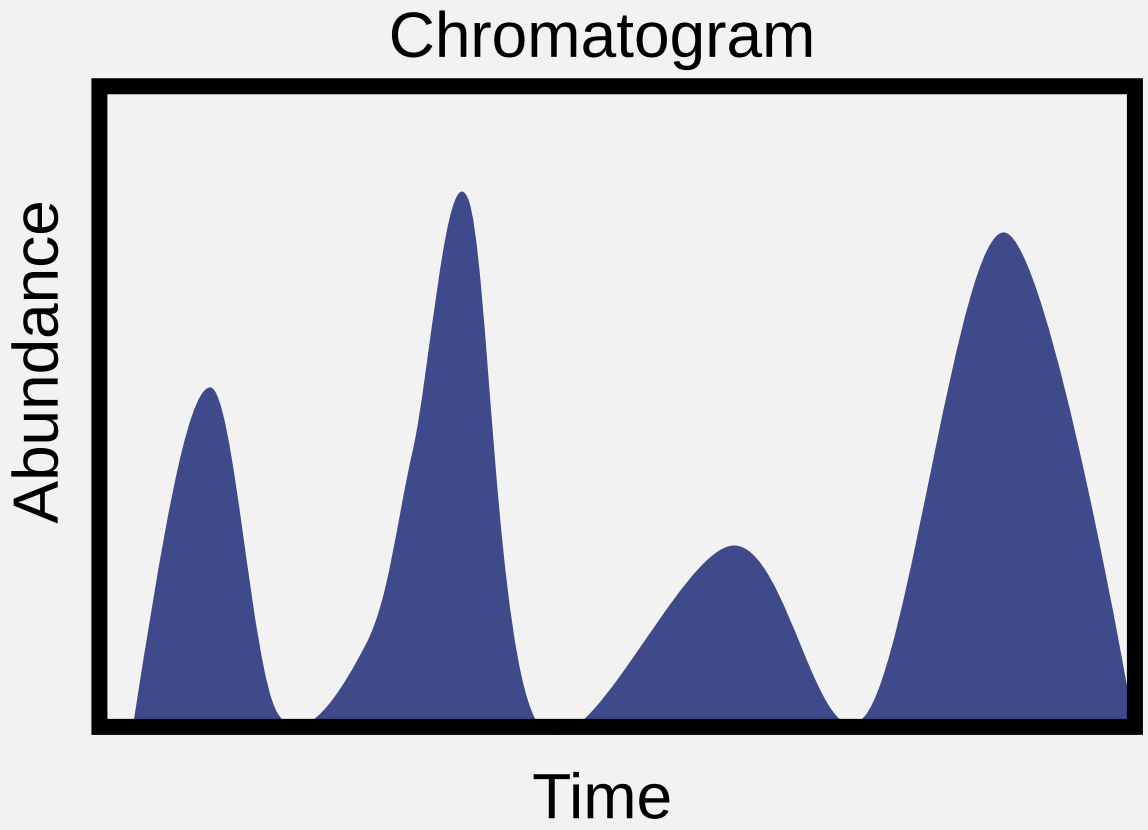
Rapid Screening

Unknown Screening

Targeted Methods:

How much Compound X do I have?

- Select compounds
- Specific matrix
- Analytical Standards
- Quantitative
- Closed Analysis



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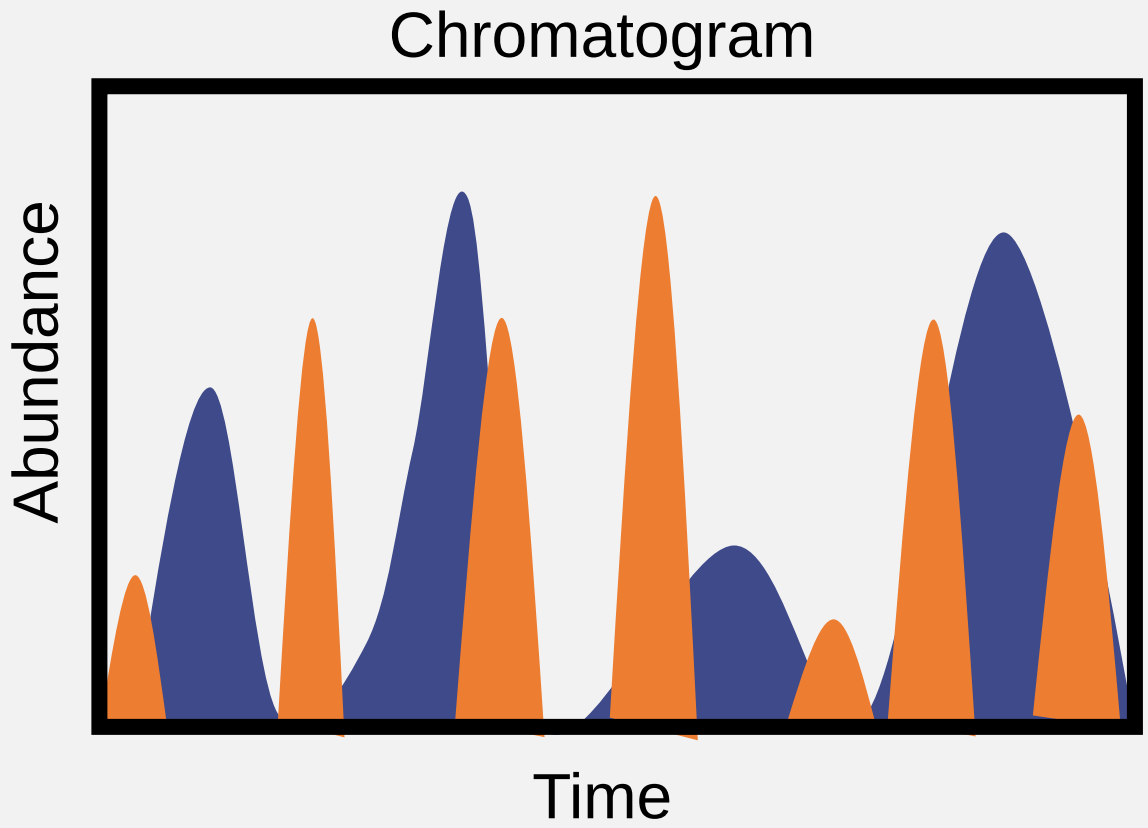

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Why explore non-targeted analysis?

- TSCA inventory >86,000 chemicals in commerce (2019)
  - 100s-1000s of suspect PFASs
- >219 million entries in the CAS registry
- Current standard methods include a very limited number of chemicals

We will only find what we are looking for!

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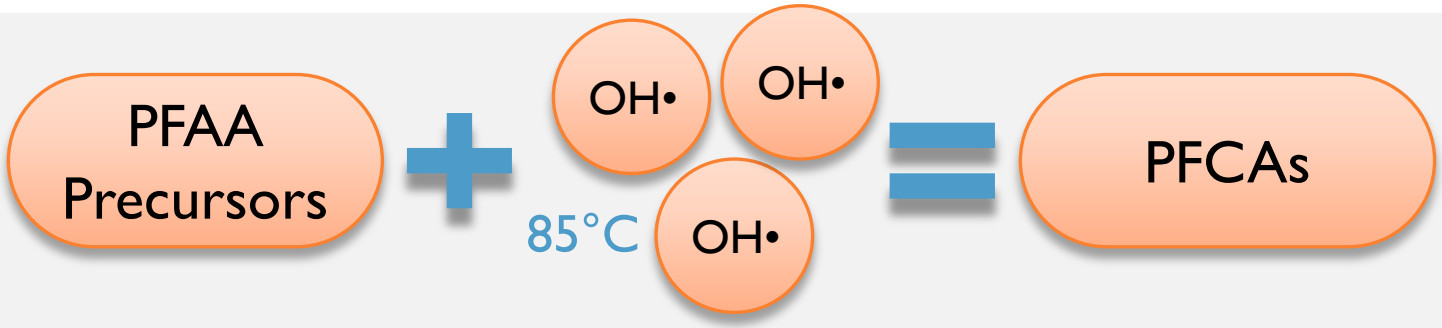
How much transformable PFAS?



	Pre-Treatment (ng/L)	Post-Treatment (ng/L)
PFBA	ND	46
PFPeA	15	15
PFHxA	11	42
PFHpA	ND	6.3
PFOA	13	14
Total PFCAs	**39**	**148.3**
	PFCA Difference:	**109.3 ng/L**

TOP Assay

Cons:

- Matrix effects quench rxn
- Un-measureable transformation products
- Not robust

Pros:

- Quantify oxidizable precursors with some chain length information

AOF/EOF

Cons:

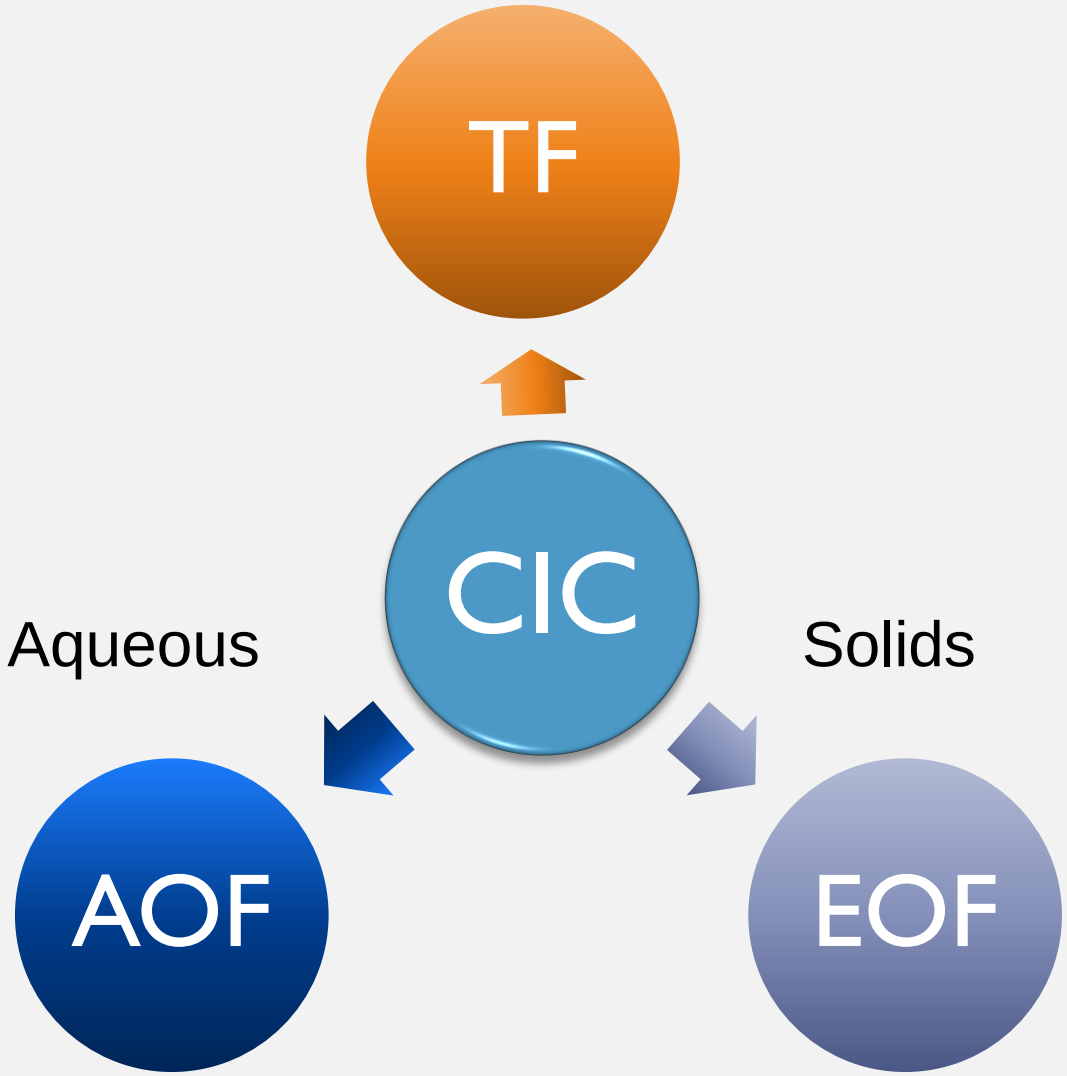
- Not PFAS specific
- High reporting limits

Pros:

- EPA Method 1621 - AOF
- Robust analysis
- Single result

CIC: Combustion Ion Chromatography

How much organic fluorine?



NTA

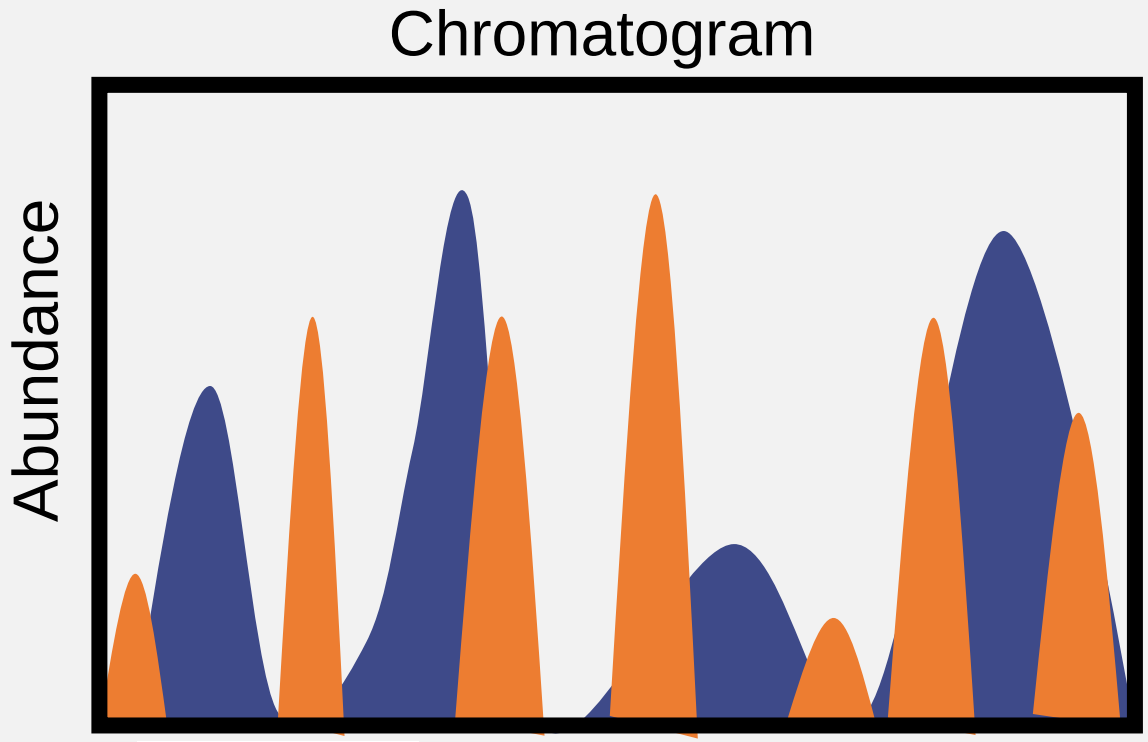
Cons:

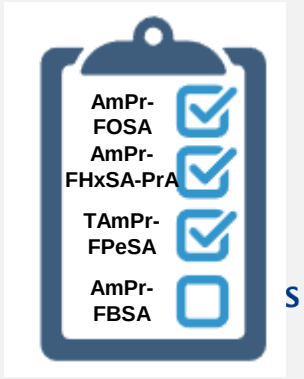
- High Resolution Mass Spectrometry
- Semi-Quantitative

- Pros:
- User Defined Compound Lists
- No Standards required
- Open Ended Analysis

Non-Targeted & Suspect Screening

What is in my sample?





Non-Targeted Analysis in the Wild West

High Resolution
Accurate Mass
Mass Spectrometry

What is in my sample?

Image generated with AI

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Target Analysis "Known Knowns"	Suspect Screening "Known Unknowns"	Non-Targeted Screening "Unknown Unknowns"	Retrospective analysis
Know what to look for	Suspect list of compounds to look for	No compounds to look for	Reanalyze data using new knowledge to discover previous contamination
Analytical standards Quantitative	No standards Semi-Quantitative or Qualitative only	No standards	No standards
Is Compound X in my sample? How much?	Which compounds from the list are in the sample?	What is in my sample? How do these two samples compare statistically?	What was in my sample?

Non-Targeted Analysis (NTA) by LC-HRMS

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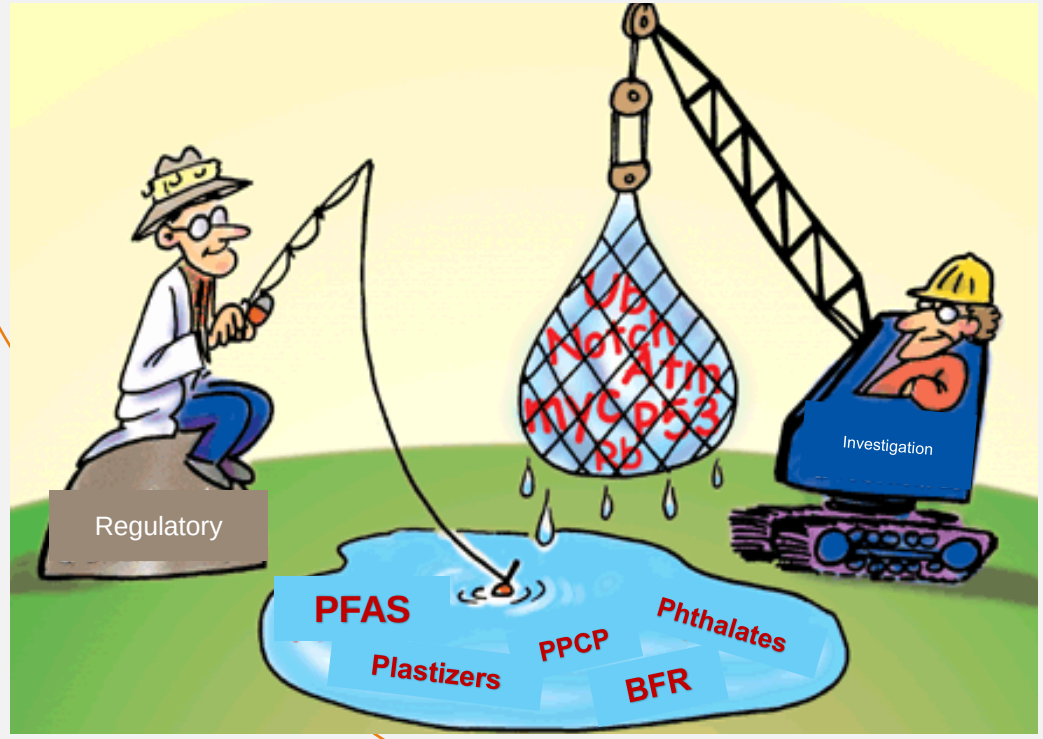
Target AND Non-Targeted



- Applications:
  - Analyte confirmation, site investigation, suspected contamination, AFFF characterization, forensics, source tracking, non-regulatory work
- Results:
  - Client Driven: Qualitative or semi-quantitation results
- Resources: BP4NTA & ITRC CECs

Drinking Water

EPA Method 533
25 PFAS

EPA Method 537.1
18 PFAS

Screening

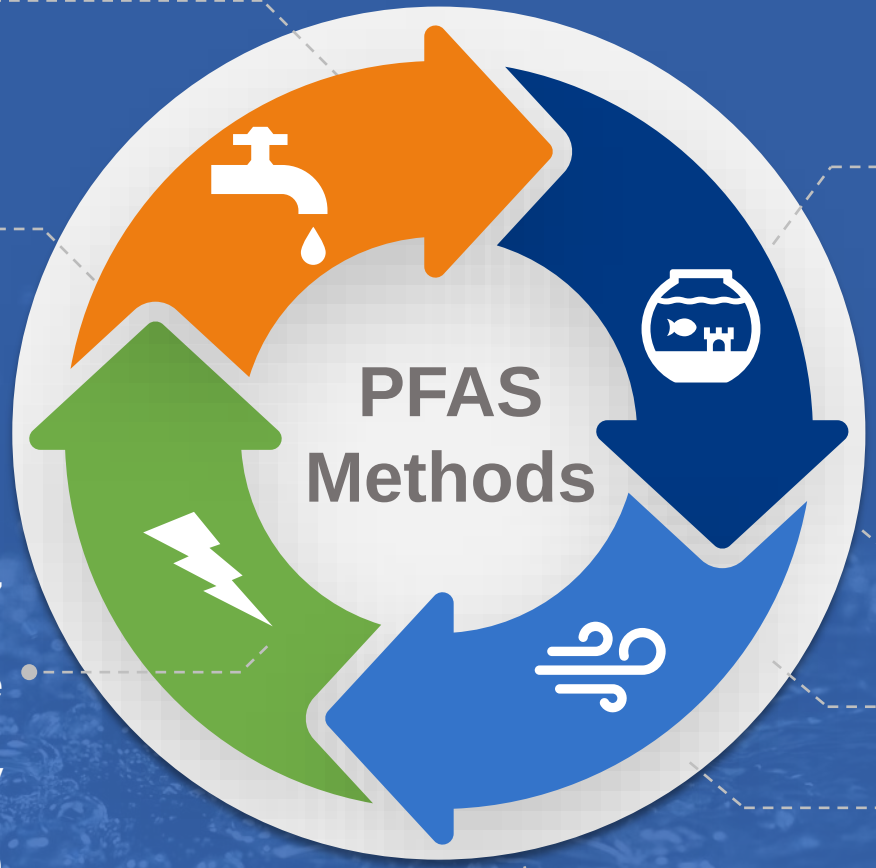
ASTM Method 8421/EPA Method 8327

EPA Method 1621 Adsorbable Organic Fluorine

Total Oxidizable Precursor (TOP) Assay

Extractable Organic Fluorine (EOF)

Non Targeted Analysis & Suspect Screening



Non-Potable Water, Solid, & Tissue

EPA Method 1633
40 PFAS

Air

OTM 45- Source Air

OTM 50- Source Air

TO-13A – Ambient Air

TO-17 – Indoor Air & Soil Vapor

THANK YOU

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