The Analysis for PFAS: An Evaluation of Current Methods, Proposed Methodologies and the Application of New Technologies

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Method Selection

Pre-Planning

Quality, Regulatory & Laboratory Drivers

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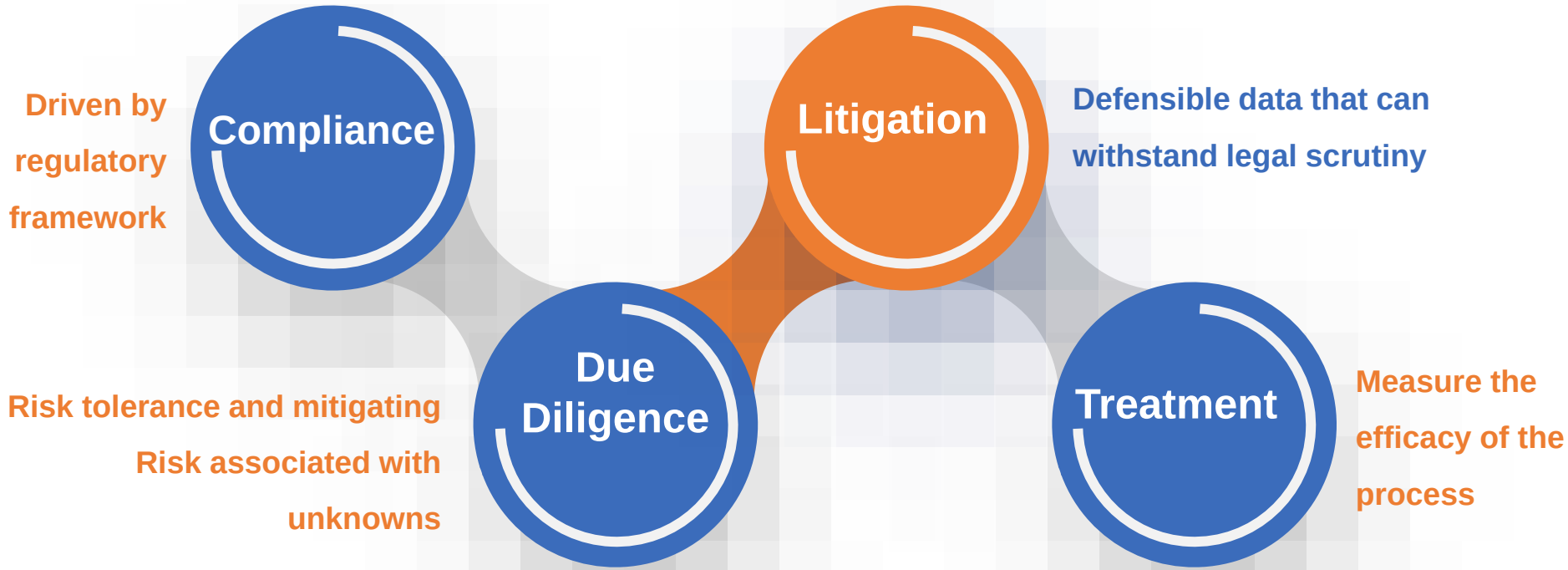
What Are The Data Being Used For?

QUALITY DRIVERS



EPA DRINKING WATER METHODS

EPA 537.1
EPA 533

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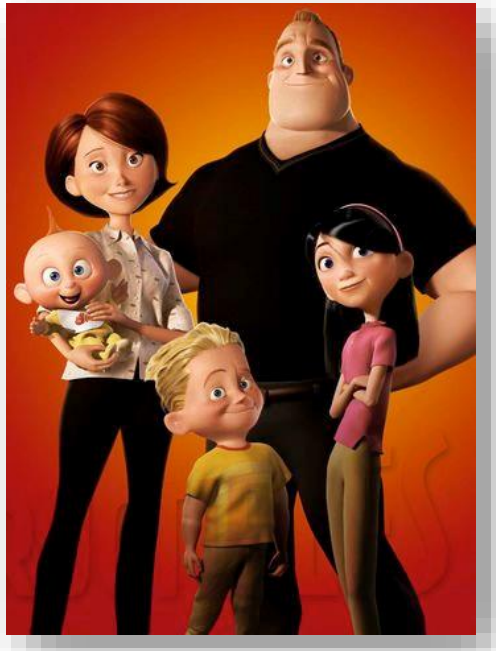
EPA PFAS Methods

Drinking Water

533	537.1
Drinking Water	Drinking Water
Branched/Linear Isomers -YES	Branched/Linear Isomers -YES
14 of the same and 15 unique compounds	14 of the same and 4 unique compounds
SPE WAX	SPE SDVB
Hold Time: 28/28 days	Hold Time: 14/28 days
LCMSMS with confirmation ion	LCMSMS - no confirmation ion
Isotope Dilution	Internal standard
Recovery Correction - YES	Recovery Correction – NO
RLs: Not defined	RLs: 2ppt - 40ppt

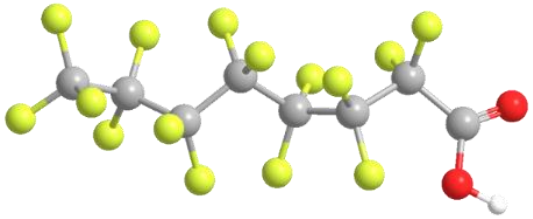
Labeled Analogues



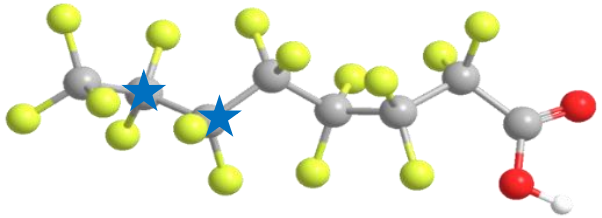
The Parr Family = Native PFOS

+ =

The Incredible Family = Labeled PFOS



+ ★=



★ = ^{13}C

Isotope Dilution

Benefits of Isotope Dilution

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What affects the native analyte will equally affect the isotope

Calibration

Most accurate and precise method

Target analytes are quantitated against structurally similar materials, the isotopes themselves

Matrix Mitigation

Expands ability to process a broader range of matrices

Compound Identification

Reduces the potential for false positives

Reduces the potential for error; corrects for retention time shifts

NON-POTABLE WATER & SOLIDS

User-Defined Isotope Dilution Method
EPA 8327
EPA Draft 1633 Method
Air Methods

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Comprehensive PFAS Testing

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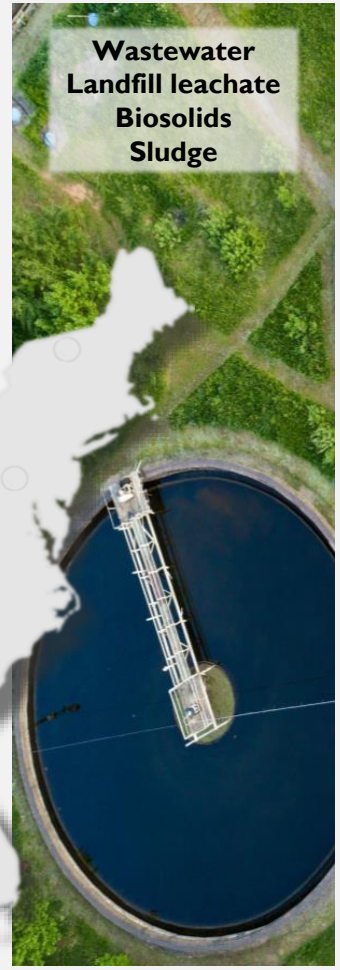

In-line SPE

LEAF

537.1

QSM

ISM

Isotope Dilution

Direct Injection

533

SPLP

Methods Distribution

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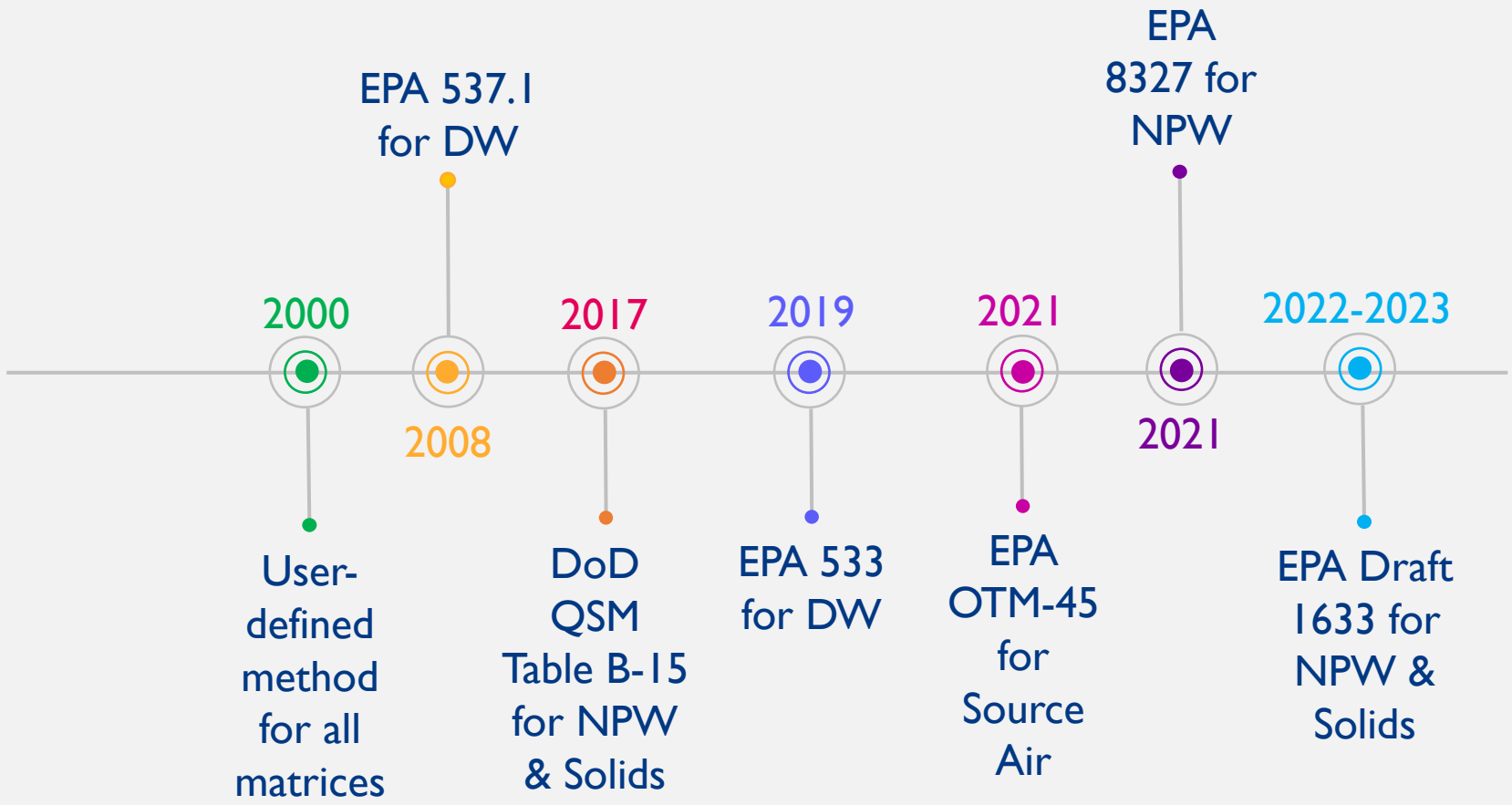
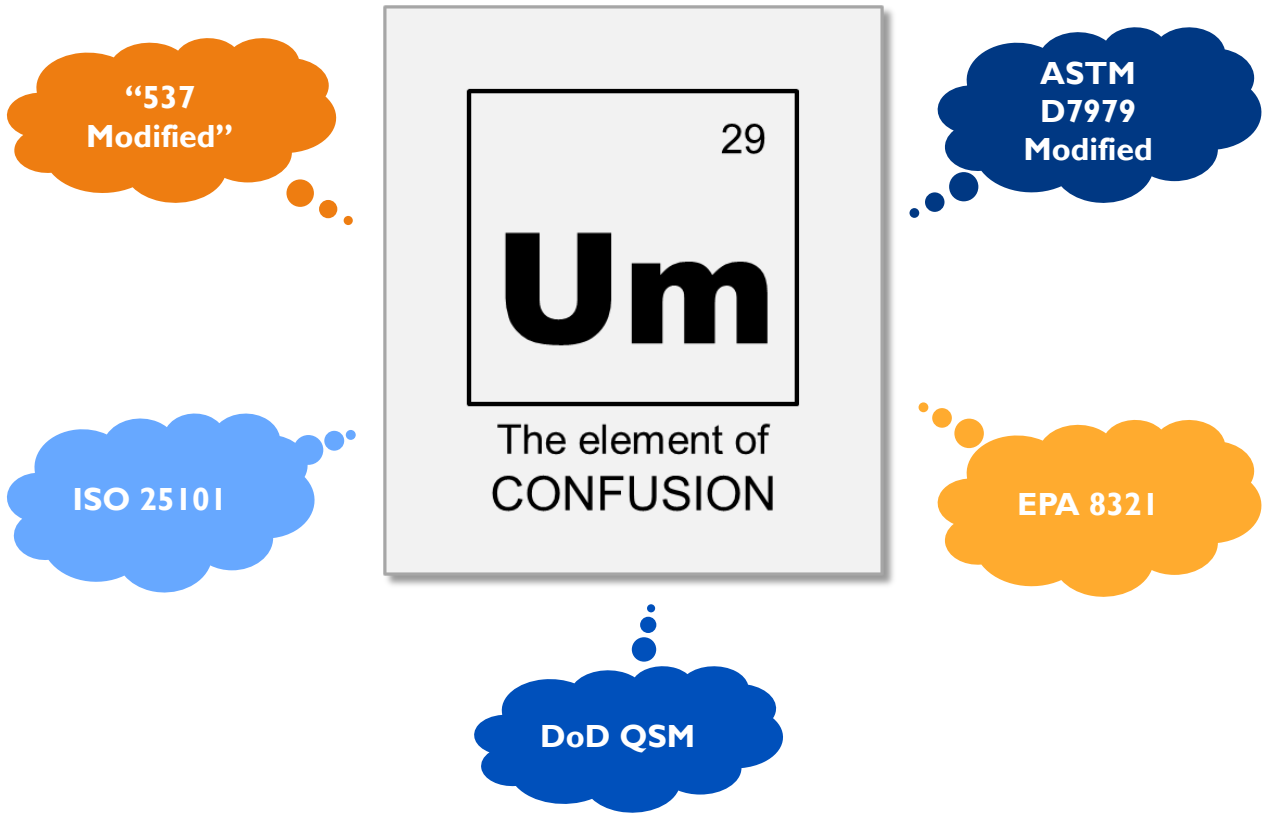
Utilizes Internal/ External Std. Quantitation and unique techniques

Utilizes Isotope Dilution and other consistent techniques



What were labs using for the past 20 years?



User-Defined Methods: PUT TO THE TEST!

Complex Matrices

- Biphasic
- Biosolids
- Tissues
- Dispersions
- Activated Carbon
- Cosmetics
- Concrete

Audits & PTs

- NELAC
- DoD ELAP
- Client/Program Specific Audits
- Semiannual PT
- NMI International Round Robin
- DOW Study

3rd Party Validation

- >85% of all PFAS data includes a validation package
- >300,000 sample data validated

LCMSMS/GCMSMS Analysis

Compounds Included in EPA Draft 1633 (RLs = 2-5ng/L)

- Perfluorobutanoic acid (PFBA)
- Perfluoropentanoic acid (PFPeA)
- Perfluorohexanoic acid (PFHxA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorodecanoic acid (PFDA)
- Perfluoroundecanoic acid (PFUnA)
- Perfluorododecanoic acid (PFDoA)
- Perfluorotridecanoic acid (PFTriA)
- Perfluorotetradecanoic acid (PFTeA)
- Perfluorobutanesulfonic acid (PFBS)
- Perfluoropentanesulfonic acid (PFPeS)
- Perfluorohexanesulfonic acid (PFHxS)
- Perfluoroheptanesulfonic Acid (PFHpS)
- Perfluorooctanesulfonic acid (PFOS)
- Perfluorononanesulfonic acid (PFNS)
- Perfluorodecanesulfonic acid (PFDS)
- Perfluorododecanesulfonic acid (PFDoS)
- Perfluorooctanesulfonamide (FOSA)
- NEtFOSA
- NMeFOSA
- NMeFOSAA
- NEtFOSAA
- NMeFOSE
- NEtFOSE
- 4:2 FTS
- 6:2 FTS
- 8:2 FTS
- 9Cl-PF3ONS
- 11Cl-PF3OUdS
- DONA
- HFPO-DA (GenX)
- 3:3 FTCA
- 5:3 FTCA
- 7:3 FTCA
- NFDHA
- PFMBA
- PFMPA
- PFEESA

Target Compounds Not Part of EPA Draft 1633 (RLs = 2-5ng/L)

- 10:2 FTS
- 6:2 FTCA
- 8:2 FTCA
- 10:2 FTCA
- 6:2 FTUCA
- 8:2 FTUCA
- 10:2 FTUCA
- PFECHS
- PFPrS
- PFPrA
- PFMOAA
- PFECAG
- PFO4DA
- PFO3OA
- PFO2HxA
- R-EVE
- NVHOS
- Hydro-EVE Acid
- Perfluoro-n-octadecanoic acid (PFODA)
- Perfluoro-n-hexadecanoic acid (PFHxDA)
- EVE Acid
- PFO5DA
- PMPA
- PEPA
- MTP
- PS Acid
- Hydro-PS Acid
- R-PSDA
- Hydrolyzed PSDA
- R-PSDCA
- 6:2 diPAP
- 8:2 diPAP
- 6:2/8:2 diPAP
- 10:2 diPAP
- 10:2 FTOH (RL=1ug/L)
- 8:2 FTOH (RL=1ug/L)
- 7:2 FTOH (RL=1ug/L)
- 6:2 FTOH (RL=1ug/L)
- 4:2 FTOH (RL=1ug/L)

EPA *Draft* 1633 for Non-Potable Water & Solids

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Compared to: User-Defined Methods and DoD QSM Table B-15

SIMILARITIES

- Applicable to a variety of solids and aqueous matrices
- Solid Phase Extraction using WAX
- Isotope Dilution Quantitation using all available isotopes
- Ion Transitions, monitoring ratios
- *Using non-Extracted Internal Standards (NEIS) for quantitation of extracted internal standards (EIS)
- **Use of carbon cleanup

*QSM 5.3 dropped it, but they are bringing it back with B-24

**User-defined methods use stacked carbon vs. loose carbon

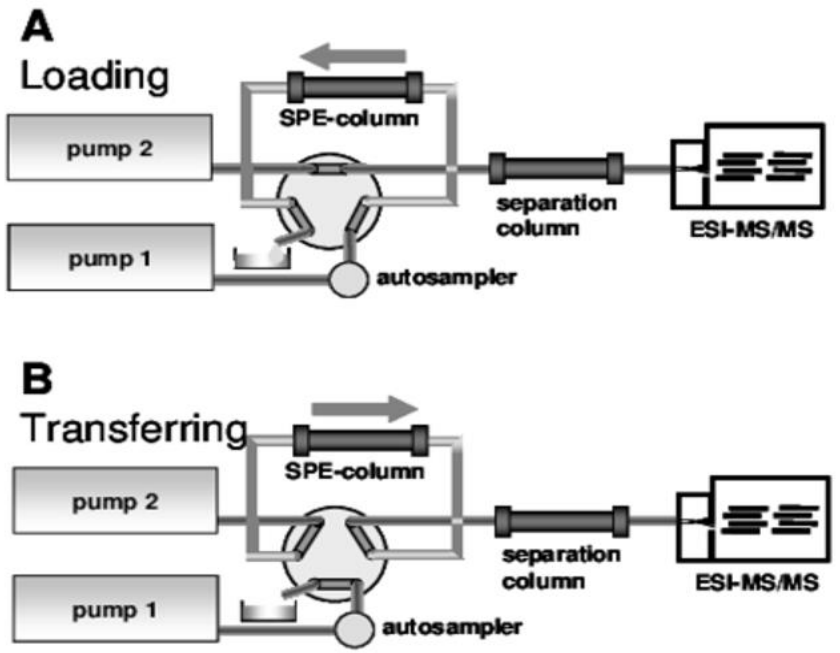
DIFFERENCES

- Frozen storage requirements
- Soil/Tissue Prep: concentration step
- S/N Ratio
- Waters Oasis WAX SPE Cartridge with loose carbon cleanup
- TDCA Check: 60 sec window specification
- E-flagged results: complex dilution scheme
- Mass transitions vary for some

How 8327 Compares to Draft 1633

EPA 8327

Specifications
Applies to non-potable water (NPW)
Applies to 24 compounds
External Standard
Direct Injection – no SPE
Recovery Correction - NO
Hold Time: 28/30 days
LCMSMS with confirmation ion
Branched/Linear Isomers -YES
RLs: 10ppt



EPA Draft 1633

Specifications
Applies to NPW, soil, tissue
Applies to 40 compounds
Isotope Dilution
SPE WAX
Recovery Correction - YES
Hold Time: Varies, 90/90 days option when frozen, 7/28 days when refrigerated
LCMSMS with confirmation ion
Branched/Linear Isomers -YES
RLs: 2ppt

537.1

Drinking Water –

18 Compounds

SVDBE SPE Extraction,

External Standard Quantitation

533

Drinking Water –

25 Compounds

WAX SPE Extraction,

Secondary Ion Confirmation,

Isotope Dilution Quantitation

A great example of collaboration applied in real world applications

EPA 8327
24 Compounds
Non-Potable Water

OTM-45

Source Air –

up to 50 Compounds

Sample collection and analysis references standard EPA methods and isotope dilution

Draft 1633

Non-Potable Water & Solids –

40 Compounds

WAX SPE Extraction

Secondary Ion Confirmation

Isotope Dilution Quantitation

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

EMERGING TECHNOLOGIES

TOP Assay
Total Organic Fluorine (TOF)
Non-Target Analysis (NTA)

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Total Oxidizable Precursors

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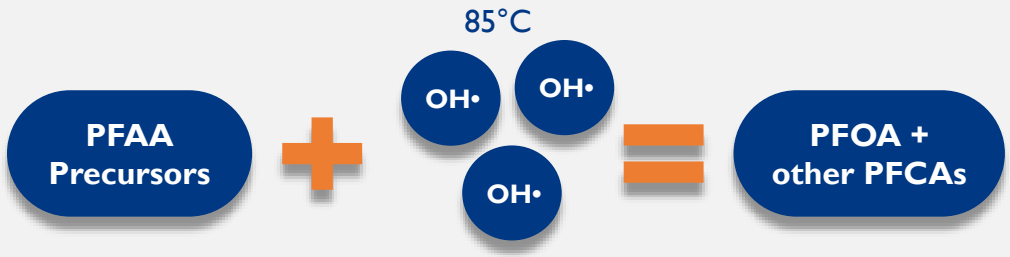
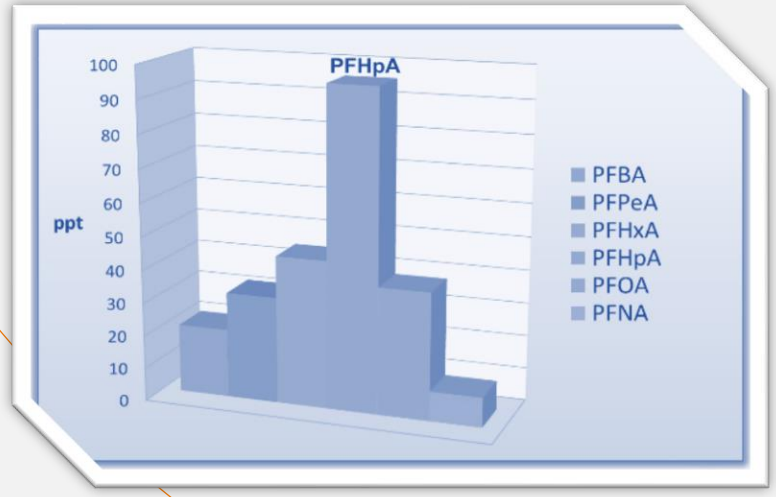
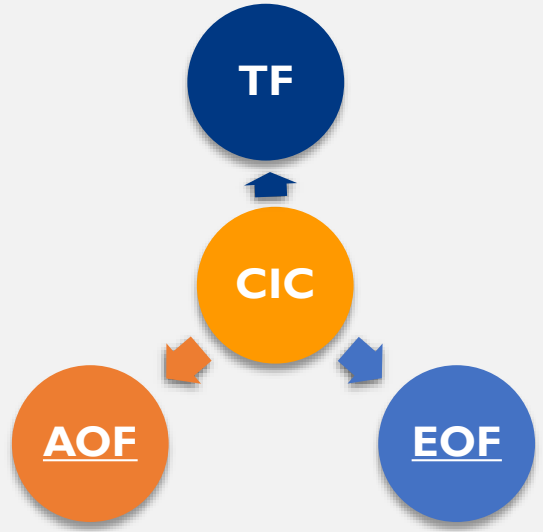
TOP Assay





TOP Conversion of 8:2 FTS

Total Organic Fluorine Analysis



CIC: Combustion Ion Chromatography

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

TOF & TOP Standardization Efforts

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HARVARD School of Engineering and Applied Sciences

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

ASTM

Improving Measurement Reliability of the PFAS TOP Assay

Final | 20 June 2019

SERDP DOD · EPA · DOE

ESTCP

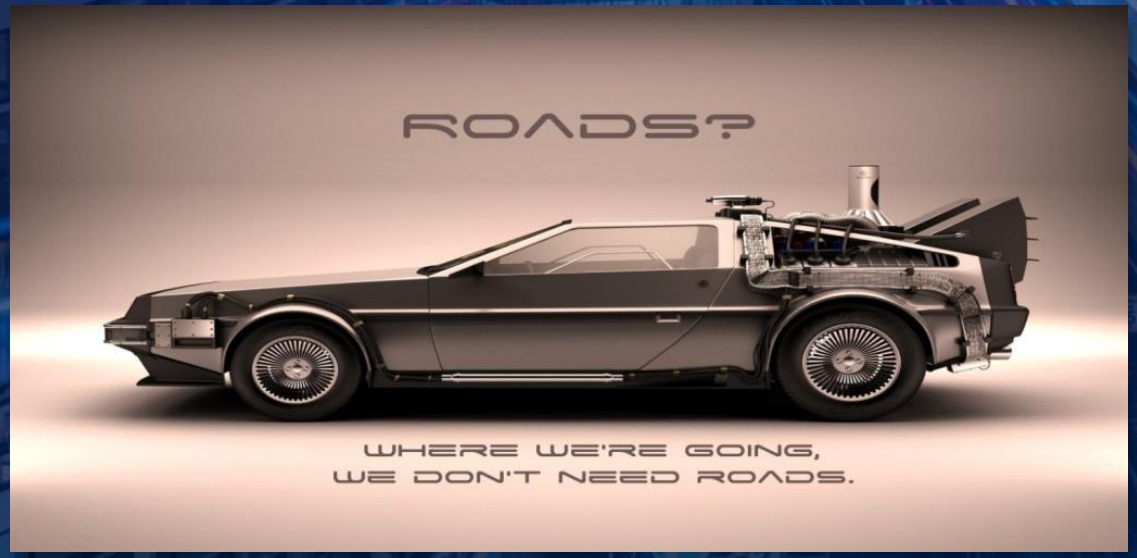
Non-Target Analysis

LC-QToF-MS

Liquid Chromatography

Quadrupole Time of Flight

Mass Spectrometry



Targeted Analysis

Suspect Screening Analysis

Non-Targeted Analysis

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Targeted PFAS

All Matrices – Up to 80 Analytes

Strengths: Selectivity

Sensitivity at ~1-5ppt

Can be used for risk assessment

Weaknesses: Limited list of compounds

TOP Assay

All Matrices – Oxidizable Precursors

Strengths: Sensitivity at ~1-5ppt

Specific to 'unknowns' with potential to convert to risk drivers

Weaknesses: Not specific

Does not complete a mass balance

Non-Target Analysis

All Matrices – Unknowns

Strengths: Ability to identify 'unknowns' with specificity

Ability to conduct novel compound identification

Weaknesses: Limited to current libraries

Limited quantitation

Total Organic Fluorine

All Matrices – Organic Fluorine

Strengths: Closest to a mass balance

Weaknesses: Sensitivity at ~1ppb

No selectivity

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

THE NEXT FRONTIER

Sub-ppt Reporting Limits

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Source Air

EPA OTM 45

Application: Semivolatile and particulate-bound PFAS from Source Air Emissions

Sample Collection: Based off of EPA Method 0010

Sample Preparation: Based off of 3542

Analysis: LCMSMS with Isotope Dilution based off of EPA Method 533

Ambient Air

Modified TO-13A / LCMSMS

Application: Semivolatile and particle-bound PFAS in Ambient Air

Sample Collection: PUF/XAD Cartridge based off of EPA Method TO-13A

Sample Preparation: Methanol Extraction based off of User-defined method

Analysis: User-defined method for PFAS by LCMSMS with Isotope Dilution

Vapor

Modified TO-17 / GCMSMS

Application: Volatile PFAS in Indoor Air and Soil Vapor

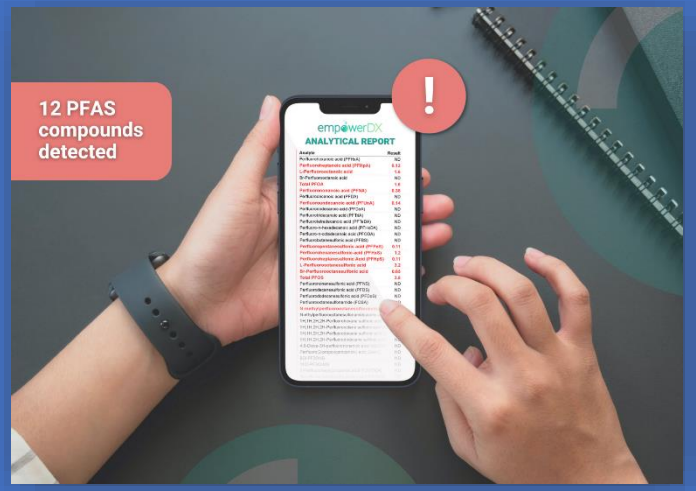
Sample Collection: Thermal Desorption Tube based off of EPA Method TO-17

Sample Preparation: Thermal Desorption based off of EPA Method TO-17

Analysis: User-defined method for PFAS by GCMSMS

https://www.epa.gov/sites/production/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf

PFAS in Human Serum / Blood



PFAS analysis from a single drop of blood, sampled by the end user

Ultra-Low Level PFAS

7500 LCMSMS

CA PFOA: 0.007ppt
CA PFOS: 1ppt
MN PFOS: 0.05ppt
EPA HA PFOA: 0.004 ppt
EPA HA PFOS: 0.02 ppt
EPA HA GenX: 10 ppt
EPA HA PFBS: 2000 ppt

What can it do?

- Direct injection valid for 70+ compounds
- 2ppt reporting limits with standard volumes of 250mLs or less
- Sub-ppt analysis in our sights

QUESTIONS?

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