Waters™

# PFAS Analysis | Building a Comprehensive Capability

**Khalid Ghaffar**
**Regional Business Development Manager**

# Perfluoro and Polyfluoro alkylated Substances (PFAS)

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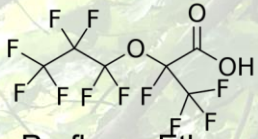
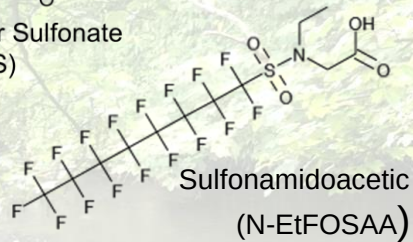
Perfluoro Carboxylic Acid (PFOA)


Perfluoro Sulfonic Acid (PFOS)

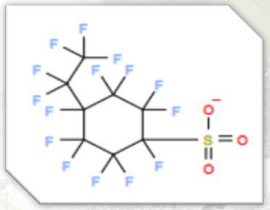

Perfluoro Ethers (GenX)


Perfluoro Telomer Sulfonate (6:2 FTS)


Sulfonamidoacetic acid (N-EtFOSAA)


Sulfonamides (FOSA)


Perfluoro Telomer Acid (FHEA or 6:2 FTA)


Cyclic (PFecHS)

- PFAS = Poly- or Per- fluorinated hydrocarbon chains with various functional groups on at least one end.
- First created in the 1930s with widespread applications
- Stable and persistent in the environment (POP) and Bio-accumulative
- Identified in environmental samples worldwide
- Most humans have PFAS in their blood

**Dangerous PFAS Chemicals Are in Your Food Packaging**

CR found 'forever chemicals' in bowls, bags, plates, and wrappers, even from some companies that say they've phased them out

***C&EN "Pesticide breakdown products found in hundreds of US streams***

*Extensive environmental survey of pesticides and their transformation products reveals potential for hidden toxicity"*

Sludge explained: What you need to know about "forever chemical" contamination on some Maine farms

By Annie Ropeik Maine

PUBLISHED 6:00 AM ET Mar. 08, 2022

*Some of the worst PFAS contamination in Maine is linked to sludge from paper mills that used the chemicals in protective coatings, but almost all biosolids tend to contain at least low levels of PFAS.*

PFAS contamination may be an emerging food safety issue *Food Business News (September 14, 2021)*

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CBS NEWS HEALTH WATCH

Raincoats, undies, school uniforms: Are your clothes dripping in "forever chemicals"?

healthwatch

BY HANNAH NORMAN

MARCH 30, 2023 /5:00 AM /KAISER HEALTH NEWS

HAWAII NEWS NOW

Bottled water distributed to hundreds after toxic ‘forever chemicals’ found in Kunia well

Published: Mar. 24, 2023

The Guardian

**Toxic ‘forever chemicals’ found in toilet paper around the World**

*Research finds waste flushed down toilets and sent to sewage plants probably responsible for significant source of water pollution*

CBS NEWS

Eating one fish from U.S. lakes or rivers likened to drinking month's worth of contaminated water

JANUARY 17, 2023 / 8:04 AM / AFP

# Why do we care?

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Exposure to PFAS can lead to adverse health outcomes in humans

- Increased cholesterol levels
- Decreased vaccine response in children
- Changes in liver enzymes
- Increased risk of high blood pressure or pre-eclampsia in pregnant women
- Small decreases in infant birth weights
- Increased risk of kidney or testicular cancer

cancer (for PFOA), and thyroid hormone disruption (for PFOS, PFBS).

Harvard University, School of Public Health
"PFAS exposure linked with worse COVID-19 outcomes"

## People can be exposed through water, air, soil, packaging, food, and more





# Testing for PFAS requires a comprehensive analysis solution

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1

## Sample prep

- SPE cartridges
- Sample preparation apparatus (manual vacuum manifold or an automated system)
- Nitrogen sample evaporator

2

## Instruments

- Ultra-Performance Liquid Chromatography (UPLC)
- Tandem quadrupole mass spectrometer (MS/MS)
- PFAS hardware kit
- Analytical columns

3

## Informatics

- Instrument control and acquisition software
- Data processing and reporting
- Output to LIMS system or similar database
- Local quality system

4

## CRM and PT

- Certified reference materials (CRM)
- Proficiency testing (PT) program for analysts

# PFAS Testing Options – Total Solution for Successful Applications

Waters™

*Consumables + Instrument + Methods + Software + Customer Education + Services*

Xevo™ TQ-S micro

**SPE enrichment prior to analysis.** Sample prep allows for use of mid-level sensitivity for MS

Xevo™ TQ-XS

**Large volume/direct inject applications** and SPE enrichment methods. Limited sample volume situations (e.g., serum). Applications requiring trace level detection limits

Xevo™ TQ ABSOLUTE

**Achieve ultra-lower limits of quantitation** to meet regulatory requirements with the most sensitive LC-MS/MS on the market

## Chemistry

**PFAS Kit** with isolator column, analytical column, PEEK tubing, cartridges, standards, and more

**Oasis WAX** for PFAS is a quality controlled SPE

**Sep-Pak PS2**
6 cc Cartridge, for Method 537.1

Sep-Pak®

## Data Management

MassLynx™

waters_connect™

# Getting Ready for Analysis: LC modifications for PFAS

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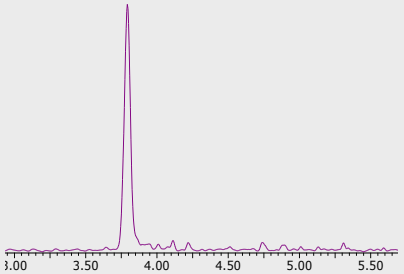
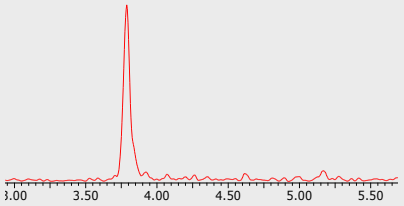
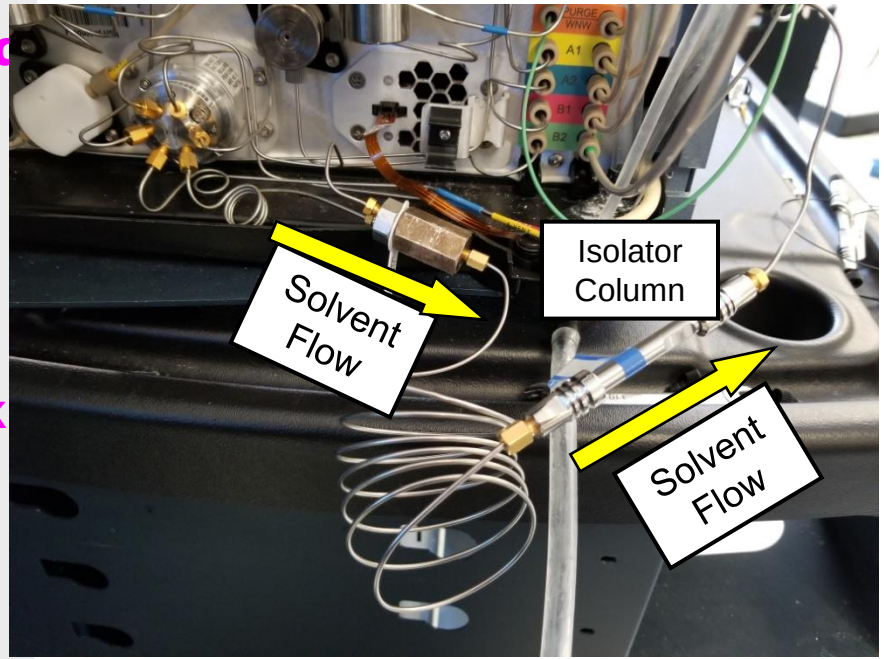
## No LC Modifications

**PFOA standard**




**PFOA in blank**

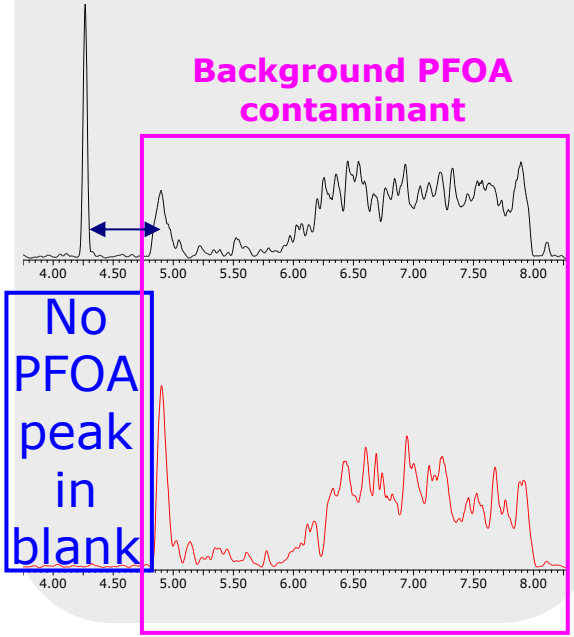



## PFAS Kit Installed

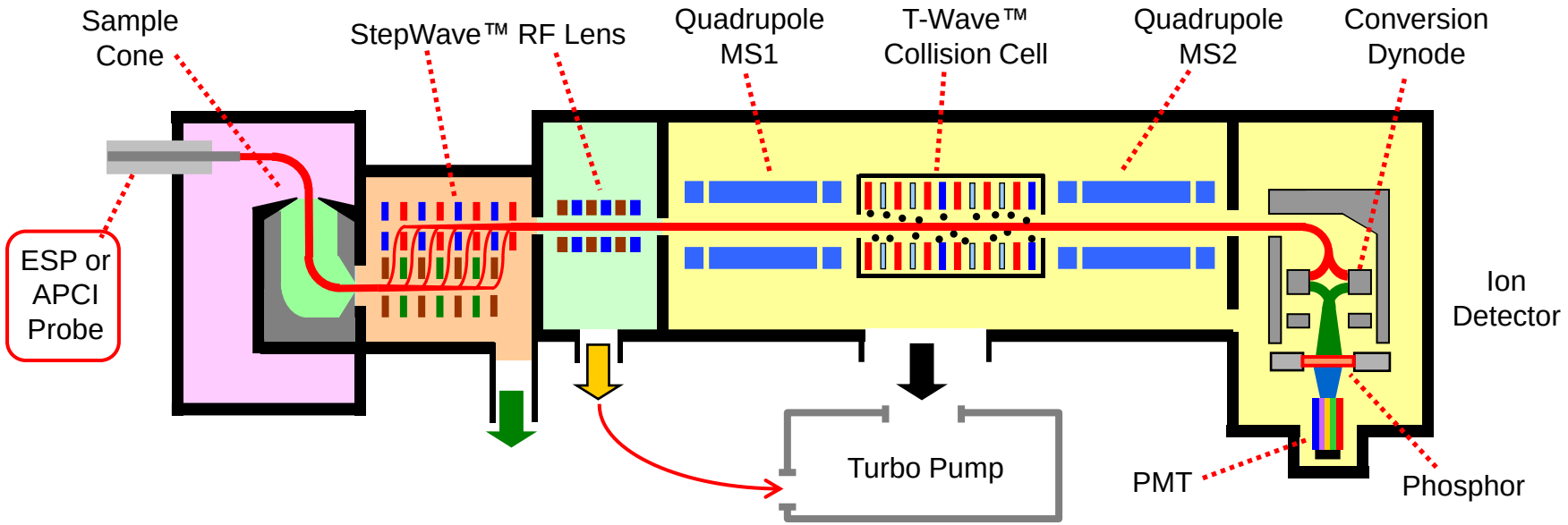
**PFOA standard**

**Background PFOA contaminant**



# What is a Tandem Quadrupole MS?

- Tandem Quadrupoles consist of 2 mass analysers(quads) and a collision cell, enabling **more selective** analyses to be performed compared to a single quadrupole or other non MS detection mode.
- Their selectivity has made them the industry standard for MS based quantitation.



# LC-MS/MS has been selected by regulators for PFAS for the technology's selectivity and sensitivity

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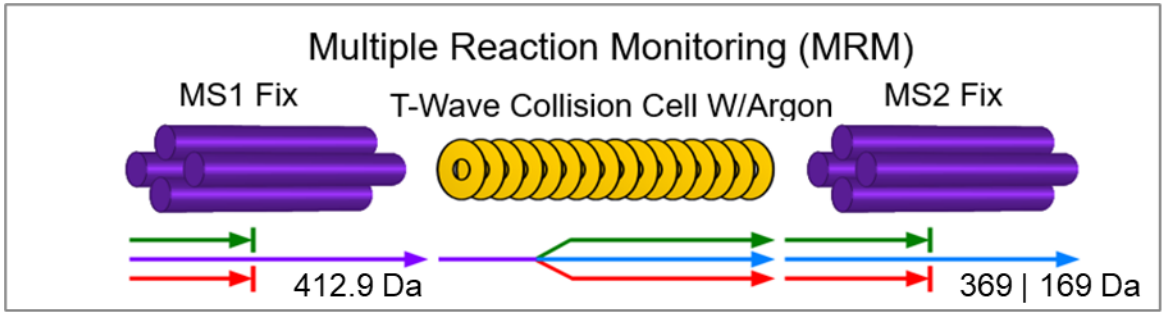
| | |
|---|---|
| High selectivity | Reduce or eliminate matrix interferences |
| High sensitivity | Trace levels - low reporting limits |
| Quantitative accuracy | Reproducibility, stability ,dynamic range and accurate quantitation of targets at low levels in matrix |
| Robustness | Complex sample matrices, reduced sample clean-up |




Waters ACQUITY™ Premier UPLC™ + Xevo™ TQ Absolute MS

Waters ACQUITY UPLC + Xevo TQ-S micro MS

# Targeted PFAS Environmental Methods Using LC-MS/MS

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| | ASTM 7979 / 8421 | ASTM 7968 / 8535 | EPA 533 | EPA 537.1 | EPA 1633 | EPA 8327 | EU 2020/2184 | EU 2022/2388 | ISO 25101 | ISO 21675 |
|---|---|---|---|---|---|---|---|---|---|---|
| Matrix | SW GW WW | Soils | DW | DW | Aqueous (not DW), Soil, Solids, Fish Tissue | Non potable water (SW, GW, WW) | DW | Food | DW GW SW | DW GW SW WW < 2 g/L solid particulate matter |
| Prep | Dilute, filter | Dilute, filter | Oasis WAX | Sep-Pak PS2 | Oasis WAX GCB | Dilute, filter | Direct Inject | Oasis WAX | Oasis WAX | Oasis WAX |
| Waters Collateral | App Note 720006329 | App Note 720006764 | App Note 720006808 | App Note 720006695 | App Note 720008117 | App Note 720006329 | App Note 720007413 | App Note 720007482 | App Note 720006471 | App Note 720006471 |
| Column | CSH Phenyl Hexyl 2.1x100mm | CSH Phenyl Hexyl 2.1x100mm | BEH C18 2.1x100mm | BEH C18 2.1x100mm | BEH C18 2.1x50mm | CSH Phenyl Hexyl 2.1x100mm | ACQUITY Premier BEH Shield RP18 Column | BEH C18 2.1x100mm | BEH C18 2.1x100mm | BEH C18 2.1x100mm |
| Minimum Instrument | TQ Absolute | TQ Absolute | TQ-S micro | TQ-S micro | TQ-S micro | TQ Absolute | TQ Absolute | TQ Absolute | TQ-S micro | TQ-S micro |
| Number of compounds | 24 / 44 | 24 / 44 | 25 | 18 | 40 | 24 | 20 | 30 | 2 | 30 |

# On Apr 10, 2024 US EPA finalized historic regulations to limit PFAS in drinking water

**PFAS National Primary Drinking Water Regulation** overview:

- An enforceable 4 parts per trillion (ppt) limit on PFOA and PFOS in drinking water
- A non-enforceable maximum contaminant level goal for PFOA and PFOS at zero
- A limit of 10 ppt on three other categories of PFAS: PFNA, PFHxS, and “GenX” chemicals
- A hazard index for mixtures of 2+ of the above PFAS, plus PFBS
- Public Water Systems (PWS) must complete initial monitoring by 2027 and implement solutions by 2029. From 2027+, they will be required to complete ongoing compliance monitoring

Announcement of the new regulations here: https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

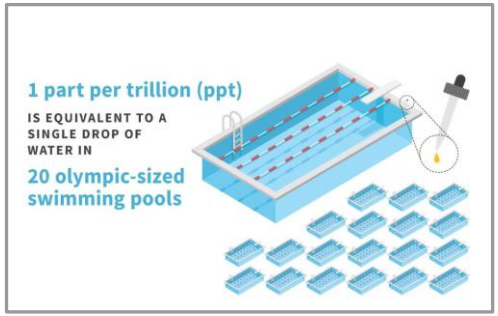
# Putting **ng/L** into perspective

Nanograms of compound per liter of solution (aka part-per-trillion (ppt))

- **One** part per 1,000,000,000,000 ($10^{12}$) parts

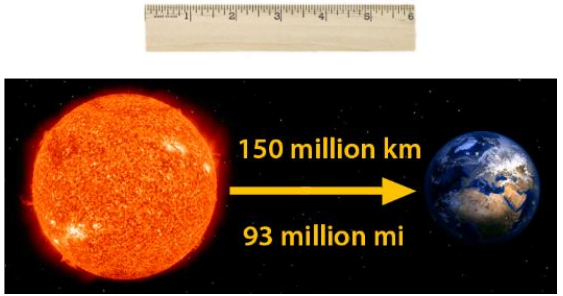
## Some ways to visualize one ng/L ….

1 drop of water in 20 Olympic-sized swimming pools




One second of time in approximately 31,700 years

Traveling 6 inches out of a 93-million-mile journey to the sun[1]




1. The earth is 93 million miles (avg.) from the sun

# Analytical Requirements: Drinking Water Methods Required to Support Testing

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**Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)**

| | |
|---|---|
| HFPO-DA | PFNA |
| NEtFOSAA | PFOS |
| NMeFOSAA | PFOA |
| PFBS | PFTA |
| PFDA | PFTrDA |
| PFDoA | PFUnA |
| PFHpA | 11Cl-PF3OUdS |
| PFHxS | 9Cl-PF3ONS |
| PFHxA | ADONA |


SepPak PS2 cartridge

**Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry**

| | |
|---|---|
| 11Cl-PF3OUdS | 4:2FTS |
| 9Cl-PF3ONS | PFHxS |
| ADONA | PFHxA |
| HFPO-DA | PFMPA |
| NFDHA | PFMBA |
| PFBA | PFNA |
| PFBS | 6:2FTS |
| 8:2FTS | PFOS |
| PFDA | PFOA |
| PFDoA | PFPeA |
| PFEESA | PFPeS |
| PFHpS | PFUnA |
| PFHpA | |


Oasis WAX cartridge

537.1: Waters App Note 720006695

533: Waters App Note 720006808

# Targeted Analysis with Enhanced Sensitivity

Xevo TQ Absolute

# Xevo TQ Absolute - Key Sustainability Benefits

*Harness Absolute Power*

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XEVO™ TQ ABSOLUTE

- Up to **15x more sensitivity** for challenging negative ionizing compounds due to detector design improvements. Xevo TQ Absolute **Signal:Noise >5 million to one** for reserpine and chloramphenicol compared to **Agilent's 6495D, 4 million to one.**
- Uses **45% less bench space** than the leading competitor
- Uses **~50% less power & gas** and generate **~50% less heat** than the leading competitor
- Save up to **50% on data review** time using waters_connect for Quantitation
- **MyGreenLab certification**: Xevo TQ Absolute scores well on a range of sustainability criteria including manufacturing, shipping, product and packaging content, end of life and energy consumption.
- **Environmental Impact Factor**: Xevo TQ Absolute consumes **one third of the in-use energy** compared to **Agilent 6495D** and the **overall ACT label* rating score was half that of the Agilent 6495D**.

*The **ACT Environmental Impact Factor Label** was designed to address the need of both scientists and procurement specialists for clear, third-party verified information about the environmental impact of laboratory products.

ACT. The Environmental Impact Factor Label — US

**Waters Xevo TQ Absolute Triple Quadrupole Mass Spectrometer**

Wexford, Ireland
**SKU** 176005117

Environmental Impact Scale
1 — Decreasing Environmental Impact — 10

| | |
|---|---|
| **Manufacturing** | |
| Manufacturing Impact Reduction | 1.0 |
| Renewable Energy Use | Yes |
| Responsible Chemical Management | 1.0 |
| Shipping Impact | 7.9 |
| Product Content | 5.0 |
| Packaging Content | 5.0 |
| **User Impact** | |
| Energy Consumption (kWh/day) | 19.3 |
| Water Consumption (gallons/day) | N/A |
| Product Lifetime | 3.0 |
| **End of Life** | |
| Packaging | 5.2 |
| Product | 6.5 |
| **Innovation** | |
| Innovative Practices | -1.0 |
| **Environmental Impact Factor:** | **52.9** |
| Label Valid Through: | December 2025 |

act.mygreenlab.org

# USEPA Working for Water Protection and Reducing Human Exposure

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**June 2023**

## EPA Announces New Drinking Water Health Advisories for PFAS Chemicals, $1 Billion in Bipartisan Infrastructure Law Funding to Strengthen Health Protections

| Compound | US EPA Health Advisory Level (ng/L) | UCMR 5 Minimum Reporting Level (ng/L) |
|---|---|---|
| PFOA | 0.004 (interim) | 4 |
| PFOS | 0.02 (interim) | 4 |
| PFBS | 2000 | 3 |
| GenX | 10 | 5 |

# PFAS Lab Background: Found Everywhere, In Everything

- PFAS from fluoropolymers and coating are ubiquitous in common sampling and analytical equipment and can easily contaminate solvents and reagents
- Laboratory contamination is common and near impossible to eliminate
  - Perfluorobutane sulfonic acid and its potassium salt (PFBS) extremely common
- Such contamination leads to reporting of false positives and/or higher reporting limits due to elevated background

**Essential mitigation options:**

- Avoid all products likely to contain fluoropolymers – e.g. vials with Teflon seals. Us HDPE, polypropylene or polyethylene materials
- Minimize risks from contaminated dust and air
- Screen all analytical consumables, solvents and reagents including water purifying systems
- Carry out extensive use of procedural blanks from sample storage
- Traceability systems for the consumables used in the laboratory
- Training !
- Modifications to the LC system fitting a PFAS Installation Kit

# Sensitivity – Controlling the Background in a Routine Laboratory

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[ WHITE PAPER ]

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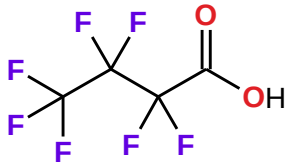
Best practices for monitoring PFAS contamination in a routine shared-space commercial laboratory

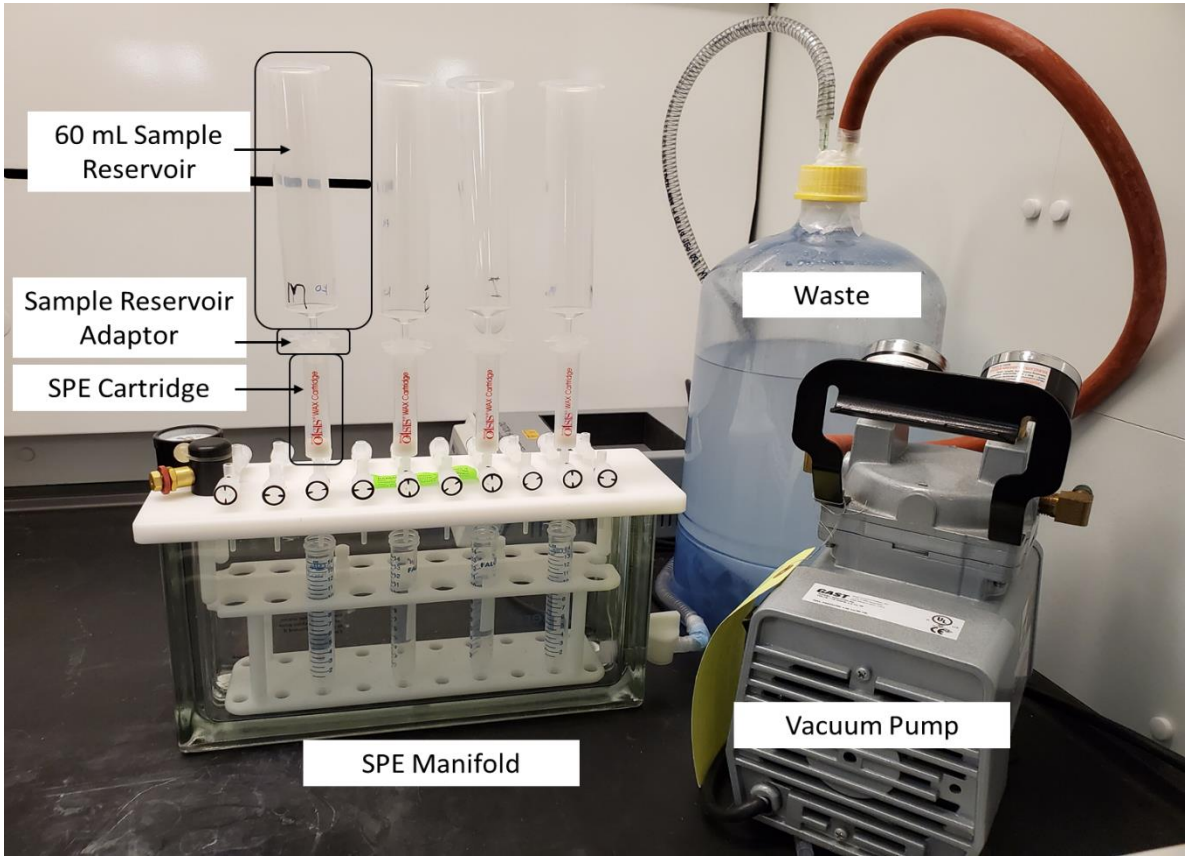
Nicola Dreolin, Henry Foddy, Kari Organtini, Stuart Adams, Ken Rosnack, Peter Hancock
Waters Corporation, Milford, MA, USA and Waters Corporation, Wilmslow, UK.

Link to White Paper




| Common Sources of PFAS Contamination to Avoid | |
|---|---|
| External Sources | Direct Sources |
| Clothing/Lab coats treated with waterproofing materials | PTFE (Teflon) containers lined caps, and tubing |
| Waterproof papers, notebooks, binders | Aluminum foil |
| Cosmetics and personal care products (sanitizers, lotions, etc.) | Pipette tips branded as being "low retention" |
| Teflon tape | Permanent markers |
| Latex gloves | Vacuum grease |
| Antifog eyewear wipes and sprays | Glass transfer pipettes |
| Soaps and dishwashing detergents | PTFE filters |

# What about SPE + Xevo TQ Absolute for EPA HALs?

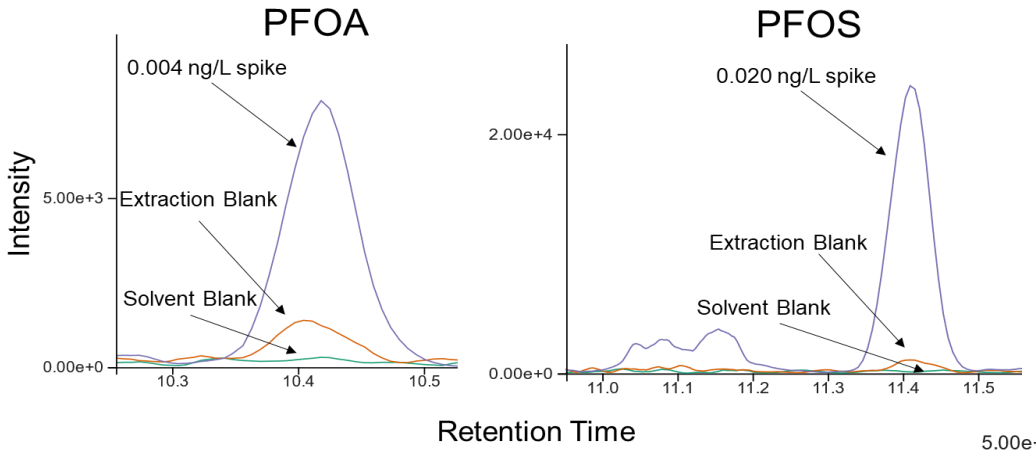



- Enrichment needed
  - *A 500-fold sample enrichment was performed using Oasis™ WAX for PFAS SPE cartridges*

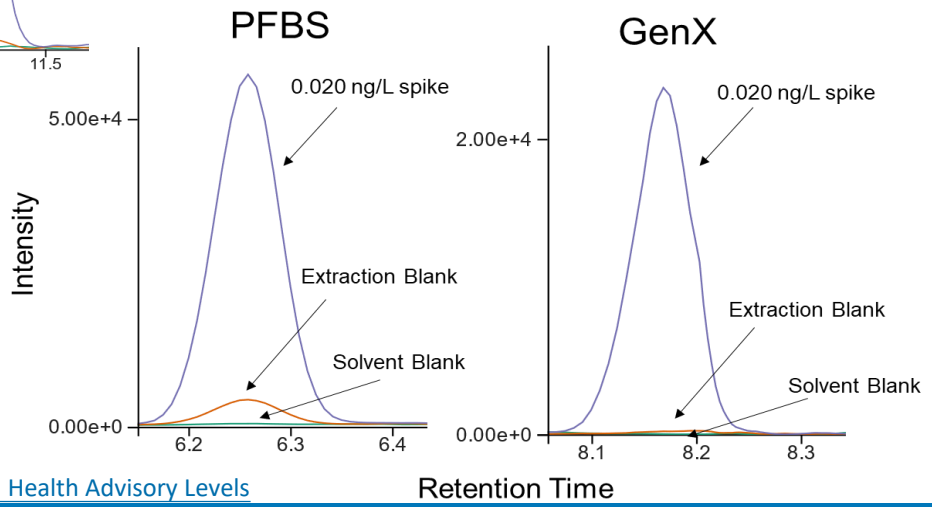
  250 ml to final volume 0.5 ml
- Highly Sensitive MS/MS
  - *Enhanced negative ion mode sensitivity of the Xevo TQ Absolute*
- Blanks will be challenging!
  - *Background PFAS contamination from routine materials in laboratories must be highly controlled*

*Best practices for monitoring PFAS contamination in a routine shared-space commercial laboratory*

# Sensitivity - EPA HALs Testing




- Critical assessment of the background of the laboratory vs the response from the spiked samples
- Blanks response <30% of the method LOQ




- It may be impossible to completely eliminate contamination during sample preparation but <u>it can be controlled to an acceptable amount</u>.

App Note: Ultra Trace Detection of PFAS in Drinking Water to Meet New USEPA Interim Health Advisory Levels

# Limit of Quantitation at 0.001 ng/l (ppt)

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| Compound | Labratory 1 LOQ ng/L | Labratory 1 S:N of LOQ | Labratory 2 LOQ ng/L | Labratory 2 S:N of LOQ | EPA HAL ng/L | Interim minimum reporting level ng/L |
|---|---|---|---|---|---|---|
| PFOA | 0.001 | 10 | 0.001 | 10 | 0.004 (interim) | 4 |
| PFOS | 0.001 | 12 | 0.001 | 27 | 0.02 (interim) | 4 |
| PFBS | 0.0009 | 24 | 0.002 | 27 | 2,000 | 3 |
| HFPO-DA (GenX) | 0.004 | 21 | 0.004 | 10 | 10 | 5 |

Limit of quantitation (LOQ) and signal:noise (S:N) for each PFAS determined in both laboratories using two different TQ Absolute systems

# EPA method 1633 Available for Non-Drinking Water Matrices:

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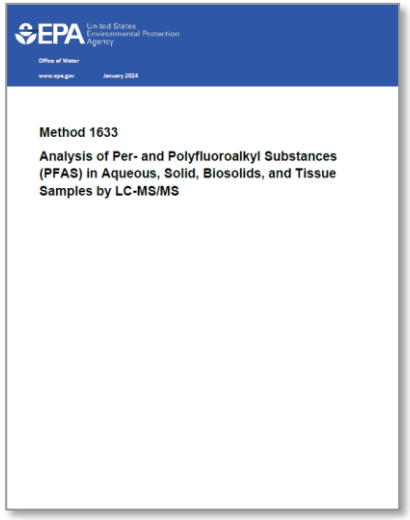



Newly finalized method (January 2024) to test for **40 PFAS compounds** in **wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue**

Created by the **US EPA's Office of Water**, partnership with the **US Department of Defense**'s Strategic Environmental Research and Development Program (SERDP)

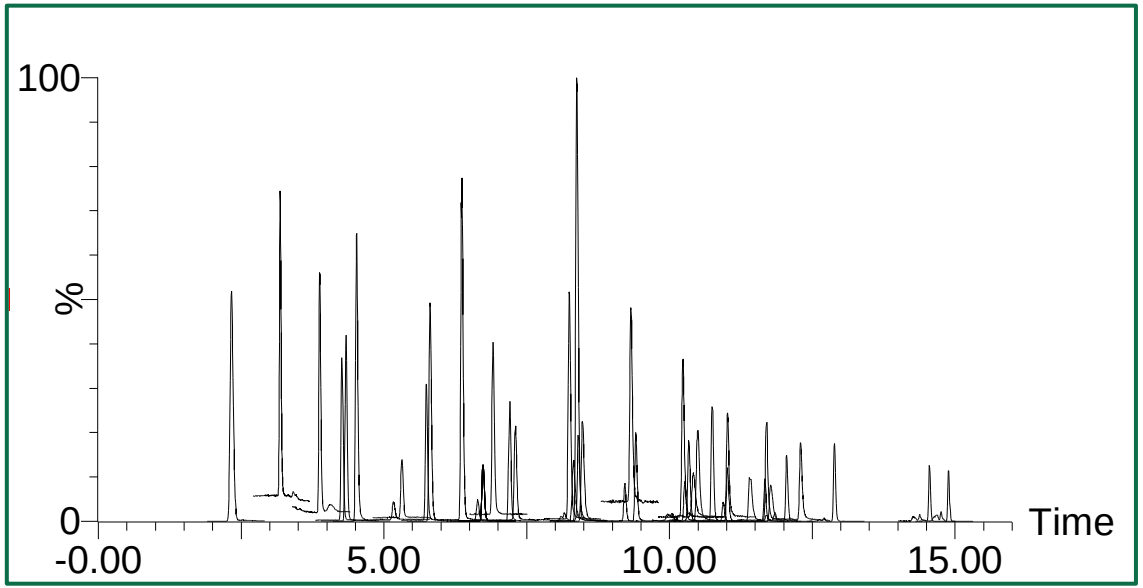
Validated through a **multi-laboratory study** to finalize method and add performance criteria

Intended to be used for:

- Clean Water Act Compliance (wastewater discharge permits – NPDES)
- Superfund sites
- Remediation and investigation programs (including for DoD installations)

Source: US Environmental Protection Agency

# Demonstration of Performance for 1633

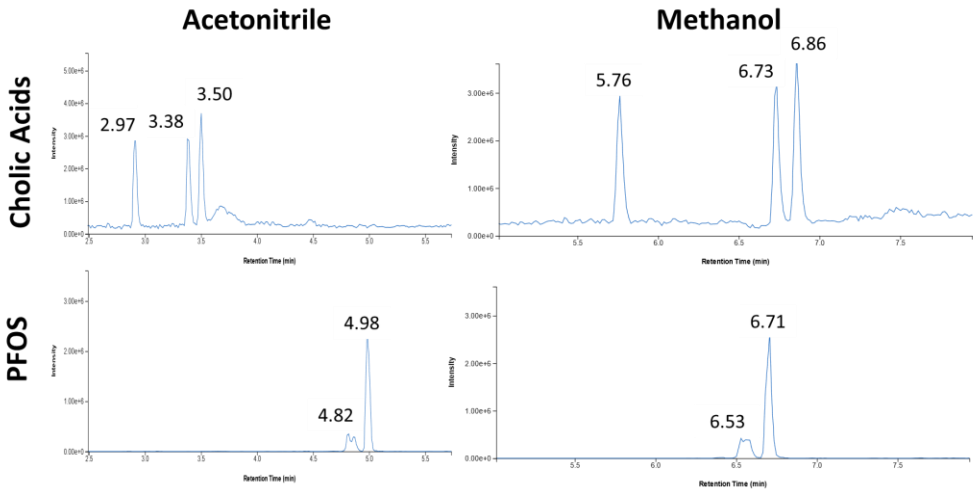



**46 native PFAS** covering both EPA 1633 and ASTM 8421 lists

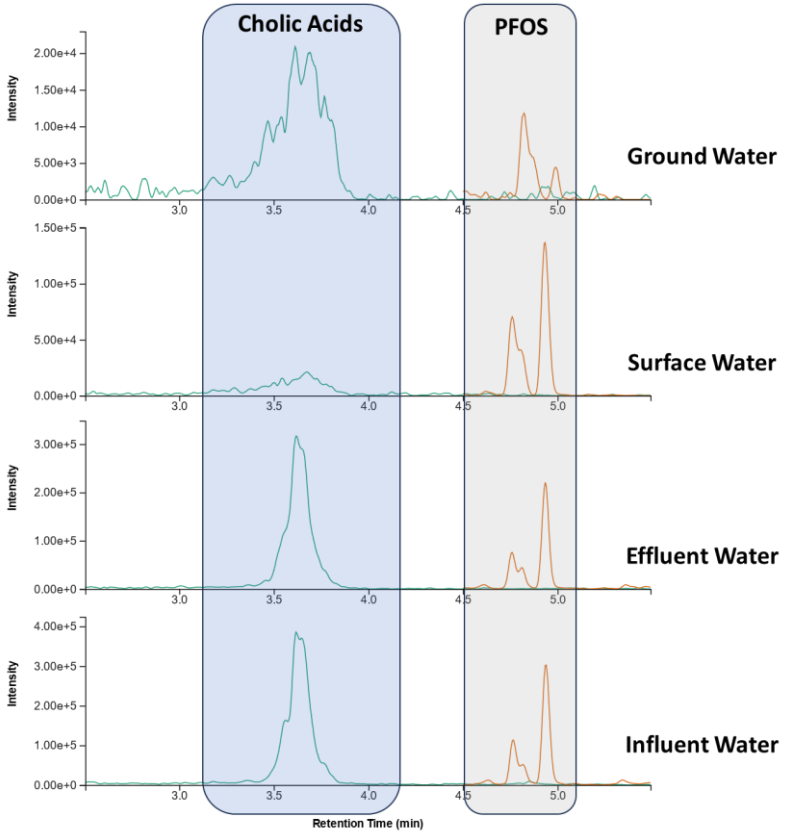
- Minimum Levels on the TQ Absolute are 20x lower than those reported in the EPA 1633 draft methods (on the Xevo TQ-S micro)
- S:N values at the minimum level were all ≥ 3 as required by EPA 1633

All initial calibration requirements in EPA 1633 are easily met on the Xevo TQ Absolute

# LC Gradient Optimization




- Cholic acids (TDCA, TCDCA, TUDCA) can cause interference with PFOS in the mass spectrometer due to the similarity in parent and fragment masses
- EPA 1633 requires a 1 min resolution of the cholic acids from PFOS
- Methanol is typically used for PFAS methods, but does not resolve cholic acids from PFOS
- Acetonitrile provides more than 1 minute separation of cholic acids from all PFOS isomers



# PFAS analysis by EPA 1633 – results from LC-MS/MS

Certified reference material (CRM) validation

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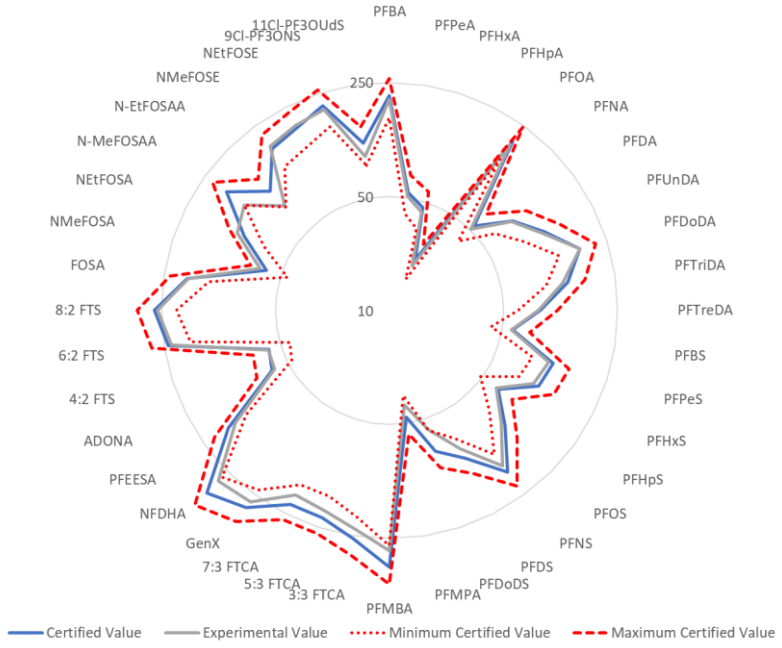
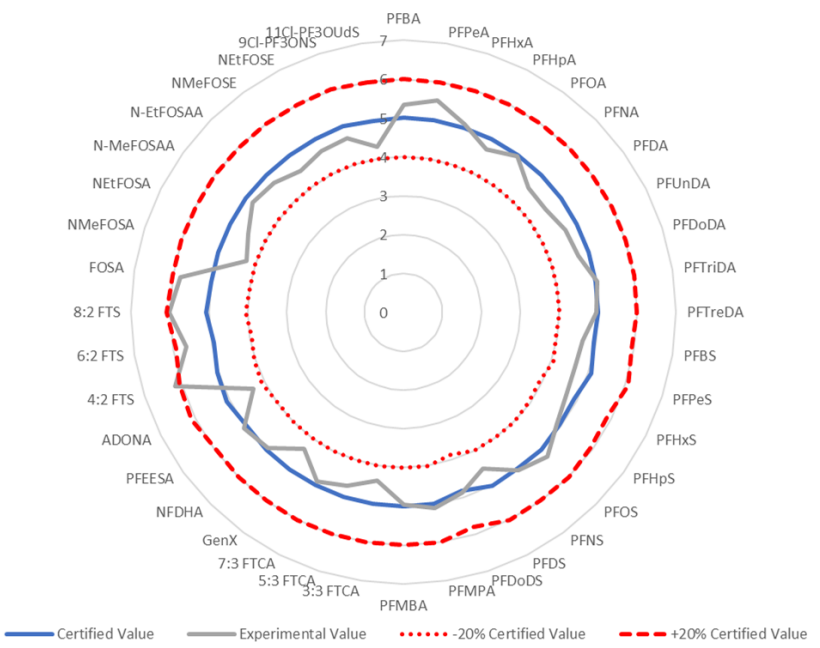
## PFAS in **wastewater** CRM




Mean trueness of 92%
Trueness range of 73 – 112%

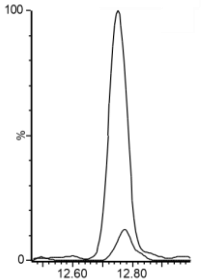
## PFAS in **soil** CRM

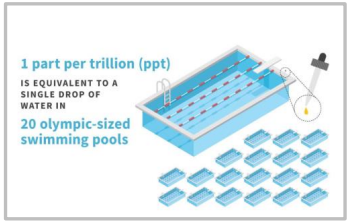


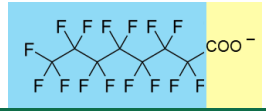

Mean trueness of 97%
Trueness range of 85 – 120%

# Solid-phase extraction (SPE) - why we use it for PFAS analysis

- Regulatory compliance
  - US EPA 533, 537.1, and 1633 require solid phase extraction clean up steps
  - Reproducibility across laboratories running same method
- Clean up from complex matrices
  - Environmental waters, solids, biosolids, and other samples contain interferences
  - Reduce ion suppression and background
- Concentration of PFAS
  - Measuring at low levels (ng/L)
  - Increase limits of detection
- Selectivity in extraction
  - Use of WAX sorbent more specific to PFAS



# PFAS impacts to our Food Supply

Waters™

The Guardian

## Thousands of toxins from food packaging found in humans – research

**Metals and PFAS linked to serious health issues are among compounds found, highlighting need for further scrutiny**

Research found that among the worst offenders is plastic, a material that is largely unregulated and can contain thousands of chemicals. Photograph: Aleaimage/Getty Images/iStockphoto

*Tom Perkins*
*Fri 27 Sep 2024 07.00 EDT*

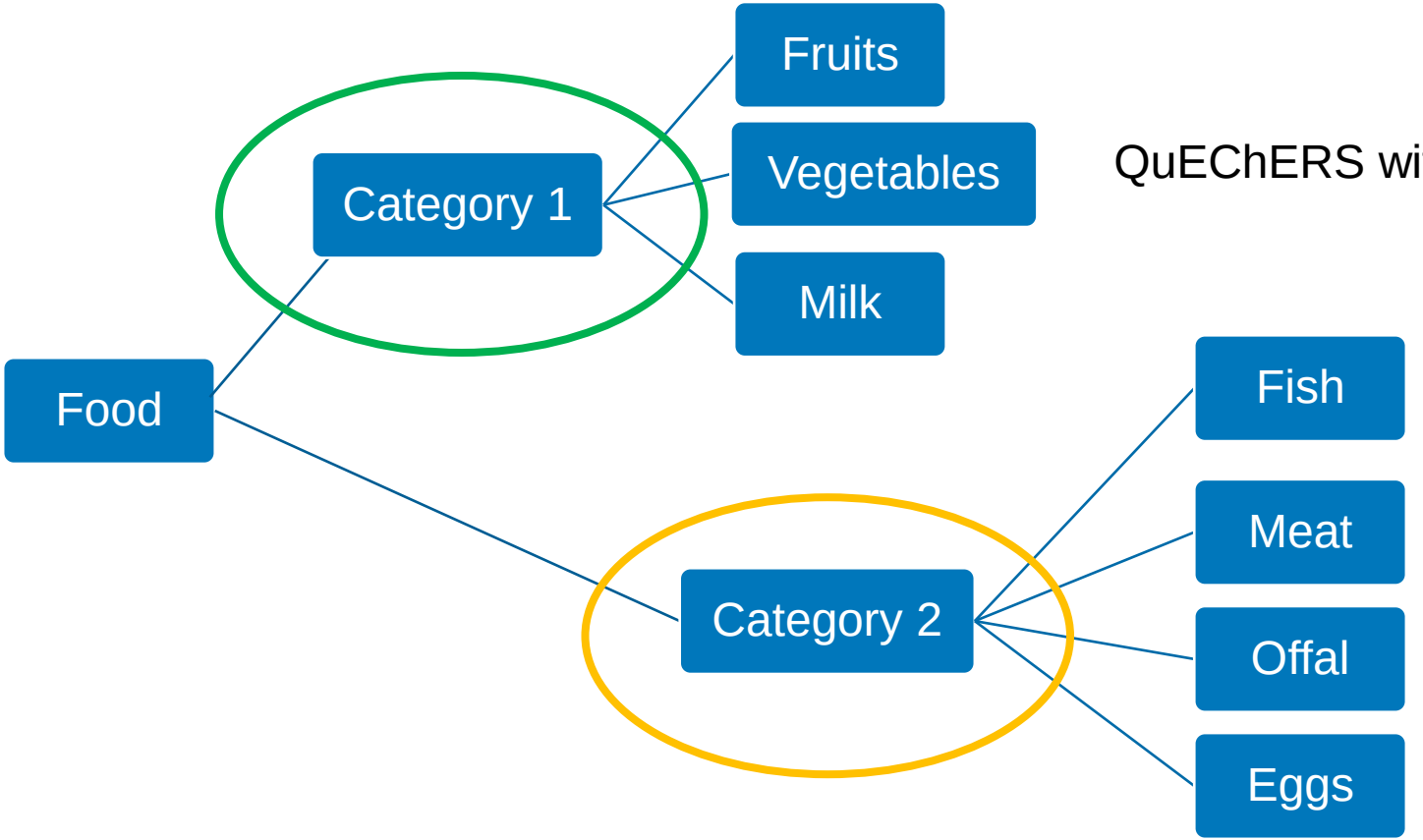
## 'Forever Chemicals' Are Found in Some Milk, Including Organic

A Consumer Reports investigation highlights gaps in how the U.S. tests and regulates PFAS in food

PHOTO ILLUSTRATION: CHRIS GRIGGS/CONSUMER REPORTS, GETTY IMAGES

By Lauren Kirchner · Data visualizations by Andy Bergmann
May 2, 2024

# Sample Preparation Protocols for Food




QuEChERS with dSPE

Alkaline digestion in methanol with WAX SPE

(FOSA is not recovered well using the WAX procedure)

# Produce and Milk

| Produce | Commodity Class |
|---|---|
| Romaine Lettuce | High Water |
| Russet Potato | High Starch |
| Whole Carrot | Low Water |
| Strawberry | High Sugar |
| Cranberry | High acid and sugar |

Produce: Waters App Note 720007333

Milk App Note coming soon

# QuEChERS Method for Produce and Milk

Waters™

5 g produce

+ 5 mL water

Spike Internal Standard (surrogate)

+ 10 mL ACN

+150 µL Formic Acid

Shake

Add AOAC Quechers Salts (6g $MgSO_4$, 1.5g Sodium Acetate)

Shake

Centrifuge

5 mL supernatant to 15 mL dSPE tube (900mg $MgSO_4$, 300mg PSA)

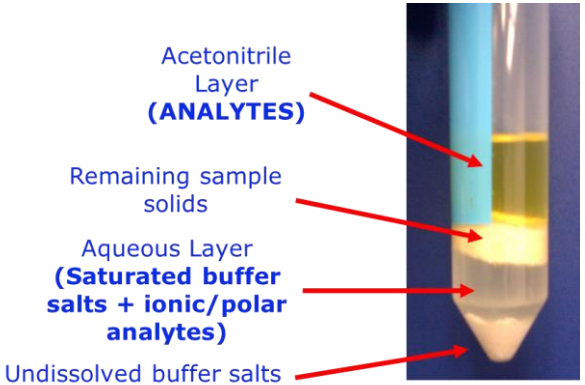
Shake

Centrifuge

Dilute 1:1 in 2mM ammonium acetate

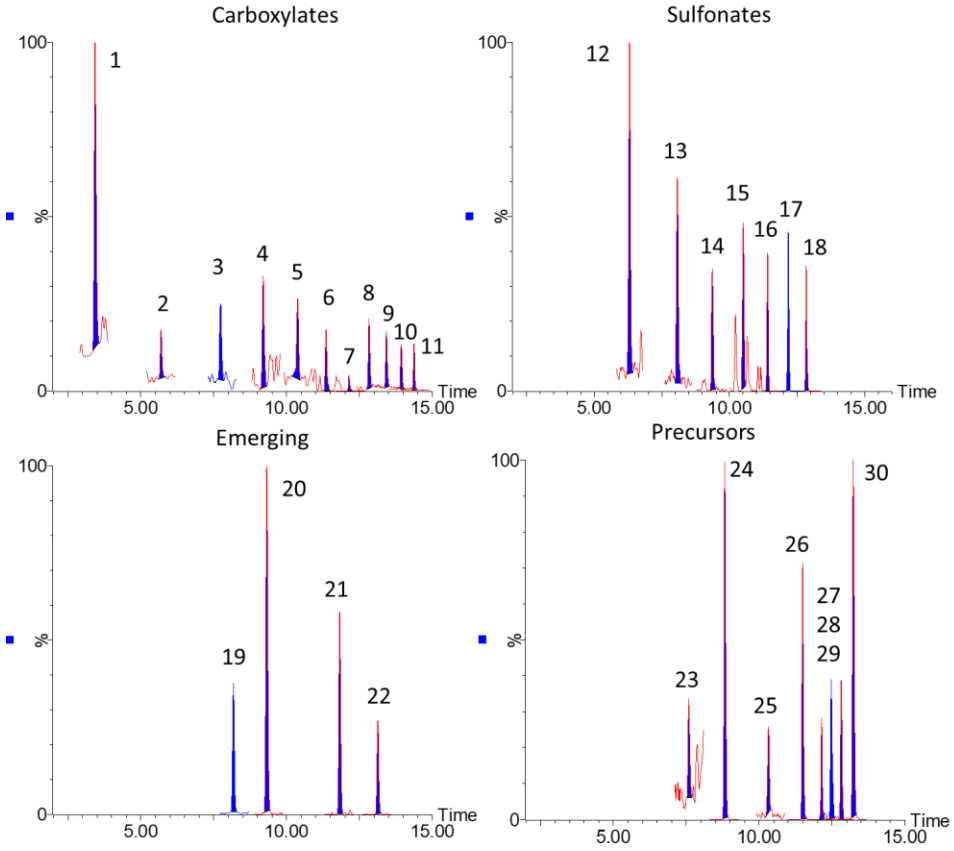
Spike Internal Standard

Inject



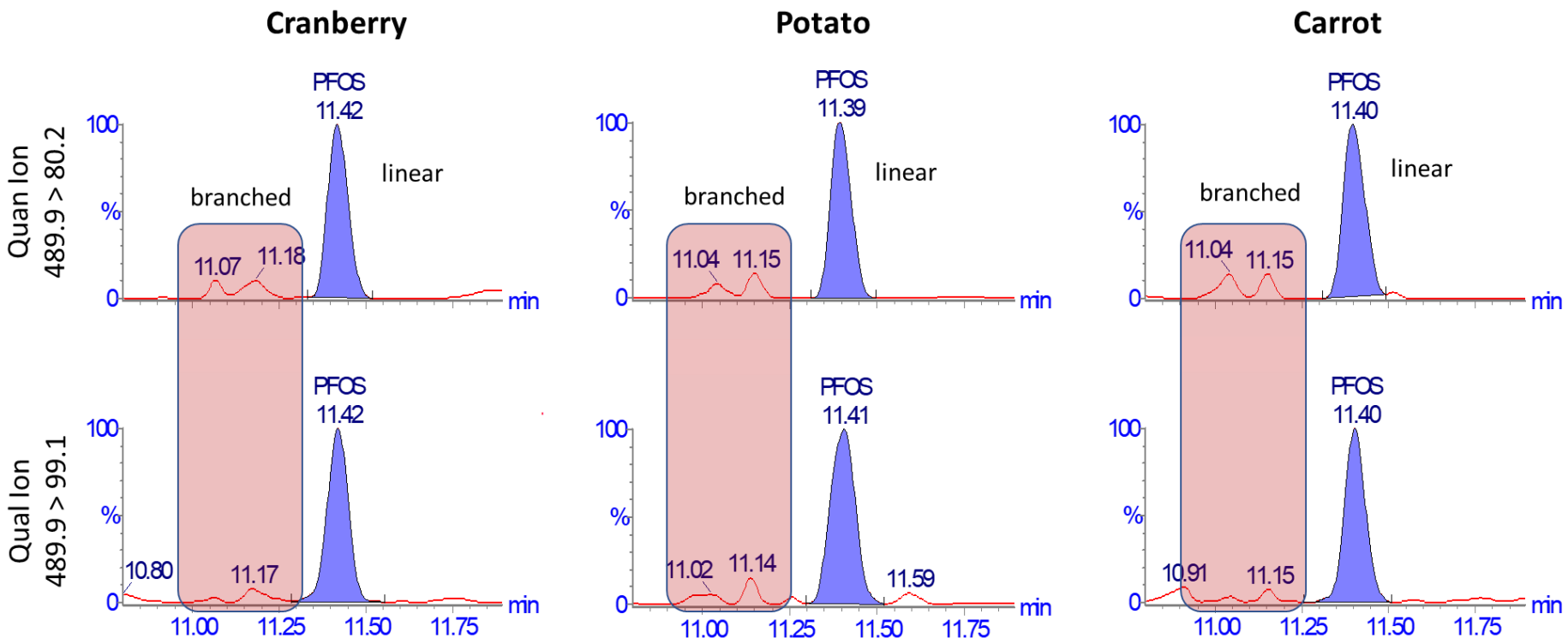

**Quick, Easy, Cheap, Effective, Rugged, Safe = QuEChERS**

# Extracted Ion Chromatograms




ACQUITY UPLC™ I-Class with Xevo™ TQ-XS

# Linear and Branched Isomers for Complete Assessment



# PFAS Quantitation in Milk


1. 5 g produce
   Spike Surrogates at 1 ng/g (MPFAC-24ES + M3HFPO-DA)
   Add 5 mL of water
2. Add 10 mL Acetonitrile + 150 µL Formic Acid
   Shake for 1 minute
3. Add AOAC QuEChERS Salts (6 g MgSO4, 1.5 g Sodium Acetate)
   Shake 5 minutes
   Centrifuge 5 minutes at 4,000 rpm
4. Transfer 5 mL supernatant to 15 mL dSPE tube (900 mg $MgSO_4$, 300 mg PSA)
   Shake 5 minutes
   Centrifuge 5 minutes at 4,000 rpm
5. Dilute 1:1 in 2mM ammonium acetate
   Centrifuge 5 minutes at 4,000 rpm
   Spike Internal Standard equivalent to 1 ng/g (MPFAC-C-IS)

Milk App Note 720007687

# Extracted Ion Chromatograms 0.1 ng/g each PFAS

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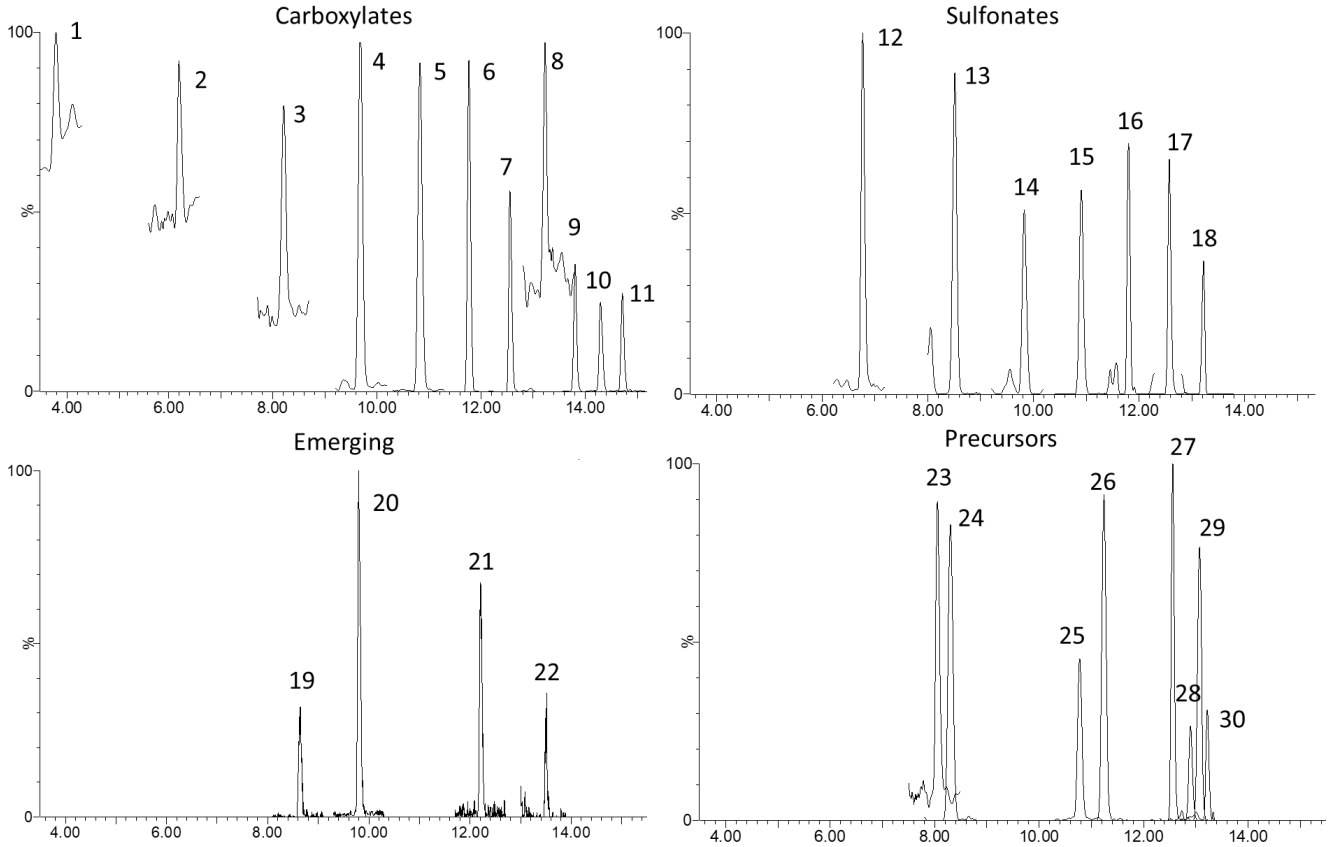


# Matrix Matching or Isotope Dilution?

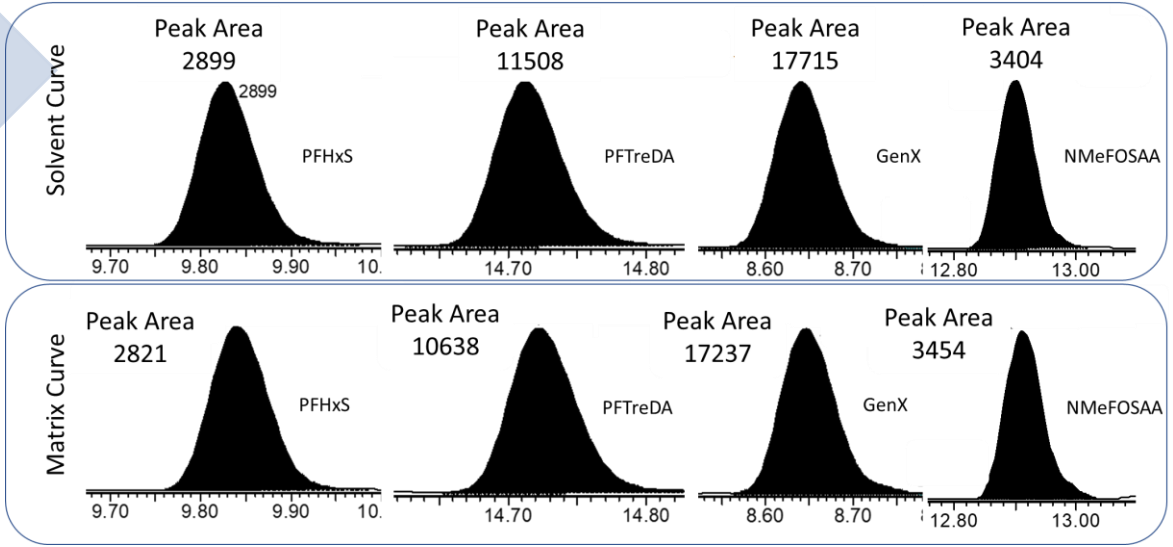
Waters™

**Matrix Matched Curve**

- Use only two internal standards
  - $^{13}C_8$-PFOA and $^{13}C_8$-PFOS
- Makes an estimate for recovery
- Calibration is performed in similar conditions as sample

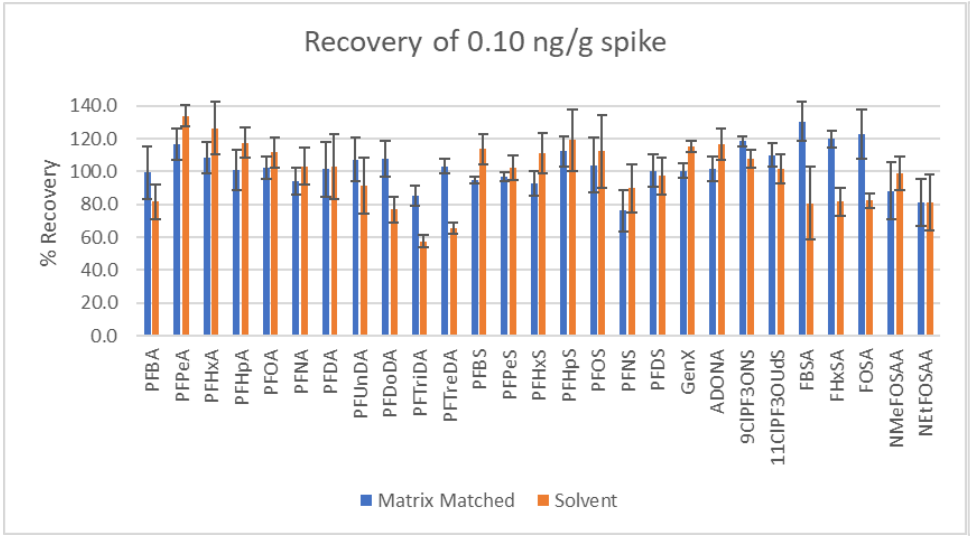
**Solvent Curve**

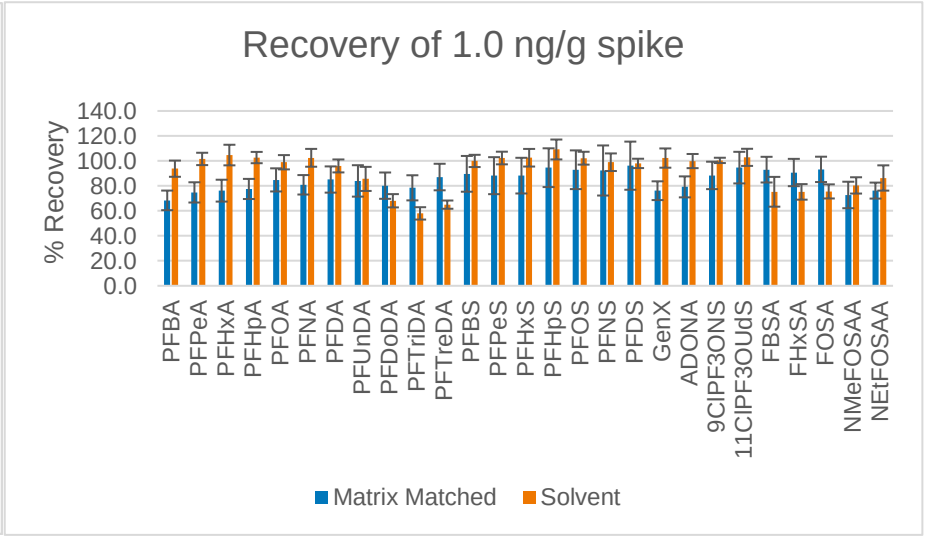
- Use isotope dilution
  - 23 $^{13}C$ and $D_2$ labelled standards used
- Accounts more accurately for recovery
- Internal standards also account for matrix effects




Peak area comparison of PFHxS, PFTreDA, GenX, and NMeFOSAAin 100 ng/L points of both the solvent and matrix matched curves.

# Recovery of PFAS in Spiked Milk Samples - What Works Best?



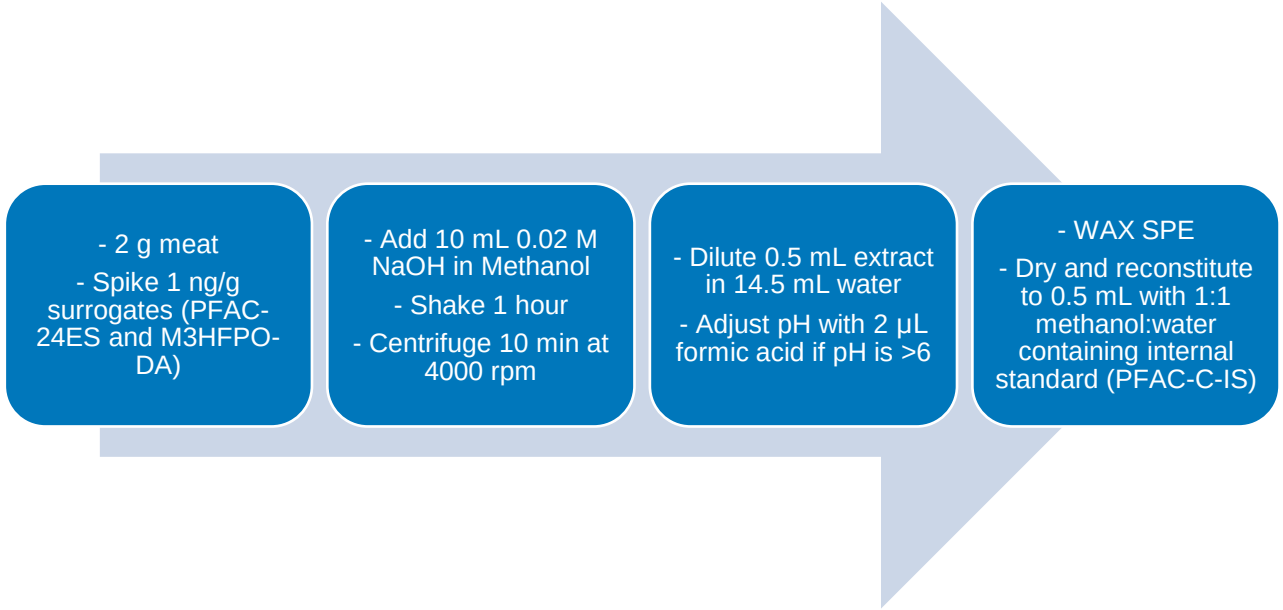




*Mean percent accuracy*

- 85% matrix matched - less costly (stds) but need an available clean matrix; how many different matrices being supported?
- 97% solvent curve with isotope dilution – can be expensive to obtain all the standards, however, greater accuracy and more flexible for wider range of sample types

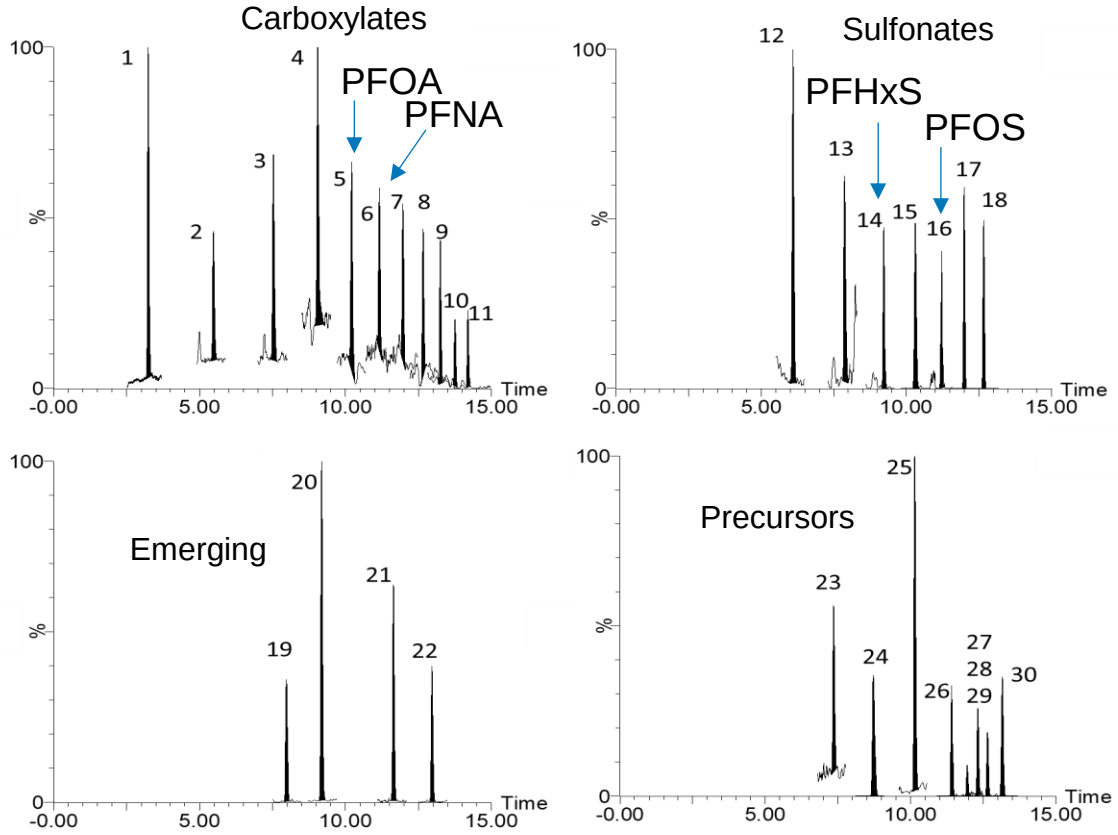
# Meats, Fish, Egg

| Sample Type |
| --- |
| Whole Egg |
| Salmon |
| Tilapia |
| Ground Beef |
| Beef Liver |
| Beef Kidney |




Waters App Note 720007482

# Salmon Spiked at 0.1 µg/kg – Digestion & WAX SPE Prep




ACQUITY BEH $C_{18}$ (2.1 x 100 mm, 1.7 µm)

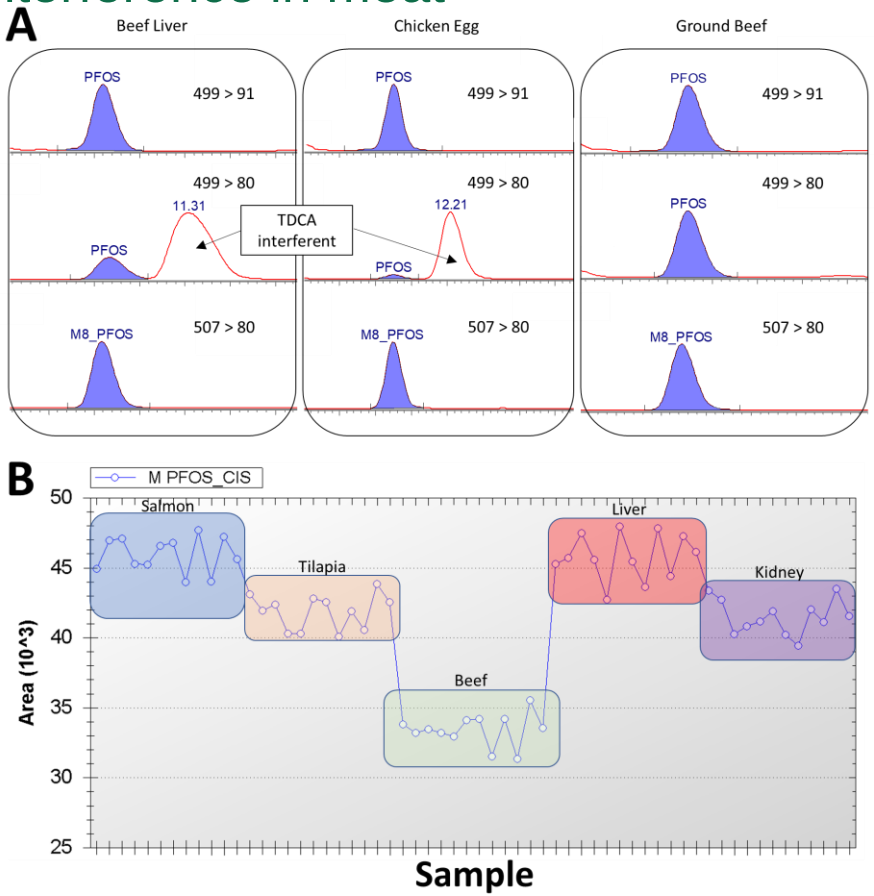
- Chromatograms shows the 30 PFAS evaluated in the method spiked into salmon extract at 0.1 µg/kg (100 ppt)
  - Peak assignments are located in the Appendix of the application note

Even though the extraction method results in 5x dilution of sample concentration, the sensitivity of the TQ-XS allows for trace level detection of PFAS in matrix samples.

# Taurodeoxycholic acid (TDCA) interference in meat

. (A) chromatograms of PFOS MRM transitions 499 > 91 and 499 > 80 and M8-PFOS in beef
liver, chicken egg, and ground beef showing taurodeoxycholic acid (TDCA) as an interferent in 499>80 transition in liver and egg.

(B) M-PFOS injection standard peak area (y-axis) over 12 sample injections of each sample matrix (x-axis): salmon, tilapia, beef, liver, and kidney



# Cosmetics

1 g sample + 10 mL methanol → Sonicate 30 minutes → Filter with 0.22 um GHP syringe filter → Dilute 1:1 with 2mM ammonium acetate

| Sample | compound | conc [ng/mL] | conc [ng/g] |
|---|---|---|---|
| Eye Shadow | PFBA | 0.29 | 2.9 |
| Eye Shadow | PFHxA | 0.02 | 0.2 |
| Eye Shadow | PFOA | 0.12 | 1.2 |
| Eye Shadow | PFTeDA | 0.02 | 0.2 |
| Eye Shadow | PFBS | 0.02 | 0.2 |
| Foundation | PFBA | 0.18 | 1.8 |
| Foundation | PFOA | 0.01 | 0.1 |
| Foundation | PFTeDA | 0.02 | 0.2 |

Environ. Sci.: Processes Impacts,2018,20, 1680

# 96 Well WAX SPE procedure for Human Serum and Plasma

**Pretreat Samples (50 µL) – spike isotope dilution standards, PPT with 3x ACN, dilute with 5x 1% Formic Acid**

**Condition Plate**

200 µL 2% ammonia/methanol

200 µL methanol

200 µL 1% Formic Acid

**Load Sample**

**Wash Plate**

200 µL 1% Formic Acid

200 µL 1:3 ACN:Water

**Elute**

50 µL methanol

50 µL 2% (v/v) ammonia/methanol → 2x

Dilute with 50 µL 2% ammonium acetate containing Injection Standards


Oasis WAX 96 well µElution plate

2 mg per well

Waters App Note 720007114

# Human Pooled Serum and Plasma Samples

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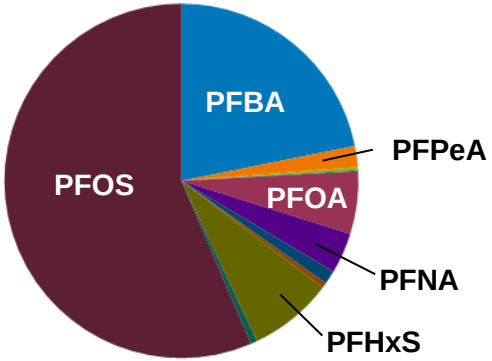
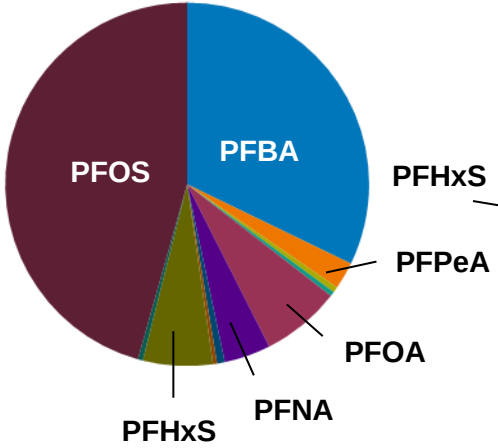
## Serum Lot 1



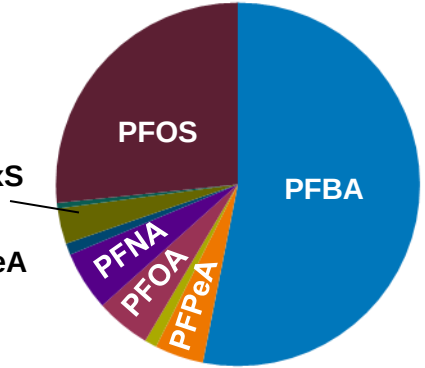

Total PFAS = 18.96 ng/L

## Serum Lot 2



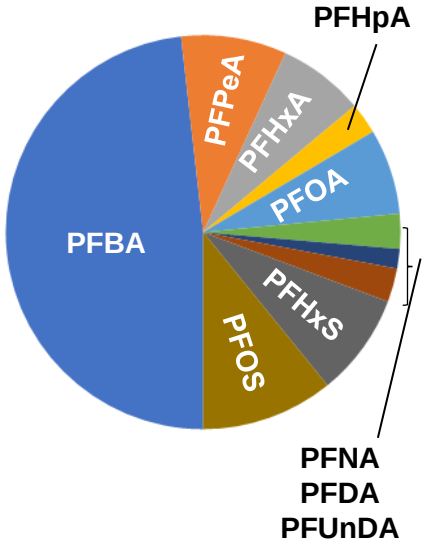

Total PFAS = 14.44 ng/L

## Serum Lot 3




Total PFAS = 8.86 ng/L

## Plasma



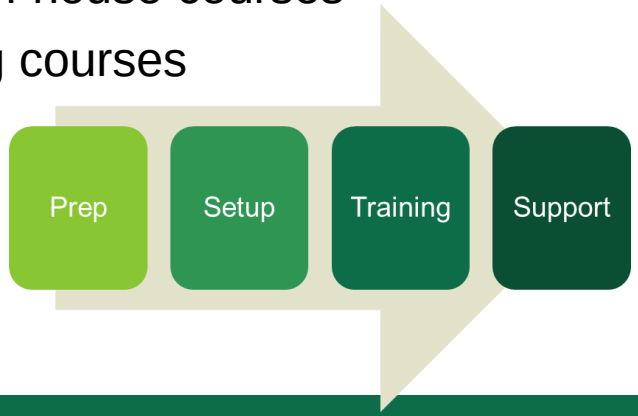

Total PFAS = 1.71 ng/L

# Education and training are fundamental to successfully establishing a PFAS analysis capability

Waters™

## Waters can help!

- Custom onsite training
- Virtual training
- Advanced method consultation
- Education subscriptions
- Certified in-house courses
- E-learning courses





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# A Comprehensive Workflow Solution for PFAS

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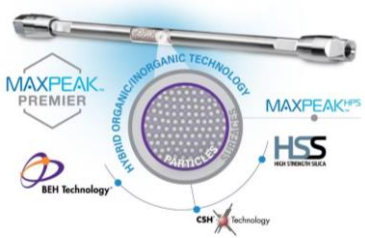
Oasis SPE

PFAS Base Hardware Only Kit


Atlantis Premier BEH C18 AX
50 mm used as Isolator Column

waters_connect
for Quantitation



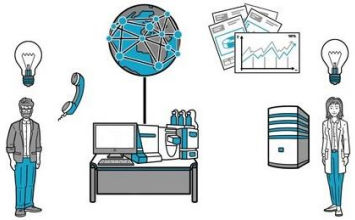

ACQUITY Premier Analytical Columns
Atlantis Premier AX Analytical Column

Native
PFAS
Precision
and
Recovery
Standard
Solution

PP Vials
& Caps

**ACQUITY Premier**

**Xevo TQ Absolute**

Analytical Professional Services

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Certified Reference Materials

Quick Response PTs

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# Waters

# Beyond PFAS – LC-MS/MS Applications for Environmental Testing

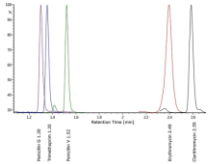
Waters™

## PPCPs in Water using LC-MS/MS

**SOLUTIONS**

- Application Note: Analysis of Macrolides and Three Other Antibiotic Classes at Low ppt Levels in WWTP Effluent and Surface Waters by LC-MS/MS

- Targeted method for the determination of PPCPs in wastewater using US EPA Method 1694.
- UPLC with Tandem Mass Spectrometry water
- Suitable for monitoring various water sample matrices with minimal sample preparation
- 200 mg Oasis HLB Solid Phase Extraction (SPE) Cartridges



*Basic UPLC conditions at 100 ng/L fortified in surface water*

| Basic UPLC | Class | R2 | MQL (ng/L) | *Absolute SPE recovery (%) | Method recovery (%) | WWTP effluent (ng/L) | Surface water (ng/L) |
|---|---|---|---|---|---|---|---|
| Clarithromycin | Macrolide | 0.997 | 1.1 | 56 | 93 | 24 | 2.7 |
| Erythromycin | Macrolide | 0.99 9 | 0.5 | 91 | 110 | 215 | 23 |
| Penicillin G | ß-lactam | 1.00 0 | 10.0 | 84 | 78 | - | - |
| Penicillin V | ß-lactam | 1.00 0 | 20.0 | 82 | 103 | - | - |
| Trimethoprim | - | 1.00 0 | 0.6 | 70 | 99 | 30 | 2.6 |
| Acidic UPLC | | | | | | | |
| Azithromycin | Macrolide | 0.998 | 1.1 | 49 | 90 | 21 | <1.1 |
| Doxycycline | Tetracycline | 0.997 | 1.1 | 74 | 101 | - | - |
| Ciprofloxacin | Fluoroquinolone | 0.998 | 32.0 | 55 | 71 | - | - |
| Norfloxacin | Fluoroquinolone | 0.998 | 21.0 | 48 | 62 | - | - |
| Sulfamethoxazole | Sulfonamide | 0.99 9 | 1.3 | 62 | 96 | 208 | 32 |

*Three macrolides and six other important antibiotics analyzed with off-line SPE and UPLC-ESI-MS/MS in positive mode at basic and acidic UPLC conditions*



## Chlorinated Acid Herbicides in Water

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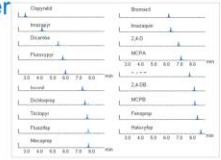
**Analyze, Without the Need to Derivatize**



**CHALLENGES**

- Lengthy preparation steps with derivatization
- Poor chromatography with historic GC-ECD, or GC-MS methods

**SOLUTIONS**

- Targeted method for the determination of 20 acidic herbicides in water samples that is suitable for monitoring both drinking water and surface waters with minimal sample preparation
- No lengthy and dangerous derivatization required
- Short analytical run time



## Link to Temple University Publication on PPCPs in the Delaware River

Waters™

ACS Environmental Science. 7(4): 302–315.
DOI: 10.1016/envsci.2020019
Received: 13 May 2020
Accepted: 06 July 2020
Published: 09 July 2020

http://www.acspress.com/journal/envsci

*Research article*

**Occurrence and aquatic toxicity of contaminants of emerging concern (CECs) in tributaries of an urbanized section of the Delaware River Watershed**

**Bjordje Vilimonovic[1], Gangadhar Andaluri[2], Robert Hannah[2], Ruminder Suri[2,*], A. Ronald MacGillivray[2]**

[1] SNF - Water and Environmental Technology (WET) Center, Civil and Environmental Engineering Department, Temple University, Philadelphia PA, USA
[2] Delaware River Basin Commission (DRBC), West Trenton, NJ, USA

* **Correspondence:** Email: ruminder.suri@tumple.edu; Tel: +12152942376.

**Abstract:** The presence of contaminants of emerging concern (CECs) in environmental matrices is an ongoing issue. This research project was carried out to increase our understanding of the loading, distribution and potential risk of CECs by sampling large and small tributaries in a specific area of the Delaware River watershed (in northeast USA) that is highly urbanized and significantly impacted by wastewater treatment plant effluents. Fifteen target compounds were selected for analysis based on their high frequency of detection in a previous multiyear study conducted on the Delaware River mainstem. Ten sampling sites were chosen on tributaries receiving numerous municipal and industrial discharges. Sampling locations were above and below potential source discharges. Sampling was designed to assess seasonal differences in CECs loadings. The measured environmental concentrations of the target compounds present a detailed picture of urban and industrial impacts on sub-watershed receiving waters. An index of concern ranking system was applied to the sample locations by comparing measured environmental concentrations, existing target computed water quality criteria or predicted no effects levels and developing a concern summary variable. Trichlorabun and diphenhydramine demonstrated to be compounds of high relative risk (RR) to the aquatic life of the Pennsylvania tributaries to the Delaware River.



**Table 1.** Compounds of interest.

| Analyte | Therapeutic category | Description |
|---|---|---|
| Carbamazepine | Anti-epileptic drugs | Prescription drug, anticonvulsant, mood-stabilizer, treatment of attention deficit hyperactivity disorder (ADHD) |
| Clarithromycin | Antibiotic | Prescription drug, a macrolide antibiotic |
| Dehydronifedipine | A metabolite of a nifedipine | An inactive metabolite of prescription cardiac drug |
| Diltiazem | Antihypertensive | Prescription drug, anticonvulsant, mood-stabilizer, treatment of ADHD |
| Diphenhydramine | Antihistamine | Prescription and over-the-counter drug, an antihistamine used to treat allergies |
| Erythromycin | Antibiotic | Prescription drug, a macrolide antibiotic |
| Gemfibrozil | Lipid regulator | Prescription drug, lipid-lowering agent |
| Guanylurea | Degradant of metformin | Metformin biodegradation |
| Ibuprofen | Non-steroidal anti-inflammatory | Prescription and over-the-counter drug, a non-steroidal anti-inflammatory drug used for pain |
| Metformin | Anti-diabetic | A prescription drug for diabetes treatment |
| Ranitidine | Antihistamine | Prescription and over-the-counter drug for peptic ulcer and gastroesophageal reflux disease treatment |
| Sulfamethoxazole | Antibiotic | Prescription drug, a bacteriostatic antibiotic frequently used in combination with trimethoprim |
| Thiabendazole | Fungicide/ parasiticide | Prescription and veterinary drug as a parasiticide also used as an agricultural fungicide |
| Triclocarban | Personal care product | Antibacterial, antifungal agent |
| Trimethoprim | Antibacterial | Prescription drug, a bacteriostatic antibiotic frequently used in combination with sulfamethoxazole |



## Anionic Polar Pesticide Solution

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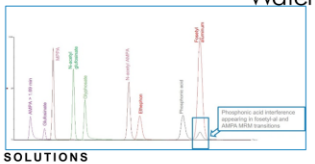
**Analyze, Without the Need to Derivatize**




**CHALLENGES**

- Difficulty with chromatographic retention
- Several polar anionic pesticides share mass transitions or can degrade in solution or via in source fragmentation, generating interferences in MRMs and thus false positives.

**SOLUTIONS**

- Anionic Polar Pesticide Column exhibits stable retention times, even across different commodities.
- AMPA is the first eluting peak with retention 3.5 times greater than the column void volume.
- Column resolves such false detections

# Want to learn more? Additional resources for PFAS in Food

Waters™

- Analysis of 28 EU Regulated and Recommended PFAS in Food via LC-MS/MS – Part 1: Vegetable, Fruit, and Baby Food
- Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Animal Products with an Enhanced Sensitivity LC-MS/MS Method using Fish Reference Materials as a Case Study
- QuEChERS Extraction of Per- and Polyfluoroalkyl Substances (PFAS) from Edible Produce with Sensitive Analysis on Xevo TQ-XS
- Total Workflow for the Sensitive Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Fish, Meat, Edible Offal, and Eggs
- Evaluation of the Performance of a Total Workflow Approach for the Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Fish, Using an Interlaboratory Study
- Matrix Matching or Isotope Dilution? A Comparison of Two Quantitation Approaches to Determine PFAS in Dairy Milk
- Optimization of Source and Transmission Parameters for a Mix of Labile and Stable Per – Or Polyfluoroalkyl Substances (PFAS) Using the Xevo™ G3 QTof Mass Spectrometer

# References

| | |
|---|---|
| Company Name: | Eurofins Eaton Lab |
| Contact Person: | Dr. Bruce (Yongtao) Li |
| Telephone Number: | 574-233-4777 |
| Email: | yongtaoli@eurofinsus.com |
| Address Line 1: | 110 S Hill Street |
| Address Line 2: | South Bend, Indiana 46617, USA |
| Comments | Lab has TQ-S, TQ-XS and TQ Absolute |

| | |
|---|---|
| Company Name: | Rhode Island State Health Laboratories |
| Contact Person: | Evan Philo, Principal Laboratory Scientist / Food Testing Coordinator |
| Telephone Number: | 401-222-5553 |
| Email: | Evan.Philo@health.ri.gov |
| Address Line 1: | 50 Orms St. |
| Address Line 2: | Providence RI, 02904 |
| Comments | TQ-Absolute for PFAS analysis in water |

| | |
|---|---|
| Company Name: | US EPA Region 5 Lab |
| Contact Person: | Larry Zintek |
| Telephone Number: | 312 886 2995 |
| Email: | Zintek.lawrence@epa.gov |
| Address Line 1: | 77 West Jackson Blvd |
| Address Line 2: | Chicago, Il 60604 |
| Comments | Multiple TQ-XS and TQ-Absolute systems for PFAS analysis |

| | |
|---|---|
| Company Name: | Suffolk County Water Authority |
| Contact Person: | Amanda Comando |
| Telephone Number: | 631 218 1128 |
| Email: | acomando@scwa.com |
| Address Line 1: | 260 Motor Parkway |
| Address Line 2: | Hauppauge, NY 11788 |
| Comments | Multiple TQ-S/TQ-XS systems |

| | |
|---|---|
| Company Name: | Complete Environmental Testing |
| Contact Person: | Jeff Smith, Lab Director |
| Telephone Number: | 203 377 9984 |
| Email: | jsmith@cetlabs.com |
| Address Line 1: | 80 Lupes Dr |
| Address Line 2: | Stratford, CT 06615 |
| Comments | Multiple TQ-XS for PFAS analysis |

| | |
|---|---|
| Company Name: | Katahdin Analytical Services |
| Contact Person: | Michael Flanders, President and CEO |
| Telephone Number: | 207-874-2400 |
| Email: | mflanders@katahdinlab.com |
| Address Line 1: | 600 Technology Way |
| Address Line 2: | Scarborough, ME-04074 |
| Comments | 3 x TQ Absolute systems for PFAS analysis in drinking water and other matrices |

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# Thank you

**khalid_ghaffar@waters.com**