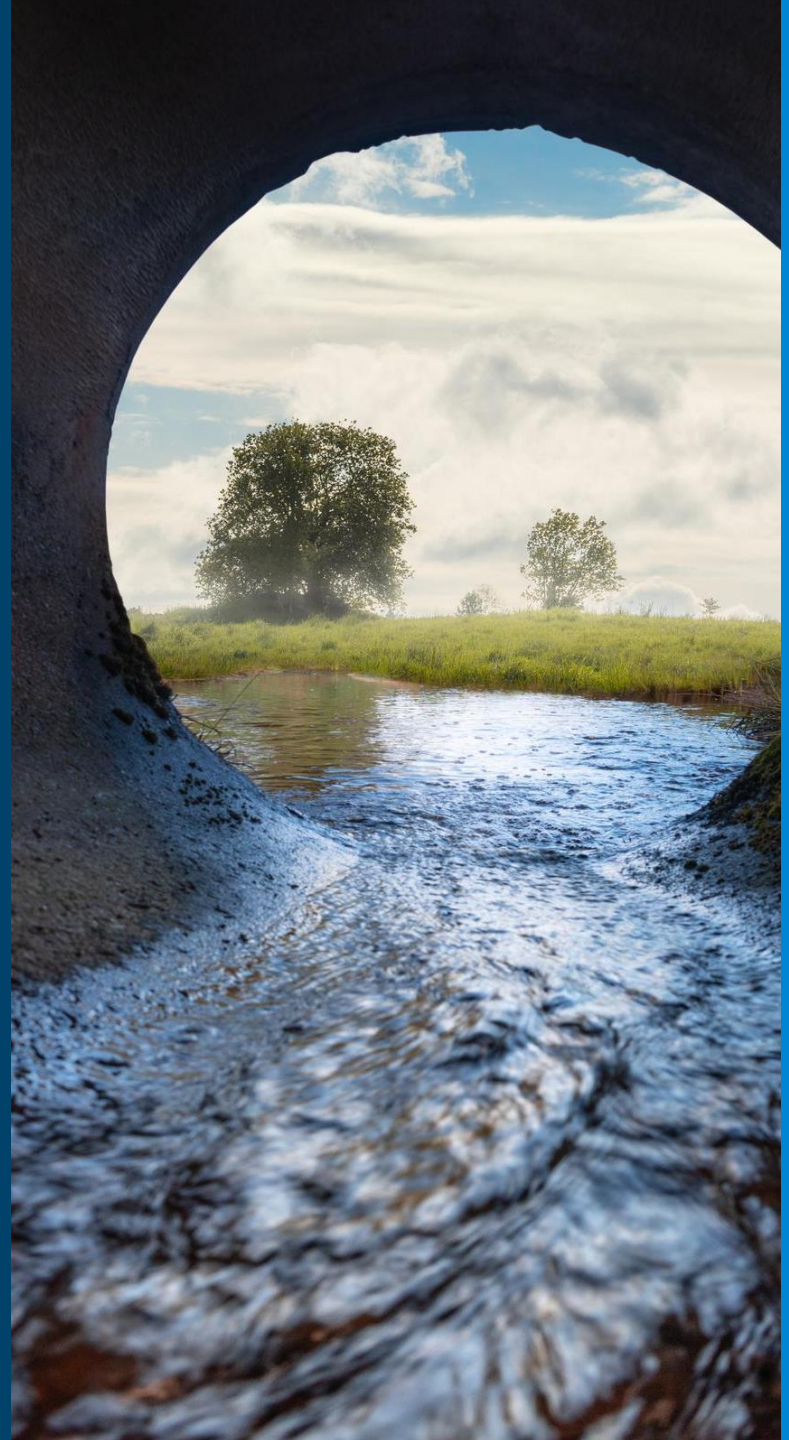
# Emerging Contaminants

## Comprehensive Targeted Workflows

Chris Snelling
Agilent Technologies



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# PFAS

## Per/Poly Fluoroalkyl Substances

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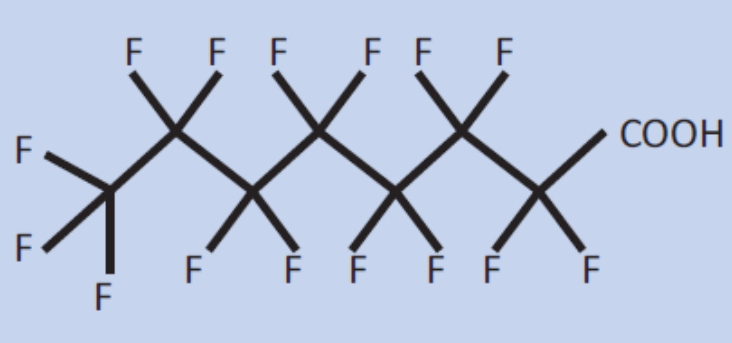
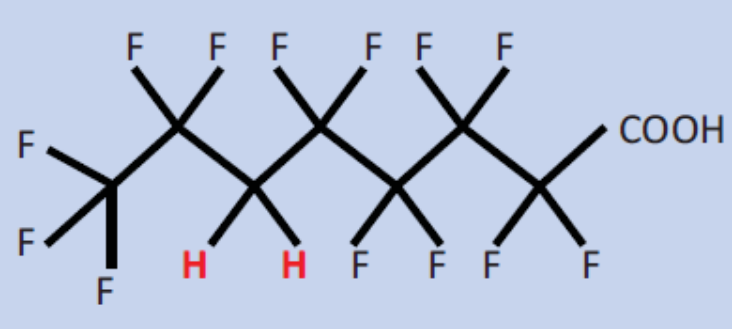
# Terminology

## Perfluoroalkyl substance




***ALL*** H atoms linked to C in alkyl chain are substituted with F

## Polyfluoroalkyl substance



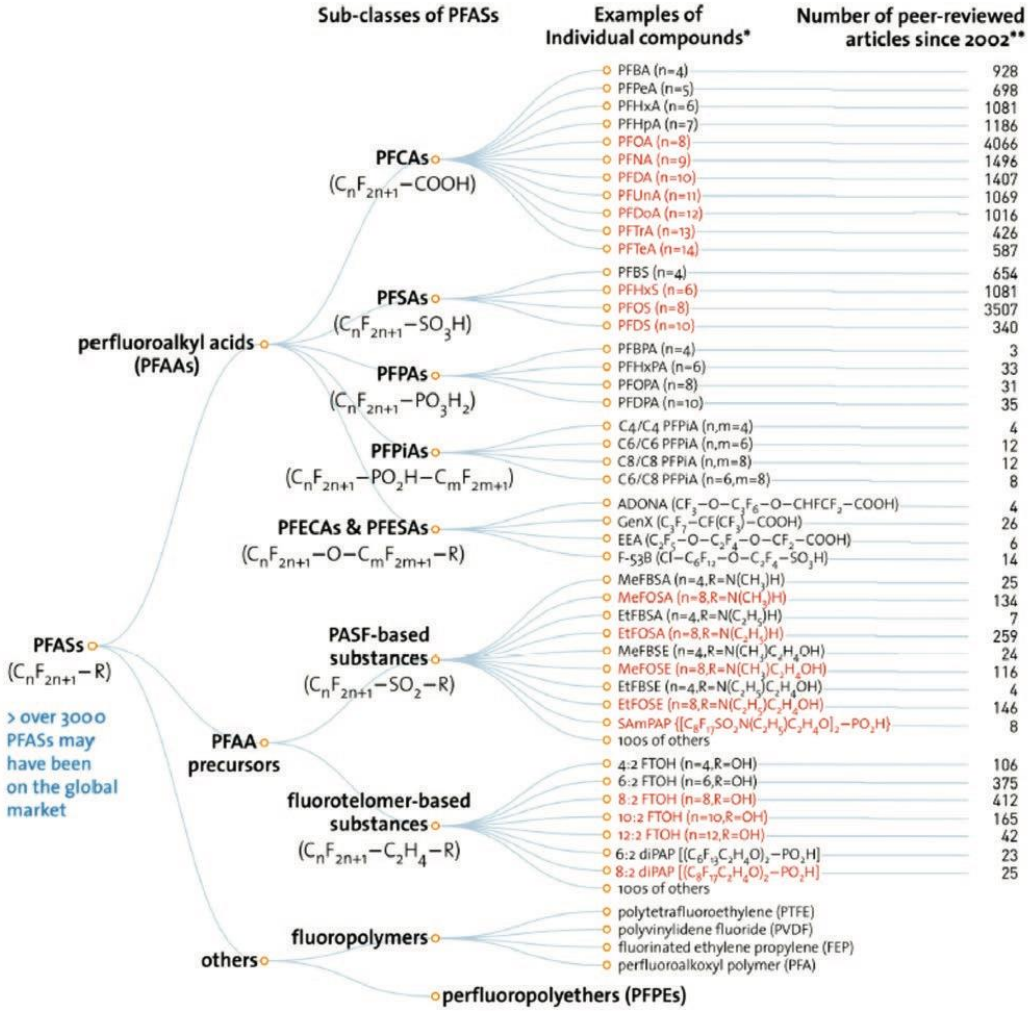

***SOME*** *(but not all)* H atoms linked to C in alkyl chain are substituted with F

# PFAS Classifications and Terminology

## >4000 PFAS compounds in commerce

### Common Acronyms

| | |
|---|---|
| PFCA | Perfluoroalkylcarboxylic acid |
| PFOA | Perfluorooctanecarboxylic acid |
| PFAS | Perfluoroalkylsulfonate |
| PFOS | Perfluorooctanesulfonate |
| PFASi | Perfluoroalkylsulfinate |
| FOSA | Perfluorooctanesulfonamide |
| FOSAA | Perfluorooctanesulfonamidoacetic acid |
| FOSE | Perfluorooctanesulfonamidoethanol |
| FTOH | Fluorinated telomer alcohol (-OH functional group) |
| FTA | Fluorinated telomer acid |
| FTUA | Fluorinated telomer unsaturated acid |
| FTS | Fluorinated telomer sulfonate |
| PFAPA | Perfluoroalkylphosphonic acid |
| PFPi | Perfluoroalkylphosphinate |
| PAP | Mono-substituted polyfluoroalkylphosphate ester |
| diPAP | Di-substituted polyfluoroalkylphosphate ester |
| PFAI | Perfluoroalkyl iodide |
| SFA | Semifluorinated alkane |
| FTI | Fluorinated telomer iodide |
| FTO | Fluorinated telomer olefin |
| FTAC | Fluorinated telomer acrylate |




Wang, Z *et al.* (2017). *Environ. Sci. Technol.* 51, 2508-2518.

# Current Standard & Consensus Methods Available

| Method | Matrix Tested | No. of analytes | Sample preparation procedure | Quantification Technique | Sample (mL)/Injection (uL) Volume | Year |
|---|---|---|---|---|---|---|
| EPA 537 | Drinking Water | 14 | Solid phase extraction | Internal standard correction | 250/10 | 2008 |
| EPA 537.1 | Drinking Water | 18 | Solid phase Extraction | Internal standard correction | 250/10 | 2018 |
| EPA 533 | Drinking Water | 25 | Solid phase extraction | Isotope dilution | 250/10 | 2019 |
| EPA 8327 | Surface water, Ground water, Wastewater influent and effluent | 24 | Dilute & shoot | External calibration (isotope dilution also allowed) | 5/30 | 2019 |
| EPA 1633 (3rd Draft) | Wastewater, Soil, Biota, Sediment, Groundwater | 40 | Solid Phase Extraction | Isotope Dilution | 500/2 | 2022 |
| ASTM 8421 | Surface water, Ground water, Wastewater influent and effluent | 44 | Dilute & shoot | External calibration (isotope dilution also allowed) | 5/30 | 2022 |
| ASTM 7968 | Soil and solids | 21 | Organic extraction with MeOH | External calibration | 5g/30 | 2015 |
| ISO/DIS 21675:2019 | Drinking Water, Sea water, Fresh water, wastewater (<0.2% solids) | 30 | Solid phase extraction | Internal standard correction | 500/5 | 2019 |

# National Primary Drinking Water Regulations

## Selected Per- and poly-fluoroalkyl substances (PFAS)

- PFAS rule references

| Contaminant | MCLG[1] (mg/L)[2] | MCL[1] (mg/L)[2] | HBWC[9] (mg/L)[2] for Hazard Index Calculation |
|---|---|---|---|
| Hazard Index PFAS (HFPO-DA, PFBS, PFHxS, and PFNA) | 1(unitless) | 1(unitless) | Not applicable |
| HFPO-DA (commonly knowns as GenX Chemicals) | 0.00001 | 0.00001 | 0.00001 |
| PFBS | No individual MCLG | No individual MCL | 0.002 |
| PFHxS | 0.00001 | 0.00001 | 0.00001 |
| PFNA | 0.00001 | 0.00001 | 0.00001 |
| PFOA | zero | 0.0000040 | Not applicable |
| PFOS | zero | 0.0000040 | Not applicable |

4 ng/L! (4 ppt)

## TNI PT for Accreditation
## Fields of Proficiency Testing with PTRLs
## *Drinking Water*
## *Effective: January 1, 2025*

Blue = New Analyte  Magenta = Changes

| Matrix | EPA Analyte Code | TNI Analyte Code | CAS Number | Analyte[2] | Conc Range | Acceptance Criteria[3,4,5,6] a | b | c | d | TNI PTRL[7] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | **PAH** | µg/L | | | | | µg/L |
| Drinking Water | 0122 | 5580 | 50-32-8 | Benzo(a)pyrene[1] | 0.2 to 2.5 | 0.8471 | -0.0040 | 0.1854 | 0.0547 | 0.02 |
| | | | | **Dioxin** | pg/L | | | | | pg/L |
| Drinking Water | 0252 | 9618 | 1746-01-6 | 2,3,7,8-Tetrachlorodibenzo- p-dioxin (2,3,7,8-TCDD)[1] | 20 to 100 | 0.8642 | 1.4865 | 0.1392 | 1.1445 | 11 |
| | | | | **PFAS** | ng/L | | | | | ng/L |
| Drinking Water | 2813 | 9490 | 763051-92-9 | 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2822 | 6948 | 39108-34-4 | 1*H* ,1*H* , 2*H* , 2*H* -Perfluorodecane sulfonic acid (8:2FTS) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2821 | 6946 | 757124-72-4 | 1*H* ,1*H* , 2*H* , 2*H* -Perfluorohexane sulfonic acid (4:2FTS) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2820 | 6947 | 27619-97-2 | 1*H* ,1*H* , 2*H* , 2*H* -Perfluorooctane sulfonic acid (6:2FTS) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2815 | 6951 | 919005-14-4 | 4,8-Dioxa-3*H*-perfluorononanoic acid (ADONA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2814 | 6952 | 756426-58-1 | 9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid (9Cl-PF3ONS) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2816 | 9460 | 13252-13-6 | Hexafluoropropylene oxide dimer acid (HFPO-DA) (GenX) | 10 to 200 | | ±30% fixed acceptance limit | | | 7 |
| Drinking Water | 2817 | 4846 | 2991-50-6 | N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2818 | 4847 | 2355-31-9 | N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2827 | 6956 | 151772-58-6 | Nonafluoro-3,6-dioxaheptanoic acid (NFDHA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2826 | 6957 | 113507-82-7 | Perfluoro(2-ethoxyethane)sulfonic acid (PFEESA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2823 | 6965 | 377-73-1 | Perfluoro-3-methoxypropanoic acid (PFMPA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2825 | 6966 | 863090-89-5 | Perfluoro-4-methoxybutanoic acid (PFMBA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2801 | 6918 | 375-73-5 | Perfluorobutanesulfonic acid (PFBS) | 10 to 200 | | ±30% fixed acceptance limit | | | 7 |
| Drinking Water | 2819 | 6915 | 375-22-4 | Perfluorobutanoic acid (PFBA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2807 | 6905 | 335-76-2 | Perfluorodecanoic acid (PFDA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2808 | 6903 | 307-55-1 | Perfluorododecanoic acid (PFDoA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2829 | 9470 | 375-92-8 | Perfluoroheptanesulfonic acid (PFHpS) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2802 | 6908 | 375-85-9 | Perfluoroheptanoic acid (PFHpA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2803 | 6927 | 355-46-4 | Perfluorohexanesulfonic acid (PFHxS) | 10 to 200 | | ±30% fixed acceptance limit | | | 7 |
| Drinking Water | 2809 | 6913 | 307-24-4 | Perfluorohexanoic acid (PFHxA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2804 | 6906 | 375-95-1 | Perfluorononanoic acid (PFNA) | 10 to 200 | | ±30% fixed acceptance limit | | | 7 |
| Drinking Water | 2805 | 6931 | 1763-23-1 | Perfluorooctanesulfonic acid (PFOS) | 10 to 200 | | ±30% fixed acceptance limit | | | 7 |
| Drinking Water | 2806 | 6912 | 335-67-1 | Perfluorooctanoic acid (PFOA) | 10 to 200 | | ±30% fixed acceptance limit | | | 7 |
| Drinking Water | 2828 | 6934 | 2706-91-4 | Perfluoropentanesulfonic acid (PFPeS) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2824 | 6914 | 2706-90-3 | Perfluoropentanoic acid (PFPeA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2810 | 6902 | 376-06-7 | Perfluorotetradecanoic acid (PFTA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2811 | 9563 | 72629-94-8 | Perfluorotridecanoic acid (PFTrDA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |
| Drinking Water | 2812 | 6904 | 2058-94-8 | Perfluoroundecanoic acid (PFUnA) | 10 to 200 | | ±40% fixed acceptance limit | | | 6 |

# Rulemaking at DEQ

DEQ's mission is to be a leader in restoring, maintaining and enhancing the quality of Oregon's air, land and water.



## PFAS 2025

**How to Find Rules and Rulemaking Documents**

**Search DEQ Rulemaking Documents**

**Search Official Version Of The Rules**

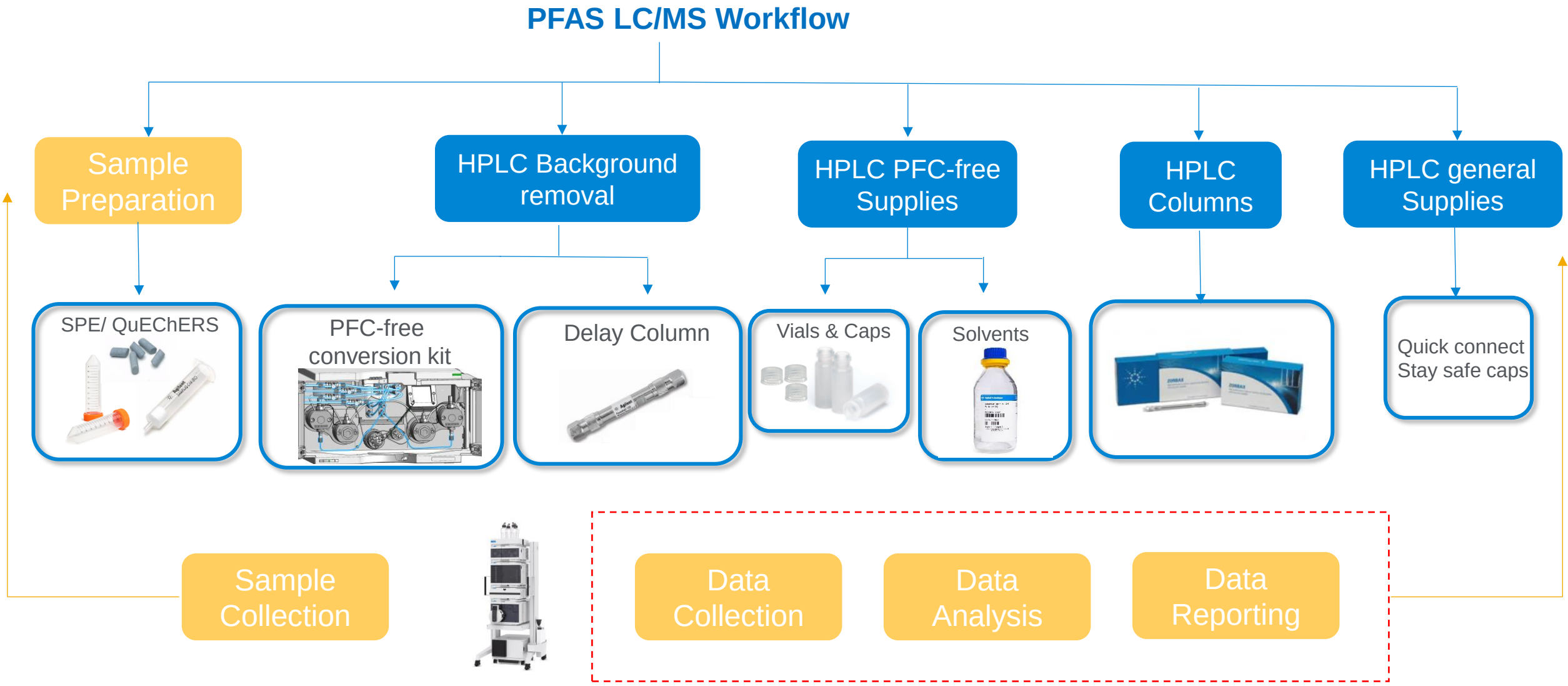
**Greenhouse Gas Emissions Program 2021**

### Proposed rule

Rulemaking contact: Sarah Van Glubt, 503-709-8253, PFAS.2025@deq.oregon.gov

This rulemaking proposes to include two per- and polyfluoroalkyl substances (PFAS), perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), including their salts and structural isomers, in the definition of hazardous substances in Oregon Administrative Rule (OAR) 340-122-0115 (30) which would give the Department authority to require investigation and removal and remedial actions of PFOA and PFOS releases and align with the US Environmental Protection Agency's approach. PFOA and PFOS are among the most commonly detected PFAS, are known or suspected carcinogens, and have been shown to exhibit toxicity effects to humans and wildlife even at low levels of exposure.

# PFAS Sample Prep & Analysis: Basic Workflow Overview
# Address background and contamination issues with a robust workflow



# SLIMS - Automation of EPA Workflows for PFAS

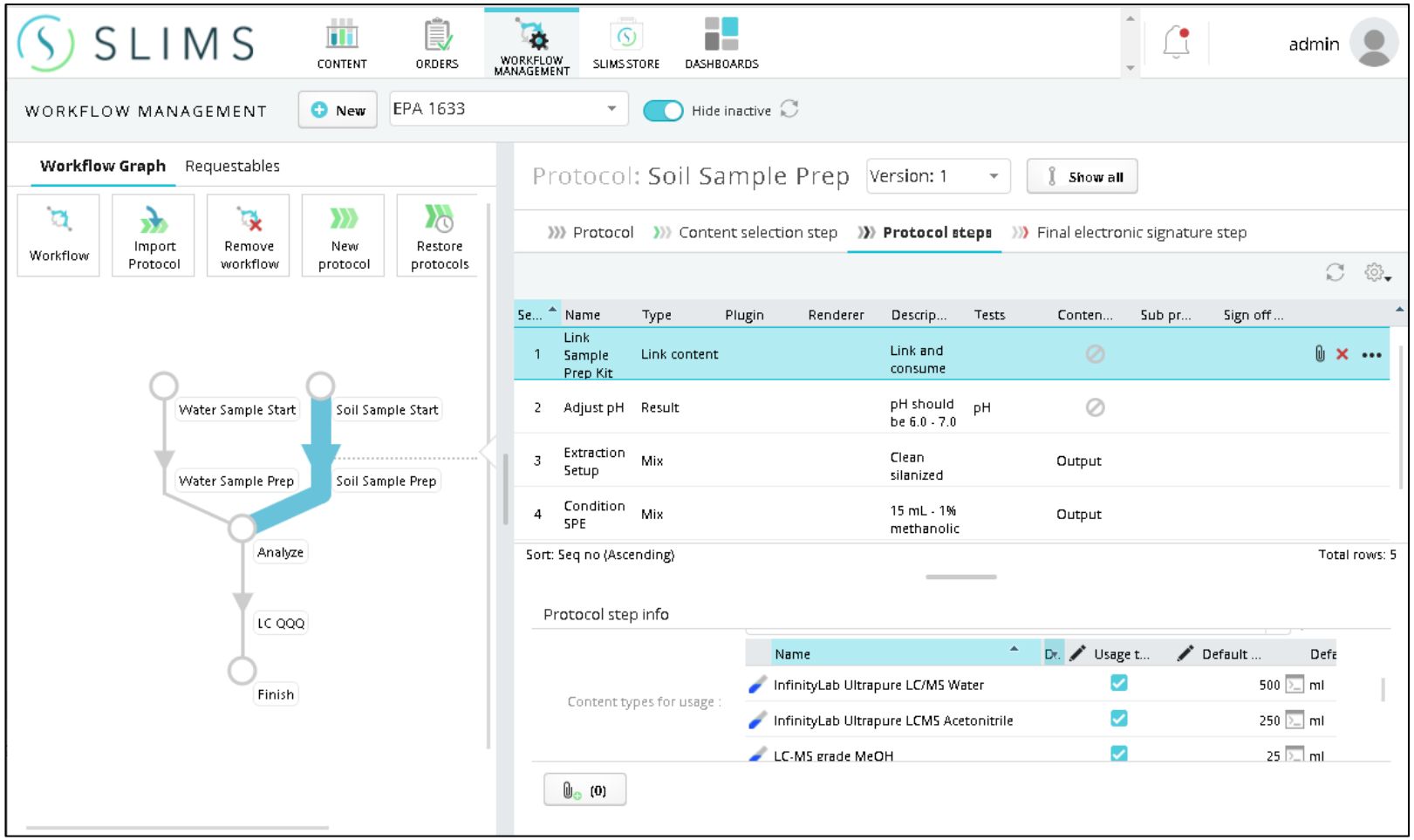
Sample Management

Inventory Management

Workflow Execution

- Sample Prep
- Masshunter Integration
- Results Evaluation

Dashboard & Reporting



# PFAS Analysis Workflow Consumables, Supplies and Hardware

Wastewater
(500mL)

Centrifuge tubes
50 mL (5610-2039)

Carbon S
(5610-2093)

Empty SPE tubes,
60 mL (12131012)

SPE Adapters
(12131001)

Glass Wool,
Silanized
(8500-1572)

Bond Elut PFAS
WAX 150 mg, 6 mL
(5610-2152)

Vac Elut SPS 24
(12234003)

Centrifuge tubes
15 mL (5610-2039)

Nylon Filters
(5190-5092)

Syringes
(9301-6476)

Polypropylene AS Vials
(5191-8151, 5191-8150)

1290 Infinity II LC
system

6495 triple
quadrupole LC/MS

PFC-free kit (5004-0006)
PFC delay column (5062-8100)
Analytical column Eclipse Plus
C18, 2.1 x 100 mm, 1.8 µm
(959758-902)

PFAS MRM Database (G1736AA)

# Solid Phase Extraction – Bond Elut PFAS WAX

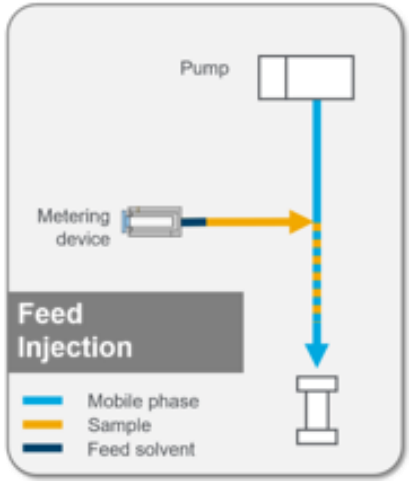
Specifically designed, developed and manufactured for PFAS applications

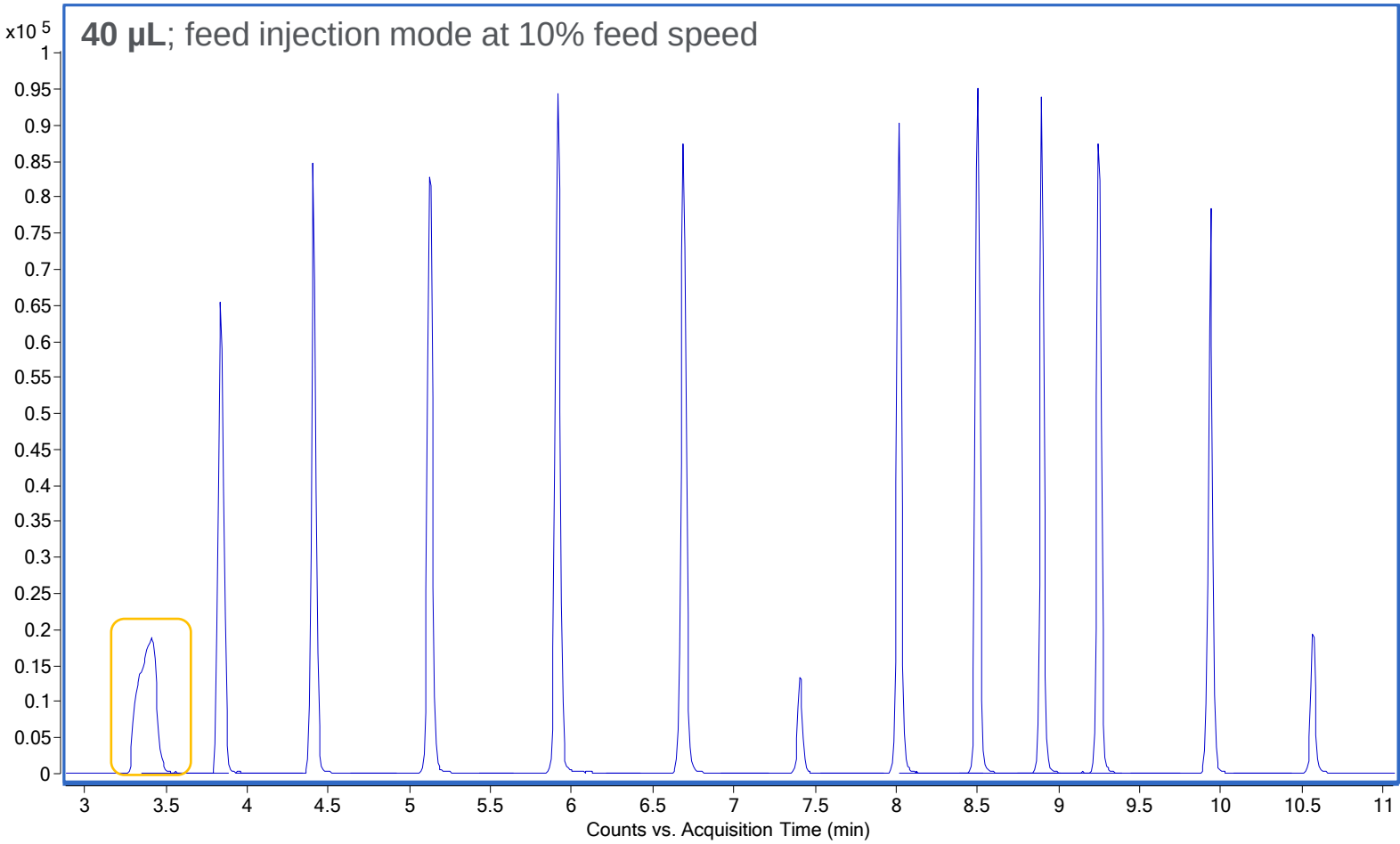
- Cleanliness
- Sorbent and cartridge formats compatible with all existing regulated methods
  - EPA method 533 for drinking water
  - EPA method 1633 (draft) for aqueous, solids, biosolids, and tissue samples
  - ISO 21675:2019 for drinking water, sea water, fresh water, and wastewater
- Performance equivalent to other commercial cartridges
- Fits into Agilent's existing PFAS workflows

# New way to overcome strong solvent effects at high injection volumes

## Improve peak shape and sensitivity of early eluting PFAS

- New 1260 Infinity II Hybrid Multisampler (G7167C)
- Feed injection valve
- Allows dilution during injection
- Classic injection mode simulation by fast feed speed



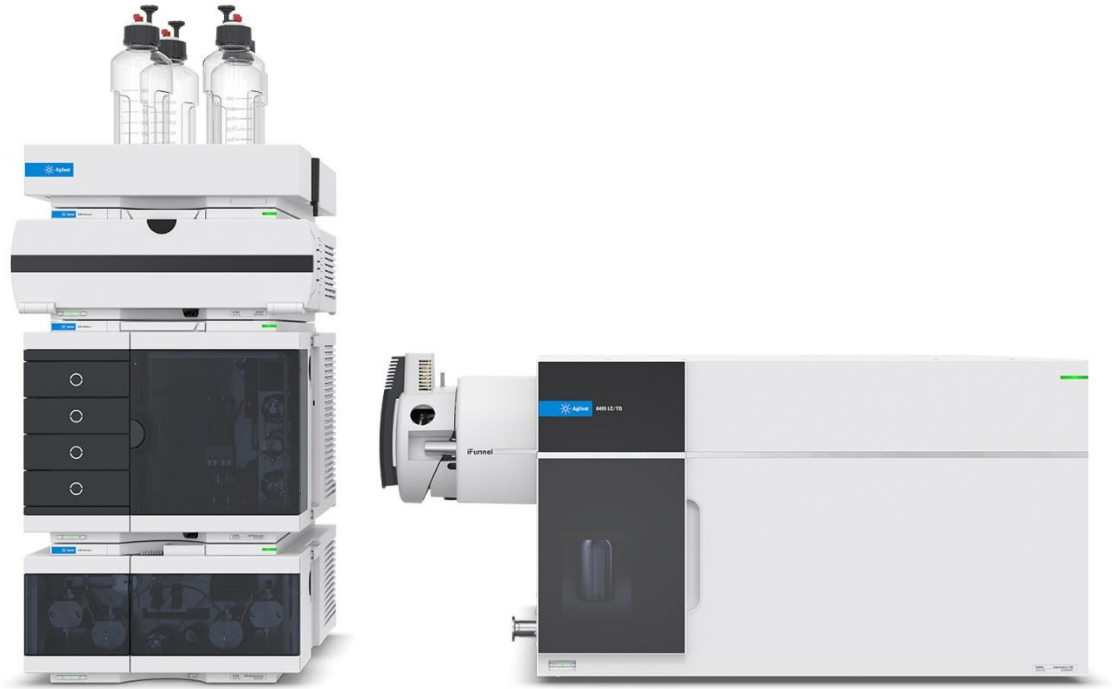



# The 6495 Triple Quadrupole LC/MS with iFunnel technology

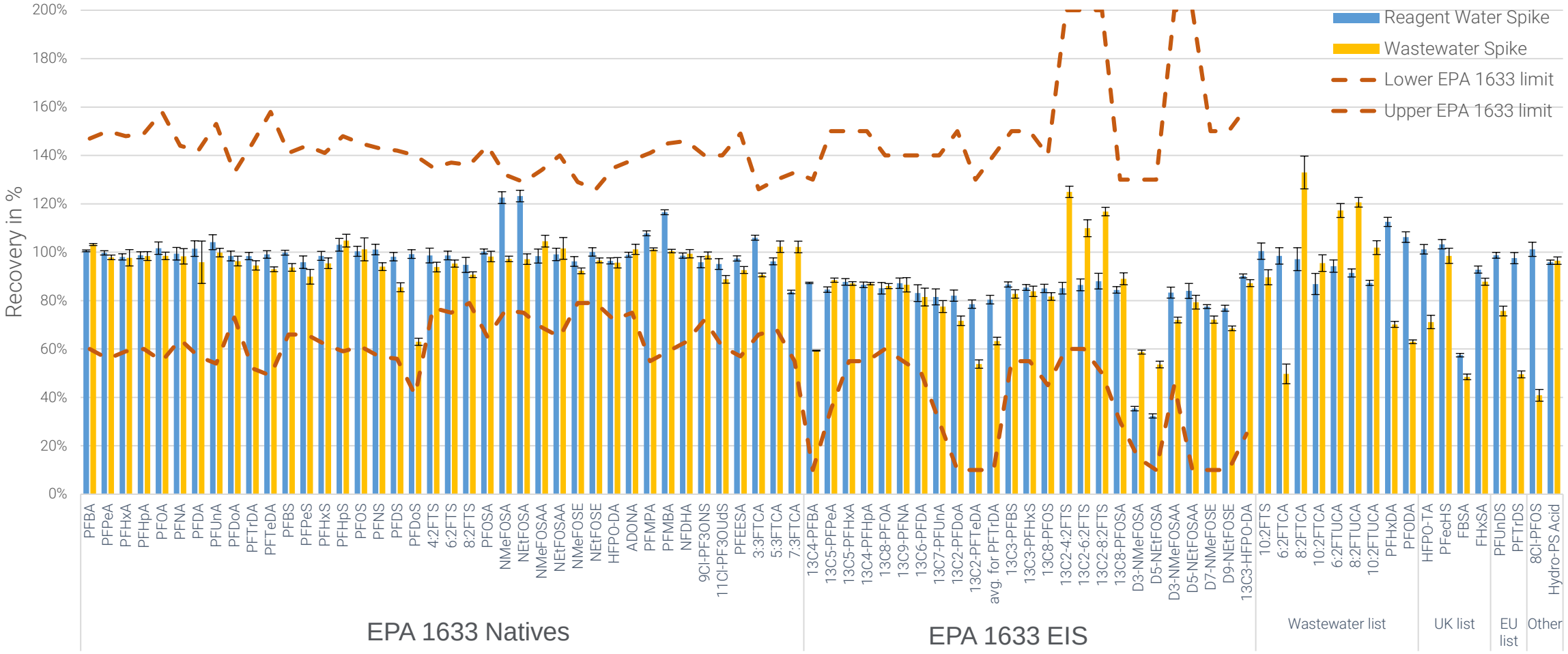
## Reliability & Robustness for demanding applications.

Born out of our drive for innovation and improvement, Agilent's 6495 Triple Quadrupole LC/MS is an innovative, powerful, and reliable mass spectrometer for customer applications demanding the lowest limits of detection, sampling speed, and signal reproducibility.

Experience the highest level of confidence with the 6495 Triple Quadrupole LC/MS.

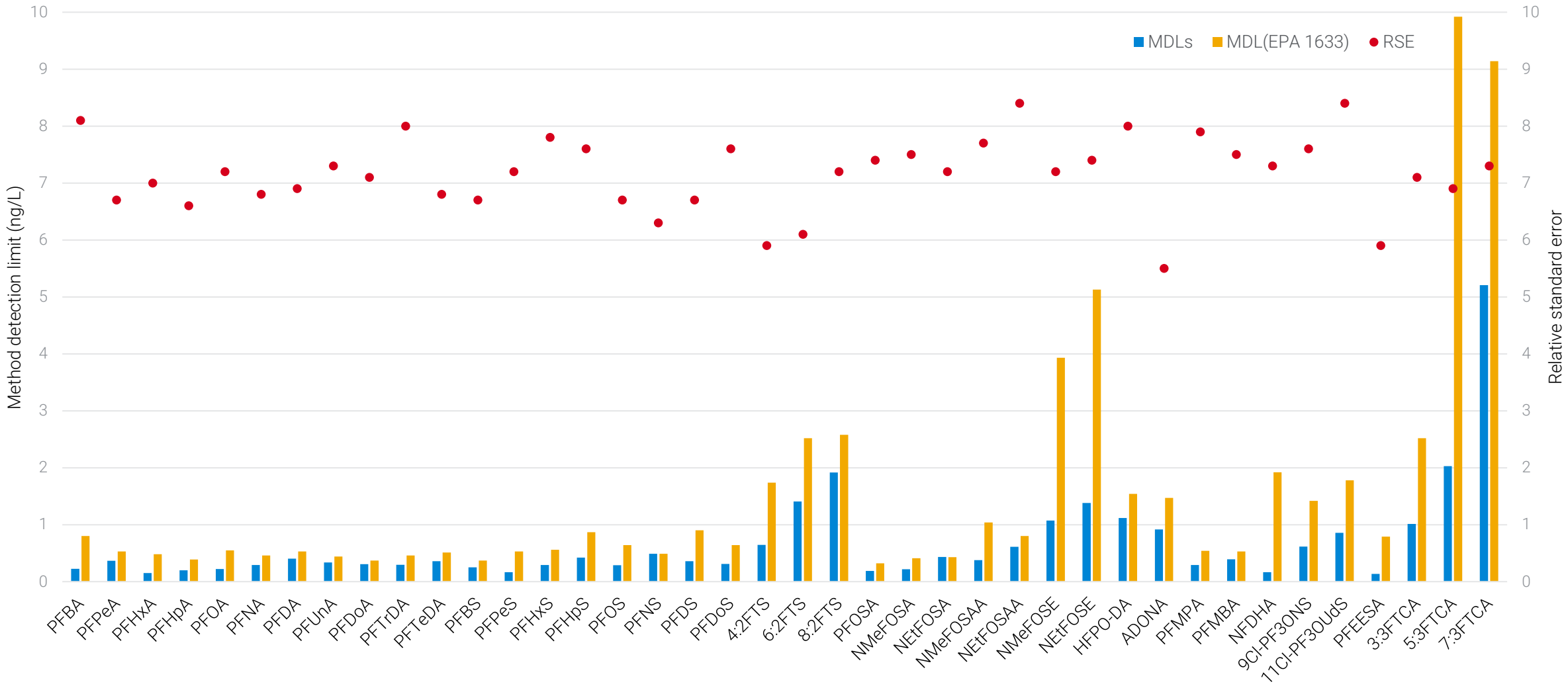


# Comprehensive Workflow for PFAS Analysis in Wastewater



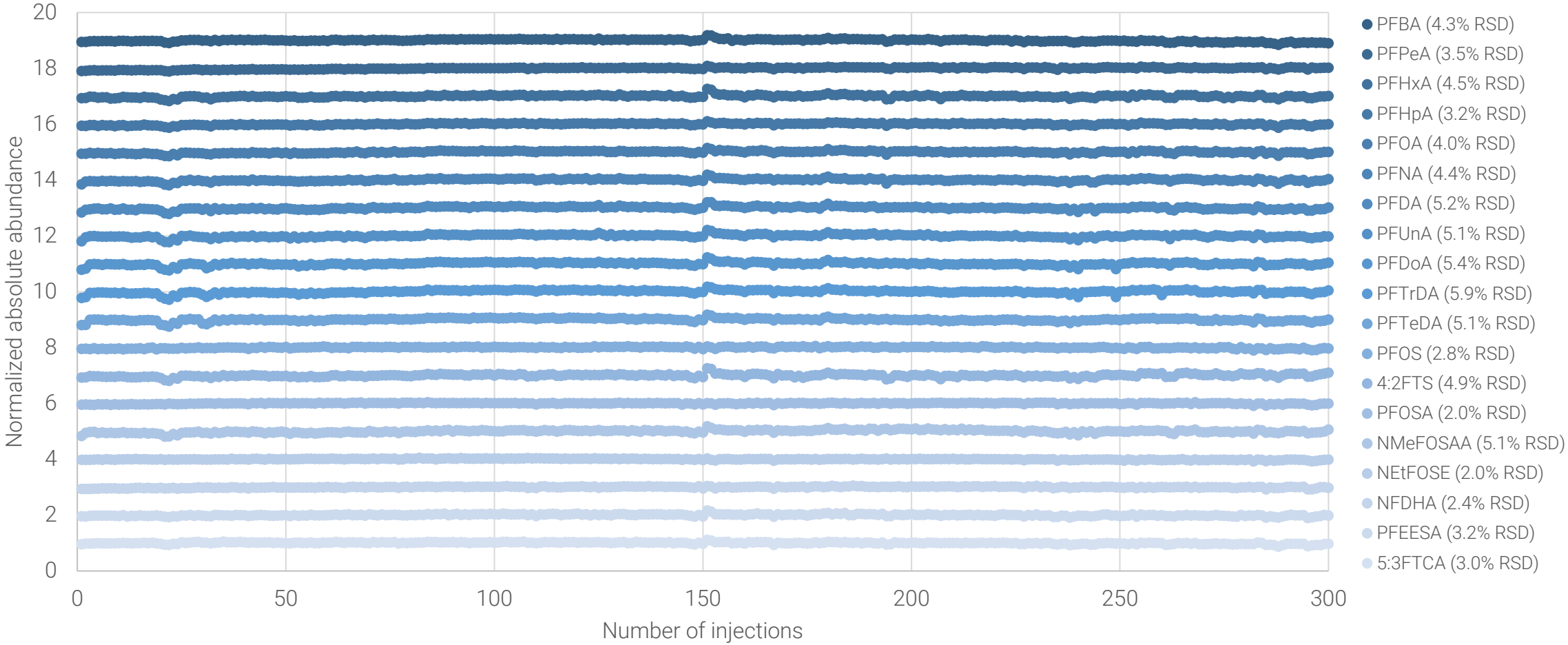

Poster Thursday 075

# Method Detection Limit and Relative Standard Error

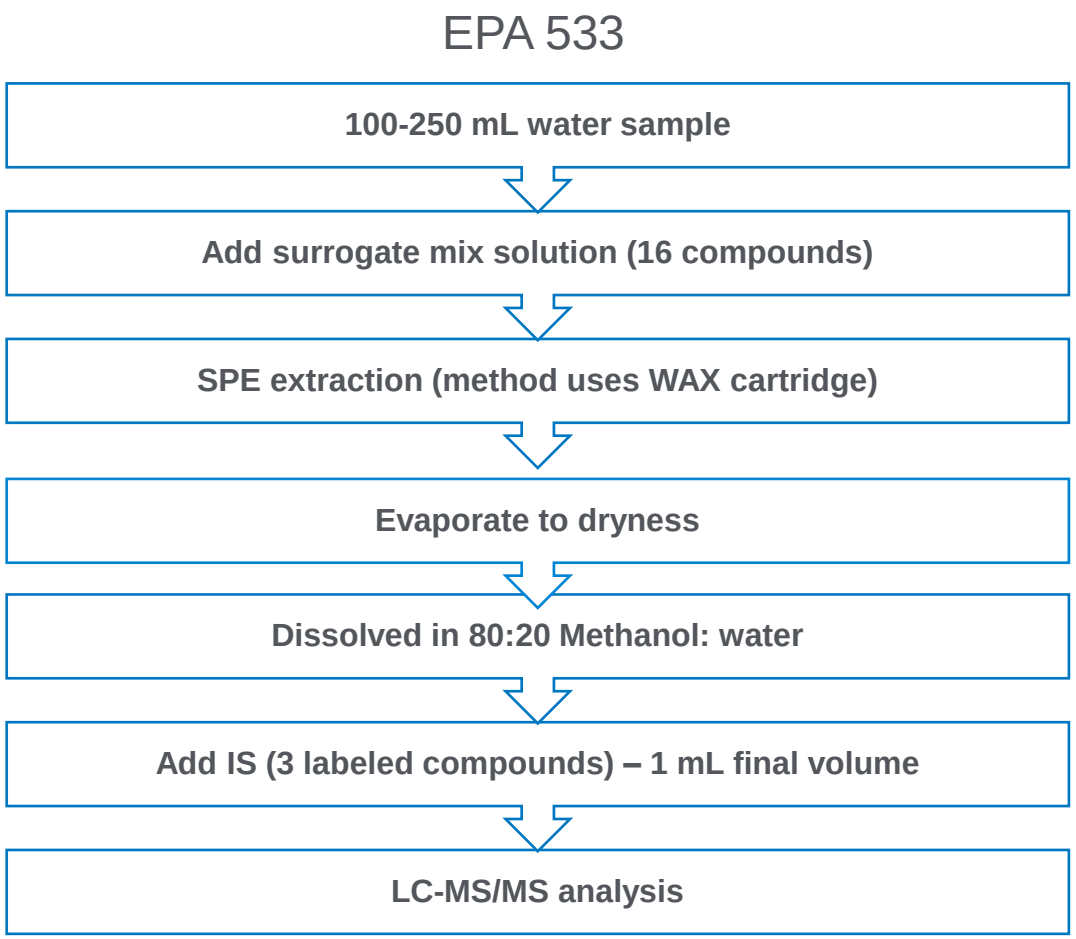


# 6495 LC/TQ Robustness

## >300 injections run over 80+ hours; RSD <6% for all 40 PFAS in EPA 1633



# EPA 533

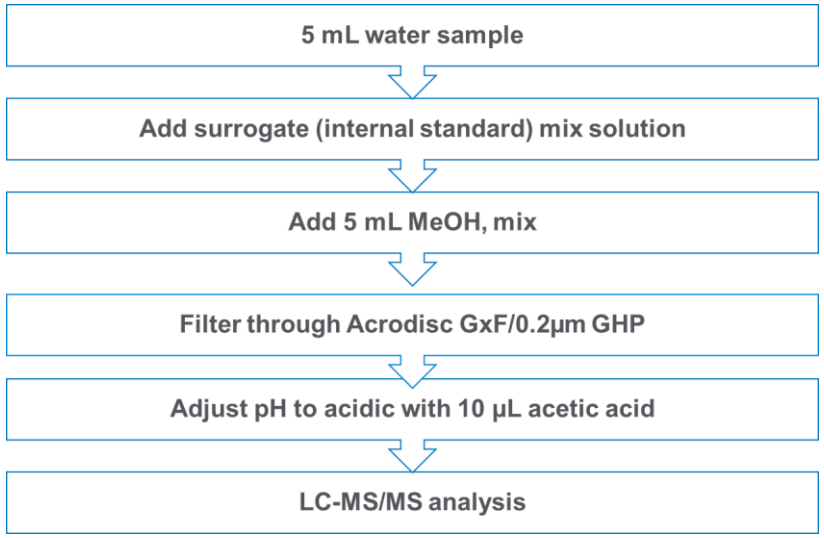


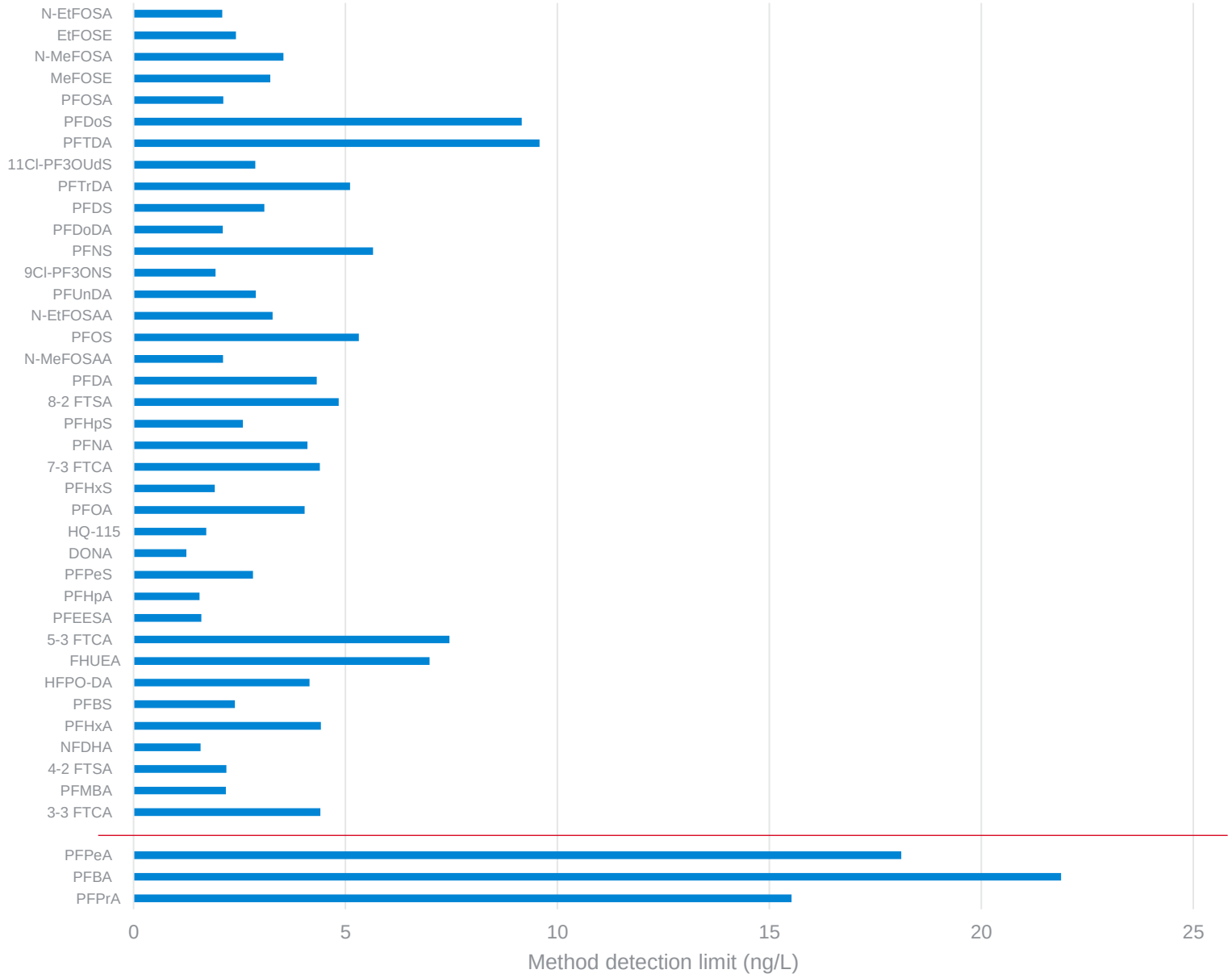

| | 3rd Generation iFunnel LOQ (ng/L) | 4th Generation iFunnel LOQ (ng/L) |
|---|---|---|
| PFBS | 0.01 | 0.004 |
| HFPO-DA | 0.01 | 0.01 |
| PFOA | 0.02 | 0.01 |
| PFHxS | 0.02 | 0.01 |
| PFNA | 0.03 | 0.03 |
| PFOS | 0.2 | 0.03 |

2.5- 7x Improvement

# PFAS Analysis (ASTM 8421)

- Dilute and Shoot method
- Reporting range 10 – 400 ng/L
- Injection volume: **10 uL**



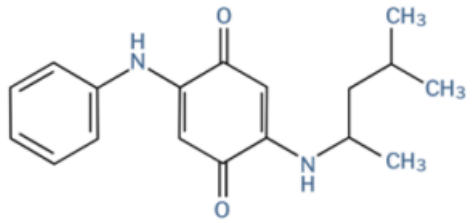

Enhanced Sensitivity with 6495!

# PFAS Workflows Conclusions

- A comprehensive workflow including sample management, preparation, consumables, data acquisition/analysis, and reporting developed for the PFAS analysis.
- Reliable sample preparation with excellent recovery.
- 6495 LC/ TQ showed excellent reproducibility and robustness for targeted analysis
- Instrument sensitivity allowed the reduced injection volume for dilute and shoot method
- Now a Fully Mature Workflow

# 6-PPD Quinone

## p-Phenylenediamine Quinone

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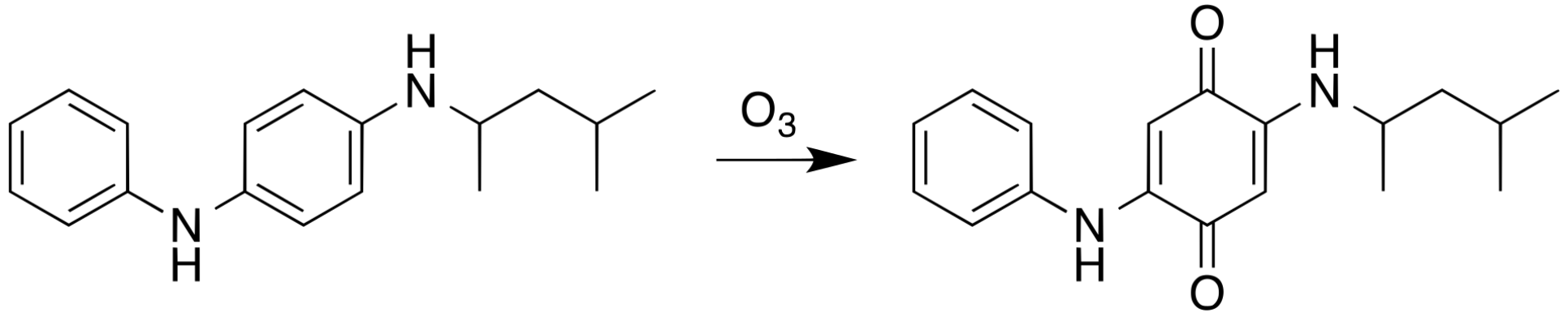
# Oxidative Formation of 6-PPD Quinone from 6-PPD



| Species | $LC_{50}$ (µg/L) | Test duration (h) |
|---|---|---|
| Coho salmon (*Oncorhynchus kisutch*) | 0.04, [24] 0.08, [25] 0.095 [2] | 24 |
| White-spotted char (*Salvelinus leucomaenis pluvius*) | 0.51 [26] | 24 |
| Brook trout (*Salvelinus fontinalis*) | 0.59 [3] | 24 |
| Rainbow trout/steelhead (*Oncorhynchus mykiss*) | 0.64,[29] 1.0,[3] 2.26 [5] | 96 |
| Chinook salmon (*Oncorhynchus tshawytscha*) | 67.3 [24], 82.1 [25] | 24 |
| Sockeye salmon (*Oncorhynchus nerka*) | Not acutely toxic at 50 [25] | 24 |
| Atlantic salmon (*Salmo salar*) | Not acutely toxic at 12.2 [28] | 48 |
| Brown trout (*Salmo trutta*) | Not acutely toxic at 12.2 [28] | 48 |
| Arctic char (*Salvelinus alpinus*) | Not acutely toxic at 12.7 [3] | 24 |
| Southern Dolly Varden (*Salvelinus curilus*) | Not acutely toxic at 3.8 [26] | 48 |
| Cherry salmon (*Oncorhynchus masou masou*) | Not acutely toxic at 3.5 [26] | 48 |

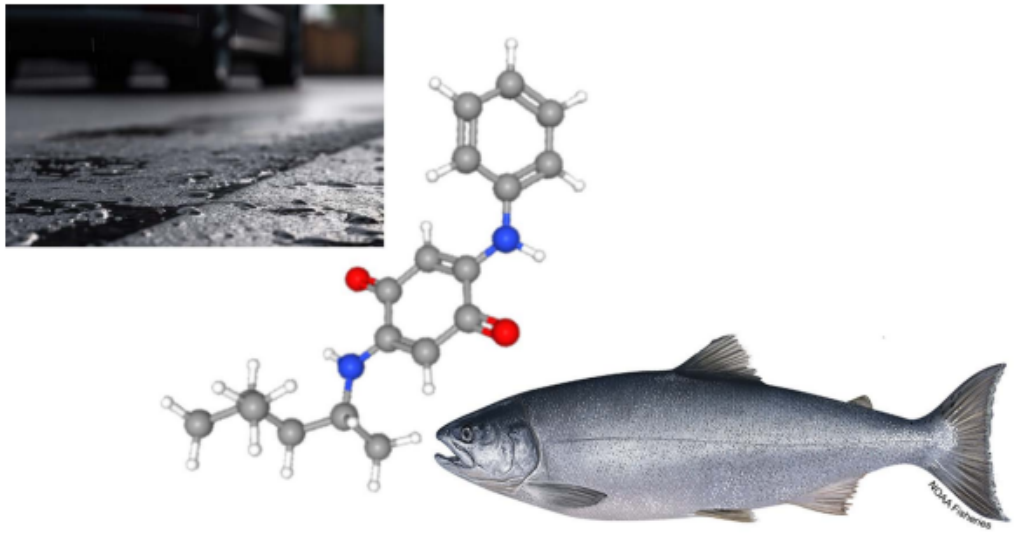
EPA United States Environmental Protection Agency

Office of Water

www.epa.gov December 2023

# DRAFT Method 1634

## Determination of 6PPD-Quinone in Aqueous Matrices Using Liquid Chromatography with Tandem Mass Spectrometry (LC/MS/MS)



# 6-PPD Quinone in Stream Water Method via LC-MS/MS

| Compound Name | Precursor Ion (*m/z*) | Product Ion (*m/z*) | Ret. Time (min) | Fragmentor (V) | Collision Energy (V) | Cell Accelerator Voltage | Polarity |
|---|---|---|---|---|---|---|---|
| 6PPD-Quinone | 299.2 | 241.1 | 3.52 | 105 | 32 | 4 | Positive |
| 6PPD-Quinone | 299.2 | 215.1 | 3.52 | 105 | 16 | 5 | Positive |
| 6PPD-Quinone | 299.2 | 187.1 | 3.52 | 105 | 32 | 5 | Positive |
| $D_5$-6PPD-Quinone | 304.2 | 246.1 | 3.49 | 110 | 36 | 4 | Positive |
| $D_5$-6PPD-Quinone | 304.2 | 220.1 | 3.49 | 110 | 20 | 4 | Positive |
| $D_5$-6PPD-Quinone | 304.2 | 192.1 | 3.49 | 110 | 36 | 5 | Positive |

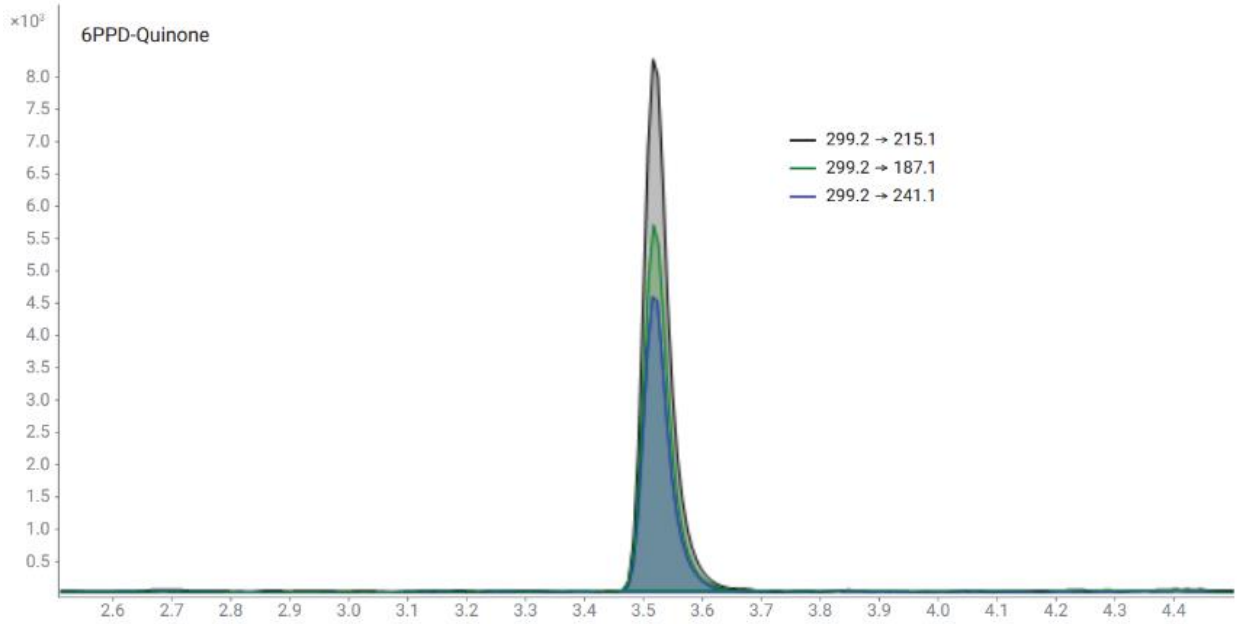



**Figure 1.** 6PPD-quinone chromatography at 0.2 ng/mL.

6PPD-quinone was quantitated using a calibration curve from 0.01 to 50 ng/mL using quadratic fit, 1/x weighting, and including the origin. The R2 value was greater than 0.999.

Method recovery (accuracy) in HPLC water was 113.5% and in stream water was 112.6%. Precision, expressed as %RSD, was 3% in HPLC water and 1% in stream water for n = 5 replicates at 5 ng/mL. The LCMRL of 6PPD-quinone was 0.023 ng/mL. There was no contribution to the 6PPD-quinone signal from the LC system.

# 6-PPD Quinone In Salmon Tissue

Weigh out 2g sample, add 5ml ACN

↓

Shake then centrifuge at 5000 rpm for 5 minutes

↓

Transfer supernatant to clean tube, then repeat extraction with another 5ml ACN

↓

Combine supernatants

Add 2.5ml water and gently invert

↓

Pass 2.5ml of mixture through Captiva EMR-Lipid cartridge

↓

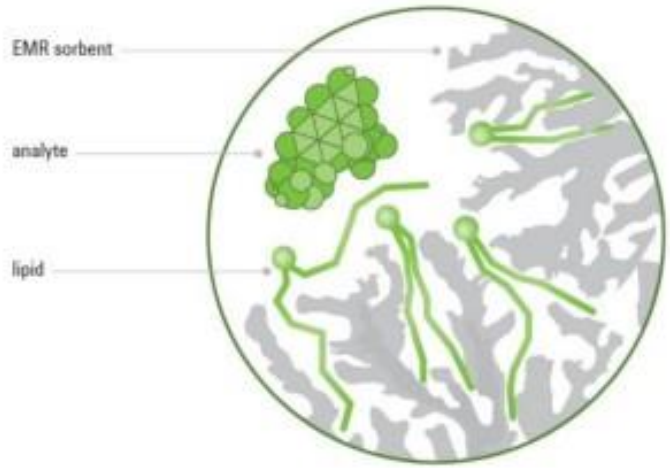
Do a secondary elution with 625µl 80% ACN:20% water

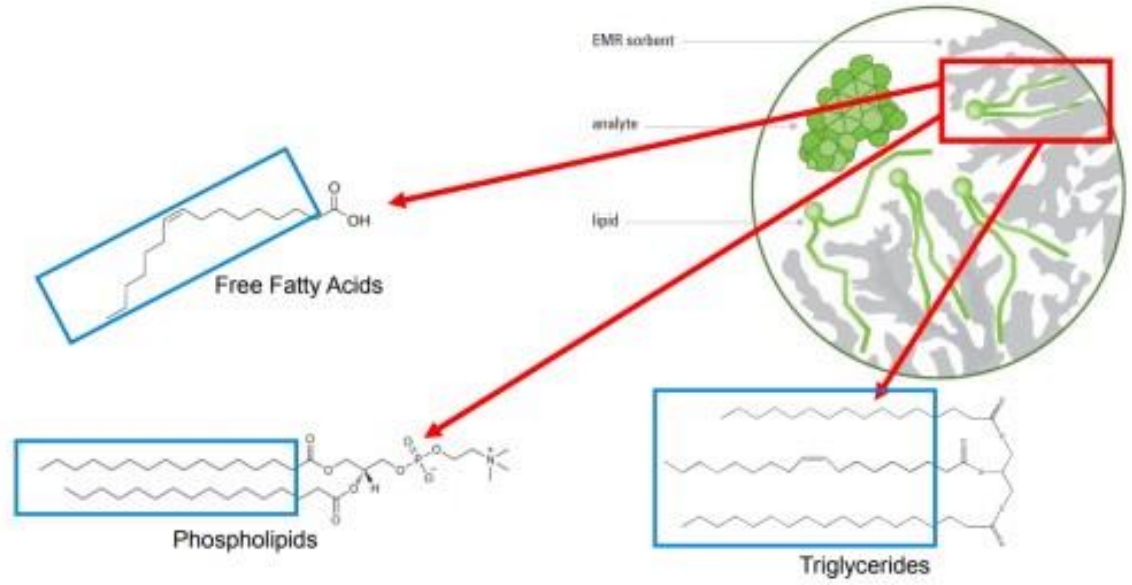
↓

Dry down final product and reconstitute in 1ml mobile phase starting conditions

**EMR sorbent technology effectively traps lipids through two mechanisms:**

- ✓ **Size exclusion** – Unbranched hydrocarbon chains (lipids) enter the sorbent; bulky analytes do not
- ✓ **Sorbent chemistry** – Lipid chains that enter the sorbent are trapped by hydrophobic interactions



# LC-MS/MS
## New Contaminants, New Tools, New Solutions

# Agilent

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