Evaluation of a New Polymeric Weak Anion Exchange Solid Phase Extraction Sorbent for PFAS

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Purpose

- Goals for developing a new polymeric weak anion exchange SPE cartridge
- Performance evaluation and comparison to other commercial sorbents
- Validation results for EPA method 533 and EPA method 1633

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Introduction

- Bond Elut PFAS WAX SPE

New!

Property	Specification
Base Polymer	Poly(styrene-co-divinylbenzene) (PSDVB)
Functionalized	Diamino ligand
Chemistry	Weak anion exchange (WAX) and hydrophobic retention
WAX pKa	> 8
Particle size	45 µm

Part Number	Description
5610-2150	Bond Elut PFAS WAX, 150 mg, 6 mL, 30/pk
5610-2151	Bond Elut PFAS WAX, 200 mg, 6 mL, 30/pk
5610-2152	Bond Elut PFAS WAX, 500 mg, 6 mL, 30/pk

Introduction

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

PFAS Workflow for Drinking Water Analysis (Example)

Sample
250 mL

Empty SPE cartridge, 60 mL (12131012)

Adapter cap for Bond Elut Cartridges (12131001)

Bond Elut PFAS WAX 500 mg, 6 mL (5610-2152)

Vac Elut SPS 24 (12234003)

Centrifuge tubes (15 mL) (5610-2039)

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

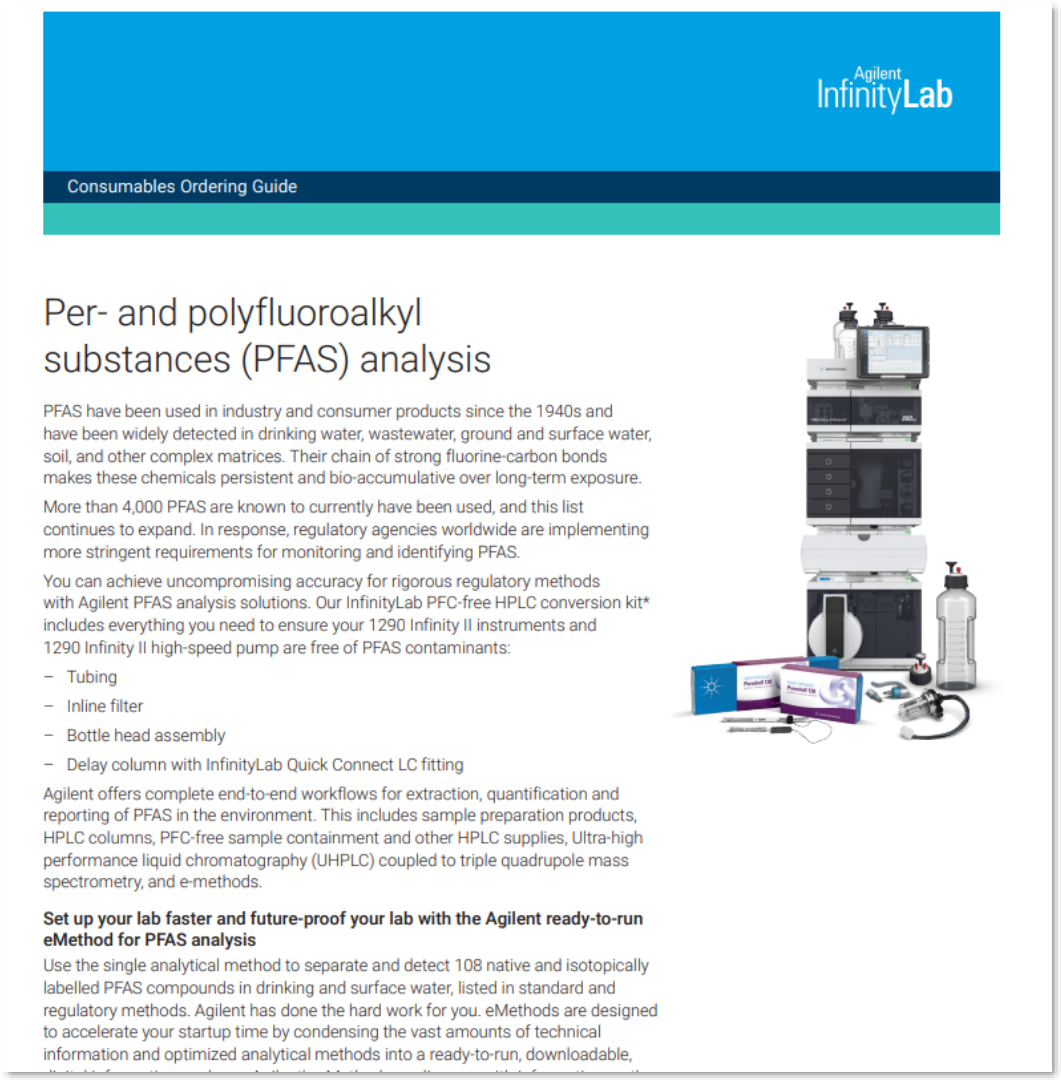
1290 Infinity II LC system

6470B 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)

Ordering Guide for PFAS Analyses



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Consumables Ordering Guide

Per- and polyfluoroalkyl substances (PFAS) analysis

PFAS have been used in industry and consumer products since the 1940s and have been widely detected in drinking water, wastewater, ground and surface water, soil, and other complex matrices. Their chain of strong fluorine-carbon bonds makes these chemicals persistent and bio-accumulative over long-term exposure.

More than 4,000 PFAS are known to currently have been used, and this list continues to expand. In response, regulatory agencies worldwide are implementing more stringent requirements for monitoring and identifying PFAS.

You can achieve uncompromising accuracy for rigorous regulatory methods with Agilent PFAS analysis solutions. Our InfinityLab PFC-free HPLC conversion kit* includes everything you need to ensure your 1290 Infinity II instruments and 1290 Infinity II high-speed pump are free of PFAS contaminants:

- Tubing
- Inline filter
- Bottle head assembly
- Delay column with InfinityLab Quick Connect LC fitting

Agilent offers complete end-to-end workflows for extraction, quantification and reporting of PFAS in the environment. This includes sample preparation products, HPLC columns, PFC-free sample containment and other HPLC supplies, Ultra-high performance liquid chromatography (UHPLC) coupled to triple quadrupole mass spectrometry, and e-methods.

Set up your lab faster and future-proof your lab with the Agilent ready-to-run eMethod for PFAS analysis

Use the single analytical method to separate and detect 108 native and isotopically labelled PFAS compounds in drinking and surface water, listed in standard and regulatory methods. Agilent has done the hard work for you. eMethods are designed to accelerate your startup time by condensing the vast amounts of technical information and optimized analytical methods into a ready-to-run, downloadable,

Ordering guides for:

- EPA 537.1
- EPA 533
- EPA 1633 (draft Aug 2021)
- EPA 8327
- ASTM D7979
- ISO 21675:2019
- Agilent eMethod G5285AA/M5660AA Single method for 108 PFAS compounds.

https://www.agilent.com/cs/library/brochures/brochure-PFAS-consumables-5994-2357EN-agilent-HR.pdf

Target Compounds

Target Compounds

48 compounds across multiple methods + 17 additional compounds (65 total)

Acronym	ASTM D7968	EPA 537.1	ASTM D7979	EPA 8327	EPA 533	ISO 21675	EPA 1633	Added
PFBA	X		X	X	X	X	X	
PFPeA	X		X	X	X	X	X	
PFHxA	X	X	X	X	X	X	X	
PFHpA	X	X	X	X	X	X	X	
PFOA	X	X	X	X	X	X	X	
PFNA	X	X	X	X	X	X	X	
PFDA	X	X	X	X	X	X	X	
PFUnDA	X	X	X	X	X	X	X	
PFDoDA	X	X	X	X	X	X	X	
PFTrDA	X	X	X	X		X	X	
PFTDA	X	X	X	X		X	X	
PFHxDA						X		
PFODA						X		
PFBS	X	X	X	X	X	X	X	
PFPeS				X	X		X	
PFHxS	X	X	X	X	X	X	X	
PFHpS				X	X	X	X	
PFOS	X	X	X	X	X	X	X	
PFNS				X			X	
PFDS				X		X	X	
PFDoS							X	
4-PFecHS	X		X					
HFPO-DA		X			X	X	X	
DONA		X			X	X	X	
PFMPA					X		X	
NFDHA					X		X	
PFMBA					X		X	
6:2 FTCA	X		X					
8:2 FTCA	X		X					
10:2 FTCA	X		X					
3:3 FTCA	X						X	
5:3 FTCA	X		X				X	
7:3 FTCA	X		X				X	
6:2 FTUCA								X

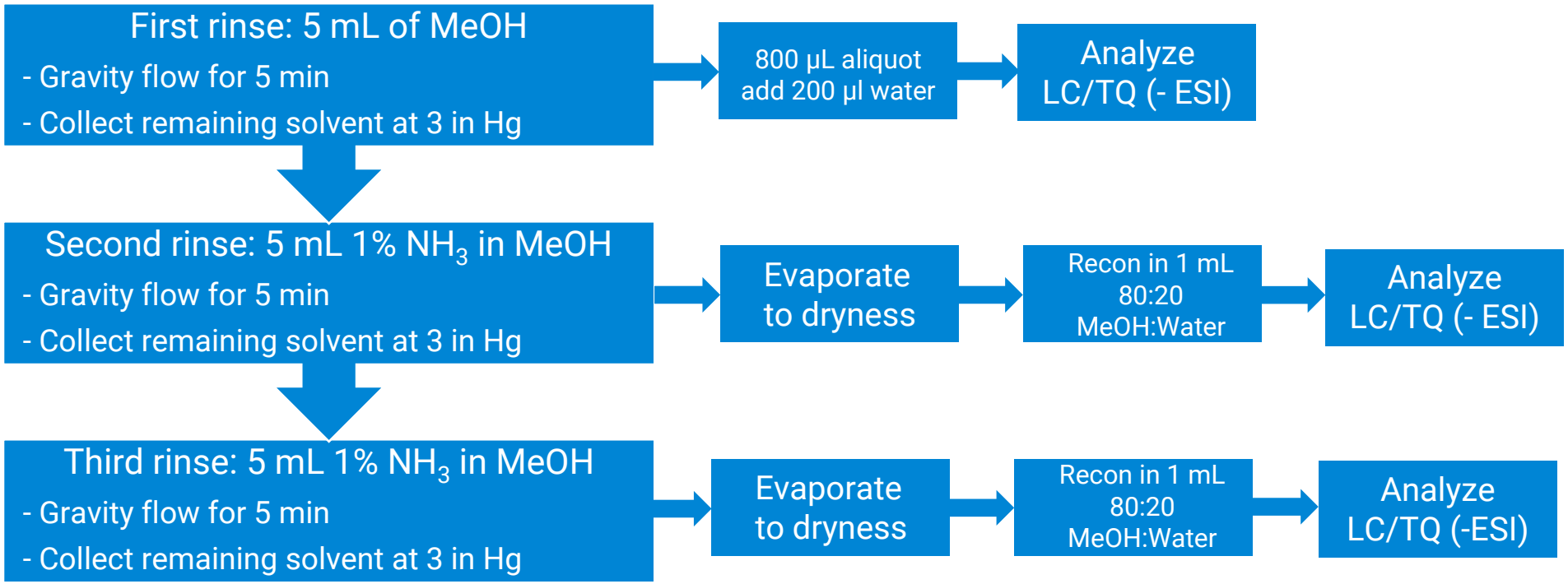
Acronym	ASTM D7968	EPA 537.1	ASTM D7979	EPA 8327	EPA 533	ISO 21675	EPA 1633	Added
8:2 FTUCA			X			X		
10:2 FTUCA								X
PFHxPA								X
PFOPA								X
PFDPA								X
Cl-PFHxPA								X
6:2 diPAP								X
6:2/8:2 diPAP								X
8:2 diPAP						X		
PFEESA					X		X	
9Cl-PF3ONS		X			X	X	X	
11Cl-PF3OUdS		X			X		X	
4:2 FTSA				X	X		X	
6:2 FTSA				X	X	X	X	
8:2 FTSA				X	X	X	X	
10:2 FTSA								X
FBSA								X
FHxSA								X
PFOSA				X		X	X	
FDSA								X
N-MeFOSA						X	X	
N-EtFOSA						X	X	
FOSAA								X
N-MeFOSAA		X		X		X	X	
N-EtFOSAA		X		X		X	X	
MeFOSE							X	
EtFOSE							X	
6:6 PFPi								X
6:8 PFPi								X
8:8 PFPi								X
diSAmPAP								X
Total: 65	21 (2017)	18 (2018)	21 (2019)	24 (2019)	25 (2019)	30 (2019)	40 (2021)	17

Cartridge Cleanliness

Experimental

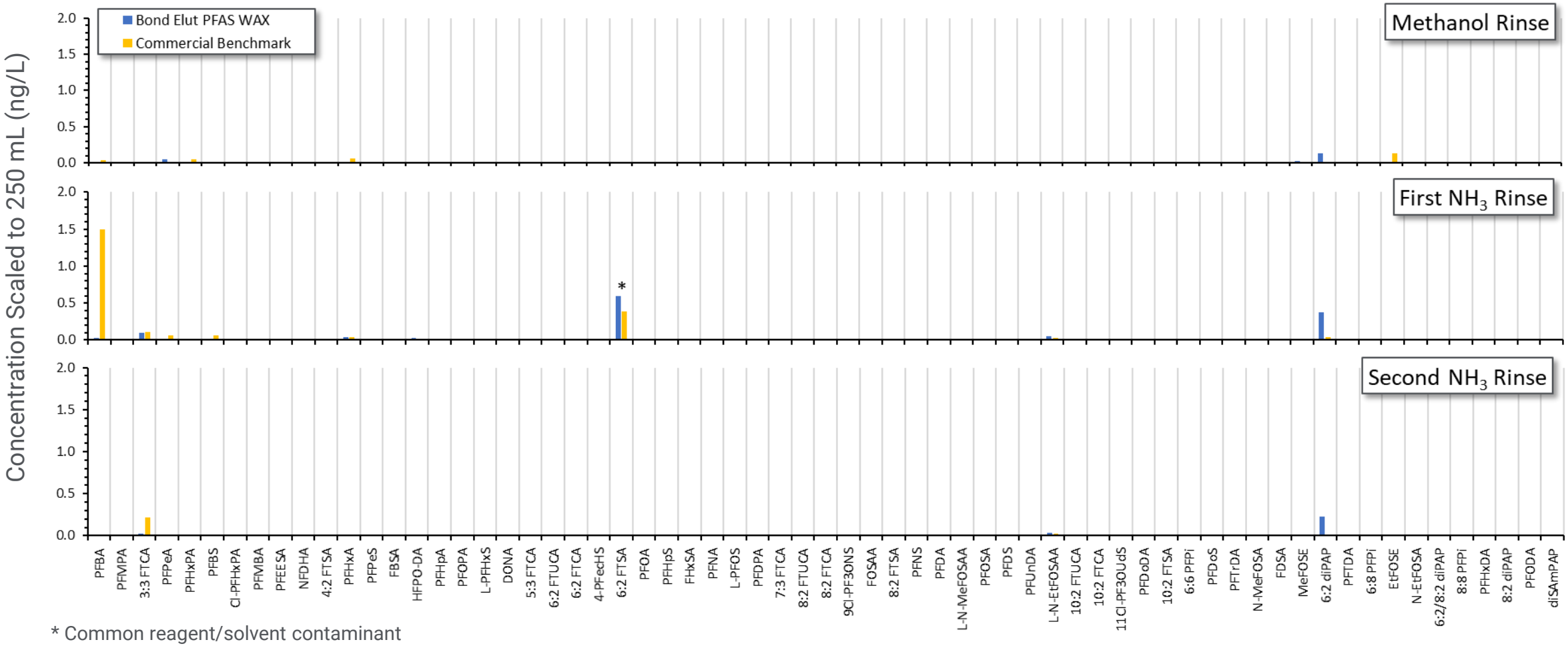
Targeted PFAS contamination testing (500 mg/6 mL)

- Three different batches, 2 replicates per batch
- One benchmark, 2 replicates



Targeted Blank Results

- External calibration (no internal standard correction)
- Estimated concentrations scaled to 250 mL sample volume
- Most concentration extrapolated between zero and lowest calibrant, background subtracted



* Common reagent/solvent contaminant

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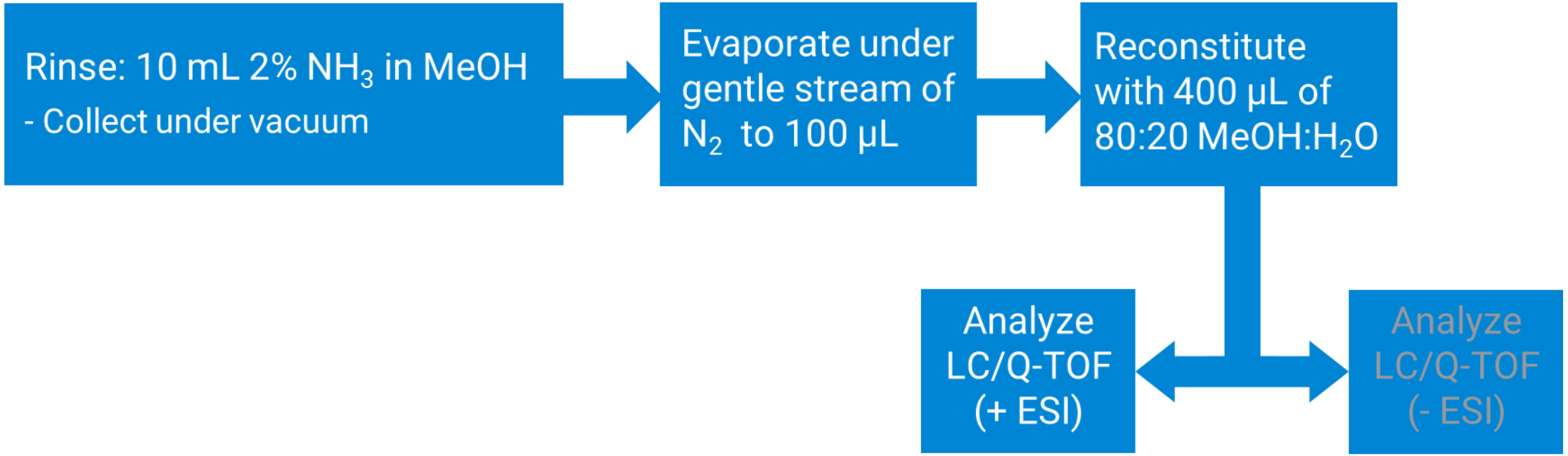
Experimental

Untargeted PFAS contamination testing (500 mg, 6 mL)

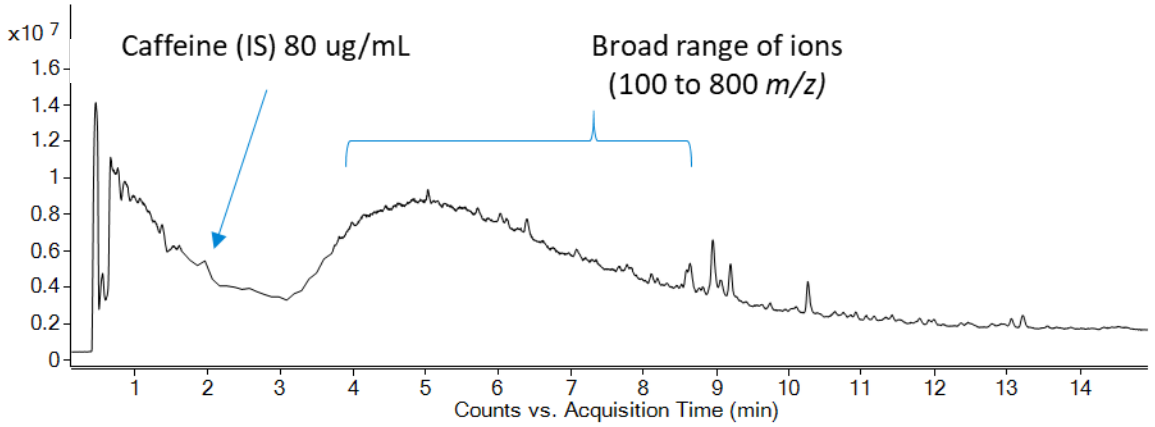
- One batch
- Two benchmark cartridges



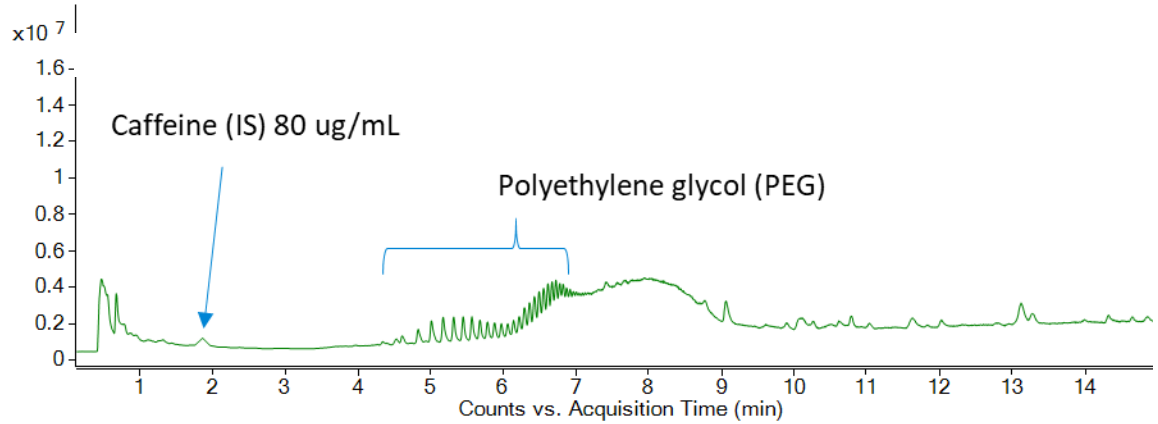
Untargeted Blank Results

Comparison to other commercial sorbents (positive ion mode)

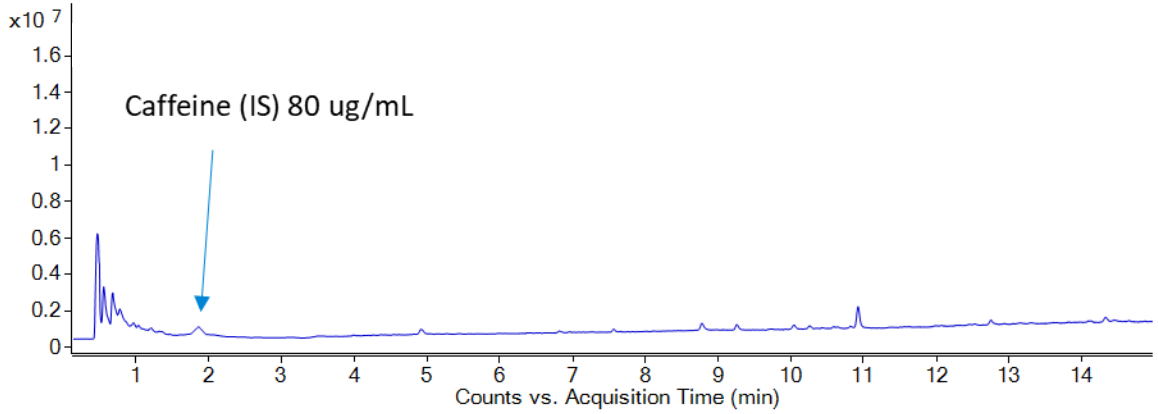
Benchmark Cartridge A



Benchmark Cartridge B

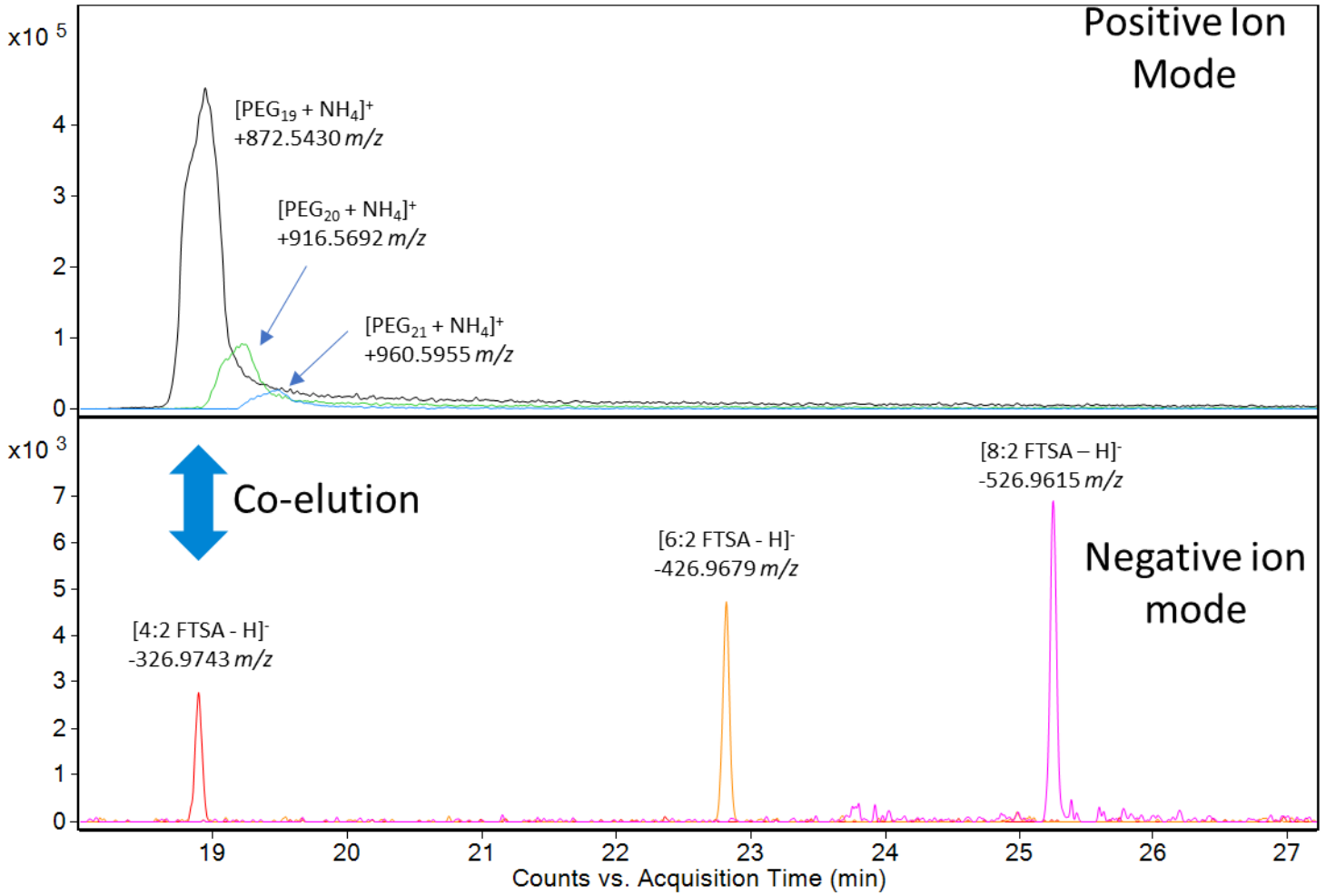


Bond Elut PFAS WAX



Untargeted Blank Results

Co-elution with PEG – matrix ionization enhancement



Calculated concentration/recovery

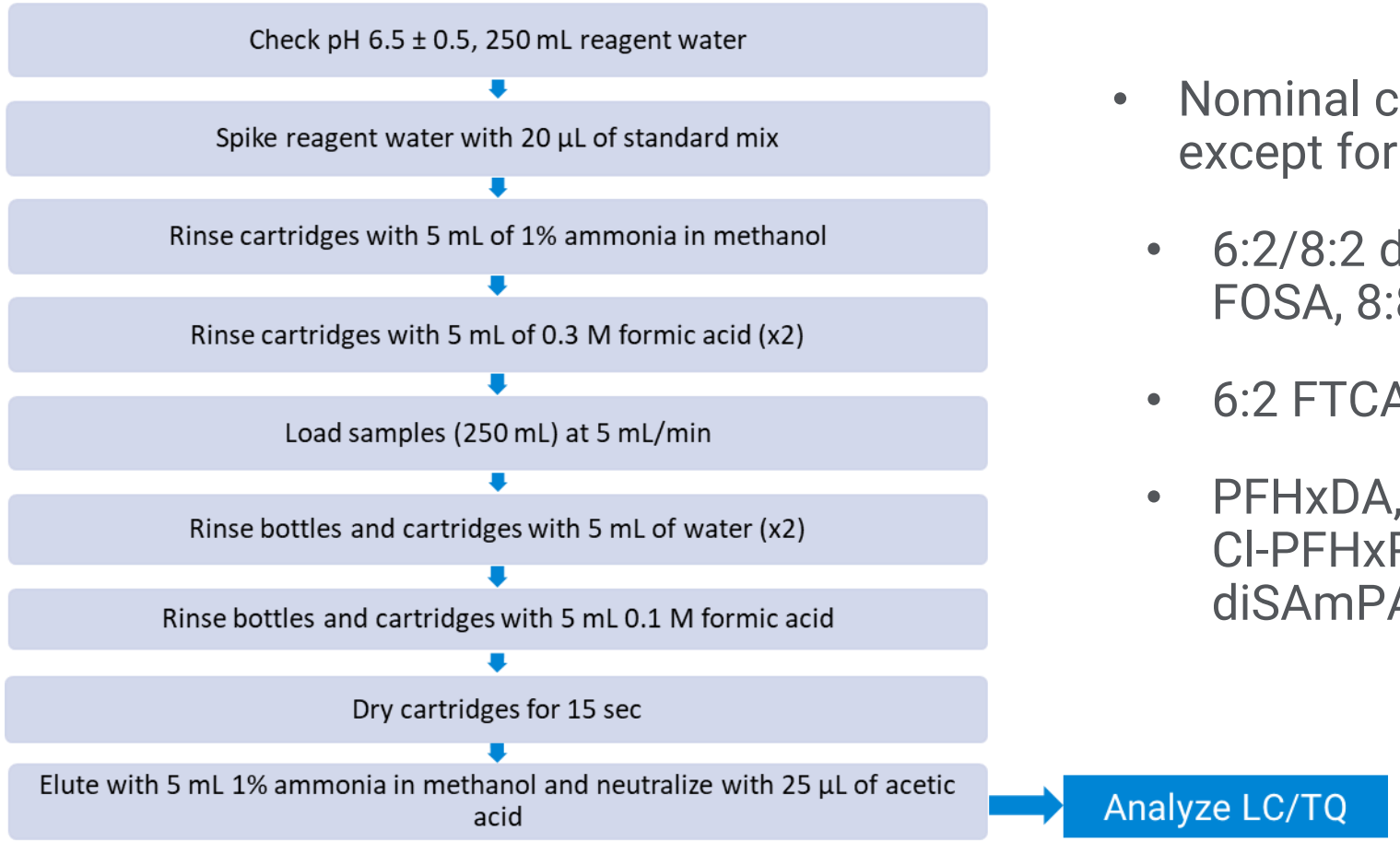
Compound	Calculated concentration (ng/L)	Actual concentration (ng/L)	Recovery (%)
4:2 FTSA	760	500	152
6:2 FTSA	496	500	99
8:2 FTSA	464	500	93

Spike Recoveries

Experimental

PFAS recovery testing (500 mg/6 mL)

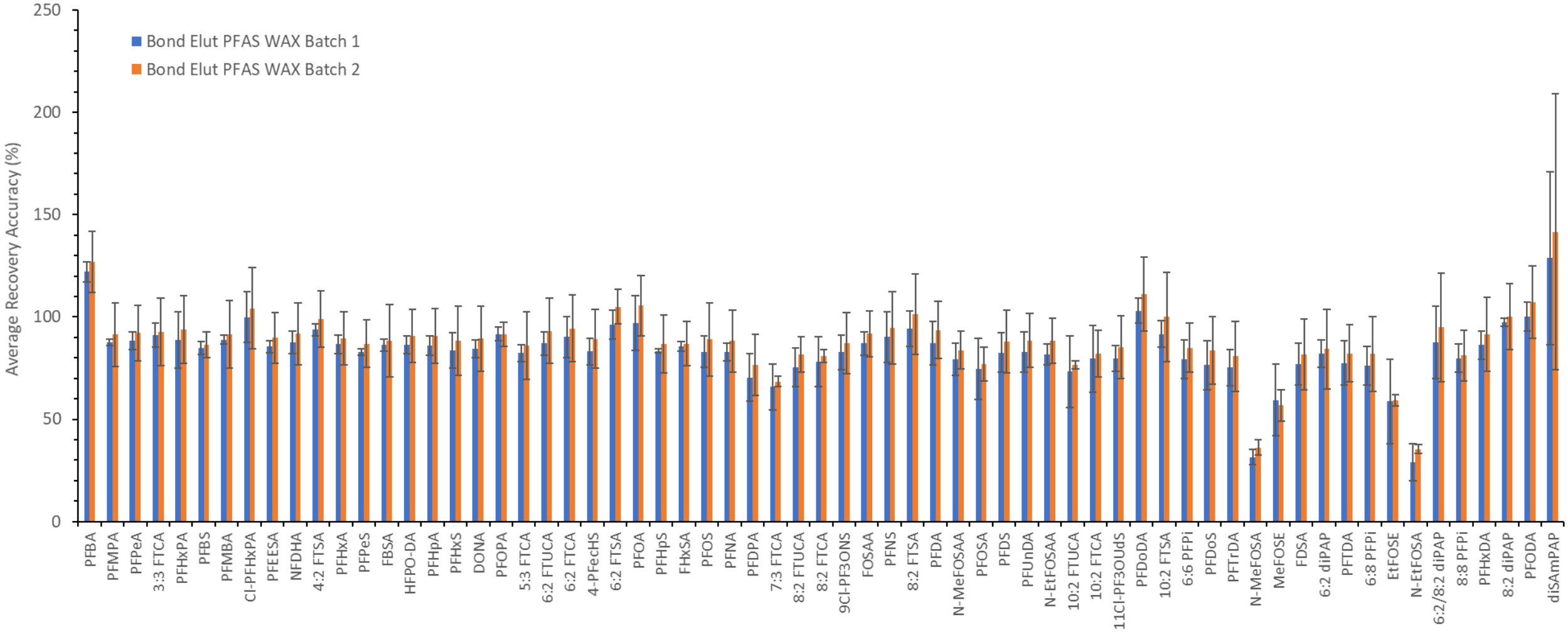
- Two different batches, 3 replicates per batch



- Nominal concentration 20 ng/L in 250 mL except for:
  - 6:2/8:2 diPAP, 8:2 diPAP, Me-FOSA, Et-FOSA, 8:8 PFPi at 40 ng/L
  - 6:2 FTCA, 8:2 FTCA, 10:2 FTCA at 200 ng/L
  - PFHxDA, PFODA, PFHxPA, PFOPA, PFDPA, Cl-PFHxPA, FOSAA, MeFOSE, EtFOSE, diSAmPAP at 80 ng/L

Recovery Results - Accuracy

- External calibration (no internal standard correction)
- Error bars represent 95% CI, N=3



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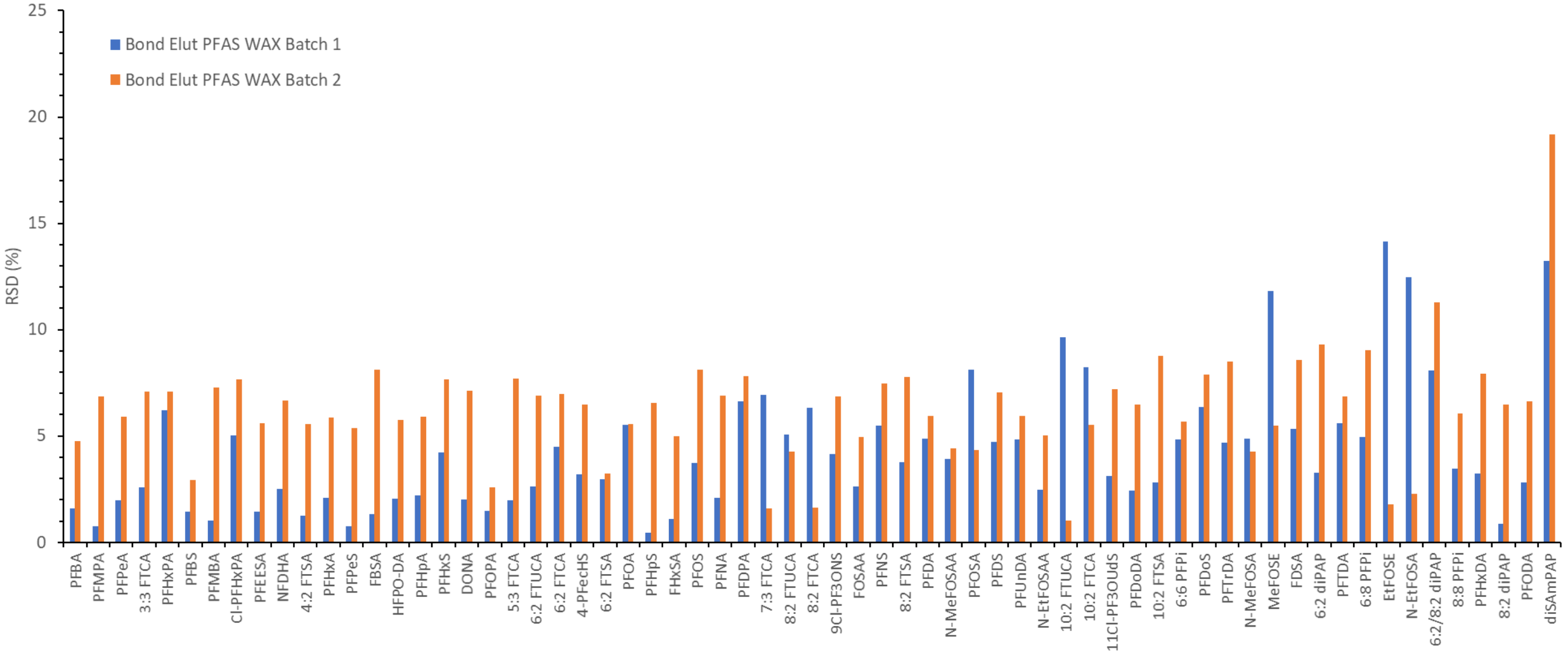
Recovery Results - Precision

- External calibration (no internal standard correction)



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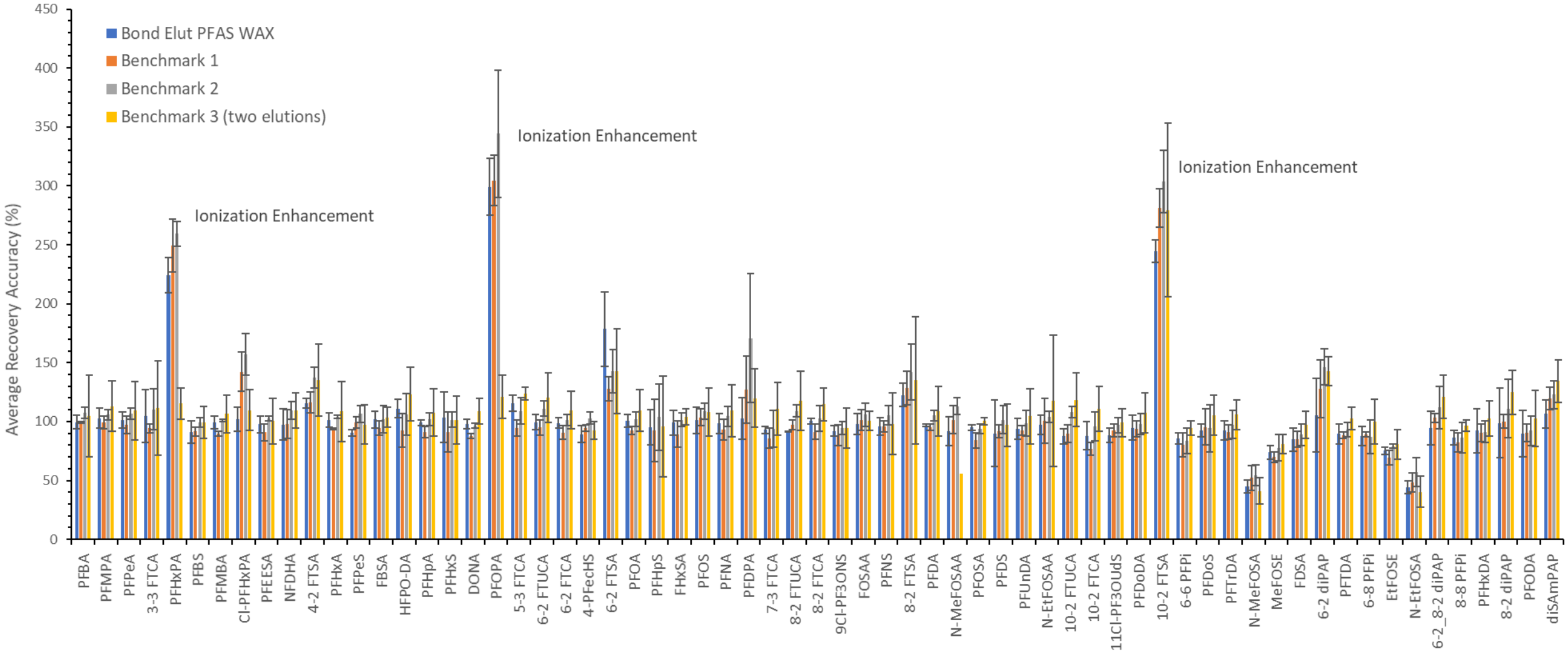
Recovery Results – Benchmark Comparison (65 targets)

- External calibration (no internal standard correction)
- Error bars represent 95% CI, N=3



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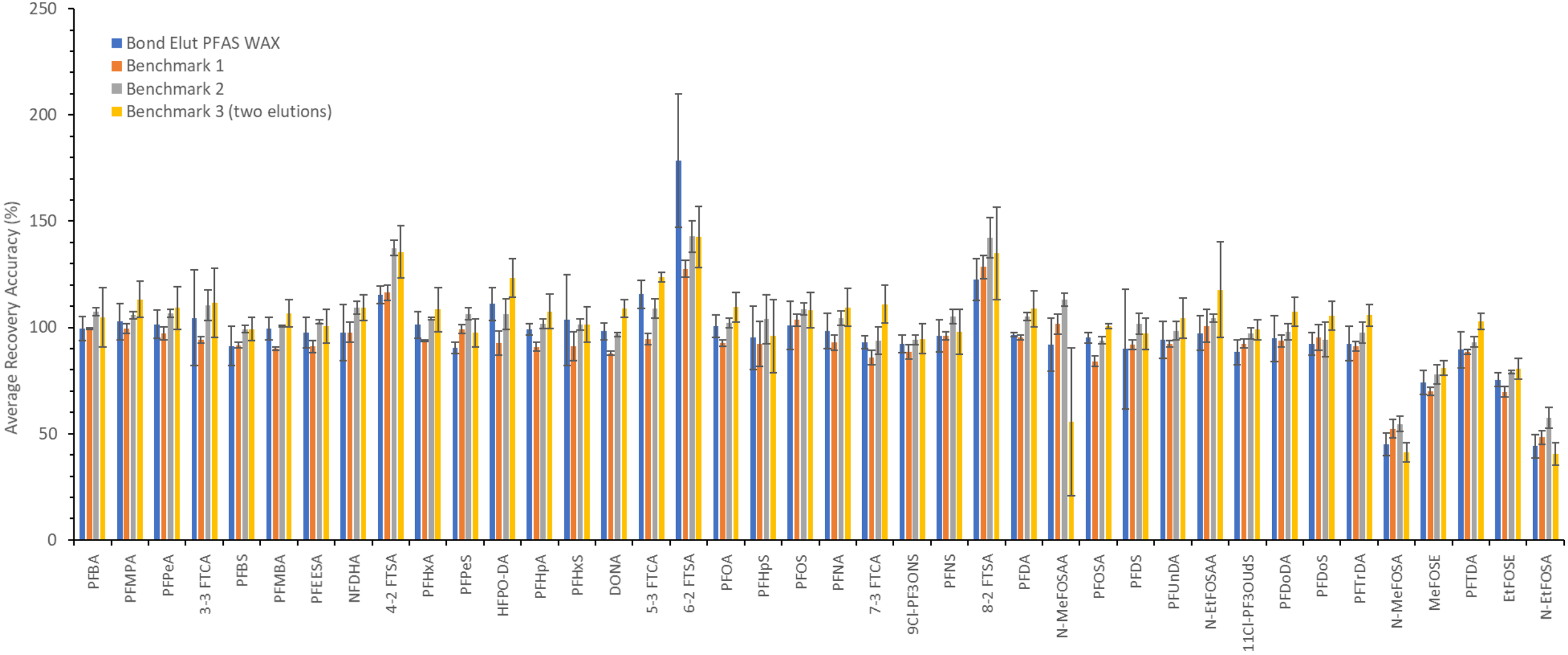
Recovery Results – Benchmark Comparison (EPA 533/1633 Targets)

- External calibration (no internal standard correction)
- Error bars represent 95% CI, N=3



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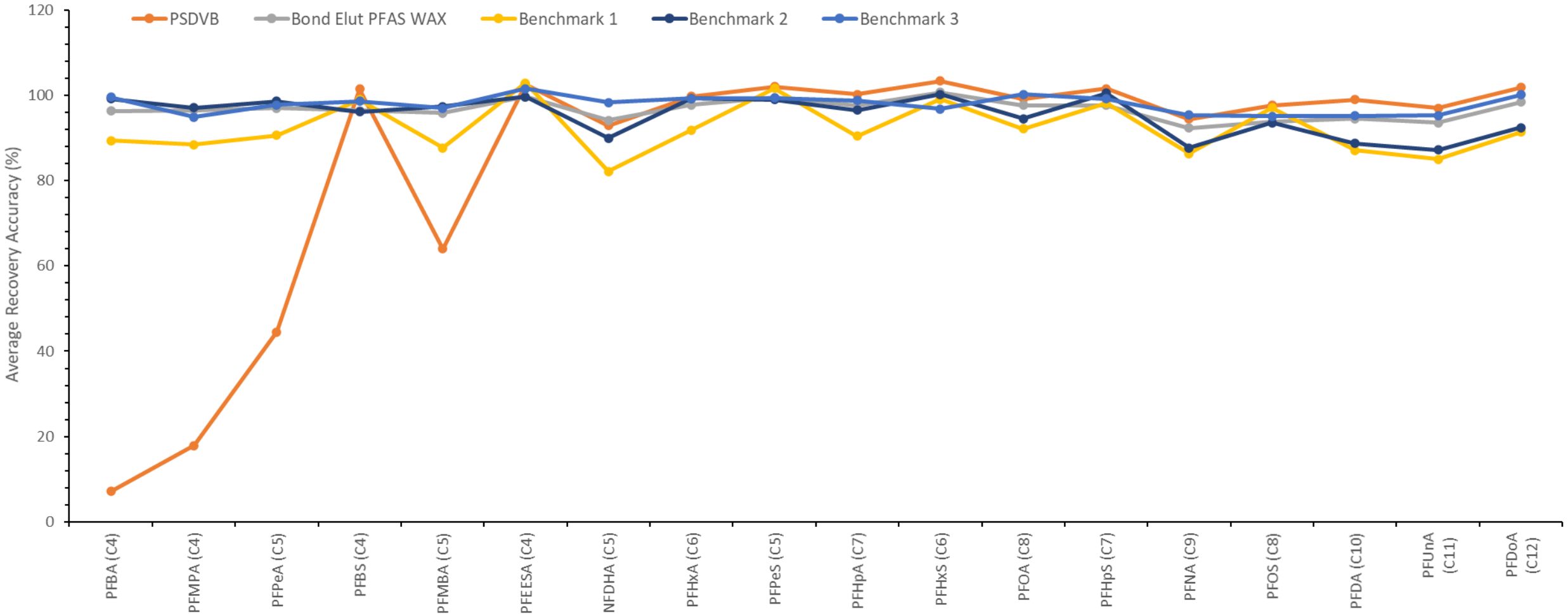
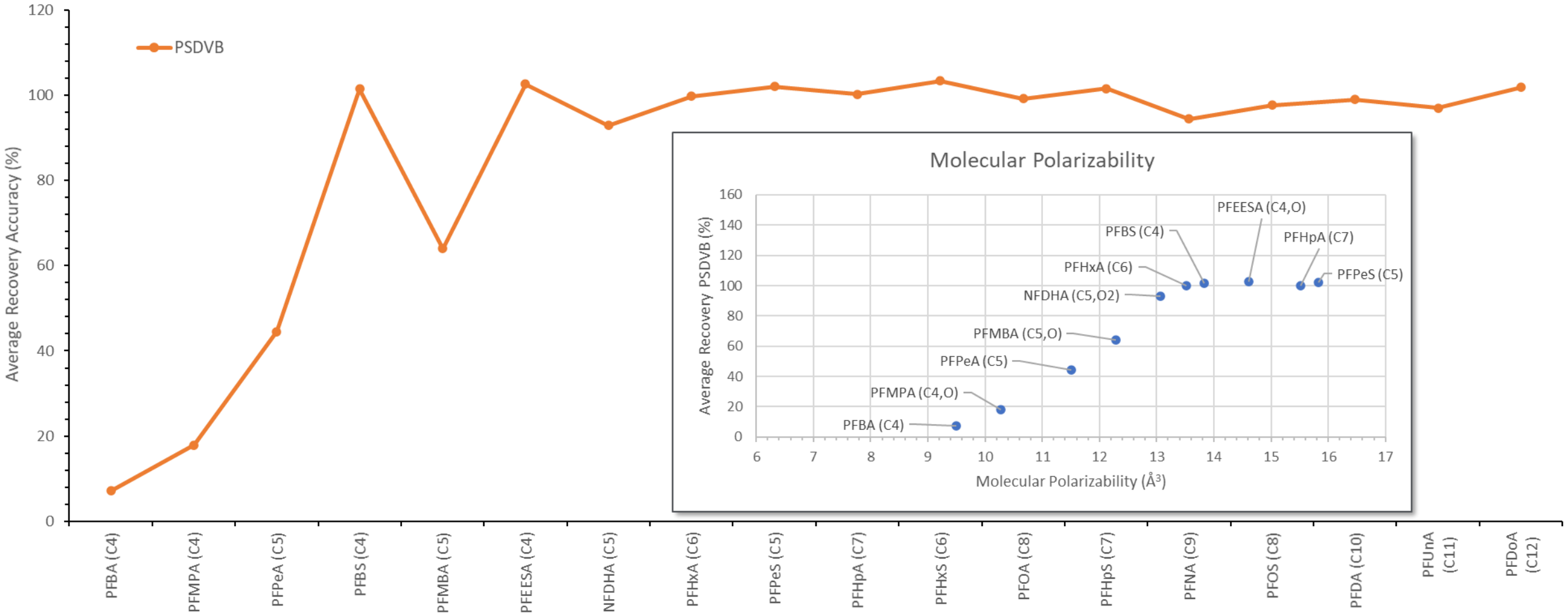
Recovery Results – PSDVB and Benchmark Comparison

- External calibration (no internal standard correction)



Recovery Results – PSDVB

- External calibration (no internal standard correction)
- Estimated average molecular polarizability (Miller's model) calculated using ChemDoodle (ver 11.10.0, iChemLabs LLC)



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Applications – EPA Method 533

Experimental Approach

- Follow EPA method 533
  - Determination of PFAS in drinking water by LC/MS/MS
- Targets
  - 25 EPA method 533 targets
- Quantitation
  - Co-extracted isotopically labeled internal standards
- Blank analysis
  - Determines minimum reporting limit (MRL) – MRL 3x blank at minimum
- Matrix spike recovery
  - Low level spike - 2 ng/L – check recovery 50-150%
  - High level spike – 20 ng/L – check recovery 70-130%
- Test samples
  - Municipal tap water sample

Experimental

Extraction Procedure – EPA method 533

Place SPE cartridges and 15 mL centrifuge collection tubes on Agilent Vac Elut SPS 24 manifold. Rotate cowling to the waste position.

↓

Rinse each SPE cartridge with 10 mL methanol.

↓

Add 60 mL reservoirs and adapters to each SPE cartridge.

↓

Rinse each cartridge with 10 mL of 0.1 M phosphate buffer. Close the stopcock and add an additional 3 mL of 0.1 M phosphate buffer.

↓

Fill the reservoirs with 60 mL of sample and adjust flow rate to approximately 5 mL/min (vacuum pressure 3 to 5 inHg).

↓

Repeat the filling step until the 250 mL sample volume has been transferred.

↓

Rinse the bottles, reservoirs, and cartridges with 10 mL of 1 g/L ammonium acetate.

↓

Dry the cartridges for 5 minutes at a vacuum pressure of 15 to 20 inHg.

↓

Rotate the cowling on the Vac Elut SPS 24 manifold to the collect position.

↓

Elute the cartridges by rinsing the sample bottles, reservoirs, and cartridges with 5 mL of 2% ammonium hydroxide in methanol.

↓

Repeat the elution with a second 5 mL portion of 2% ammonium hydroxide in methanol.

↓

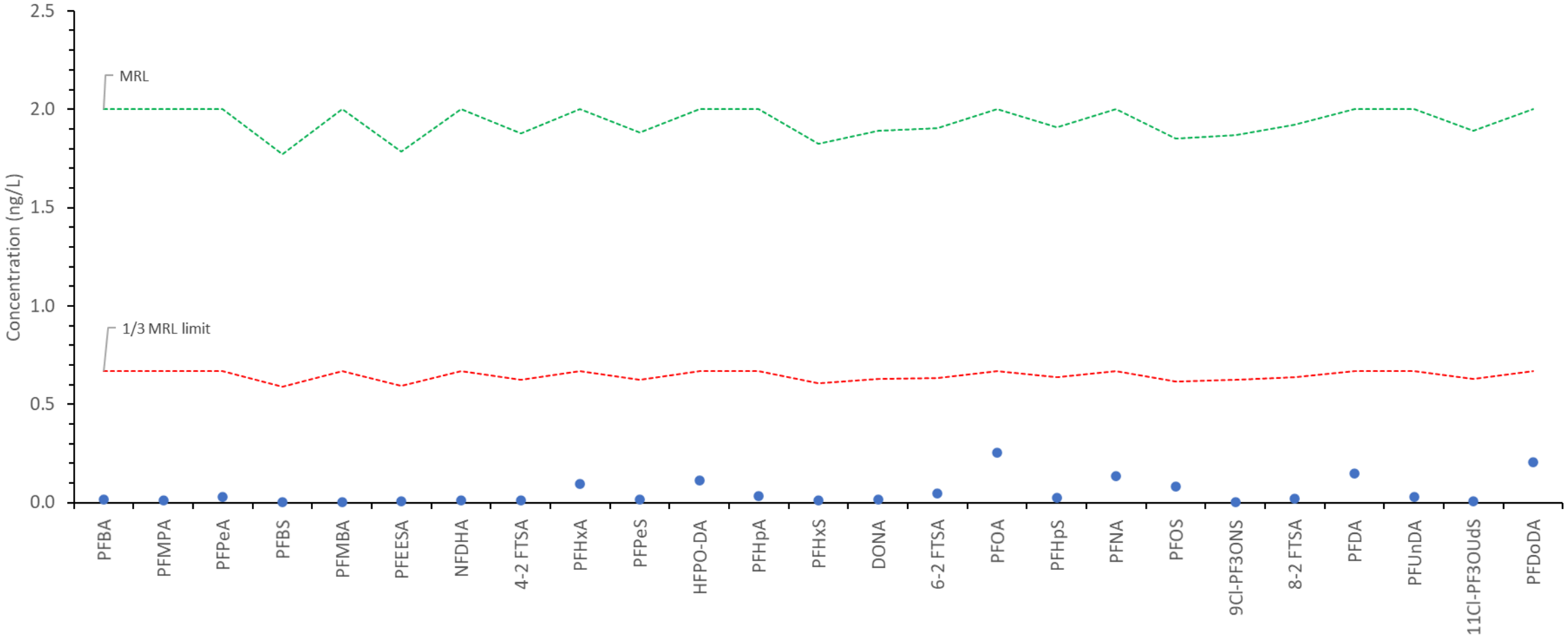
Evaporate the 10 mL extracts under a gentle stream of nitrogen at 55 to 60 °C until dry.

↓

Reconstitute extract in 1 mL of 80:20 MeOH:H_2O and analyze by LC/MS/MS.

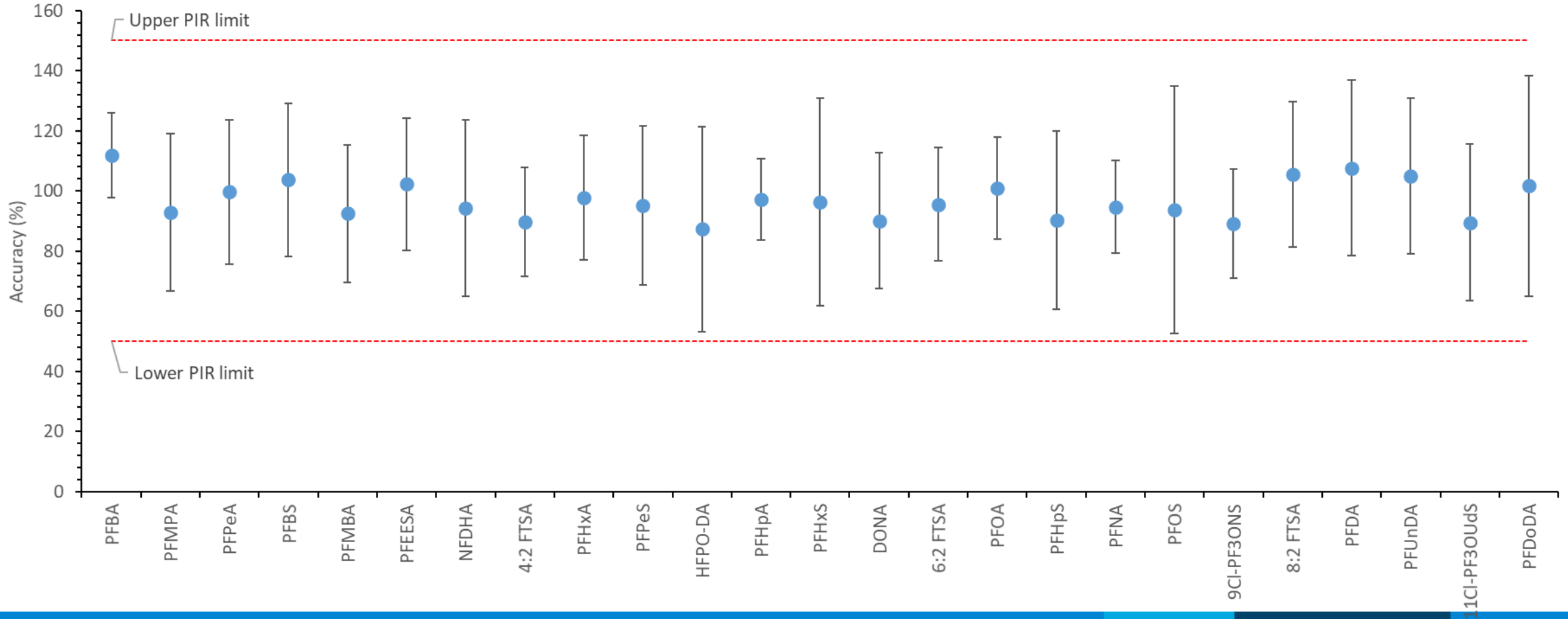
Low System Background Demonstration – EPA Method 533 Targets

- Blank extractions < 1/3 minimum reporting level (MRL)



MRL Confirmation – EPA Method 533 Targets

- MRL must fall within 50 to 150% recovery with 99.5% confidence.
- Predicted interval of results (PIR) for 8 replicate extractions at 2 ng/L.
- Average recovery 97.0% and average RSD 6.9%



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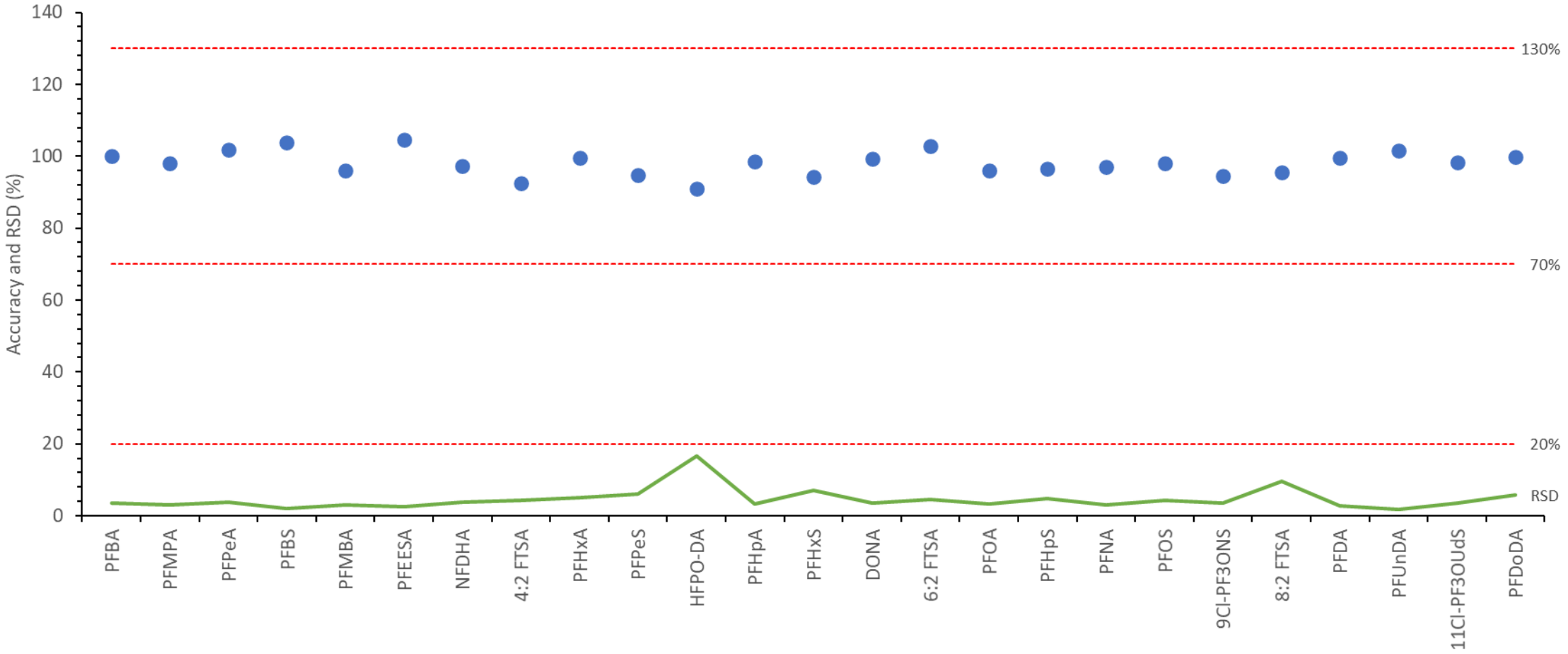
Precision and Accuracy Demonstration - EPA Method 533 Targets

- Seven replicate extractions at 20 ng/L
- Recoveries must be within 70 to 130% with an RSD < 20%
- Average recovery was 98.1% with an average RSD of 4.6%



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Tap Water Extraction

- Tap water from municipal water supply
- Tap water spike at 4 ng/L

Compound	Concentration found in tap water sample (ng/L)	Concentration in spiked in tap water sample (ng/L)	Background subtracted Spike Recovery (%)
PFBA	5.8	4.3*	107
PFMPA	< MRL	3.7	93
PFPeA	3.6	4.4*	111
PFBS	1.9	3.3*	94
PFMBA	< MRL	4.0	99
PFEESA	< MRL	3.7	104
NFDHA	< MRL	3.9	99
4:2 FTS	< MRL	3.9	105
PFHxA	3.4	4.5*	112
PFPeS	< MRL	3.6	95
HFPO-DA	< MRL	4.8	121
PFHpA	2.3	4.0*	99
PFHxS	< MRL	4.1	112

Compound	Concentration found in tap water sample (ng/L)	Concentration in spiked tap water sample (ng/L)	Background subtracted Spike Recovery (%)
ADONA	< MRL	3.9	103
6:2 FTS	< MRL	4.1	108
PFOA	3.8	4.3*	107
PFHpS	< MRL	4.2	110
PFNA	< MRL	3.9	97
PFOS	< MRL	4.4	118
9CL-PF3ONS	< MRL	4.0	107
8:2 FTS	< MRL	4.0	105
PFDA	< MRL	4.1	101
PFUnA	< MRL	3.9	98
11CL-PF3OUdS	< MRL	3.5	91
PFDoA	< MRL	4.4	111

* Concentration in drinking water subtracted from spike concentration.

Applications – EPA Method 1633 (draft)

Experimental Approach

- Follow EPA method 1633 for aqueous matrices (wastewater)
  - Analysis of PFAS in Aqueous, Solid, Biosolids, and Tissue
- Targets
  - 40 EPA method 1633 targets
- Quantitation
  - Co-extracted isotopically labeled internal standards
- Spike levels (500 mL)
  - Low level spike (MDL) – 0.5 to 12.5 ng/L
  - High level spike (P&A) – 25 to 500 ng/L
- Test samples
  - Wastewater effluent grab samples

Experimental – Aqueous Samples

Sample Preparation
- Aqueous sample size: 500 mL in HDPE bottles
- No preservative
- Add EIS directly into sample bottles – swirl to mix
- Check pH is 6.0 – 7.0

Extraction Setup
- Clean silanized glass wool packed to half height of Agilent Bond Elut PFAS WAX SPE cartridge
- Adapters and large volume reservoirs in place

Condition SPE
- 15 mL - 1% methanolic ammonium hydroxide
- 5 mL – 0.3M formic acid

Load Sample
- Pour samples into reservoir
- Pass through cartridge (**Bond Elut PFAS WAX, 150 mg, 6 mL**) at 5 mL/min

Rinse Reservoir
- 2 x 5 mL reagent water
- 5 mL 1:1 0.1M formic acid/Methanol
- Dry under vacuum for 15 seconds

Elution
- Rinse sample bottle with 5 mL 1% methanolic ammonium hydroxide
- Transfer to SPE cartridge

Carbon Cleanup
- Add 25 uL concentrated acetic acid to each sample eluate & vortex
- Add 10 mg **Carbon S** to each sample
- Hand-shake for < 5 minutes then vortex for 30 seconds
- Centrifuge for 10 minutes at 2800 rpm

Internal Standard
- Add NIS to a clean collection tube

Filter
- Install a nylon syringe filter on a 5 mL polypropylene syringe
- Decant sample supernatant into syringe barrel
- Filter entire extract into NIS collection tube & Vortex

Analysis
- Transfer an aliquot into a poly ALS vial for LCTQ analysis
- Store remaining at 0-4C

Initial Method Detection Limit (MDL) Determination

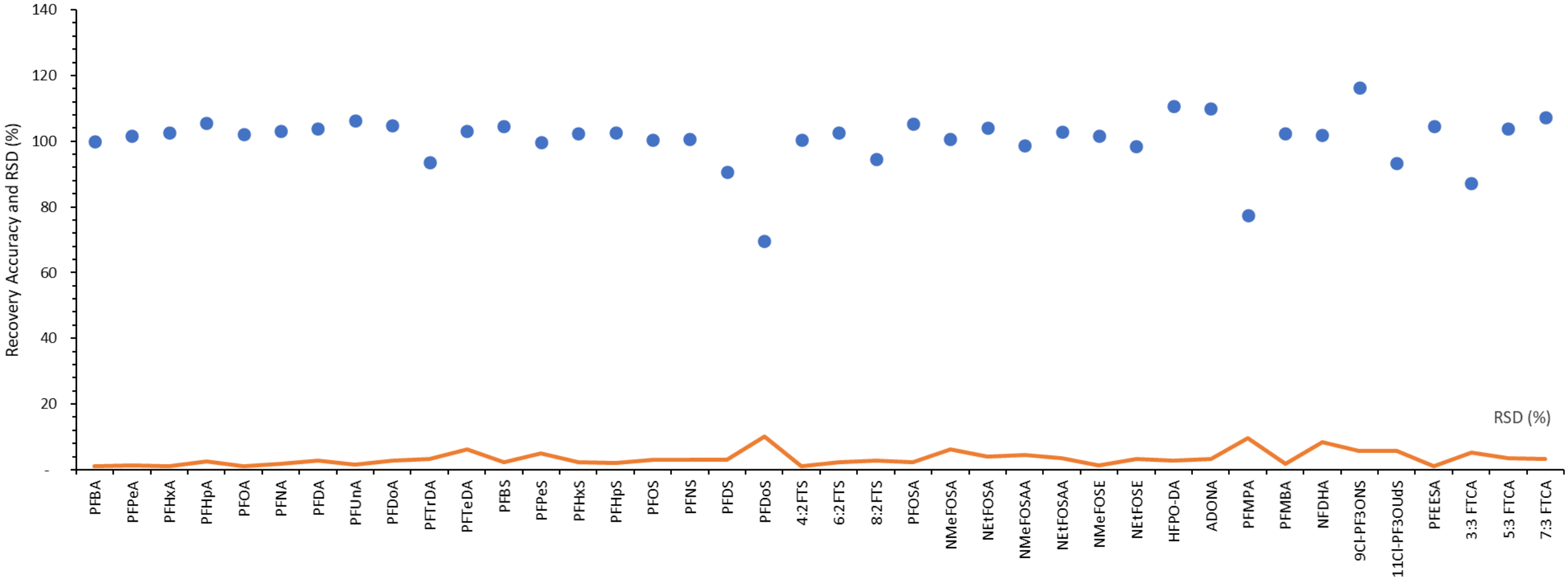
- Following 40 CFR Part 136, Appendix B
- Seven replicates in reagent water

Analyte	Bond Elut PFAS WAX Initial MDL (ng/L)	EPA Draft 1633 Aq. MDL (ng/L)
PFBA	0.38	0.33
PFPeA	0.71	0.196
PFHxA	0.09	0.318
PFHpA	0.19	0.221
PFOA	0.23	0.302
PFNA	0.15	0.221
PFDA	0.15	0.333
PFUnA	0.13	0.264
PFDoA	0.29	0.379
PFTrDA	0.33	0.238
PFTeDA	0.38	0.264
PFBS	0.12	0.245
PFPeS	0.15	0.204
PFHxS	0.26	0.217
PFHpS	0.21	0.137
PFOS	0.39	0.327
PFNS	0.15	0.303
PFDS	0.23	0.334
PFDoS	0.44	0.179
4:2FTS	0.43	2.281

Analyte	Bond Elut PFAS WAX Initial MDL (ng/L)	EPA Draft 1633 Aq. MDL (ng/L)
6:2FTS	0.58	3.973
8:2FTS	0.84	1.566
PFOSA	0.20	0.227
NMeFOSA	0.09	0.196
NEtFOSA	0.17	0.585
NMeFOSAA	0.27	0.586
NEtFOSAA	0.34	0.324
NMeFOSE	1.41	1.191
NEtFOSE	1.97	1.022
HFPO-DA	0.60	0.406
ADONA	0.26	0.779
PFMPA	0.36	0.137
PFMBA	0.13	0.177
NFDHA	0.38	0.117
9Cl-PF3ONS	0.52	1.384
11Cl-PF3OUdS	1.38	0.871
PFEESA	0.26	0.819
3:3 FTCA	0.82	0.721
5:3 FTCA	3.77	5.066
7:3 FTCA	3.27	5.942

Precision and Accuracy

- Precision and accuracy extraction studies at mid-level concentration, four replicates
- Recoveries within 70 and 166% and RSD's < 9%



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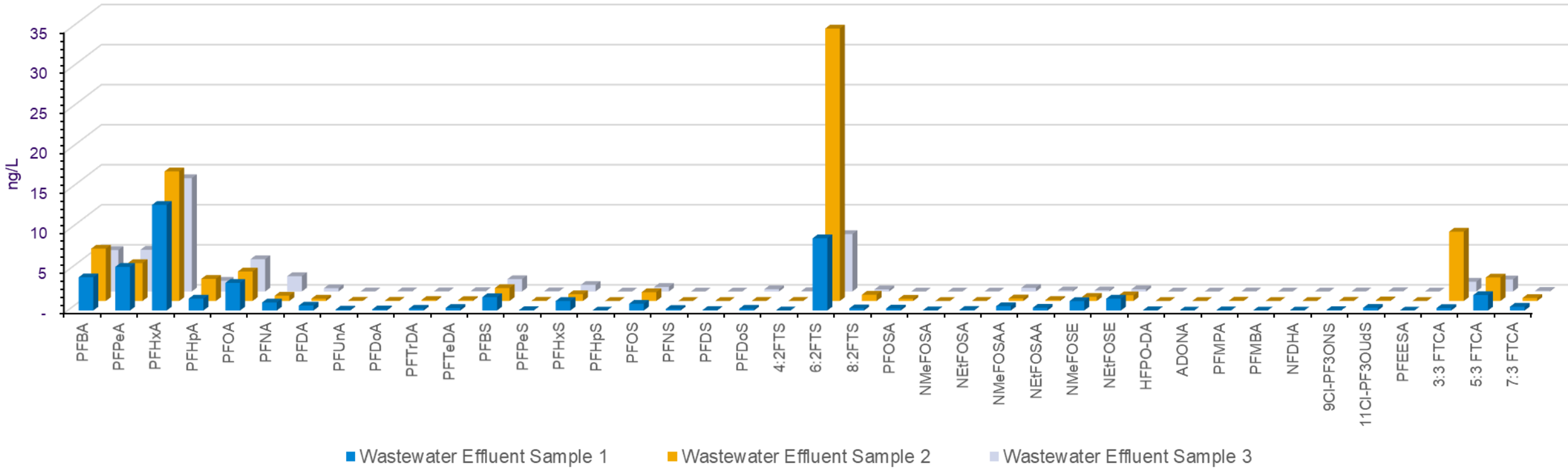
Wastewater Effluent Samples

- Three unique wastewater effluent samples were analyzed
- Perfluoroalkyl carboxylic acids were the most common group of compounds found
- 6:2 FTS was detected in all samples at up to 34 ng/L



Wastewater Effluent Spike Recovery

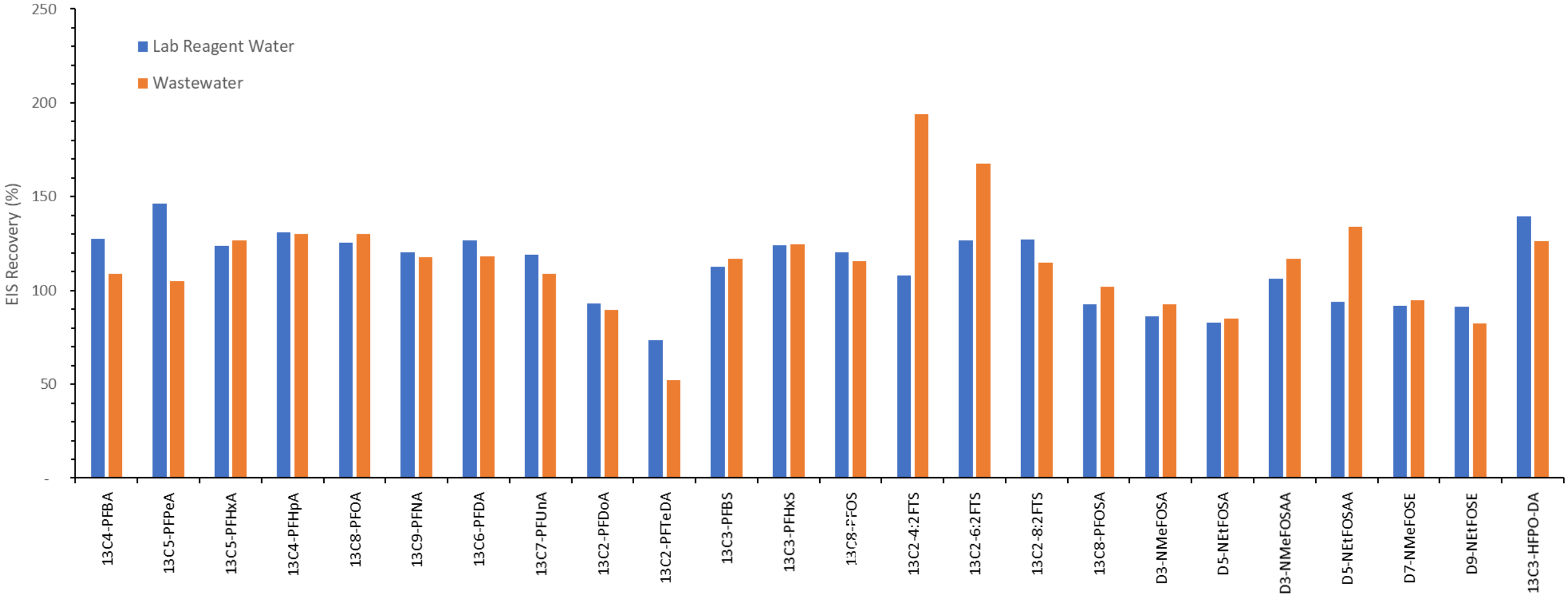
- Three to four replicates of the three wastewater samples were spiked
- Average background levels in unspiked samples were subtracted from spiked

Analyte	Spiked Concentration (ng/L)	Average Accuracy (Recovery)	Low Average Recovery Range	High Average Recovery Range
PFBA	50	91%	86%	99%
PFPeA	25	88%	84%	95%
PFHxA	12.5	93%	85%	103%
PFHpA	12.5	97%	91%	104%
PFOA	12.5	96%	87%	107%
PFNA	12.5	94%	85%	101%
PFDA	12.5	96%	90%	103%
PFUnA	12.5	95%	90%	101%
PFDoA	12.5	92%	87%	95%
PFTrDA	12.5	90%	85%	96%
PFTeDA	12.5	96%	88%	103%
PFBS	12.5	104%	92%	114%
PFPeS	12.5	92%	86%	98%
PFHxS	12.5	91%	88%	94%
PFHpS	12.5	99%	90%	105%
PFOS	12.5	97%	84%	105%
PFNS	12.5	82%	76%	87%
PFDS	12.5	70%	65%	76%
PFDoS	12.5	48%	45%	50%
4:2FTS	50	95%	90%	104%

Analyte	Spiked Concentration (ng/L)	Average Accuracy (Recovery)	Low Average Recovery Range	High Average Recovery Range
6:2FTS	50	95%	92%	99%
8:2FTS	50	89%	77%	105%
PFOSA	12.5	96%	88%	103%
NMeFOSA	12.5	89%	83%	93%
NEtFOSA	12.5	92%	81%	99%
NMeFOSAA	12.5	105%	100%	115%
NEtFOSAA	12.5	96%	92%	103%
NMeFOSE	125	92%	86%	101%
NEtFOSE	125	93%	89%	98%
HFPO-DA	50	109%	90%	120%
ADONA	50	111%	91%	122%
PFMPA	25	103%	95%	111%
PFMBA	25	102%	93%	106%
NFDHA	25	48%	39%	54%
9Cl-PF3ONS	50	100%	82%	109%
11Cl-PF3OUdS	50	74%	61%	84%
PFEESA	25	96%	93%	101%
3:3 FTCA	50	114%	97%	127%
5:3 FTCA	250	153%	136%	169%
7:3 FTCA	250	141%	117%	156%

Extracted Internal Standard (EIS) Recovery

- Three to four replicates of the three wastewater samples were spiked
- Average background levels in unspiked samples were subtracted from spiked



Fit for Purpose (Certificate of Analysis)

Certificate of Analysis (CoA)

Agilent Product Name: Bond Elut PFAS WAX, 150 mg, 6 mL, 30/pk
Agilent Part Number: 5610-2150
FG Lot Number: 6678914-01
Media Lot Number: 0006678914

Raw Materials

Component Properties			
Properties	**Specifications**	**Results**	**Methods**
Tube Purity	Proprietary	Pass	GC FID Test
Frit Purity	Proprietary	Pass	HPLC QQQ Test

Product Specifications/Analysis

Polymeric Sorbent Properties			
Properties	**Specifications**	**Results**	**Methods**
Nitrogen Loading (%N)	1.6-2.1	1.9	CHNO-S Analysis
Average Particle Size D50(µm)	40.0-55.0	46.2	Laser Diffraction
Average Pore Diameter (Å)	50.0-250.0	157.5	Nitrogen Adsorption Isotherm
Turbidity (NTU)	≤7.0	0.5	Turbidity meter
Washable Residue (mg/g)	≤1.0	0.1	Methanol and Hexane gravimetric
Ion Exchange Capacity (meq/g)	0.40-0.82	0.63	Counter Ion Titration
Cleanliness Test	Proprietary	Pass	GC FID Test
Bed Mass Consistency	Proprietary	Pass	Weight Measurement
Flow Characteristics	Proprietary	Pass	Air Flow Test
PFAS Recovery	Proprietary	Pass	HPLC QQQ Test
PFAS Cleanliness	Proprietary	Pass	HPLC QQQ Test

Visual and Microscopic Properties

Properties	Description
Color	White to Buff
Form and Appearance	Spherical, Free Flowing Beads

New!

Conclusions

- Bond Elut PFAS WAX meets the cartridge specifications in EPA, ISO and ASTM PFAS methods.
- The cartridges have very low residual contamination and provide excellent recovery for diverse PFAS compounds exceeding current methods requirements.
- Performance is equivalent to other commercial polymeric WAX cartridges.
- For more information, refer to application notes:
  - Determination of PFAS in Drinking Water Using Agilent Bond Elut PFAS WAX SPE and LC/MS/MS (5994-4960EN)
  - Analysis of PFAS in Aqueous Samples per EPA Draft Method 1633 Using Agilent's New Bond Elut PFAS WAX SPE Cartridges (5994-5148EN)