The Importance of Sorbent Mass to Sample Volume for the Extraction of PFAS from Drinking Water using Weak Anion Exchange SPE

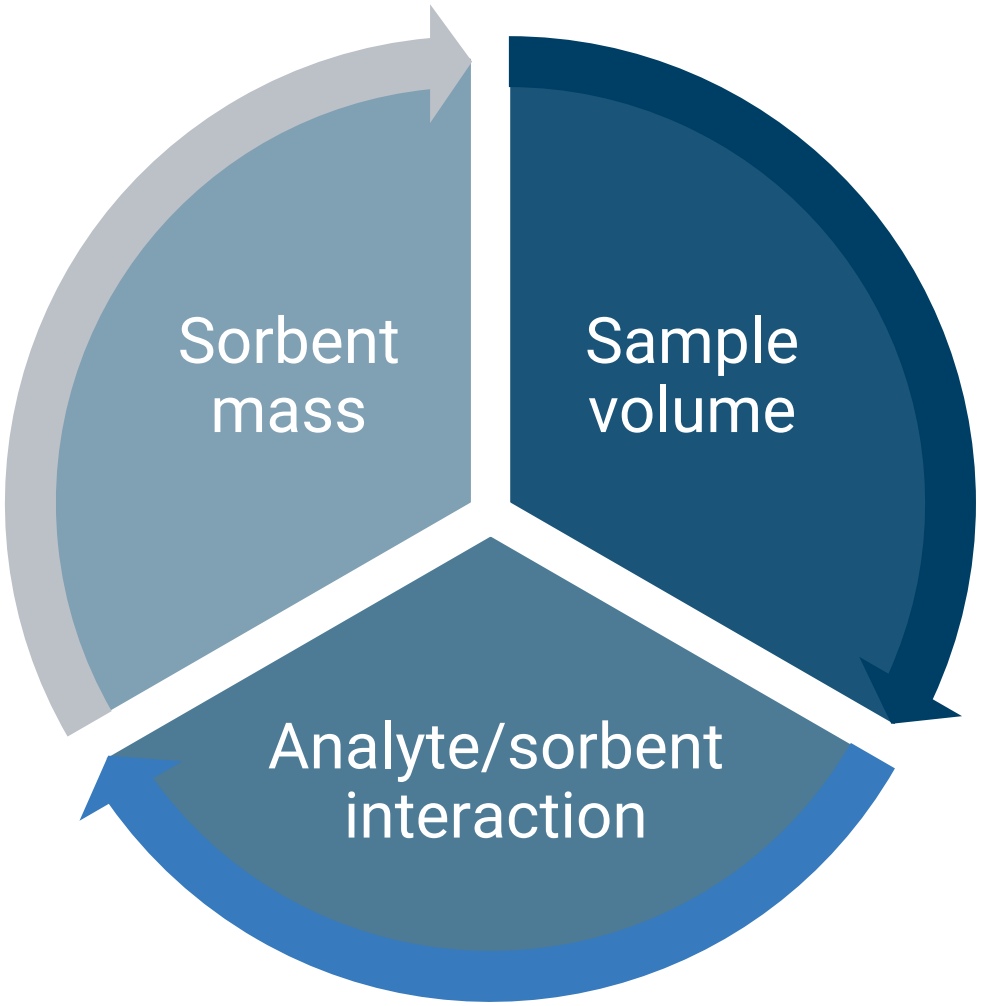
Matthew Giardina, Ph.D.
Applications Chemist

Tuesday, August 10, 2021

Outline

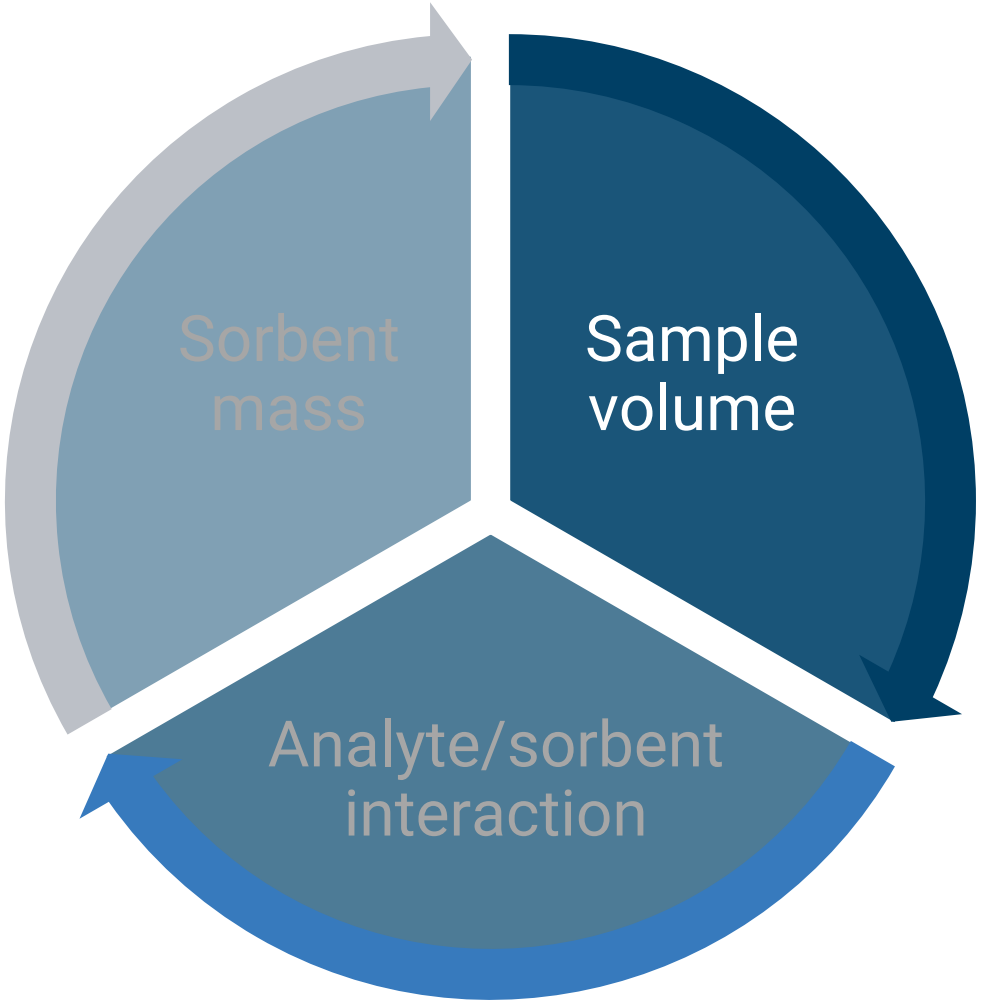
- Considerations when optimizing SPE and sorbent bed mass.
- Extraction of PFAS from drinking water using 150 mg bed mass SampliQ WAX SPE.
- Comparison between 150 and 500 mg SampliQ WAX SPE.

SPE Optimization Considerations



Wells, M. J. M. Handling Large Volume Samples: Applications of SPE to Environmental Matrices. *Solid-Phase Extraction: Principles, Techniques, and Applications* **2000**, 97–119.

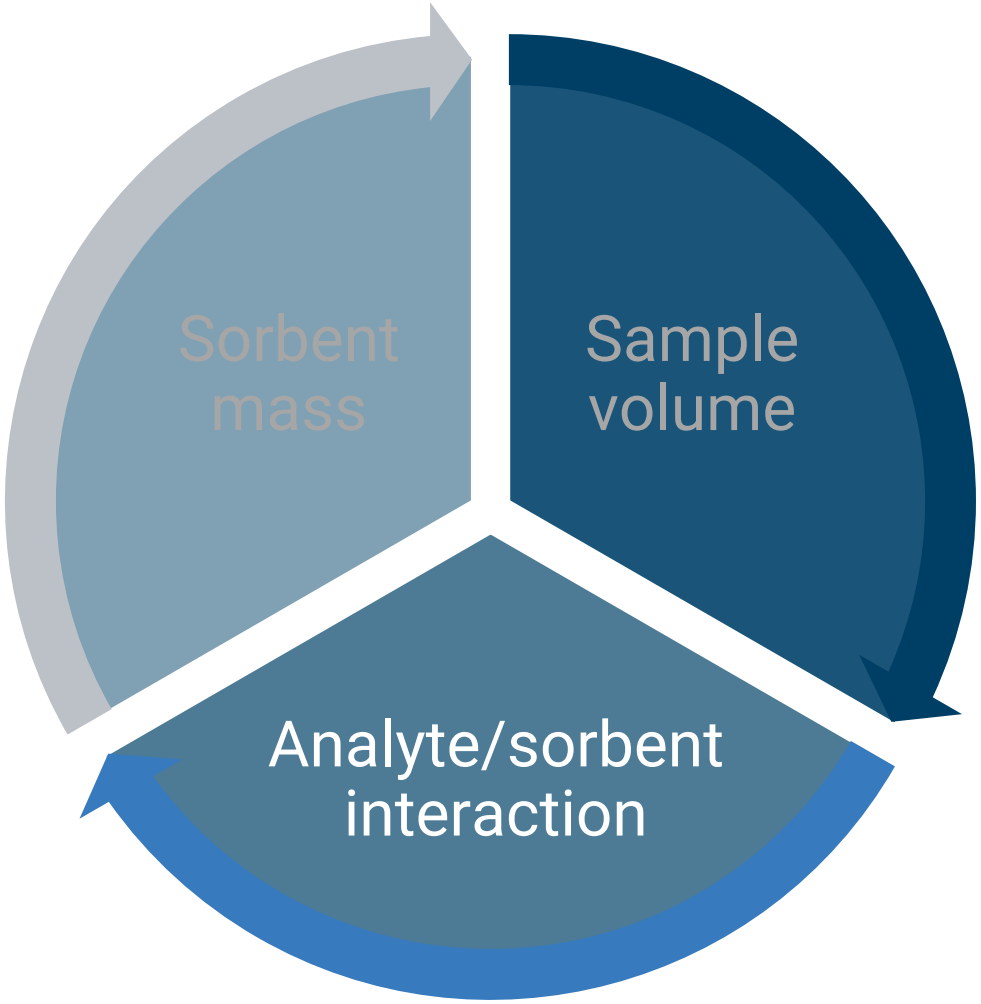
SPE Optimization Considerations



Sample volume

Analyte/sorbent interaction	• larger sample volume, stronger interaction
Sorbent mass	• larger sample volume, larger sorbent mass

SPE Optimization Considerations



Analyte/sorbent interaction

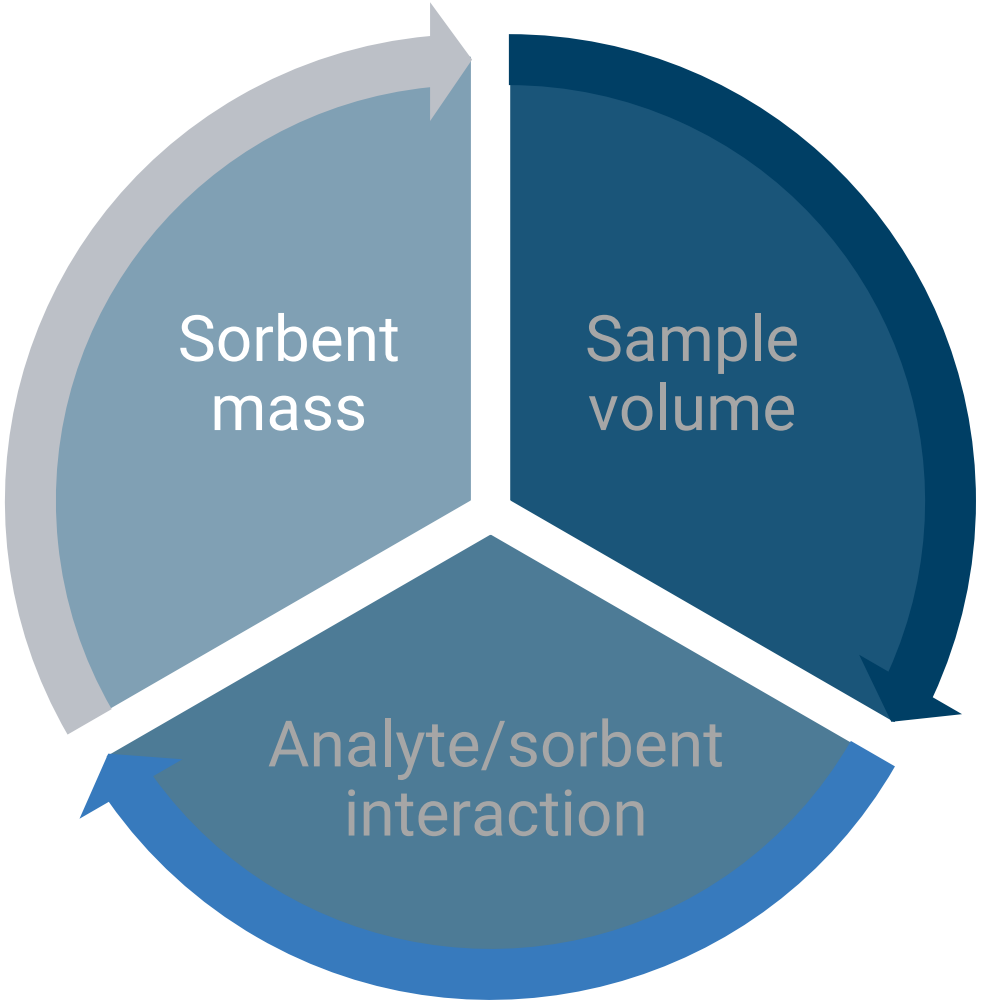
Sorbent mass

- stronger interaction, less sorbent

Sample volume

- stronger interaction, larger sample volume

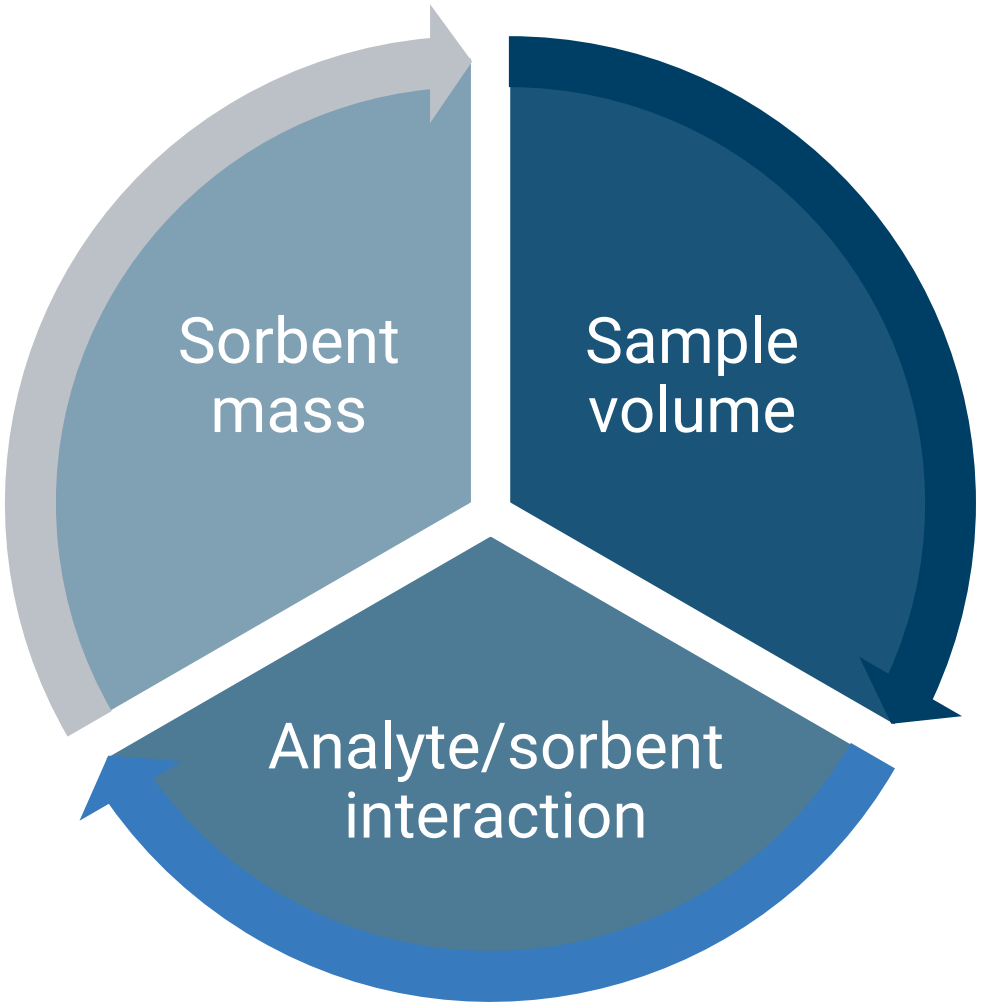
SPE Optimization Considerations



Sorbent mass

Sample volume	• larger sorbent mass, greater sample volume
Analyte/sorbent interaction	• larger sorbent mass, weaker interaction

SPE Optimization Considerations



Optimization Goal

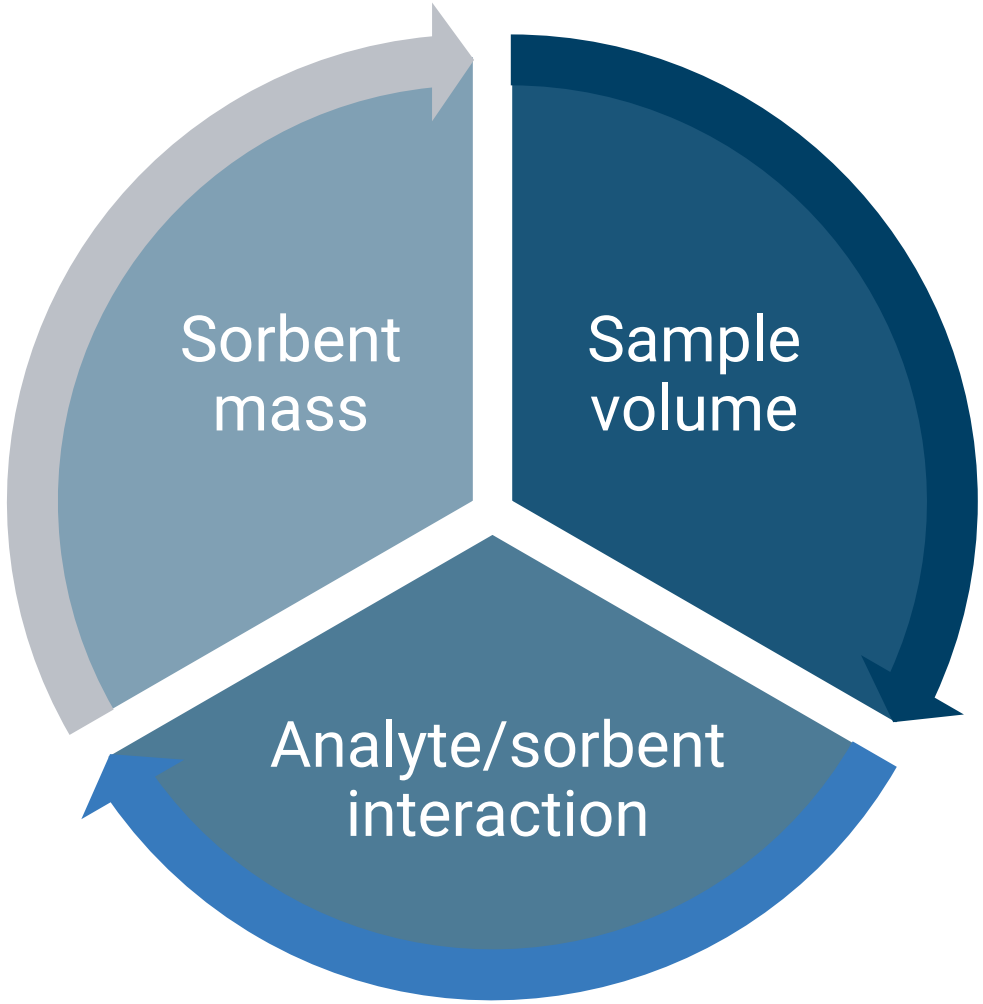
"maximize the ratio of sample volume to sorbent mass"

"minimize the elution volume and maximize the SPE concentration effect"

Wells, M. J. M. Handling Large Volume Samples: Applications of SPE to Environmental Matrices. *Solid-Phase Extraction: Principles, Techniques, and Applications* **2000**, 97–119.

SPE For PFAS in Drinking Water

500 mg typical
(200, 150 mg)



250 mL typical
(100, 500 mL)

Polymeric Weak Anion Exchange (WAX) typical
(SDVB)

Goals of the Study

- Follow protocol given in EPA 533 for the determination of 25 PFAS from drinking water.
- Use 150 mg/6 mL SampliQ WAX instead of 500 mg/6 mL WAX for 250 mL sample volume.
- See if quality control metrics can be achieved.

WHY?

Practical Benefits of Reducing Bed Mass from 500 to 150 mg

- Lower cost – cost scales with bed mass
- Less waste – sorbent and solvents
- Faster prep time – shorter elution and evaporation time
- Cleaner extracts[†] – reduces potential of coextraction of matrix interferents

[†] Majors, R. E. Sample Preparation Fundamentals for Chromatography. *Agilent Technologies*, publication number 5991-3326EN, **2013**.

Potential Drawbacks of Reducing Bed Mass from 500 to 150 mg

- Ionic interferences[†]
- Method compliance

[†] Villaverde-de-Sáa, E. *et al.* Solid-Phase Extraction of Perfluoroalkylated Compounds from Sea Water. *J. Sep. Sci.* 2015, *38*, 1942–1950.

Experimental

Experimental

Extraction Supplies & Equipment

Description	Agilent Part Number
Agilent SampliQ Wax cartridge, 6 mL tube, 150 mg, 30 µm, 30/pk	5982-3667
Adapter cap for 1, 3, and 6 mL Bond Elut cartridges, 15/pk	12131001
Empty SPE cartridge, 60 mL, 100 pk (large volume reservoir)	12131012
Agilent Vac Elut SPS 24 manifold with collection rack for 10 × 75 mm test tubes	12234003
Collection rack and funnel set for 12 or 15 mL conical tubes, for Vac Elut SPS 24 manifold	12234027
Centrifuge tubes and caps, 15 mL, 50/pk	5610-2039
Polypropylene autosampler screw top vials, 2 mL, and caps	5191-8151 and 5191-8150

Extraction Procedure

Place SPE cartridges and 15 mL centrifuge collection tubes on Vac Elut 24 and rotate cowling to the waste position.

Rinse each SPE cartridge with 10 mL of 2% ammonia in methanol (v/v).

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 3-5 in Hg).

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.

Rinse the bottles, reservoirs, and cartridges with 1 mL of methanol.

Dry the cartridges for 5 minutes at a vacuum pressure of 15-20 in Hg.

Rotate the cowling on the Vac Elut 24 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 55-60 °C until dry.

Reconstitute extract in 1 mL of 80:20 methanol:water and analyze.

Best practice!

Experimental

Analysis Supplies & Equipment

Description	Agilent Part Number
HPLC	1290 Infinity II LC System
InfinityLab PFC-free HPLC conversion kit	5004-0006
InfinityLab PFC delay column, 4.6 x 30 mm	5062-8100
ZORBAX RRHD Eclipse Plus C18, 2.1 x 50 mm, 1.8 µm	959757-902
MS/MS	6470 Triple Quadrupole
Ion source	Jet Stream ESI
Agilent MassHunter PFAS MRM database	G1736AA

Experimental

Instrumental Conditions

LC

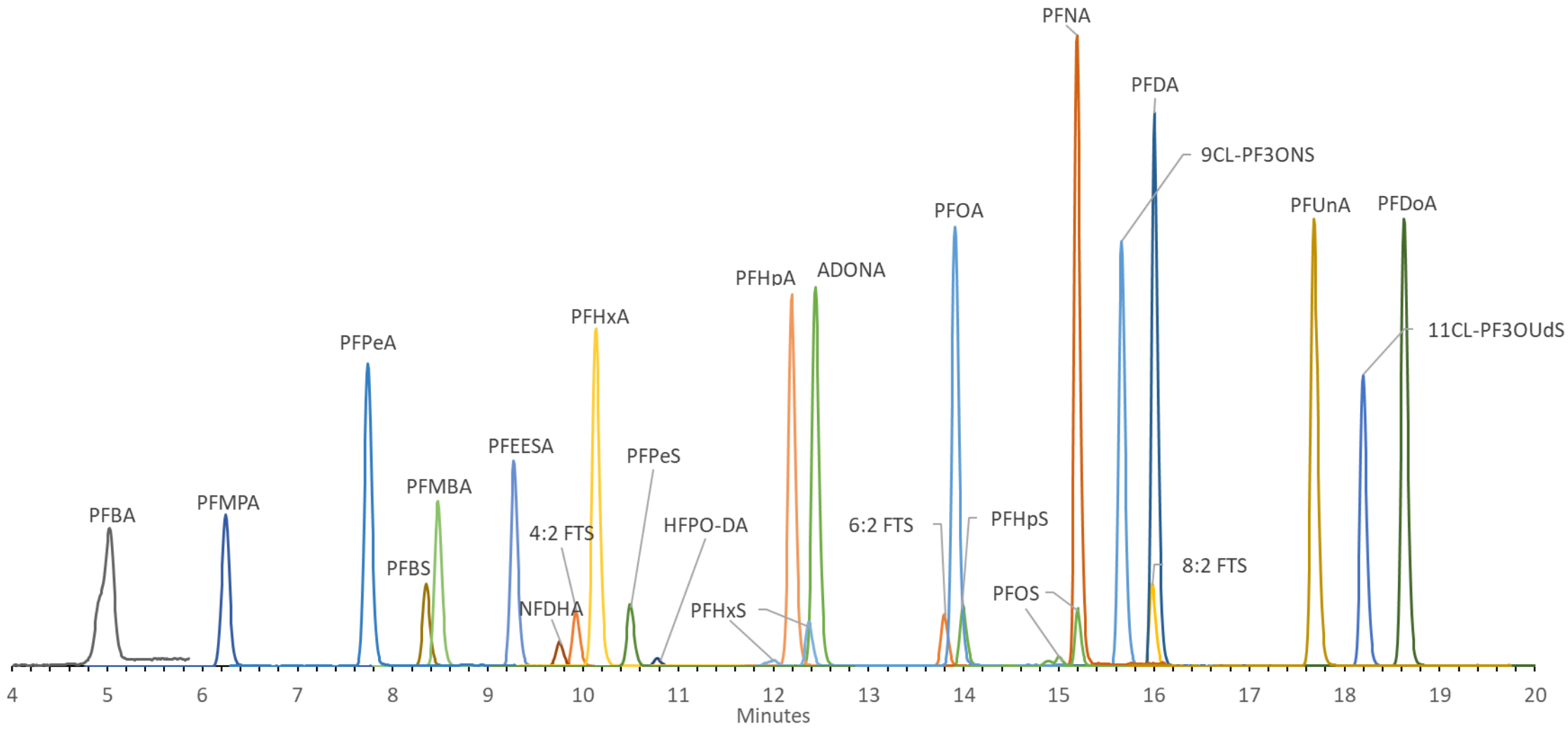
Parameter	Value
Mobile Phase	A) 20 mM ammonium acetate in water B) methanol
Injection volume	5 µL
Column temperature	30 °C
Flow rate	0.250 mL/min
Gradient	Time (min) % A % B 0 95 5 0.50 95 5 3.00 60 40 16.00 20 80 18.00 20 80 20.00 5 95 22.00 5 95 25.00 95 5 35.00 95 5

Ion Source

Parameter	Value
Polarity	Negative
Drying gas	230 °C, 4 L/min
Sheath gas	250 °C, 12 L/min
Nebulizer gas	15 psi
Capillary voltage	2,500 V
Nozzle voltage	0 V

Experimental

Chromatogram



Agilent

Agilent
Trusted Answers

Results

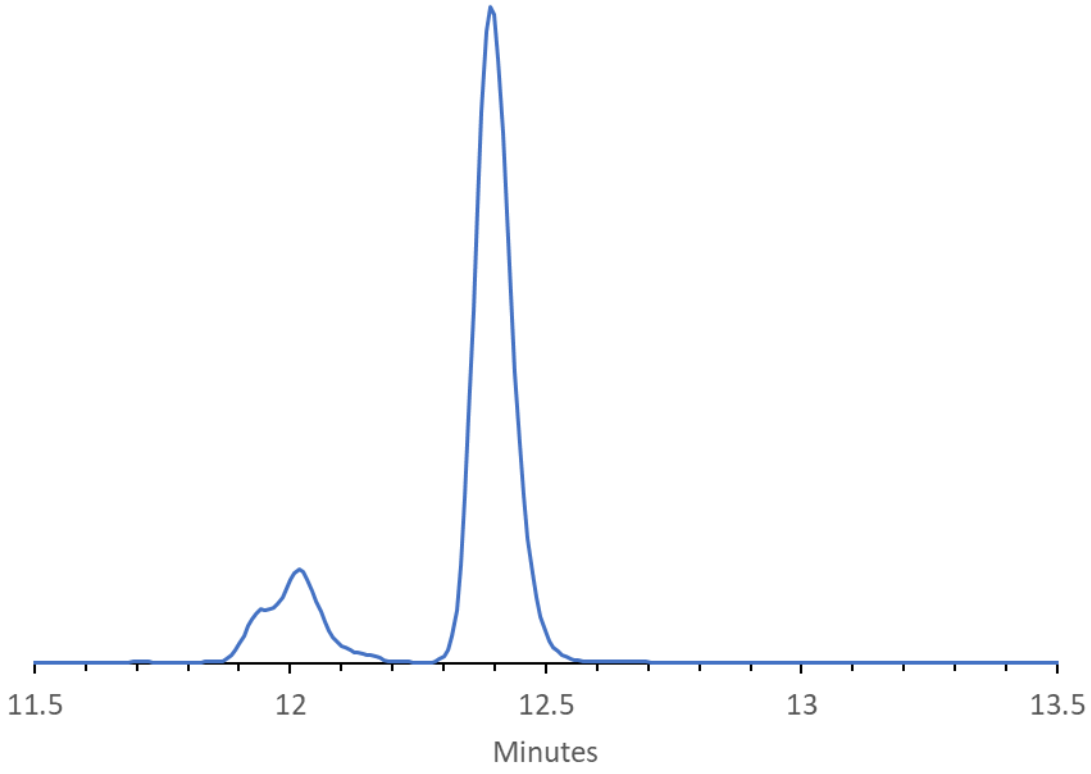
EPA 533 Requirements

- Data quality metrics are well defined in EPA 533
  - Initial demonstration of capability § 9.1
    - Establish retention time and MRM window for branched isomers
    - Demonstrate low system background
    - Demonstrate precision and accuracy
    - Confirm Minimum Reporting Level (MRL) at the 99% confidence level
    - Verification calibration with an independent Quality Control Standard (QCS)
  - QC Acceptance Criteria (On-Going QC) § 9.2
    - Pass calibration acceptance criteria (isotope dilution quantitation)
    - Monitor response of Isotope Performance Standards (IPS)
    - Monitor recovery of Isotope Dilution Analogs (IDA)
    - Determine recovery of low-level spikes into matrix
  - Performance in Representative Sample Matrix § 9.3
    - Assess precision and accuracy in representative matrix (finished drinking water)

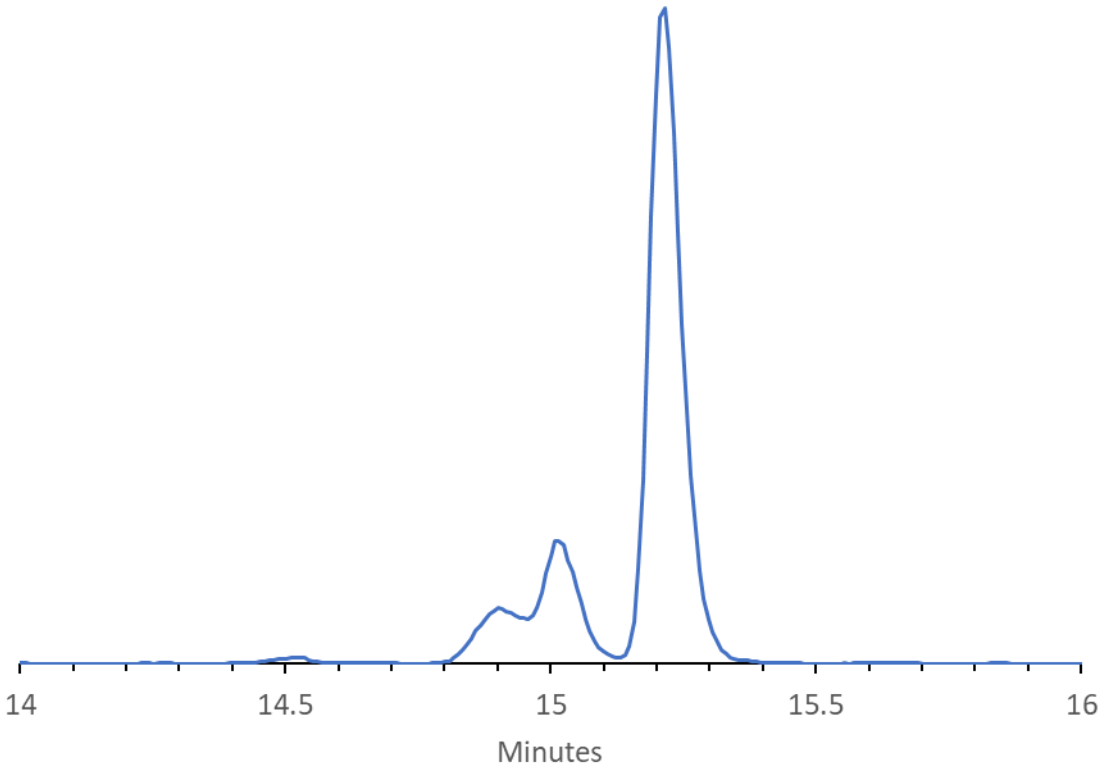
Retention Time of Branched Isomers

Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 10.2.2	Establish retention times for branched isomers	Each time chromatographic conditions change	All isomers of each analyte must elute within the same MRM window.	

PFHxS

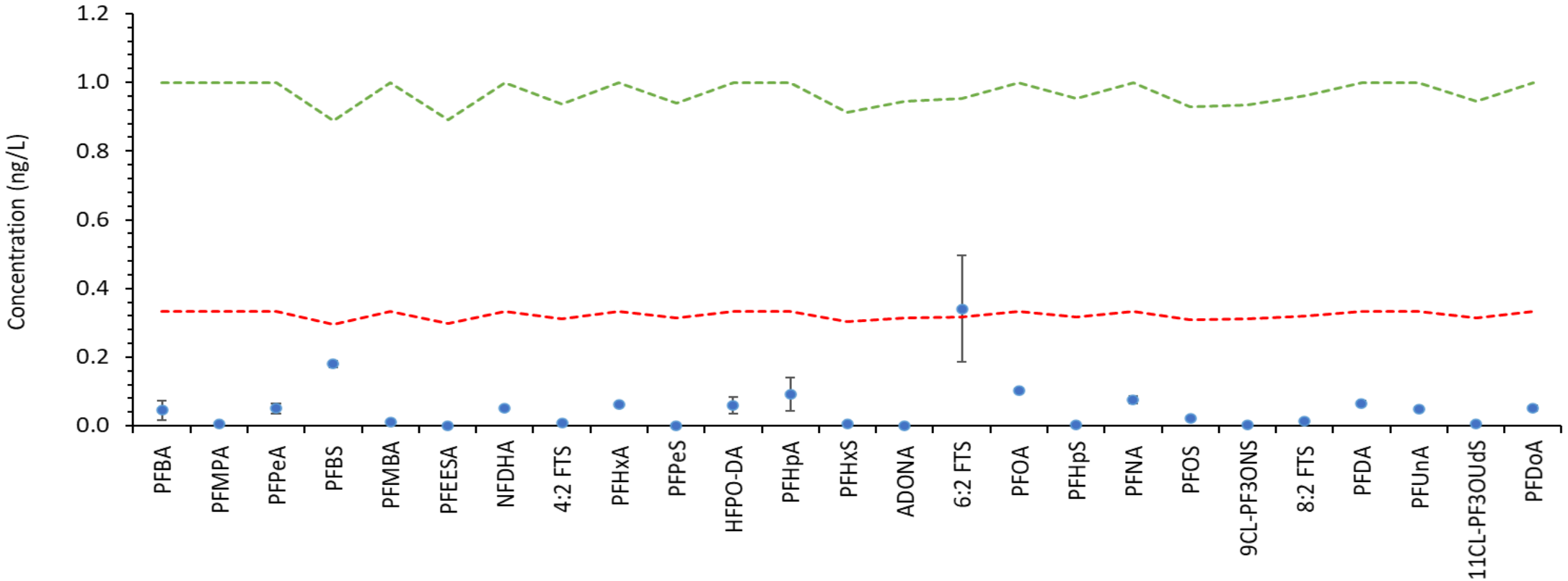


PFOS



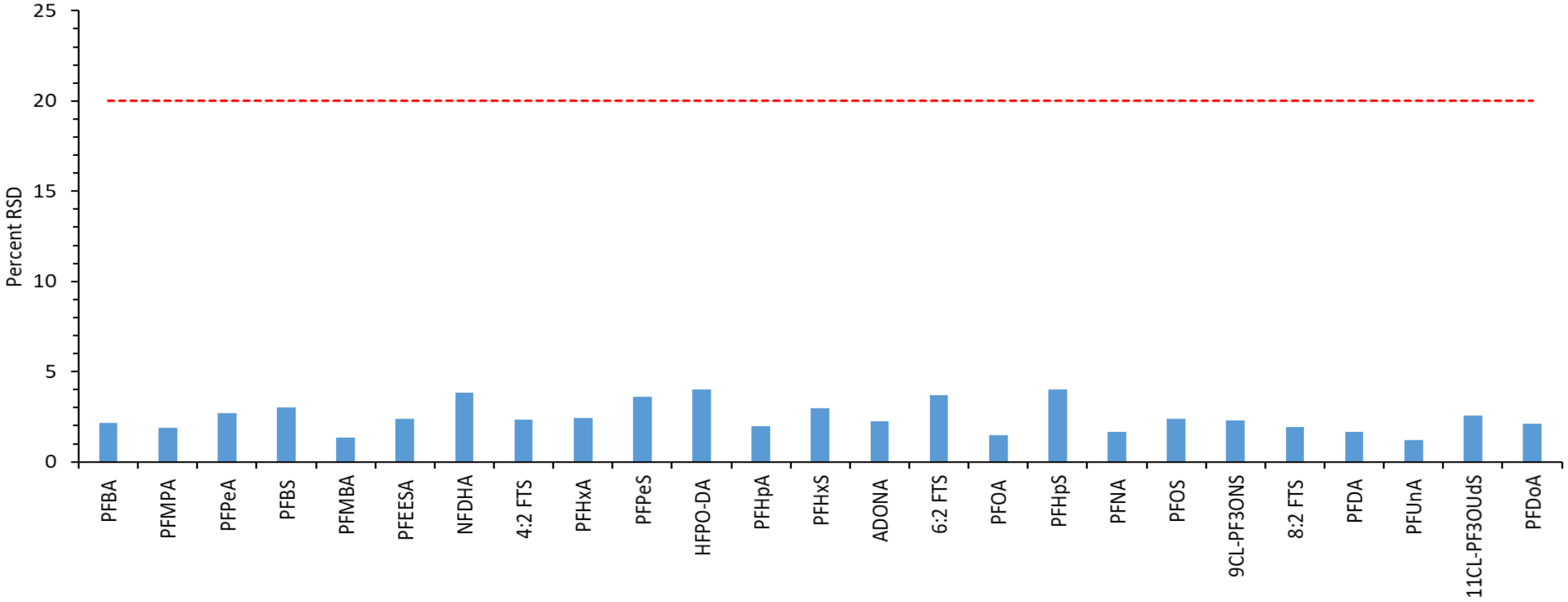
Initial Demonstration of Low Background

Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 9.1.1	Demonstrate low system background	Analyze Laboratory Reagent Blank after highest calibration standard	Demonstrate that all analytes are below 1/3 the MRL.	6:2 FTS contamination in methanol



Demonstration of Precision

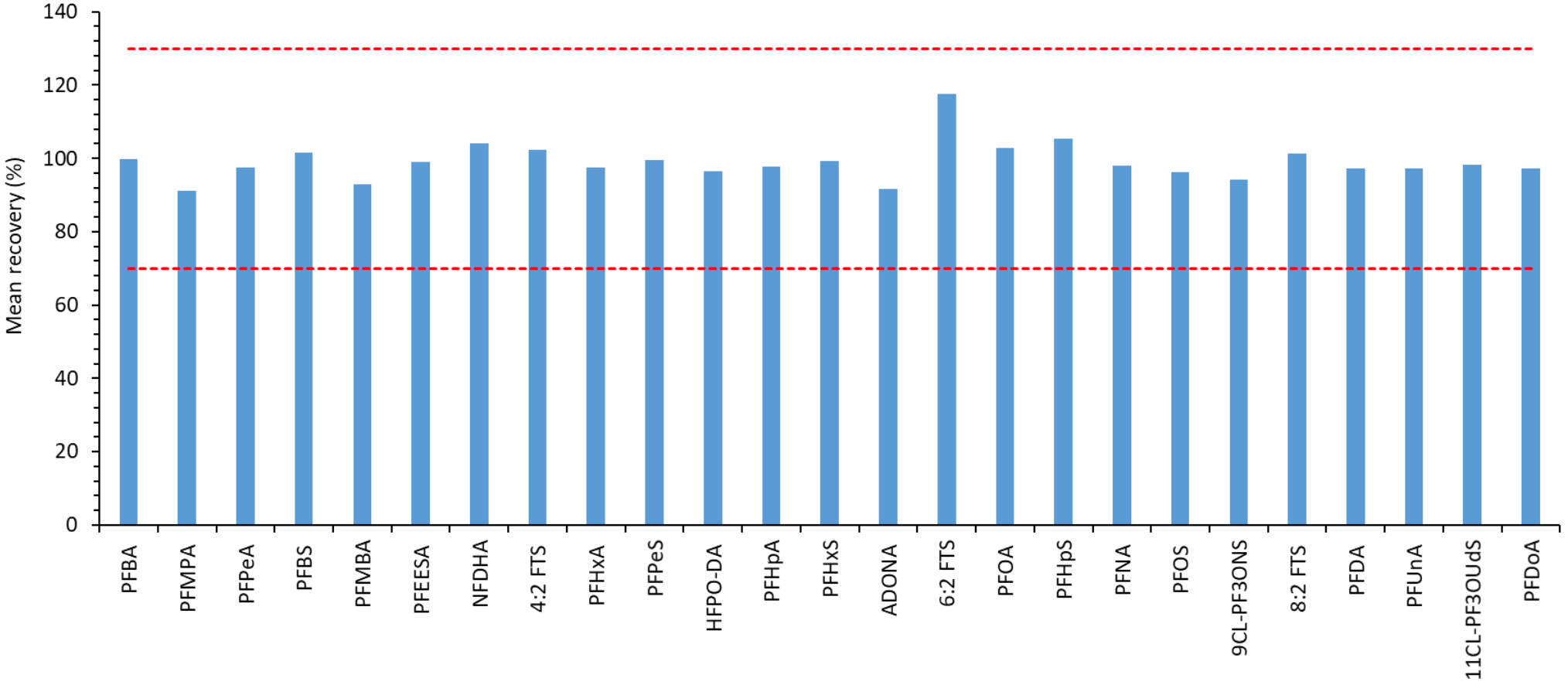
Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 9.1.2	Demonstration of precision	Extract and analyze 7 replicate Laboratory Fortified Blanks (LFBs) near the mid-range concentration.	%RSD must be <20%	Fortified concentration 5 ng/L. Average RSD was 2.5%.



Agilent

Demonstration of Accuracy

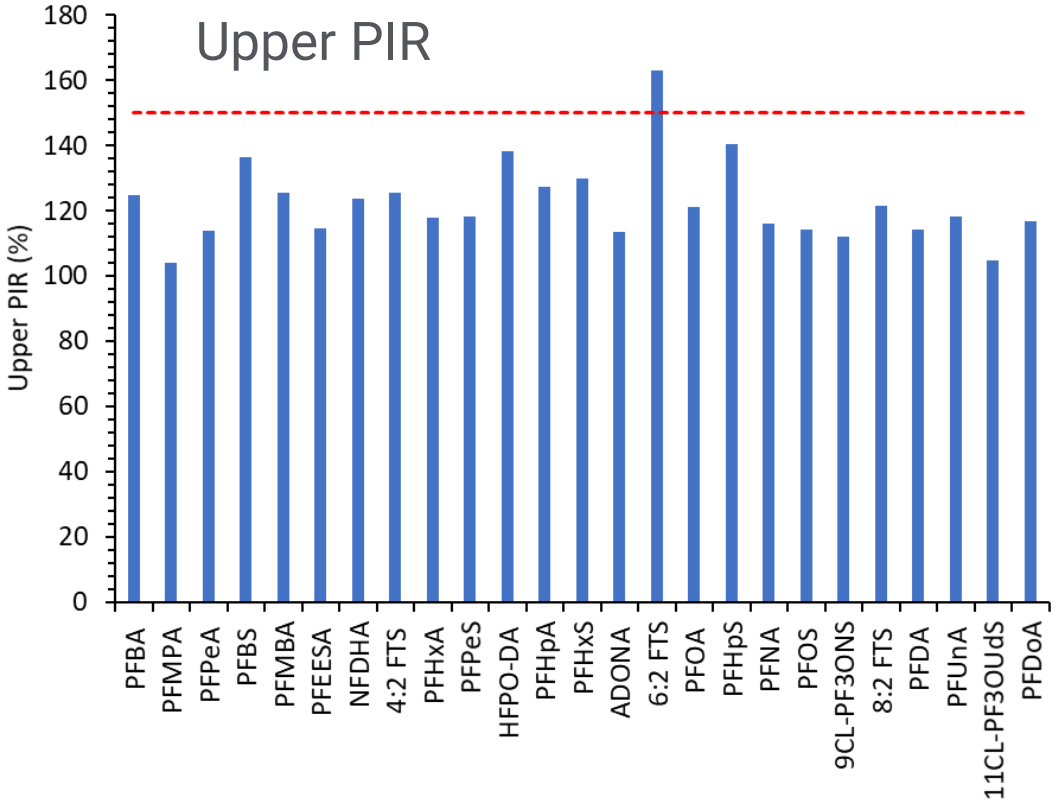
Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 9.1.3	Demonstration of accuracy	Calculate mean recovery for 7 replicates of midlevel spikes.	Mean recovery within 70-130% of true value	Fortified concentration 5 ng/L. Average recovery was 99%.

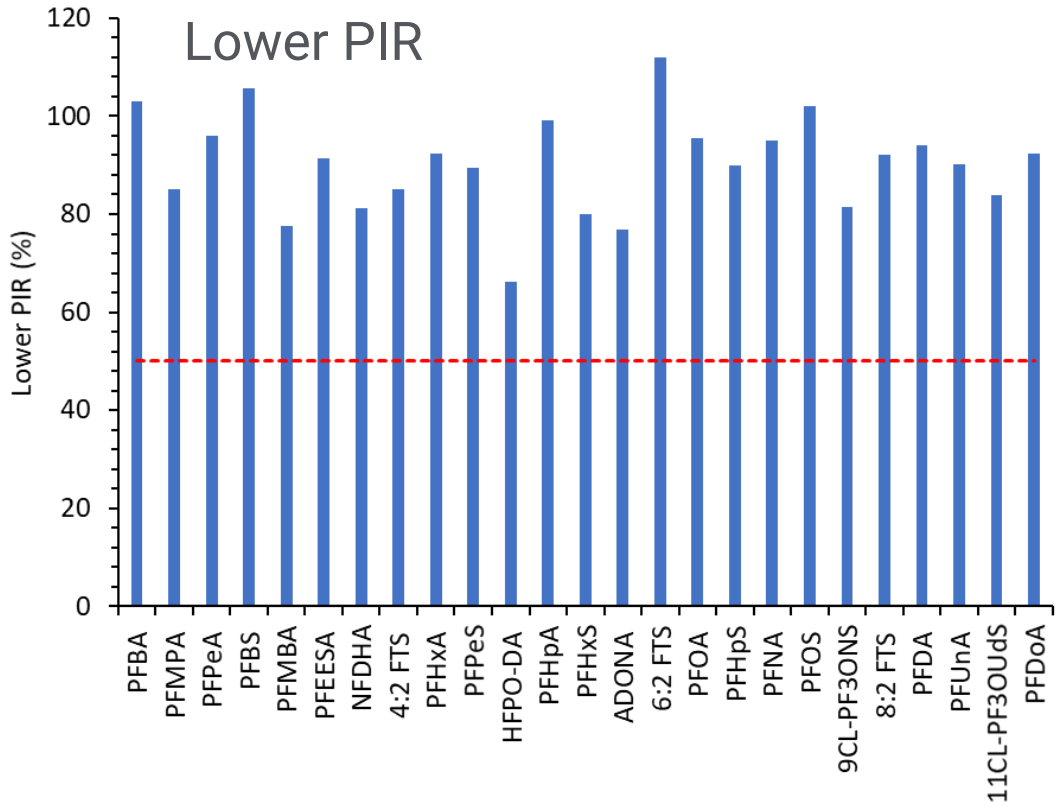


Agilent

Minimum Reporting Limit Confirmation

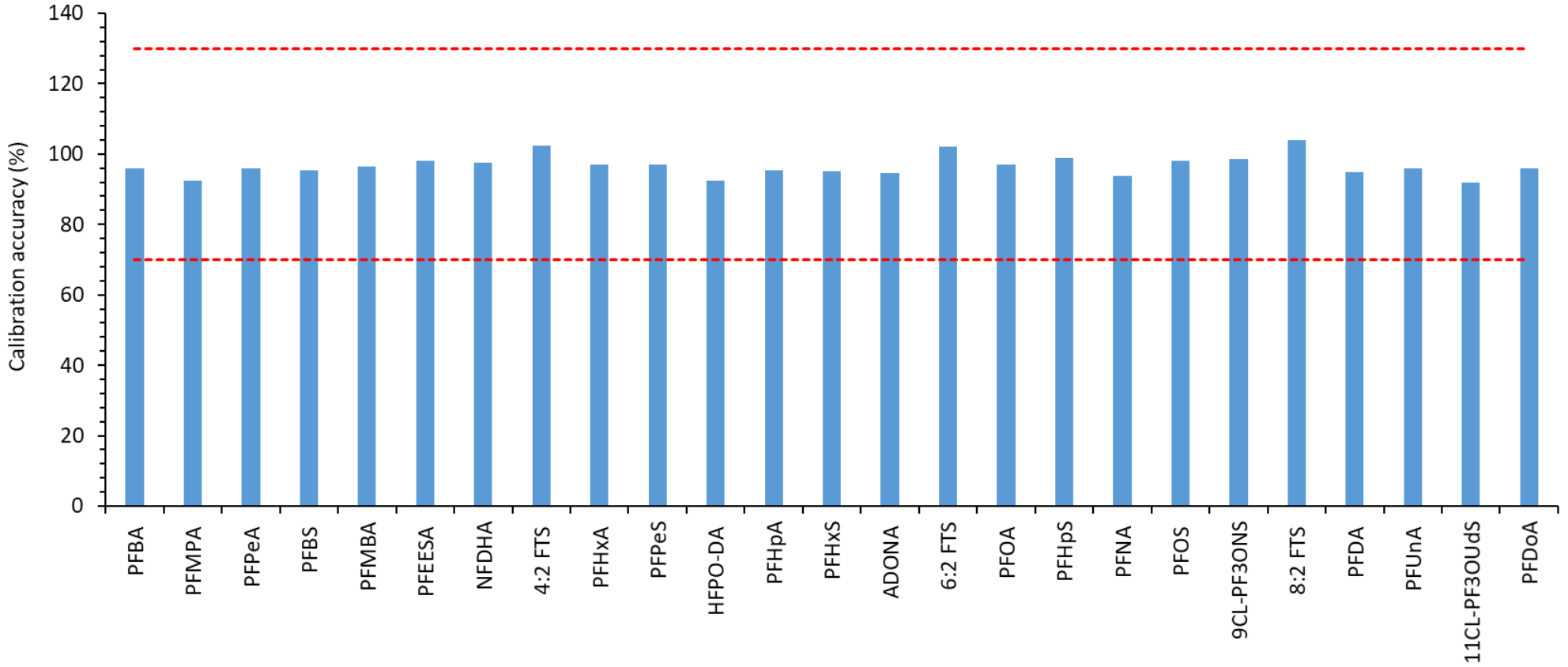
Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 9.1.4	Minimum reporting limit (MRL) confirmation.	Fortify and analyze 7 replicate LFBs at the proposed MRL concentration. Confirm that the Upper Prediction Interval of Results (PIR) and Lower PIR meet the recovery criteria.	Upper PIR ≤ 150% Lower PIR ≥ 50%	Fortified concentration 1 ng/L. 6:2 FTS above 150% limit due to methanol contamination.





Calibration Verification

Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 9.1.5	Calibration Verification	Analyze mid-level QCS.	Results must be within 70–130% of the true value.	Midlevel calibration standard at 5 ng/L. Average accuracy was 96.7%.



Initial Calibration

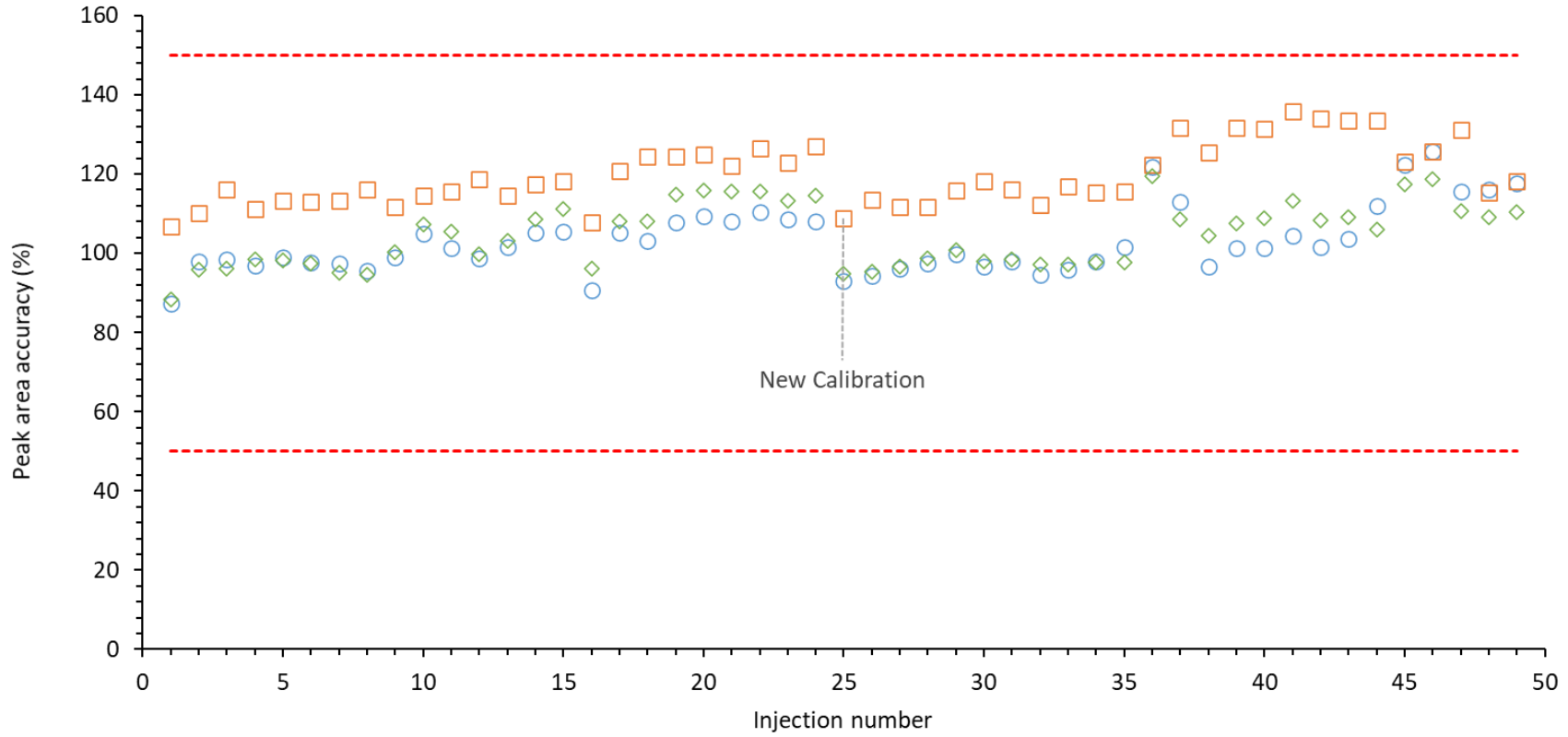
Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 10.3	Initial calibration	Use the isotope dilution calibration technique to generate a linear or quadratic calibration curve. Use at least 5 standard concentrations. Evaluate the calibration curve as described in Section 10.3.5.	When each calibration standard is calculated as an unknown using the calibration curve, analytes fortified at or below the MRL should be within 50–150% of the true value. Analytes fortified at all other levels should be within 70–130% of the true value.	

	Percent Accuracy					
	Fortified Concentration (ng/L)					
Compound	0.6	1	2	5	10	20
PFBA	109.4	110.6	107.1	101.5	105	95.6
PFMPA	105.1	103.5	106.1	102	104.9	96.1
PFPeA	108	105	105.7	101.6	104.4	96.4
PFBS	104	103	104.2	105.8	104.9	95.4
PFMBA	109.4	106	106.6	104	105.4	95.1
PFEESA	99.9	101.7	105.1	105.5	101.7	97.1
NFDHA	97.5	105.5	104.8	104.4	105.5	95.5
4:2 FTS	105.2	105.7	116.3	109.1	105	93.2
PFHxA	106	103.5	106.5	103.6	104.7	95.8
PFPeS	105.6	103.4	105.4	104.1	103.8	96.2
HFPO-DA	93.2	100.8	109.7	105.3	97.4	99.2
PFHpA	102.3	107.3	104.7	102.2	105.6	95.7

	Percent Accuracy					
	Fortified Concentration (ng/L)					
Compound	0.6	1	2	5	10	20
PFHxS	121.7	103.2	108.9	105.2	104.4	94.8
ADONA	105.4	104.4	104.4	102.1	105.3	96
6:2 FTS	125.2	107.3	112.1	107.9	106.9	92.2
PFOA	106.3	105.6	106.2	101.7	104.7	96.1
PFHpS	110.3	109.7	109.1	100.2	105.8	95.3
PFNA	101.3	106.8	105.5	101.5	105.5	95.9
PFOS	110.7	105.7	106.4	102.1	105	95.7
9CL-PF3ONS	100.3	103.5	102.7	99.5	106.7	96.3
8:2 FTS	105.2	114	108.6	110.8	106.9	92.1
PFDA	109.1	105.1	105	104.8	103.9	95.9
PFUnA	103.7	106.8	106	101.7	104.5	96.3
11CL-PF3OUdS	101.1	103.2	100.8	99.2	104.7	97.6
PFDoA	104.9	102.7	105.4	102.1	105.4	96

Isotope Performance Standards

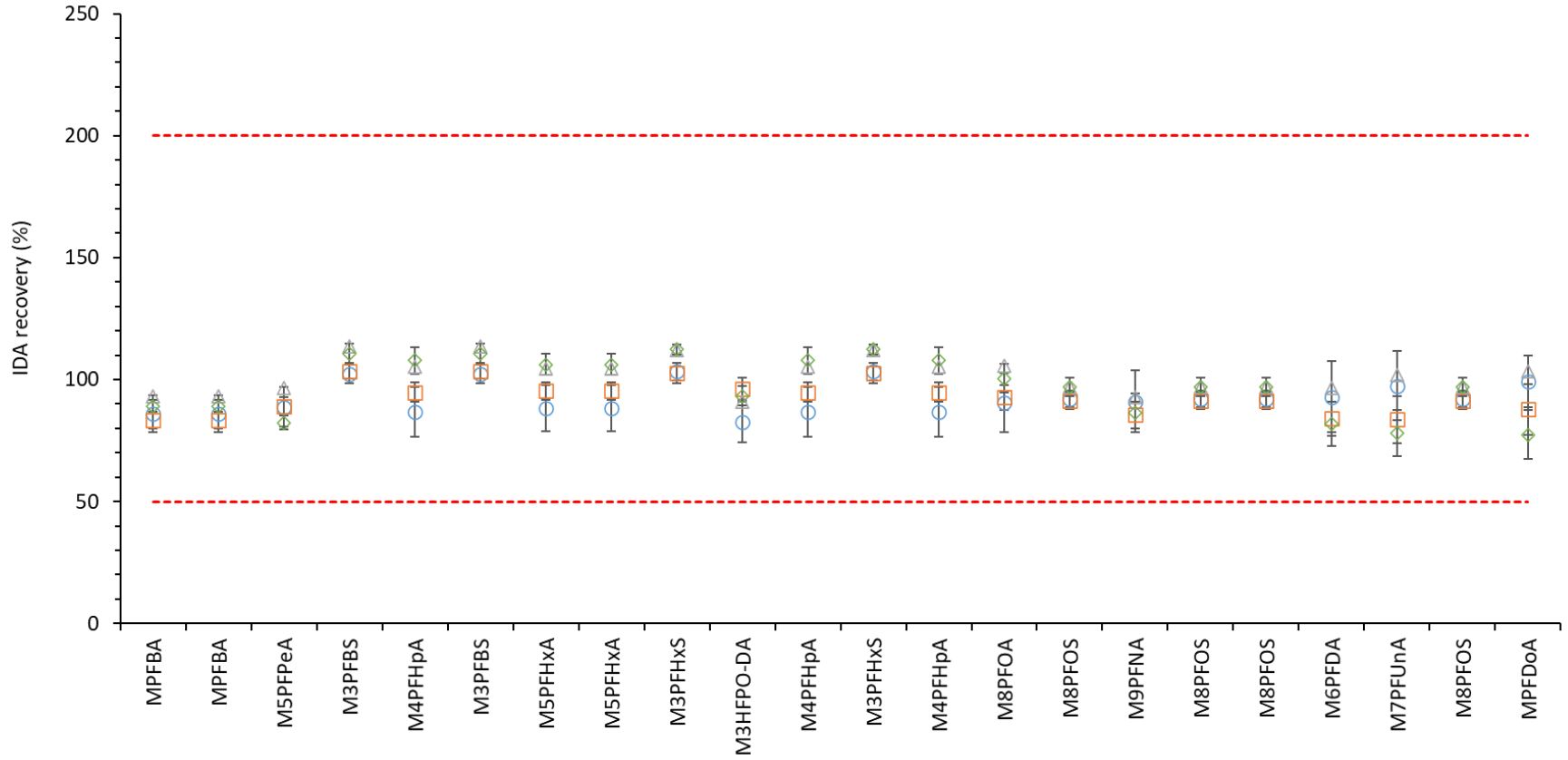
Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 9.2.4	Isotope performance standards	Isotope performance standards are added to all standards and sample extracts.	Peak area counts for each isotope performance standard must be within 50–150% of the average peak area in the initial calibration.	



M3PFBA (○), M2PFOA (□), and MPFOS (◇)

Isotope Dilution Analogs

Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 9.2.5	Isotope performance standards	Isotope dilution analogues are added to all samples prior to extraction.	50%–200% recovery for each analogue	Average IDA recovery for all compounds was 96.1%.



low-level spikes (○), mid-level spikes (□), high-level spike (Δ), and drinking water samples (◊)

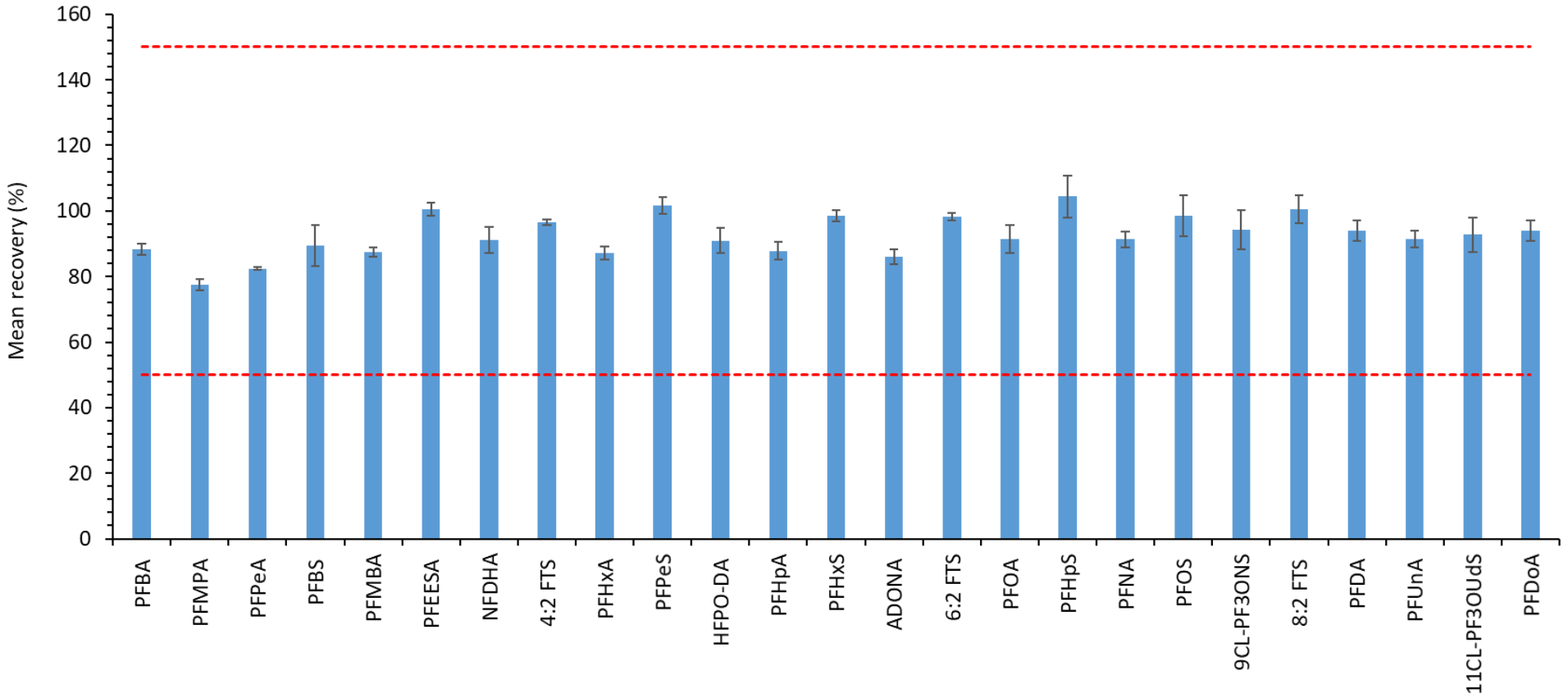
Representative Sample Matrix

- Analysis of finished drinking water sample in triplicate

Compound	Average Concentration (ng/L)	Standard Deviation (ng/L)	MRL (ng/L)	% RSD
PFBA	6.50	0.14	1.00	2.19
PFMPA	ND	-	1.00	
PFPeA	6.37	0.07	1.00	1.13
PFBS	3.05	0.02	0.89	0.75
PFMBA	ND	-	1.00	
PFEESA	ND	-	0.89	
NFDHA	ND	-	1.00	
4:2 FTS	ND	-	0.94	
PFHxA	6.37	0.16	1.00	2.50
PFPeS	ND	-	0.94	
HFPO-DA	ND	-	1.00	
PFHpA	4.11	0.06	1.00	1.42
PFHxS	2.08	0.04	0.91	1.70
ADONA	ND	-	0.94	
6:2 FTS	ND	-	0.95	
PFOA	4.92	0.02	1.00	0.50
PFHpS	ND	-	0.95	
PFNA	1.99	0.00	1.00	0.18
PFOS	ND	-	0.93	
9CL-PF3ONS	ND	-	0.93	
8:2 FTS	ND	-	0.96	
PFDA	ND	-	1.00	
PFUnA	ND	-	1.00	
11CL-PF3OUdS	ND	-	0.94	
PFDoA	ND	-	1.00	

Representative Sample Matrix

Method Reference	Requirement	Specification	Acceptance Criteria	Notes
Sect. 9.2.6/9.2.7	Laboratory Fortified Sample Matrix (LFSM)	Include one LFSM per Extraction Batch. Fortify the LFSM with method analytes at a concentration close to but greater than the native concentrations (if known).	For analytes fortified at concentrations ≤2 x the MRL, the result must be within 50–150% of the true value; 70–130% of the true value if fortified at concentrations greater than 2 x the MRL.	Average recovery at 2 ng/L spikes in triplicate was 92.7%

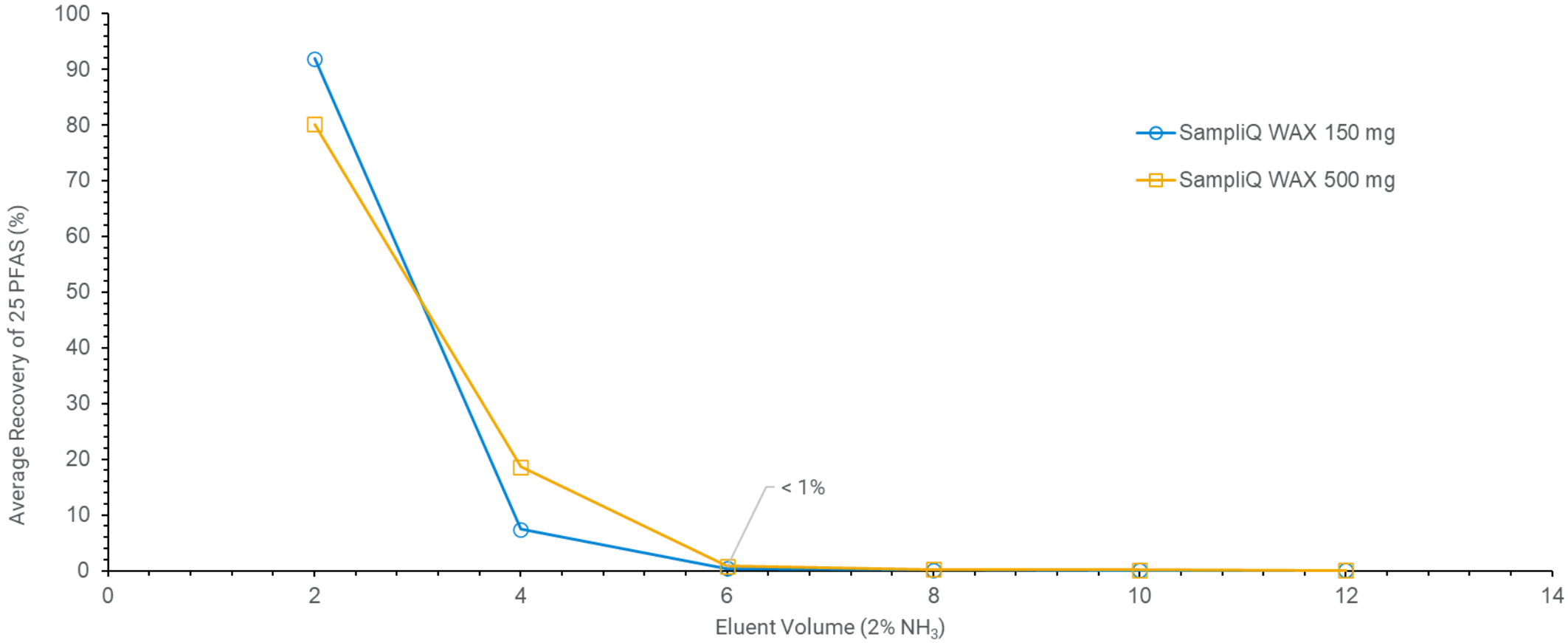


Agilent

Comparison – 150 mg and 500 mg (New Data)

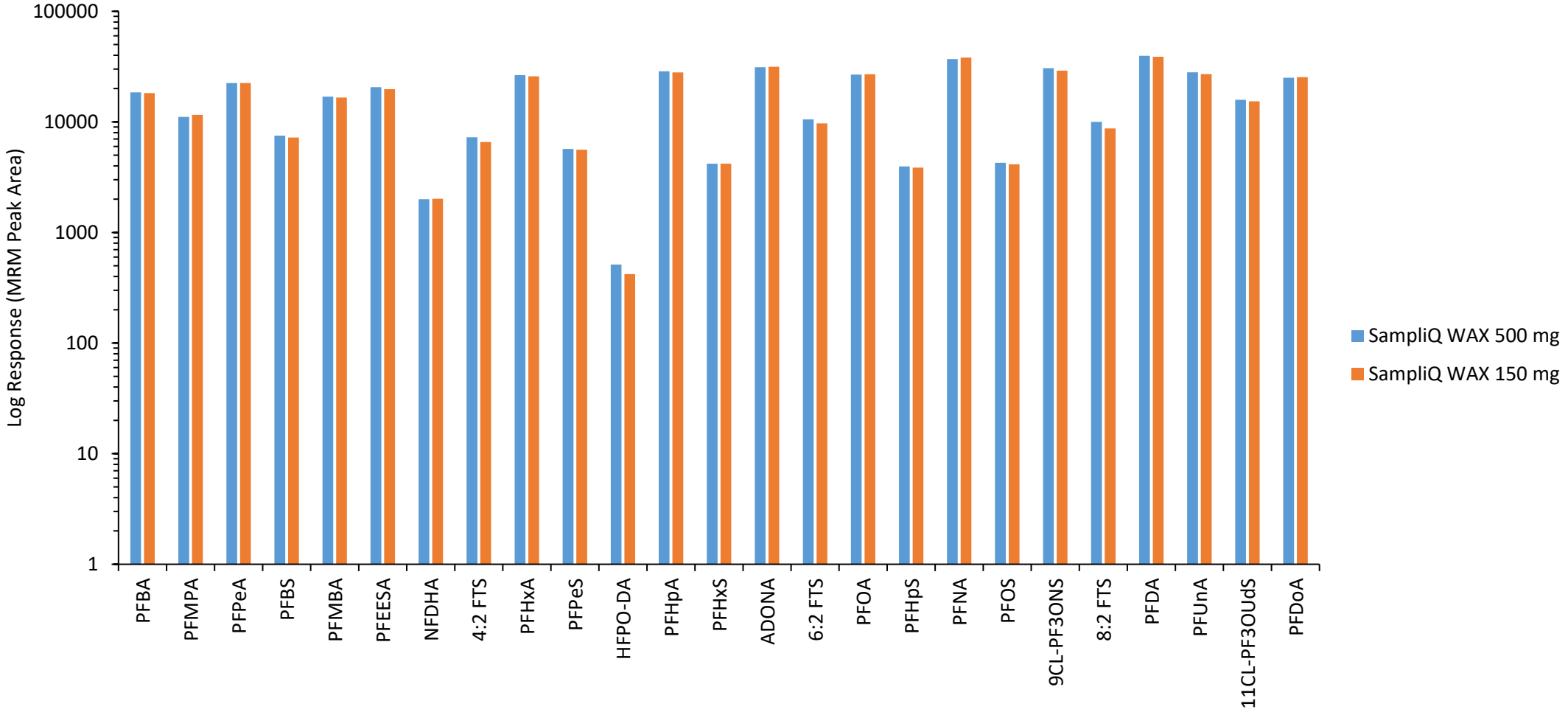
Elution Volume – 150 mg versus 500 mg

- Successive elutions with 2 mL volumes of methanol with 2% ammonium hydroxide (v/v)
- Average recovery of 25 PFAS at 125 ng/L in reagent water.



Interferences – 150 mg versus 500 mg

- Soaked & rinsed cartridges with 10 mL of > 250 ppm Cl^- after loading 125 ng/L PFAS standard in reagent water.



Conclusion

- The 150 mg/6 mL SampliQ WAX passes the rigorous EPA 533 quality control criteria under the conditions studied.
- Minimum reporting limit of nominally 1 ng/L was achieved with the exception of 6:2 FTS due to methanol contamination. An MRL of 0.5 to 0.6 ng/L is achievable for most compounds.
- Elution volume 6 mL was required for recovery of >99.5% for 150 mg SampliQ WAX.
- No difference in competitive interference observed with >250 ppm Cl^- for either 150 or 500 mg bed mass.

More Information

- Publication 5994-3616EN.
- Targeted Quantitation of Legacy and Emerging Per- and Polyfluoroalkyl Substances (PFAS) in Water Matrices, Monday, August 9, 3:45PM Analytical Chemistry Session.
- Contact: matthew_giardina@agilent.com