Analysis of Per- and Polyfluoroalkyl Substances in Drinking Water using SampliQ Weak Anion Exchange Solid Phase Extraction 150 mg Cartridge

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Abstract

Optimizing the sorbent mass-to-sample volume ratio is an important consideration when developing a solid phase extraction method. For strongly retained analytes, the sorbent mass-to-sample volume ratio may be relatively small compared to weakly retained analytes, which require a larger bed mass. Using more sorbent mass than required has some downsides including increased cost, larger elution volume, and the potential increase in co-extraction of matrix interferences. In this paper, the extraction of per- and polyfluoroalkyl substances (PFAS) from drinking water is investigated. The method uses 150 mg SampliQ WAX polymer for a 250 mL sample volume instead of the typical 500 mg sorbent mass as specified in EPA method 533. Results show that all quality control metrics listed in EPA method 533 can be achieved with a smaller sorbent mass.

Introduction

An important but sometimes overlooked consideration in optimizing an SPE method is the ratio of sorbent mass to sample volume. Clearly, there needs to be sufficient sorbent mass to retain the analytes of interest without breakthrough during sample loading and washing steps. However, defining a sufficient sorbent mass depends on the strength of sorbent-analyte interaction. For weakly interacting analytes, the sorbent mass-to-sample ratio may be relatively large to achieve a sufficient loading volume to meet required detection limits. For strongly interacting analytes, the sorbent mass-to-sample volume ratio may be relatively small, or the loading volume may be increased to yield a greater concentration factor. Another important consideration is the volume of elution solvent. Elution volume is proportional to sorbent mass and can affect the final extract concentration. Therefore, the goal for optimizing sorbent mass should be to maximize the ratio of sample volume to sorbent mass, since the final concentration depends on the loading and elution solvent volumes.[1]

Polymeric weak anion exchange is the preferred sorbent for the extraction of PFAS. The large ion exchange capacity and mixed-mode retention are important for PFAS analysis. Many of the PFAS compounds of interest are carboxylic and sulfonic acids, which are predominately in the anionic form over a wide range of pH.[2] These acids are retained through ionic sorbent-analyte interactions while the retention of neutral PFAS are achieved due to the hydrophobic polymeric substrate. The capacity of these sorbents is large ranging from 0.8 to 1.3 mEq/g for ion exchangers with surface areas up to 800 m^2/g.[3,4]

United States EPA method 533 was developed for the extraction of 25 PFAS compounds from drinking water. The method specifies the use of a polymeric WAX SPE.[5] Typically, a 500 mg sorbent mass is used for the extraction of a 250 mL drinking water sample, although a 200 mg sorbent mass can be used for sample volumes of 100 mL. This ratio ensures a more than adequate capacity to retain the analytes of interest. However, matrices and matrix interferants may be co-extracted.[6] Among interferences, the presence of dissolved salts may be the most problematic by competitively interfering with available ionic sorbent sites.[7] This has been observed for matrices with considerable ionic strength such as seawater.[8] However, the concentration of ions in drinking water is considerably lower by comparison. For example, the specific conductance of seawater is around 80 to 1,000 times that of typical tap water and therefore less likely to encounter interference from dissolved salts.[9] Therefore, the extraction of PFAS compounds from drinking water may not require a sorbent mass-to-sample ratio of 500 mg to 250 mL.

Reducing the sorbent mass-to-sample ratio for drinking water samples has many practical benefits. A lower ratio will reduce waste, lower cost per analysis, and require less time for blowdown if the elution solvent volume is reduced. From a performance point of view, lowering the sorbent mass reduces the potential of co-extraction of matrix interferants. In this application note, the use of 150 mg of SampliQ WAX polymer cartridges is investigated for the extraction of PFAS compounds from 250 mL of drinking water. This method follows the Quality Control Protocols listed in EPA method 533.

Experimental

Extraction and analysis procedures closely followed those given in EPA method 533.[5]

Spiking solution preparation

Native PFAS analytes, isotope performance standards (IPS), and isotope dilution analogs (IDA) were purchased as mixtures from Wellington Labs (Table 1). These standards were diluted to make intermediate concentration stock solutions in 80/20 methanol/water. The native PFAS analytes were diluted from 500 ng/mL to 25 ng/mL. The IPS was diluted to a final concentration of 120 ng/mL for both M3PFBA and M2PFOA, and 344 ng/mL for MPFOS. The IDS was diluted from 500 mg/mL to 120 ng/mL for all the compounds except the fluorotelomers (i.e. 4:2, 6:2, and 8:2 FTS) which had final concentrations of 480 ng/mL. The intermediate solutions were prepared and stored in 2 mL polypropylene autosampler vials (Table 2).[5]

Table 1. Compound list.

Name	Abbreviation
Native PFAS Analytes	
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS
4,8-Dioxa-3H-perfluorononanoic acid	ADONA
Hexafluoropropylene oxide dimer acid	HFPO-DA
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA
Perfluorobutanoic acid	PFBA
Perfluorobutanesulfonic acid	PFBS
1H,1H,2H,2H-Perfluorodecanesulfonic acid	8:2 FTS
Perfluorodecanoic acid	PFDA
Perfluorododecanoic acid	PFDoA
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA
Perfluoroheptanesulfonic acid	PFHpS
Perfluoroheptanoic acid	PFHpA
1H,1H,2H,2H-Perfluorohexanesulfonic acid	4:2 FTS
Perfluorohexanesulfonic acid	PFHxS
Perfluorohexanoic acid	PFHxA
Perfluoro-3-methoxypropanoic acid	PFMPA
Perfluoro-4-methoxybutanoic acid	PFMBA
Perfluorononanoic acid	PFNA
1H,1H,2H,2H-Perfluorooctanesulfonic acid	6:2 FTS
Perfluorooctanesulfonic acid	PFOS
Perfluorooctanoic acid	PFOA
Perfluoropentanoic acid	PFPeA
Perfluoropentanesulfonic acid	PFPeS
Perfluoroundecanoic acid	PFUnA

Name	Abbreviation
Isotope Performance Standards	
Perfluoro-*n*-[2,3,4-$^{13}C_3$] butanoic acid	M3PFBA
Perfluoro-[1,2-$^{13}C_2$] octanoic acid	M2PFOA
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] octanesulfonate	MPFOS
Isotope Dilution Standards	
Perfluoro-*n*-[1,2,3,4-$^{13}C_4$] butanoic acid	MPFBA
Perfluoro-*n*-[1,2,3,4,5-$^{13}C_5$] pentanoic acid	M5PFPeA
Sodium perfluoro-1-[2,3,4-$^{13}C_3$] butanesulfonate	M3PFBS
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$] hexanesulfonate	M2-4:2 FTS
Perfluoro-*n*-[1,2,3,4,6-$^{13}C_5$] hexanoic acid	M5PFHxA
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy-$^{13}C_3$)-propanoic acid	M3HFPO-DA
Perfluoro-*n*-[1,2,3,4-$^{13}C_4$] heptanoic acid	M4PFHpA
Sodium perfluoro-1-[1,2,3-$^{13}C_3$] hexanesulfonate	M3PFHxS
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-octanesulfonate	M2-6:2 FTS
Perfluoro-*n*-[$^{13}C_8$] octanoic acid	M8PFOA
Perfluoro-*n*-[$^{13}C_9$] nonanoic acid	M9PFNA
Sodium perfluoro-[$^{13}C_8$] octanesulfonate	M8PFOS
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-decanesulfonate	M2-8:2 FTS
Perfluoro-*n*-[1,2,3,4,5,6-$^{13}C_6$] decanoic acid	M6PFDA
Perfluoro-*n*-[1,2,3,4,5,6,7-$^{13}C_7$] undecanoic acid	M7PFUnA
Perfluoro-*n*-[1,2-$^{13}C_2$] dodecanoic acid	M2PFDoA

Table 2. Consumables and supplies.

Description	Agilent Part Number
Polypropylene autosampler screw top vials, 2 mL, and caps	5191-8151 and 5191-8150
Agilent InfinityLab PFC-free HPLC conversion kit	5004-0006
Agilent MassHunter PFAS MRM database	G1736AA
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
Empty SPE cartridge, 60 mL, 100 pk (large volume reservoir)	12131012
Adapter cap for 1, 3, and 6 mL Bond Elut cartridges, 15/pk	12131001
Agilent SampliQ Wax cartridge, 6 mL tube, 150 mg, 30 μm, 30/pk	5982-3667
Centrifuge tubes and caps, 15 mL, 50/pk	5610-2039

Calibration standard preparation

Calibration standards were prepared at concentrations of 150, 250, 500, 1,250, 2,500, and 5,000 ng/L using the PFAS native mix and the intermediate concentration stock solution. The IDA were added to each level a constant concentration of 4,800 ng/L for the fluorotelomers and 500 ng/L for the rest of the labeled compounds. The IPS were added at constant nominal concentrations of 1,200 ng/L for both M3PFBA and M2PFOA, and 3,600 ng/L for MPFOS. All standards were prepared in an 80/20 methanol/water diluent in 2 mL polypropylene autosampler vials and were analyzed immediately after preparation.

Laboratory reagent blanks

Laboratory reagent blanks (LRB) were prepared by adding IDA to 250 mL of reagent water (Milli-Q Integral 3) at a concentration of 19.2 ng/L for the fluorotelomers and 4.80 ng/L for rest of the labeled compounds.

Laboratory fortified blanks

Low, medium, and high laboratory fortified blanks (LFB) were prepared at concentrations of 1, 5, and 20 ng/L in 250 mL of reagent water for the native PFAS compounds. IDA were added to each level at a constant concentration of 19.2 ng/L for the fluorotelomers and 4.80 ng/L for rest of the labeled compounds. The low LFB was used for minimum reporting level (MRL) confirmation.

Drinking water samples

Six municipal water samples were collected from the same tap (Wilmington, DE). To each 250 mL water sample, 0.25 mg of ammonium acetate was added to sequester free chlorine. For laboratory fortified sample matrix (LFSM) samples, three of the drinking water samples were spiked with native PFAS compounds at a concentration of 2 ng/L. To all six samples, IDA were added at a concentration of 19.2 ng/L for the fluorotelomers and 4.80 ng/L for rest of the labeled compounds.

Extraction solvents

For cartridge cleaning and elution, a 2% ammonium hydroxide solution in methanol (v/v) was used. The solution was prepared and used the same day of extraction. A 0.1 M phosphate buffer solution at pH 7.0 was used for cartridge conditioning. It was prepared by adding 500 mL of 0.1 M dibasic sodium phosphate with 275 mL of 0.1 M monobasic sodium phosphate. The pH was verified to be approximately 7.0.

Extraction method

SampliQ WAX sorbent was used for all extractions in a 150 mg bed mass, 6 mL cartridge volume format. To reduce the number of pours required to transfer the 250 mL sample volume, each SPE cartridge was equipped with a 60 mL reservoir using a cartridge adapter. Extractions were carried out under vacuum using the Agilent Vac Elut SPS 24 manifold with a waste manifold adapter and collection rack to accommodate 15 mL centrifuge tubes. To collect extracts, 15 mL polypropylene centrifuge tubes were used. See Table 2 for a list of consumables.

The extraction method followed those listed in EPA method 533 with the addition of a basic methanol wash as a first step. The extraction sequence is listed in Figure 1.

Instrumental method

The optimized LC conditions are listed in Table 3, and optimized MS conditions are listed in Table 4. The gradient used for analysis follows the gradient listed in EPA method 533. The MRM transitions used for quantitation and retention times listed are listed in Table A1 in Appendix A. The optimal fragmentor and collision energy voltages were taken from the Agilent MassHunter PFAS MRM database (Table 2). Figure 2 shows a typical chromatogram produced at the method conditions.

Instrument calibration

For calibration, the concentration of all the PFAS present as salts were corrected to the acid concentration in solution. The isotope dilution calibration technique was used in which the response of the native PFAS were referenced to the IDA responses. A linear least-squares regression weighted by the inverse concentration (i.e. 1/x) was applied to all analytes. According to the method, acceptance criteria for the calibration is determined by the predictability of the regression model. For the lowest concentration standard, the calculated concentration must be within 50 to 150% of the actual concentration. For all other standards, the calculated concentration must be within 70 to 130% of the actual concentration. Table A2 in Appendix A list the accuracy for each PFAS at each calibration level in addition to the coefficient of determination. All compounds passed the calibration criteria.

Place SPE cartridges and 15 mL centrifuge collection tubes on a Vac Elut SPS 24 manifold 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 to 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 to 20 in Hg.

↓

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 methanol/water and analyze.

Figure 1. Extraction procedure.

Table 3. LC conditions.

Parameter	Value
LC	Agilent 1290 Infinity II LC
Analytical Column	Agilent ZORBAX RRHD Eclipse Plus C18, 2.1 x 50 mm, 1.8 µm (p/n 959757-902)
Delay Column	Agilent InfinityLab PFC delay column, 4.6 × 30 mm (p/n 5062-8100)
Column Temperature	30 °C
Injection Volume	5 µL
Mobile Phase	A) 20 mM ammonium acetate in water B) methanol
Gradient	Time (min) % A % B Flow (mL/min) 0 95 5 0.25 0.50 95 5 0.25 3.00 60 40 0.25 16.00 20 80 0.25 18.00 20 80 0.25 20.00 5 95 0.25 22.00 5 95 0.25 25.00 95 5 0.25 35.00 95 5 0.25

Results and discussion

EPA method 533 provides a rigorous set of quality control requirements for the initial demonstration of capability (IDC) and ongoing quality control. Therefore, this method was selected to evaluate the performance the 150 mg SampliQ WAX cartridges for the extraction of PFAS from 250 mL water samples.

Branched isomer resolution

The first IDC requirement is to establish the retention times of the branched isomers in the technical-grade PFAS standard and ensure they elute within the same MRM window as the linear isomers. In the PFAS standard used, both PFHxS and PFOS were present as a mixture of branched and linear isomers. Figure 3 shows the chromatograms of PFHxS and PFOS and the isomer resolution within the same transition windows.

Table 4. MS conditions.

Parameter	Value
MS	Agilent 6470 triple quadrupole LC/MS with Agilent Jet Stream ESI source
Source Parameters	
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

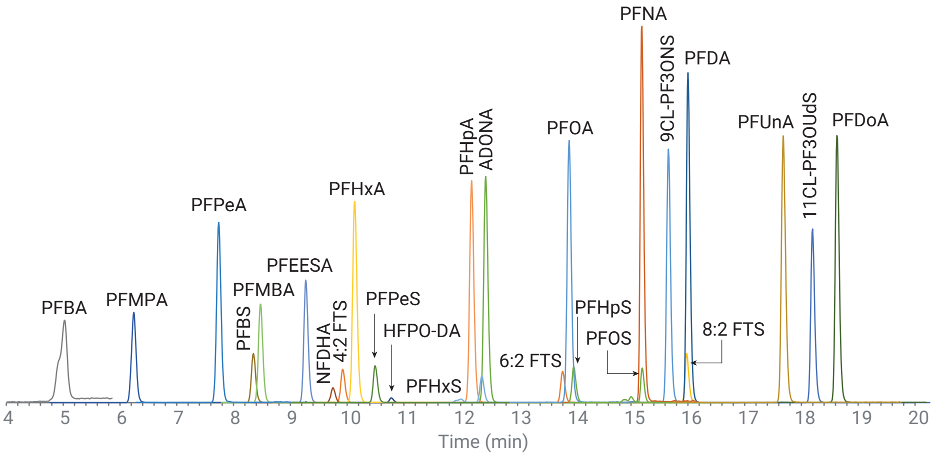

Figure 2. Chromatogram of the native PFAS in the mid-level 1,250 ng/L calibration standard.

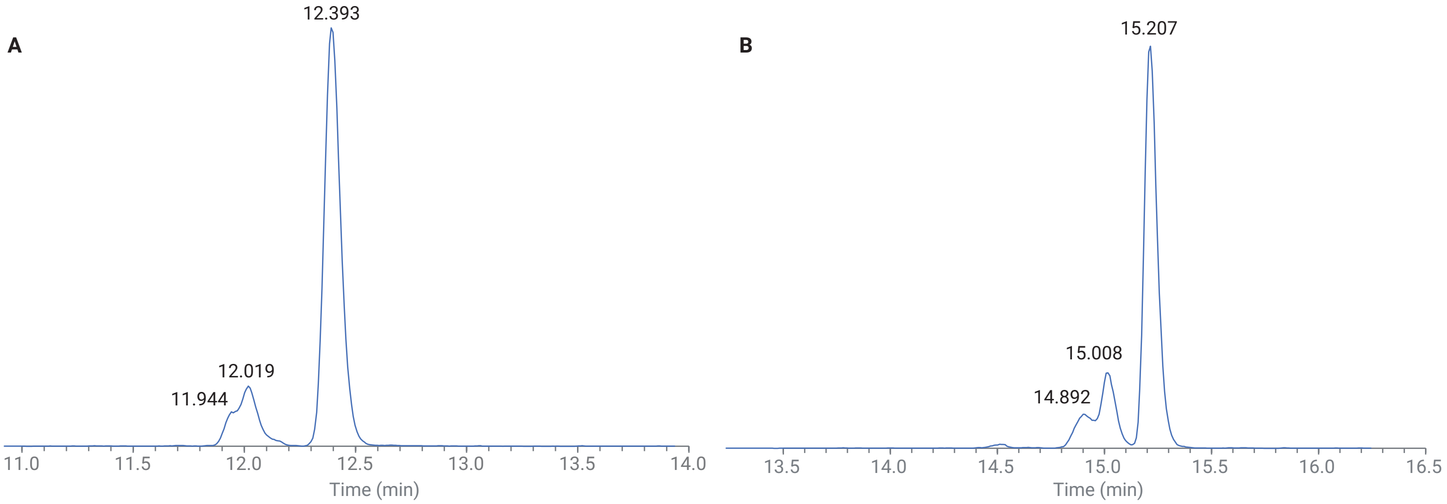

Figure 3. Resolution of branched and linear isomers captured in the same MRM window for (A) PFHxS and (B) PFOS.

Demonstration of low system background

For the next IDC requirement, the system background should be established as less than one-third the MRL. In this study, the MRL was set to a nominal concentration of 1 ng/L in 250 mL of water, which establishes a background threshold of 0.3 ng/L. Figure 4 shows the average concentration of native PFAS compounds in the LRB measured immediately after the injection of the highest concentration standard in the calibration (5,000 ng/L) for three replicates. All compounds measured in the blank had a concentration well below the 0.3 ng/L threshold except for 6:2 FTS. The source of the 6:2 FTS contamination was traced to the methanol used in the study.

Demonstration of precision and accuracy

The next two IDC requirements demonstrate extraction accuracy and precision. For these requirements, seven replicate LFBs at the mid-level concentration (5 ng/L) were extracted and analyzed. According to requirements, the relative standard deviation (RSD) must be ≤20% and the accuracy must be within 70 to 130%. Figure 5 shows the precision determination. The percent RSD for each compound was significantly lower than the 20% threshold. The average RSD across all compounds was 2.5%. Figure 6 shows the accuracy determination. For all compounds, the recovery was within the 70 to 130% accuracy window for all the compounds with an average recovery of 99%. It should be noted that four consecutive measurements for 6:2 FTS were used in the accuracy and precision determination.

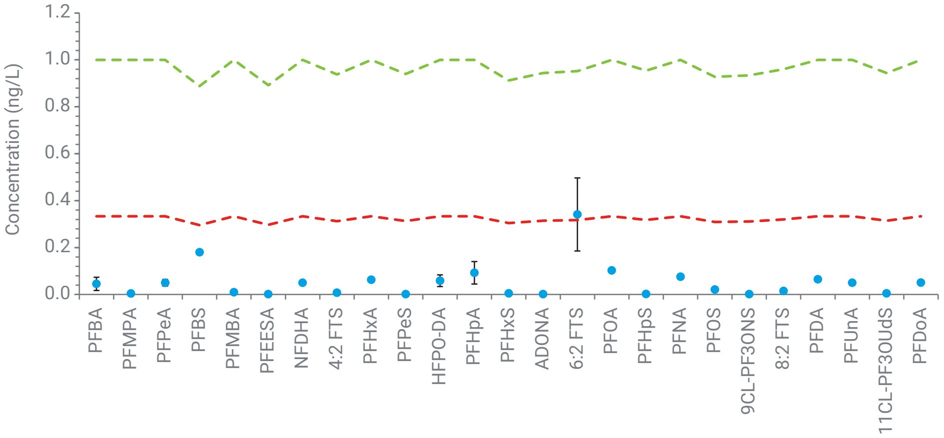

Figure 4. Demonstration of low system background. The green hashed line is the MRL level of approximately 1 ng/L, and the red hashed line is the blank threshold at approximately 0.3 ng/L. The error bars represent one standard deviation for three measurements.

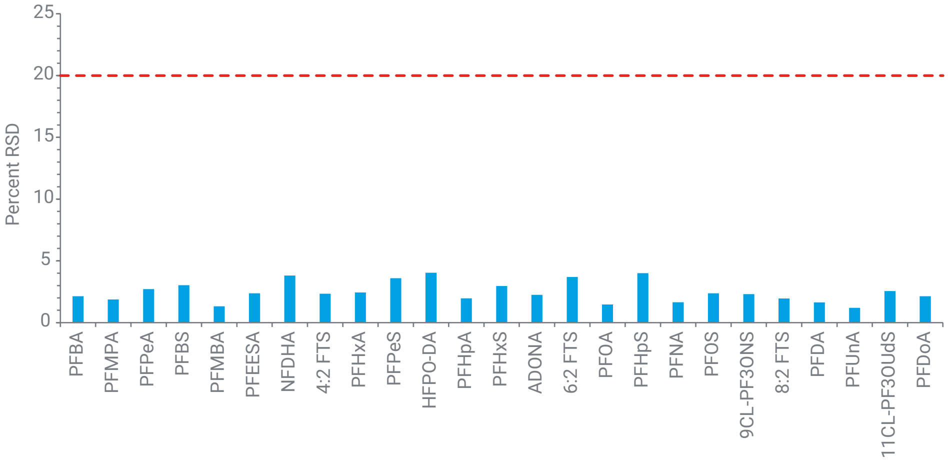

Figure 5. Demonstration of method precision for 5 ng/L PFAS in water. The hashed red line represents the 20% RSD method acceptance criteria.

Figure 6. Demonstration of accuracy for 5 ng/L of PFAS in water. The hashed red lines represent the method acceptance criteria of upper and lower accuracy limit.

MRL confirmation

The next IDC requirement is statistical verification of the MRL. The procedure ensures that MRL is the lowest true concentration for which future measurements will fall within 50 to 150% recovery with 99% confidence.[5] This requires calculation of the upper and lower limits for the prediction interval of results (PIR). The upper PIR should be equal to or less than 150%, and the lower PIR should be greater than or equal to 50%.[10] Figure 7 shows the calculated upper and lower PIR for seven replicate extracts prepared at the MRL (1 ng/L). All the PFAS compounds pass the MRL confirmation criteria at the 1 ng/L except for 6:2 FTS due to the small amount of contamination of the methanol used for extraction.

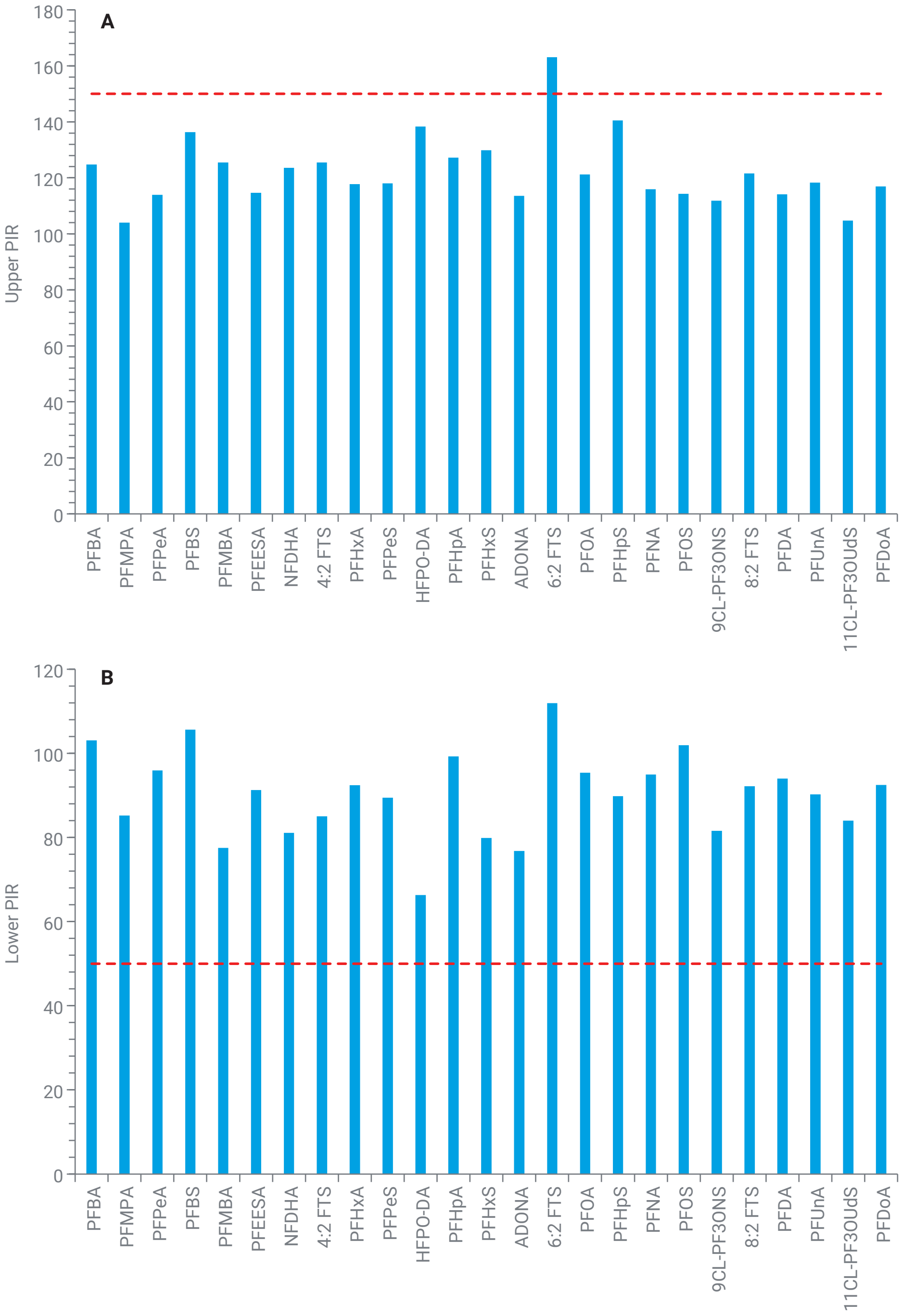

Figure 7. Calculated A) upper and B) lower PIR at fortified concentration 1 ng/L. The hashed lines represent the PIR limits.

Calibration verification

The final IDC requirement is verification of the calibration using a quality control standard (QCS). For EPA method 533, the same source can be used for the QCS as for the primary calibration standards. The results of the calibration verification at the mid-level concentration (5 ng/L) are shown in Figure 8. For all compounds, recoveries were within the required 70 to 130% range. On average, the recovery for all compounds was 96.7%.

Drinking water

Drinking water samples were prepared following the EPA 533 procedure in triplicate. Results are shown in Table 5. Eight compounds (PFBA, PFPeA, PFBS, PFHxA, PFHpA, PFHxS, PFOA, and PFNA) were found to be above the MRL. The average RSD was 1.3% for the compounds above the MRL indicating good precision for replicate measurements in matrix.

Figure 8. Calibration verification with a mid-level standard at 5 ng/L of PFAS in water. Red hashed lines represent the method acceptance criteria of upper and lower threshold limits of recovery.

Table 5. Drinking water measurements 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	<MRL	–	1.00	
PFPeA	6.37	0.07	1.00	1.13
PFBS	3.05	0.02	0.89	0.75
PFMBA	<MRL	–	1.00	
PFEESA	<MRL	–	0.89	
NFDHA	<MRL	–	1.00	
4:2 FTS	<MRL	–	0.94	
PFHxA	6.37	0.16	1.00	2.50
PFPeS	<MRL	–	0.94	
HFPO-DA	<MRL	–	1.00	
PFHpA	4.11	0.06	1.00	1.42
PFHxS	2.08	0.04	0.91	1.70
ADONA	<MRL	–	0.94	
6:2 FTS	<MRL	–	0.95	
PFOA	4.92	0.02	1.00	0.50
PFHpS	<MRL	–	0.95	
PFNA	1.99	0.00	1.00	0.18
PFOS	<MRL	–	0.93	
9CL-PF3ONS	<MRL	–	0.93	
8:2 FTS	<MRL	–	0.96	
PFDA	<MRL	–	1.00	
PFUnA	<MRL	–	1.00	
11CL-PF3OUdS	<MRL	–	0.94	
PFDoA	<MRL	–	1.00	

LFSMs were prepared in three of the drinking water samples at a concentration of 2 ng/L. The measured concentrations in the LFSMs were subtracted from the drinking water sample and the recoveries were calculated (Figure 9). According to the method, recoveries should be within 70 to 130% at twice the MRL concentration. The average recovery in matrix at the MRL was 92.7% indicating good recovery of the PFAS targets in matrix.

Absolute isotope dilution analog recoveries

An important gauge of sorbent performance in the context of extraction interferences are the absolute recoveries of the IDA. The IDA are spiked into the samples at a constant concentration before extraction and are referenced to the native PFAS analytes to compensate for matrix effects (i.e. isotope dilution quantitation). Any loss of IDA could be an indication of losses during extraction. The absolute IDA recoveries are plotted in Figure 10. These data include the seven replicate extractions of the low and mid-level spikes at 1 and 5 ng/L (respectively), the three unspiked and three spiked (2 ng/L) drinking water samples, and a high-level spike at 20 ng/L. Recoveries were calculated based on the average IDA responses for all six standards used in the initial calibration. The average recovery for the compounds was 96.1% indicating no significant interferences with sorbent recovery. It should be noted however that the flurotelomers are not shown. The absolute recoveries of these compounds exceeded the 200% threshold and were a result of ionization enhancement and not due to sorbent recovery.[5]

Figure 9. Average recoveries of the LFSM spikes at 2 ng/L for three sample replicates. Error bars represent one standard deviation. The hashed red lines indicate the recovery acceptance criteria (50 to 150%).

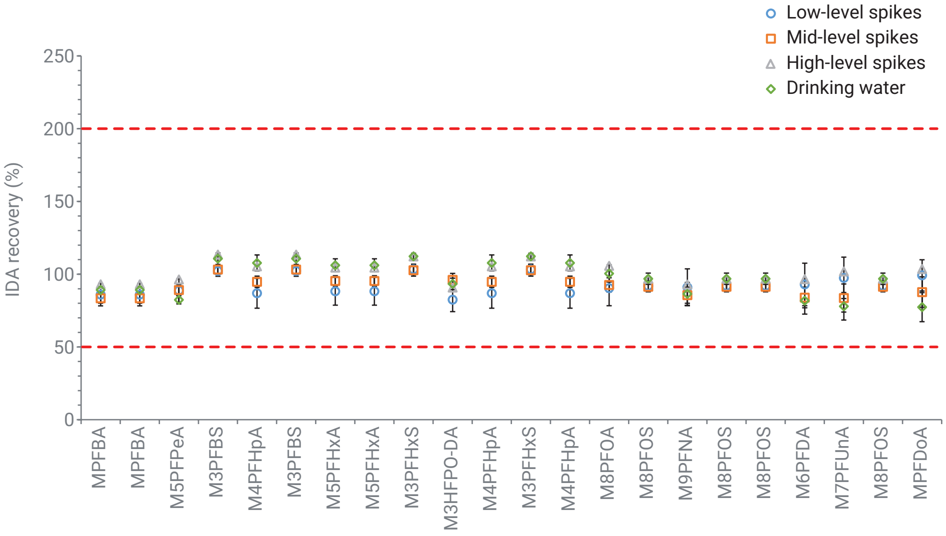

Figure 10. Absolute recoveries of IDAs in the low-level spikes, mid-level spikes, high-level spike, and drinking water samples.

Isotope performance standards responses

As a final check on the consistency of instrument response over time, the method requires that the peak area counts for the IPS are within 50 to 150% of the peak areas at the time of calibration. Figure 11 shows the IPS recovery for all the samples injected across the study with a recalibration after the 24th injection. For all IPS compounds, recoveries were within the 50 to 150% window.

Figure 11. Percent recoveries of IPS compounds: M3PFBA, M2PFOA, and MPFOS.

Conclusion

The results of this study demonstrate that the all quality performance metrics specified in EPA method 533 can be achieved with the 150 mg SampliQ WAX sorbent. No interferences or reduction in either relative or absolute recovery of the target PFAS compounds or PFAS analogs were discovered using a smaller sorbent mass-to-sample volume ratio of 150 mg to 250 mL. This indicates a sufficient sorbent capacity of the 150 mg bed mass within the context of the samples tested.

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Appendix A

Table A1. Compound MRM quantitation transitions and retention times.

Compound	Retention Time (min)	MRM Transition (Quant Ion)
Native PFAS Compounds		
PFBA	5.018	213.0 → 169.0
PFMPA	6.235	229.0 → 85.0
PFPeA	7.729	263.0 → 219.0
PFBS	8.35	299.0 → 80.0
PFMBA	8.468	279.0 → 85.0
PFEESA	9.262	315.0 → 135.0
NFDHA	9.738	295.0 → 201.0
4:2 FTS	9.916	327.0 → 307.0
PFHxA	10.119	313.0 → 269.0
PFPeS	10.479	349.0 → 80.0
HFPO-DA	10.769	285.0 → 169.0
PFHpA	12.177	363.0 → 319.0
PFHxS	12.358	399.0 → 80.0
ADONA	12.425	377.0 → 251.0
6:2 FTS	13.767	427.0 → 407.0
PFOA	13.884	413.0 → 369.0
PFHpS	13.965	449.0 → 80.0
PFNA	15.167	463.0 → 419.0
PFOS	15.174	499.0 → 80.0
9CL-PF3ONS	15.625	531.0 → 351.0
8:2 FTS	15.95	527.0 → 507.0
PFDA	15.968	513.0 → 469.0
PFUnA	17.636	563.0 → 519.0
11CL-PF3OUdS	18.155	631.0 → 451.0
PFDoA	18.591	613.0 → 569.0
IDA		
MPFBA	5.014	217.0 → 172.0
M3PFBS	5.016	216.0 → 172.0
M5PFPeA	7.728	268.0 → 223.0
M2-4:2 FTS	9.915	329.0 → 309.0
M5PFHxA	10.117	318.0 → 273.0
M3HFPO-DA	10.768	287.0 → 169.0
M4PFHpA	12.177	367.0 → 322.0
M3PFHxS	12.357	402.0 → 80.0
M2-6:2 FTS	13.774	429.0 → 409.0
M8PFOA	13.883	421.0 → 376.0
M9PFNA	15.166	472.0 → 427.0
M8PFOS	15.173	507.0 → 80.0
M2-8:2 FTS	15.95	529.0 → 509.0
M6PFDA	15.968	519.0 → 474.0
M7PFUnA	17.635	570.0 → 525.0
MPFDoA	18.59	615.0 → 570.0
IPS		
M3PFBA	8.348	302.0 → 80.0
M2PFOA	13.884	415.0 → 370.0
MPFOS	15.173	503.0 → 80.0

Table A2. Target calibration accuracy using linear least-squares regression with 1/x weighting.

	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
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

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