Application Note

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Determination of Per and Polyfluoroalkyl Substances in Drinking Water Using Agilent Bond Elut PFAS WAX SPE and LC/MS/MS

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Abstract

This application note presents the evaluation of the Agilent Bond Elut PFAS WAX solid phase extraction (SPE) cartridge for the determination of per and polyfluoroalkyl substances (PFAS) from drinking water. For the 25 target compounds in Environmental Protection Agency (EPA) method 533, the average recovery was 98.1% with an average relative standard deviation of 4.6%. In addition to the EPA method 533 targets, 26 compounds comprising different compound classes were analyzed. For these compounds, the average recovery was 99.0% with an average relative standard deviation (RSD) of 7.1%.

Introduction

Several key factors need to be considered when developing a weak anion exchange (WAX) SPE cartridge for PFAS analysis. Foremost, the resin needs to function as a mixed-mode sorbent, with a combination of ion exchange retention from the WAX ligand, and hydrophobic retention from the polymer substrate. Ion exchange is the dominant retention mechanism for the shorter-chain hydrophilic carboxylic acids ($<C_8$) and sulfonic acids ($<C_6$).[1,2] As alkyl chain length increases, the contribution from hydrophobic interaction on retention increases. For neutral PFAS without acidic functional groups (such as the sulfonamides, sulfonamide ethanols and fluorotelomer alcohols), retention is dependent on hydrophobic interactions alone.

Another aspect to consider in developing an SPE cartridge is potential contamination. The widespread use of perfluorinated compounds in industry can lead to the presence of PFAS residue in either the sorbent, SPE tube, or retaining frits. Other contaminants besides PFAS may cause interferences resulting in alterations in the electrospray ionization process leading to signal enhancement or suppression compared to the standards used for response calibration.[3] The issue of contamination is exacerbated by the low-level parts-per-trillion (ppt) reporting limits required for most methods. Largely, trace contaminants can be eliminated by including a wash step in the SPE extraction procedure prior to loading, but this may not be sufficient if there is a high concentration of contaminants.

As research into PFAS continues to expand, the list of target compounds has increased over time.[4] For example, EPA method 537, published in 2009, was developed for the determination of 14 compounds in drinking water.[5] In 2021, in EPA draft method 1633 for aqueous, solid and tissue samples, the number of target analytes has increased to 40.[6] Therefore, it is necessary to consider the extraction performance for additional targets and target classes.

A final consideration is method compliance. Most validated methods developed by standards organizations and regulatory agencies specify the use of polymeric WAX, particularly for drinking water, where target reporting limits are in the low ppt. Some methods may be more prescriptive than others, such as the U.S. EPA method 533.[7] This method specifies the use of a polymeric mixed-mode WAX, with a diamino ligand (pKa >8) of an approximate particle size of 33 µm. The method requires a bed mass to sample volume ratio of 2:1, with 500 mg sorbent and 250 mL sample volume used during validation. The use of 200 mg sorbent is acceptable for 100 mL sample volumes.

The Agilent Bond Elut PFAS WAX SPE cartridge was developed to address each of these requirements, specific to PFAS analysis. The base sorbent consists of a polystyrene divinylbenzene copolymer, functionalized with a diamino ligand. The physical properties listed in Table 1 make them fully compliant with EPA method 533. The sorbent and assembled cartridges are manufactured under strict quality control and assurance to minimize the potential of contamination or interferences. In this application note, the Bond Elut PFAS WAX 500 mg, 6 mL cartridge was used for the extraction of PFAS from drinking water by following the EPA method 533 protocol. In addition to the 25 target compounds listed in the method, another 26 compounds from diverse PFAS classes were evaluated.

Table 1. The Agilent Bond Elut PFAS WAX SPE properties.

Property	Description
Base Particle	Polystyrene divinylbenzene
Functional Group	Diamino
pKa	>8
Particle Diameter	45 µm
Available Bed Masses	500, 200, and 150 mg

Experimental

Chemicals and reagents

Native PFAS standards, isotope dilution analogues (IDA), and isotope performance standards (IPS) were purchased as individual standards from Wellington Laboratories, Inc. (Guelph, ON, Canada). HPLC-grade methanol (MeOH) was from Honeywell (Muskegon, MI, U.S.), and reagent-grade ammonium acetate and ammonium hydroxide were from Sigma-Aldrich (St Louis, MO, U.S.). Reagent water was prepared using a Milli-Q Integral 3 purification system from Millipore Sigma (Burlington, MA, U.S.).

Spiking solution preparation

For the 25 analytes listed in EPA method 533, two spiking solutions were prepared in MeOH: a high-concentration target spiking solution at 250 ng/mL and a low-concentration target spiking solution at 25 ng/mL. An IDA spiking mix was prepared in MeOH at a concentration of 250 ng/mL. Appendix A lists each of the EPA method 533 target compounds and their associated IDA.

An extended target list spiking solution with an additional 26 PFAS compounds not listed in EPA method 533 was prepared in MeOH (Appendix B). The concentration of all compounds in the extended spiking mix was 250 ng/mL except 6:2/8:2 diPAP, 8:2 diPAP, and 8:8 PFPi, with concentrations of 500 ng/mL, PFHxDA, PFDOA, PFHxPA, PFOPA, PFDPA, and Cl-PFHxPA, with concentrations of 1,000 ng/mL, and 6:2 FTCA and 8:2 FTCA, with concentrations of 2,500 ng/mL.

For each extended target, an IDA was assigned, which is listed in Appendix B. An extended target list IDA spiking solution was prepared in MeOH. The concentration of all the compounds was 250 ng/mL except $^{13}C_2$-6:2 FTCA and $^{13}C_2$-8:2 FTCA, with concentrations of 2,000 ng/mL.

An IPA solution was prepared in MeOH containing $^{13}C_3$-PFBA, $^{13}C_2$-PFOA, and $^{13}C_4$-PFOS at concentrations of 500, 500, and 1,500 ng/mL, respectively.

Calibration standard preparation

Calibration standards were prepared in 1 mL of an 80:20 (v/v) mixture of methanol and water. Seven standard levels were used for calibration, ranging from 0.25 to 25 ng/mL for all the EPA 533 and extended targets listed in Appendixes A and B except for PFHxPA, PFOPA, PFDPA, and Cl-PFHxPA, with concentrations ranging from 1 ng/mL to 100 ng/mL, and 6:2 FTCA, 8:2 FTCA, with concentrations ranging from 2.5 to 250 ng/mL. The concentration of the IDAs in the standards was 5 ng/mL for all the analogues in Appendixes A and B, except for $^{13}C_2$-6:2 FTCA and $^{13}C_2$-8:2 FTCA, with concentrations of 40 ng/mL. A 10 µL aliquot of the IPS solution was added to each 1 mL calibrant to yield concentrations of 5, 5, and 15 ng/mL for $^{13}C_3$-PFBA, $^{13}C_2$-PFOA, and $^{13}C_4$-PFOS, respectively.

Laboratory reagent blanks

Laboratory reagent blanks (LRB) were prepared by adding 20 µL of the IDA spiking mixes to 250 mL of reagent water, yielding a concentration of 20 ng/L for all the compounds except $^{13}C_2$-6:2 FTCA and $^{13}C_2$-8:2 FTCA, with concentrations of 160 ng/L.

Laboratory fortified blanks

Low-concentration laboratory fortified blanks (LFB) were prepared by adding 20 µL of the low- concentration target spiking solution to 250 mL of reagent water, yielding concentrations of 2 ng/L for the EPA method 533 targets. The low LFB was used for minimum reporting level (MRL) confirmation.

High-concentration LFBs were prepared by adding 20 µL of the high-concentration target spiking solution and 20 µL of the extended target list spiking solution to 250 mL of reagent water. This yielded concentrations of 20 ng/L for all compounds except 6:2/8:2 diPAP, 8:2 diPAP, and 8:8 PFPi, with concentrations of 40 ng/L, PFHxDA, PFDOA, PFHxPA, PFOPA, PFDPA, and Cl-PFHxPA, with concentrations of 80 ng/L, and 6:2 FTCA and 8:2 FTCA, with concentrations of 200 ng/L. IDAs were added to the LFBs using the same procedure for preparing the LRBs.

Cartridge blanks

Cartridge sample blanks were prepared by rinsing the cartridges with 10 mL of a 2% ammonia solution in MeOH. The collected rinse was concentrated to 100 µL under dry nitrogen at ambient temperature. The concentrate was diluted with 400 µL of 80:20 solution of MeOH and water. The extracts were qualitatively assessed using an Agilent 6546 LC/Q-TOF.

Drinking water sample

Municipal drinking water samples (Wilmington, DE, U.S.) were collected in 250 mL polypropylene volumetric flasks. A laboratory fortified sample matrix (LFSM) was prepared by spiking a 250 mL drinking water sample with 40 µL of the low-concentration target spiking solution yielding a concentration of 4 ng/L for the EPA method 533 targets. Ammonium acetate (0.25 g) was added to the drinking water samples to sequester chlorine.

Extraction solvents

For cartridge elution, a 2% ammonium hydroxide solution in MeOH (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.

Equipment and materials

Sample analysis was performed using an Agilent 1290 Infinity II LC system consisting of an Agilent 1290 Infinity II high-speed pump (G7120A), an Agilent 1290 Infinity II multisampler (G7167B), and an Agilent 1290 Infinity II multicolumn thermostat (G7167B). The LC system was modified for PFAS analysis using the Agilent InfinityLab PFC-free HPLC conversion kit (part number 5004-0006). The LC system was coupled to an Agilent 6470B triple quadrupole LC/MS equipped with an Agilent Jet Stream Electrospray ion source. Agilent MassHunter Workstation software was used for data acquisition and analysis. The Agilent PFAS MRM Database for triple quadrupole LC/MS (G1736AA) was used for optimized MRM settings.

The consumables and supplies used for the PFAS extraction and analysis are listed in Table 2. With exception of the Bond Elut PFAS WAX cartridges, these consumables were verified to be free from PFAS interferences and contamination in previous studies.[3,8]

Extraction method

Bond Elut PFAS WAX was used for all extractions in a 500 mg bed mass, 6 mL volume cartridge 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.

The extraction method closely followed the procedure specified in EPA method 533.[7] 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 MRM transitions used for quantitation and retention times listed are listed in Table in Appendixes A and B. The optimal fragmentor and collision energy voltages were taken from the PFAS MRM Database. Figure 2 shows a typical chromatogram produced under the method conditions.

Table 3. HPLC conditions.

Parameter	Value
Mobile Phase	A) 5 mM ammonium acetate in water B) Methanol
Injection Volume	2 µL
Column Temperature	55 °C
Flow Rate	0.400 mL/min
Gradient	Time (min) %A %B 0 85 15 1.00 85 15 1.50 45 55 5.50 30 70 7.00 20 80 12.00 0 100 14.40 0 100 14.50 85 15

Table 4. MS conditions.

Parameter	Value
MS/MS	6470B triple quadrupole LC/MS
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

Table 2. PFAS-suitable consumables and supplies.

Agilent Consumables and Supplies	Part Number
Bond Elut PFAS WAX, 500 mg, 6 mL, 30 pk	5610-2152
Polypropylene autosampler screw top vials, 2 mL, and caps	5191-8151 and 5191-8150
Centrifuge tubes and caps, 15 mL	5610-2039
InfinityLab PFC delay column, 4.6 x 30 mm	5062-8100
ZORBAX RRHD Eclipse Plus C18 column, 2.1 x 100 mm, 1.8 µm	959758-902
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

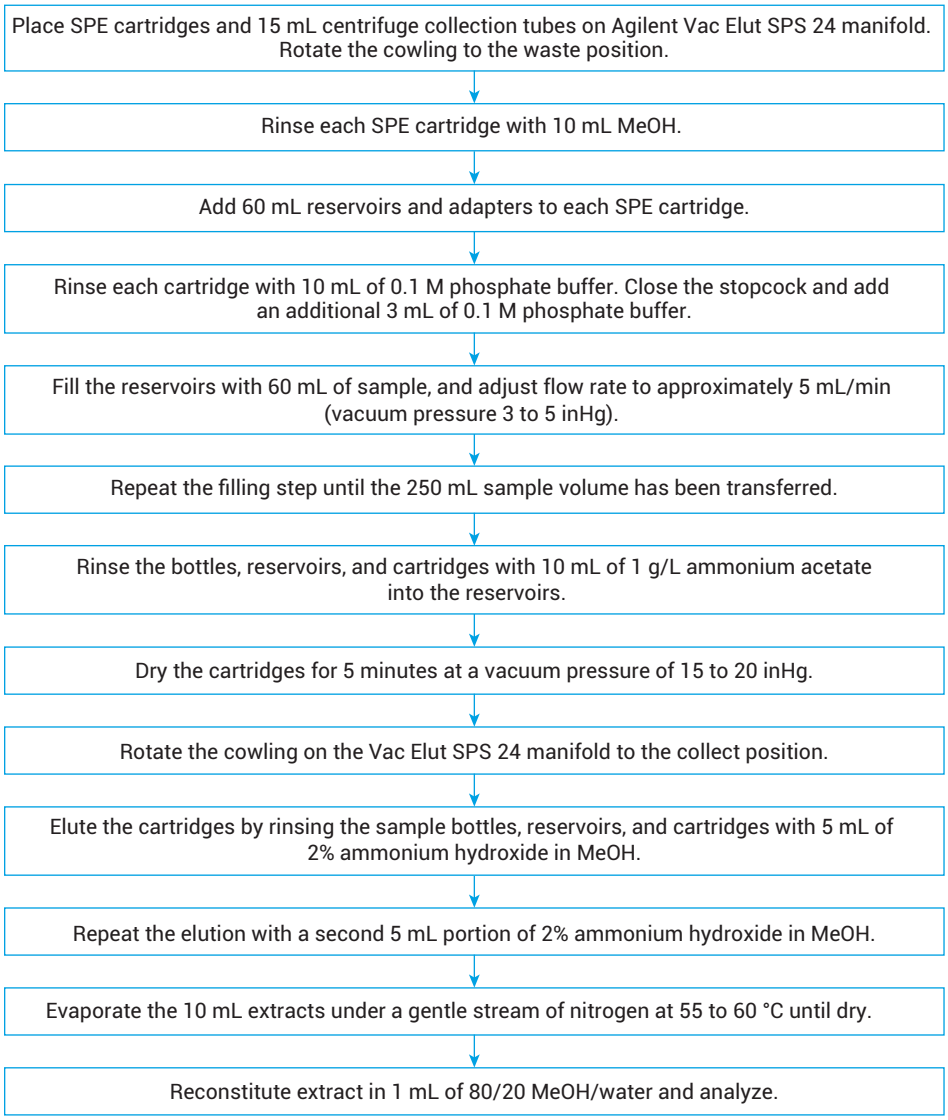

Figure 1. Extraction procedure.

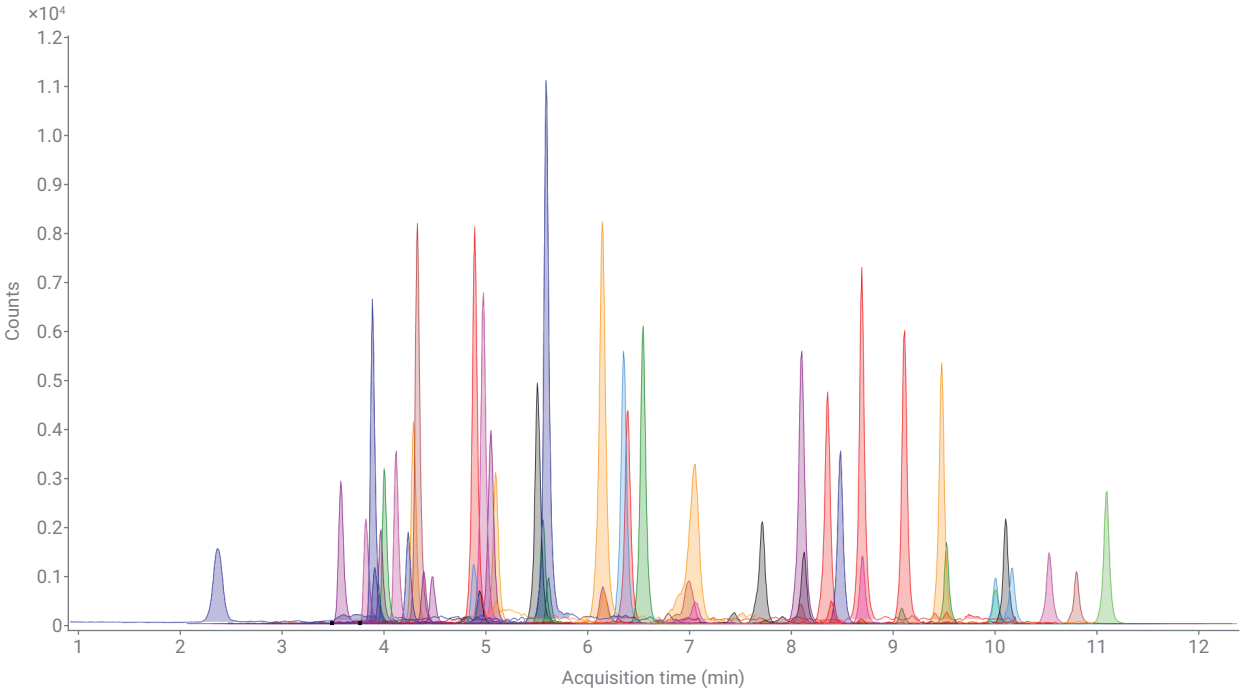

Figure 2. Target quant ion chromatogram for a standard at 5 ng/mL for most compounds (retention times listed in Appendixes A and B).

Instrument calibration

For calibration, the concentrations of all the PFAS present as salts were corrected to the acid concentrations in solution. The isotope dilution calibration technique was used, in which the response of the native PFAS were referenced to the IDA responses (Appendix A and B). Response curves were fitted using 1/x weighted linear least squares regression model and included the origin (0,0).

Results and discussion

Calibration

To evaluate the method calibration quality, the calculated concentration of each target at each calibration level was calculated based upon the response curve (Figure 3). For levels 2 to 7, the accuracy ranged from 73.1 to 129.3% with an average of 99.9%. For level 1, the accuracy ranged from 60.8 to 121.2% with an average of 95.2%. A quality control standard[7] was prepared from the target spiking solution independent of the calibration solutions at a concentration of 2.5 ng/mL for most compounds. The accuracy of the quality control standard ranged from 78.6 to 135.4% with an average of 110.4% These results are plotted in Figure 4 and demonstrate good calibration accuracy over the concentration range implemented in the study.

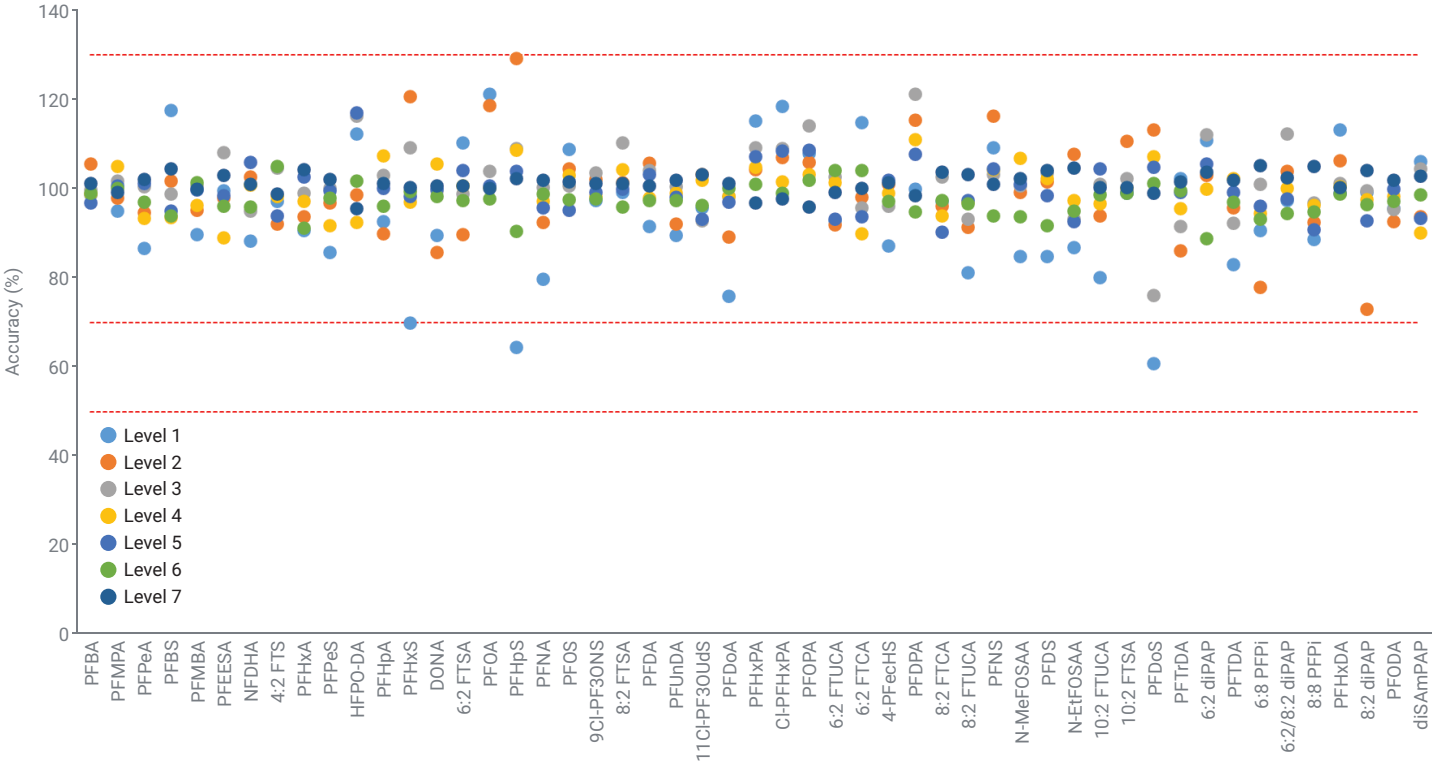

Figure 3. Calculated concentration accuracy for calibration levels 1 to 7.

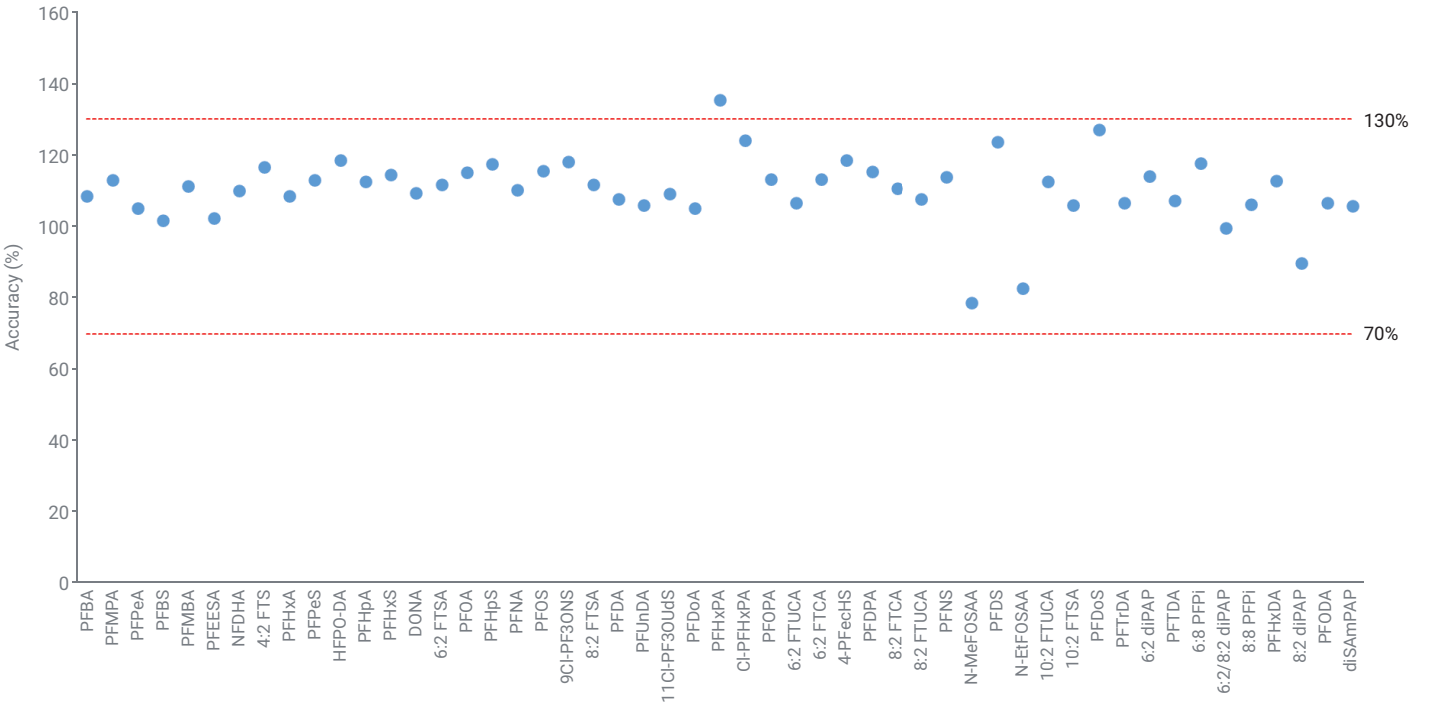

Figure 4. Calculated concentration accuracy for the quality control standard at 2.5 ng/mL for most compounds.

Cartridge blanks

The cleanliness of the Bond Elut PFAS WAX cartridge was qualitatively compared to two other commercial polymeric WAXs in the same cartridge format (500 mg, 6 mL) using LC/Q-TOF in both positive and negative mode electrospray ionization. The negative ion mode results were similar across all the cartridges tested; however, more pronounced differences were observed in positive ion mode. Figure 5 shows a total ion chromatogram comparison of the Bond Elut PFAS WAX and the two other commercial phases in positive ion mode. Caffeine was used as an internal standard at 80 µg/mL and can be seen eluting at 1.8 minutes. In the top chromatogram (Figure 5A), the elevated baseline throughout the separation consisted of a broad range of ions from 100 to 800 *m/z* and could not readily be associated with a specific contaminant. In the middle chromatogram (Figure 5B), the polymer series observed from 4.5 to 7 minutes was identified as polyethylene glycol (PEG). The bottom chromatogram is the eluate collected from the Bond Elut PFAS WAX (Figure 5C). Aside from the early eluting peaks, the Bond Elut PFAS WAX produced a much lower baseline indicating significantly lower level of contamination than the other two cartridges.

It was hypothesized that the presence of contaminants identified in positive ion mode could affect the signal response in negative ion due to matrix interference. This hypothesis was supported by the ionization signal enhancement observed for 4:2 FTSA when coeluting with PEG in a spiked extract. Figure 6 shows extracted ion chromatograms (EICs) from a reagent water spike at 500 ng/L collected in both positive and negative ion mode on the LC/Q-TOF. The top chromatogram (6A) was collected in positive ion mode showing the elution of the PEG series and the bottom chromatogram (6B) was collected in

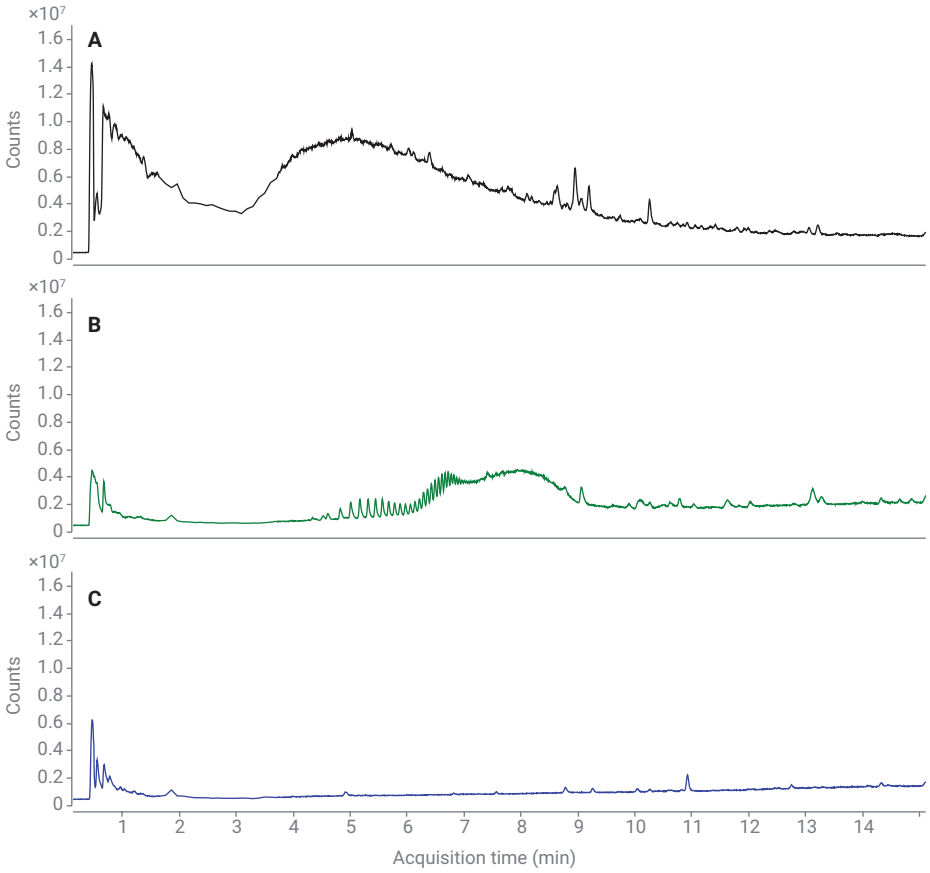

Figure 5. Cartridge blank comparison between two commercial polymeric WAXs (A, B) and the Agilent Bond Elut PFAS WAX SPE cartridge (C).

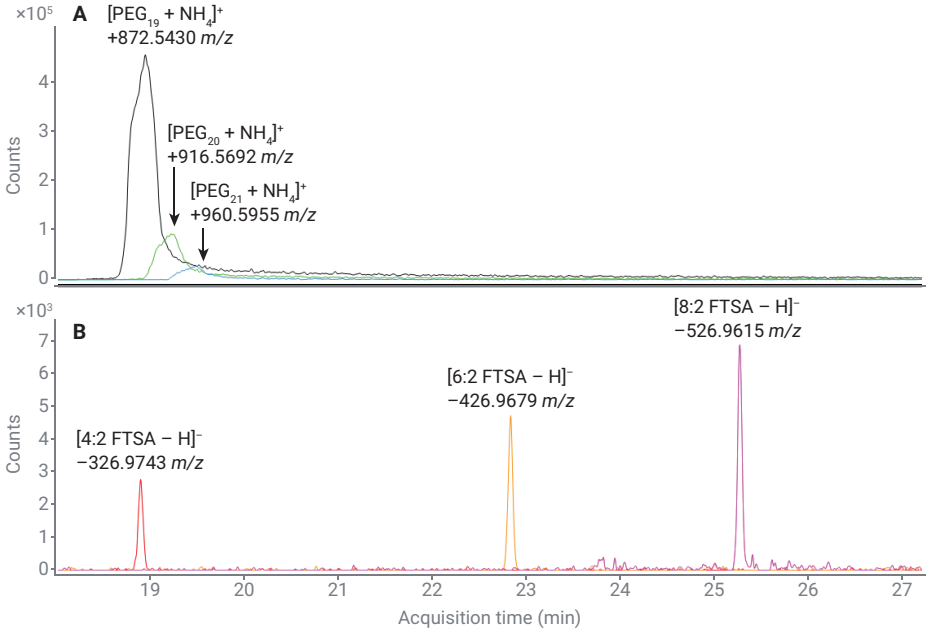

Figure 6. Coelution of 4:2 FTSA with PEG in a 500 ng/L spiked water extract analyzed in both (A) positive and (B) negative ion mode with LC/Q-TOF.

negative ion mode showing the elution of the fluorotelomer series. As observed in Figure 6, 4:2 FTSA coelutes with PEG_{19} ($C_{38}H_{78}O_{20}$); however, the other fluorotelomers 6:2 FTSA and 8:2 FTSA elute outside of the PEG series. Table 5 lists the calculated concentrations and recoveries for the fluorotelomers in extracts. The calculated concertation of 4:2 FTSA was a factor of 1.5 greater than expected. Since PEG was not present in the calibration standards, the increase in response for the 4:2 FTSA was attributed to the coelution with PEG.

Demonstration of low system background

EPA method 533 requires the demonstration of a low system background before establishing MRLs. Demonstrating low system background is accomplished by measuring the concentration of targets in an LRB sample after running the highest-level calibration standard. According to the method, the measured background concentration of targets in the LRB must be less than one-third of the MRL concentrations. In this case, the highest-level calibration standard was 25 ng/mL with a desired MRL of 2 ng/mL, therefore the background levels should be no greater than 0.67 ng/L. Figure 7 shows the results of the background measurements for the EPA 533 method targets. The blue circles represent the background concentrations, the hashed green line represents the desired MRL, and the red hashed line is one-third the desired MRL limit. All concentrations in the LRB were well below the one-third MRL threshold limit.

MRL confirmation

EPA method 533 requires statistical confirmation of the MRL. The procedure ensures that the MRL is the lowest concentration for which future measurements will fall within 50 to 150% recovery with 99.5% 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] In Figure 8, the average accuracies are plotted (blue circles) with the upper and lower PIRs represented by error bars. The PIR calculations were based on eight replicate measurements (d.f. = 7, t = 3.499) prepared at an MRL of 2 ng/L. All the PFAS compounds passed the MRL confirmation criteria at 2 ng/L.

Table 5. Recoveries of fluorotelomers in spiked water extract with PEG contaminant.

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

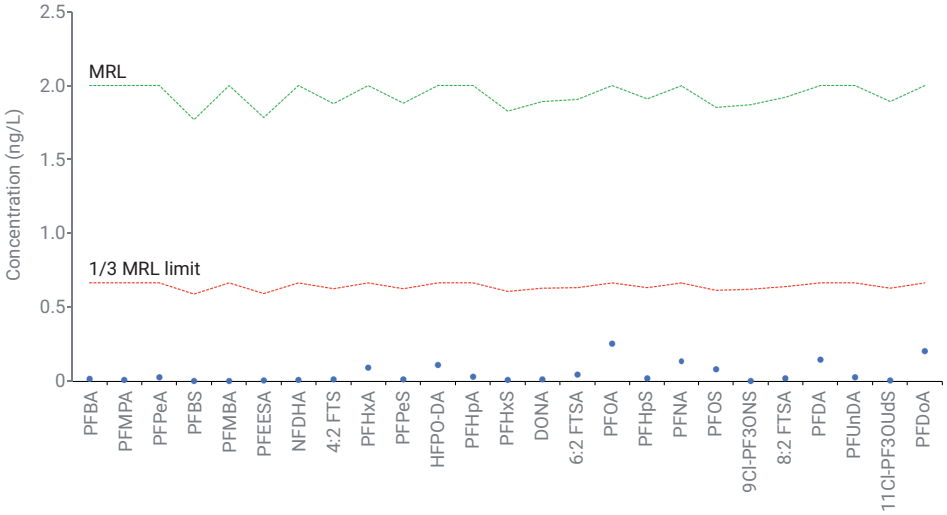

Figure 7. Demonstration of low system background. The green hashed line is the MRL level of approximately 2 ng/L, and the red hashed line is the blank threshold at approximately 0.67 ng/L.

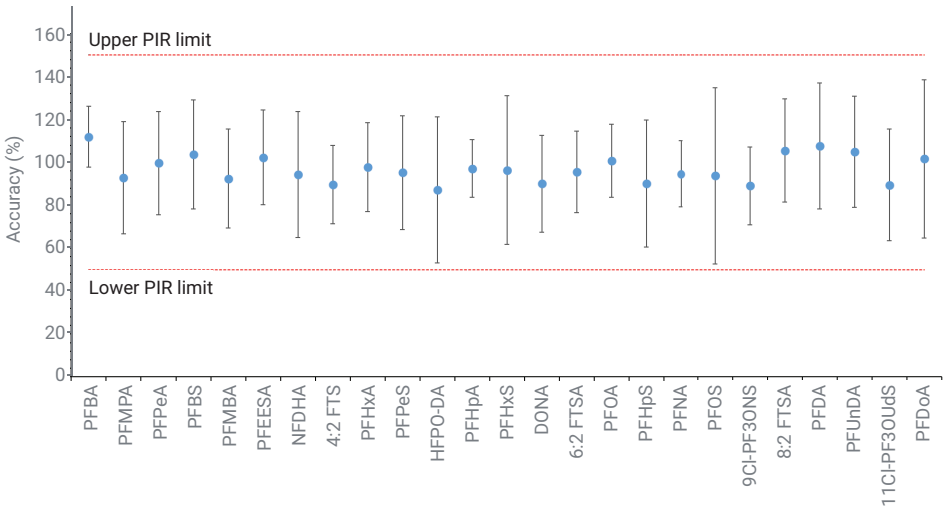

Figure 8. MRL confirmation. Average accuracy (blue circles) and PIR intervals (error bars) calculated at the MRL of 2 ng/L. The hashed lines represent the PIR limits.

Demonstration of precision and accuracy

To measure precision and accuracy, seven replicate LFBs at the midlevel concentration of 20 ng/L were extracted and analyzed. According to EPA method 533, the RSD must be ≤20% and the accuracy must be within 70 to 130% for each target. Figure 9 shows the results of the measurements. The average recoveries were well within the 70 to 130% limits and the RSDs were below the 20% threshold. Across all compounds, the average recovery was 98.1% with an average RSD of 4.6%.

Drinking water

Drinking water and drinking water spike (LFSM) samples were prepared following the EPA method 533 procedure and analyzed. Of the 25 EPA method 533 target compounds, six (PFBA, PFPeA, PFBS, PFHxA, PFHpA and PFOA) were found to be above the MRL in the drinking water sample. To test recovery of the targets in the drinking water matrix, a drinking water spike sample was prepared at a concentration of 4 ng/L. The concentration of the six targets found in the drinking water sample were subtracted from the LFSM and the recovery was calculated. The results of the drinking water and drinking water spike samples are listed in Table 6. 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 104.2% indicating good recovery of the PFAS targets in drinking water matrix.

Extended target list

In addition to the EPA method 533 target list, another 26 compounds comprising diverse compound classes were analyzed. These included phosphonic acids; fluorotelomer carboxylic acids, both saturated and unsaturated; sulfonamidoacetic acids, longer chain carboxylic and sulfonic acids; and phosphate diesters. The results of seven replicate midlevel extractions are shown in Figure 10. The extended targets had recoveries within 70 to 130% and RSDs <20%. These results indicate good sorbent performance for targets and PFAS classes outside the EPA method 533 targets.

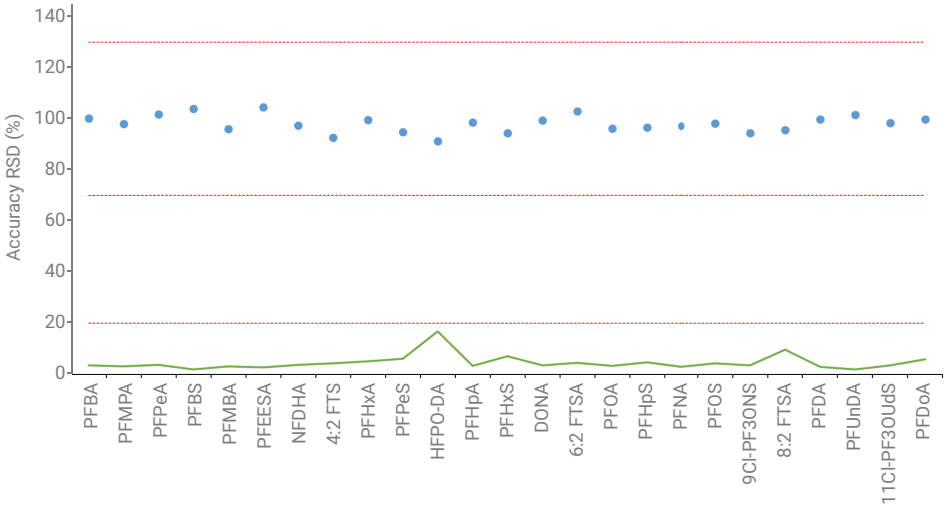

Figure 9. Recovery and precision measurements for the EPA 533 method targets at 20 ng/L. Average recoveries are represented by the blue circles and the associated RSDs are represented by the green line. The hashed lines represent the measurement limits.

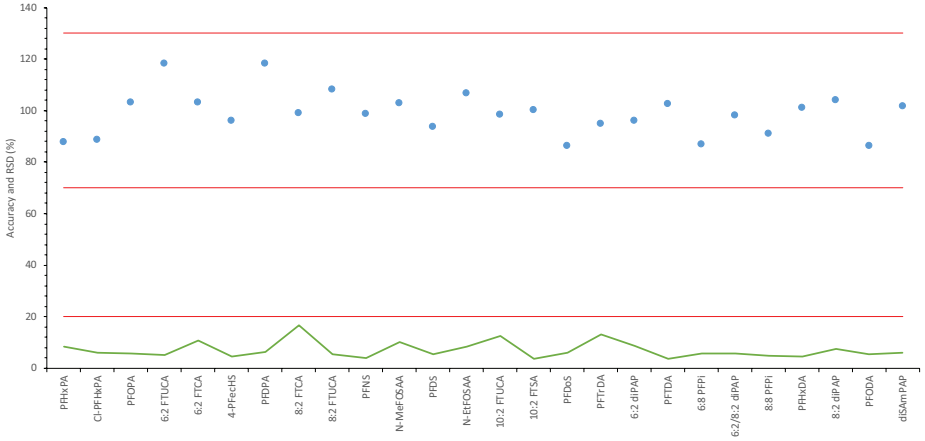

Figure 10. Average recovery (blue circles) and RSD (green line) for seven replicate midlevel spikes at 20 ng/L.

Conclusion

The results of this study demonstrate that the Agilent Bond Elut PFAS WAX SPE cartridge provides outstanding performance for the extraction of PFAS from drinking water. The cartridges demonstrated significantly lower background than other commercial cartridges. A statistically verified MRL of 2 ng/L was easily achieved with an average accuracy of 98.1% and average RSD of 4.6% for the 25 EPA method 533 target PFAS. For 26 additional targets comprising diverse compound classes, the average recovery was 99.0% with an RSD of 7.1%.

Table 6. Drinking water samples.

Compound	Concentration found in drinking water (ng/L)	Concentration in spiked drinking 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
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.

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Appendix A

EPA 533 target compounds, retention times, IDAs, and MRM transitions

Target Compound	CAS	Retention Time (min)	Target Quant Ion MRM Transition	IDA	IDA MRM Transition
PFBA	375-22-4	2.43	213 → 169	$^{13}C_4$-PFBA	217 → 172
PFMPA	377-73-1	3.57	229 → 85	$^{13}C_4$-PFBA	217 → 172
PFPeA	2706-90-3	3.89	263 → 219	$^{13}C_5$-PFPeA	268 → 223
PFBS	375-73-5	3.97	299 → 80	$^{13}C_3$-PFBS	302 → 80
PFMBA	863090-89-5	4.01	279 → 85	$^{13}C_5$-PFPeA	268 → 223
PFEESA	113507-82-7	4.12	315 → 135	$^{13}C_3$-PFBS	302 → 80
NFDHA	151772-58-6	4.25	201 → 85	$^{13}C_5$-PFHxA	318 → 273
4:2 FTSA	757124-72-4	4.29	327 → 307	$^{13}C_2$-4:2 FTSA	329 → 309
PFHxA	307-24-4	4.33	313 → 269	$^{13}C_5$-PFHxA	318 → 273
PFPeS	2706-91-4	4.39	349 → 80	$^{13}C_3$-PFHxS	402 → 80
HFPO-DA	13252-13-6	4.48	285 → 169	$^{13}C_3$-HFPO-DA	287 → 169
PFHpA	375-85-9	4.90	363 → 319	$^{13}C_4$-PFHpA	367 → 322
PFHxS	355-46-4	4.95	399 → 80	$^{13}C_3$-PFHxS	402 → 80
DONA	919005-14-4	4.98	377 → 251	$^{13}C_4$-PFHpA	367 → 322
6:2 FTSA	27619-97-2	5.57	427 → 407	$^{13}C_2$-6:2 FTSA	429 → 409
PFOA	335-67-1	5.60	413 → 369	$^{13}C_8$-PFOA	421 → 376
PFHpS	375-92-8	5.63	449 → 80	$^{13}C_8$-PFOS	507 → 80
PFNA	375-95-1	6.15	463 → 419	$^{13}C_9$-PFNA	472 → 427
PFOS	1763-23-1	6.17	499 → 80	$^{13}C_8$-PFOS	507 → 80
9Cl-PF3ONS	756426-58-1	6.55	531 → 351	$^{13}C_8$-PFOS	507 → 80
8:2 FTSA	39108-34-4	7.02	527 → 507	$^{13}C_2$-8:2 FTSA	529 → 509
PFDA	335-76-2	7.07	513 → 469	$^{13}C_6$-PFDA	519 → 474
PFUnDA	2058-94-8	8.11	563 → 519	$^{13}C_7$-PFUnDA	570 → 525
11Cl-PF3OUdS	763051-92-9	8.48	631 → 451	$^{13}C_8$-PFOS	507 → 80
PFDoDA	307-55-1	8.70	613 → 569	$^{13}C_2$-PFDoDA	615 → 570

Appendix B

Extended target compounds, retention times, IDAs, and MRM transitions

Target Compounds	CAS	Retention Time (min)	Target Quant Ion MRM Transition	IDA	IDA MRM Transition
PFHxPA	40143-76-8	3.87	399 → 79	Cl-PFOPA	515 → 79
Cl-PFHxPA	NA	3.90	415 → 79	Cl-PFOPA	515 → 79
PFOPA	40143-78-0	4.87	499 → 79	Cl-PFOPA	515 → 79
6:2 FTUCA	70887-88-6	5.06	357 → 293	$^{13}C_2$-6:2 FTUCA	359 → 294
6:2 FTCA	53826-12-3	5.11	377 → 293	$^{13}C_2$-6:2 FTCA	379 → 294
4-PFecHS	646-83-3	5.52	461 → 381	$^{13}C_8$-PFOS	507 → 80
PFDPA	52299-26-0	6.10	599 → 79	Cl-PFOPA	515 → 79
8:2 FTCA	27854-31-5	6.40	477 → 393	$^{13}C_2$-8:2 FTCA	479 → 394
8:2 FTUCA	70887-84-2	6.36	457 → 393	$^{13}C_2$-8:2 FTUCA	459 → 394
PFNS	68259-12-1	7.09	549 → 80	$^{13}C_8$-PFOS	507 → 80
N-MeFOSAA	2355-31-9	7.73	570 → 419	$^{2}H_3$-N-MeFOSAA	573 → 419
PFDS	335-77-3	8.10	599 → 80	$^{13}C_8$-PFOS	507 → 80
N-EtFOSAA	2991-50-6	8.13	584 → 419	$^{2}H_5$-N-EtFOSAA	589 → 419
10:2 FTUCA	70887-94-4	8.36	557 → 493	$^{13}C_2$-10:2 FTUCA	559 → 494
10:2 FTSA	120226-60-0	8.60	627 → 607	$^{13}C_2$-8:2 FTSA	529 → 509
PFDoS	79780-39-5	9.09	699 → 80	$^{13}C_8$-PFOS	507 → 80
PFTrDA	72629-94-8	9.12	663 → 619	$^{13}C_2$-PFDoDA	615 → 570
6:2 diPAP	57677-95-9	9.39	789 → 97	$(^{13}C_2)_2$-6:2 diPAP	793 → 97
PFTDA	376-06-7	9.49	713 → 669	$^{13}C_2$-PFTDA	715 → 670
6:8 PFPi	610800-34-5	9.54	801 → 401	$(^{13}C_2)_2$-6:2 diPAP	993 → 97
6:2/8:2 diPAP	943913-15-3	10.02	889 → 443	$(^{13}C_2)_2$-6:2 diPAP	793 → 97
8:8 PFPi	40143-79-1	10.11	901 → 501	$(^{13}C_2)_2$-6:2 diPAP	793 → 445
PFHxDA	67905-19-5	10.18	813 → 269	$^{13}C_2$-PFHxDA	815 → 770
8:2 diPAP	678-41-1	10.55	989 → 543	$(^{13}C_2)_2$-8:2 diPAP	993 → 97
PFODA	16517-11-6	10.81	913 → 369	$^{13}C_2$-PFHxDA	815 → 770
diSAmPAP	2965-52-8	11.10	1,203 → 526	$(^{13}C_2)_2$-8:2 diPAP	993 → 97

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