Application Note

Environmental

Automated Solid Phase Extraction of PFAS from Aqueous Samples

Using dual-phase Agilent Bond Elut PFAS WAX/Carbon S SPE cartridges for US EPA Method 1633

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Abstract

Key to enabling automated solid phase extraction (SPE) is the use of sorbents specifically designed and tested for Per- and Polyfluoroalkyl Substance (PFAS) analysis. In this study, five extraction protocols using Agilent PFAS WAX and Carbon S for PFAS sorbents, designed to meet the quality control requirements of US EPA Method 1633, were evaluated. The protocols included two-step extractions with single-phase Bond Elut PFAS WAX SPE cartridges and loose carbon, as well as one-step extractions with dual-phase Agilent Bond Elut layered PFAS WAX/Carbon S and Agilent Bond Elut blended PFAS WAX/Carbon S SPE cartridges. The blended sorbent configuration, containing 200 mg of PFAS WAX and 10 mg of Carbon S for PFAS, demonstrated the fewest number of recovery outliers and was selected for full method validation for aqueous sample matrices. To evaluate method effectiveness across different aqueous matrix types, PFAS analysis was carried out on groundwater samples from residential private wells, effluent from a wastewater storage lagoon, and a landfill monitoring well. Recovery of internal standards and matrix spike targets were well within acceptance limits. This study highlights the effectiveness of automated SPE coupled with PFAS-ready cartridges in improving laboratory efficiency and accuracy in PFAS analysis.

Introduction

There is an increasing focus on streamlining sample preparation and analysis methods for determining PFAS in environmental matrices. The large number of sample requests that many production laboratories receive, and the complexity of method-regulated sample preparation procedures can be a stress on laboratory resources. To address these challenges, many laboratories are adopting automation for sample preparation, which can be the most labor-intensive and error-prone aspect of sample preparation.[1]

One analysis method is US EPA Method 1633.[2] This method was developed to consolidate procedures for the extraction and quantitation of PFAS in aqueous (nonpotable water), solid (soil, biosolids, and sediment), and tissue samples. Principally, polymeric weak anion exchange (WAX) SPE is used for the selective extraction of target analytes and graphitized carbon is used to reduce matrix interferences. In the multilaboratory validation study, WAX SPE and graphitized carbon procedures required separate steps due to the manual addition of bulk carbon to the samples. Many production laboratories have opted to combine WAX and carbon sorbents into single SPE cartridges to streamline the sample preparation procedure and facilitate automation. This modification is acceptable as specified in Section 1.5 of Method 1633 if the quality control metrics of the method can be achieved.[2]

A key aspect of achieving success with automated SPE is the implementation of reliable SPE cartridges specifically designed for the method requirements and easily adaptable to automation. The Agilent PFAS WAX and Carbon S for PFAS sorbents are manufactured for PFAS applications and are lot tested to ensure low PFAS residue and maximum recovery.[3,4] Combining these sorbents in standard 6 mL SPE cartridges using low PFAS residue frits make them ideally suited for automated methods requiring both WAX extraction and carbon matrix reduction.

In this study, three types of dual-phase SPE cartridges were evaluated based on the quality control requirements for aqueous matrices as specified in US EPA Method 1633 using automated SPE. The cartridges contained PFAS WAX and Carbon S for PFAS. In the first configuration, a 200 mg bed of PFAS WAX was layered on top of a 50 mg bed of Carbon S with the sorbents separated by a frit. In the second configuration, 200 mg of PFAS WAX was mixed with 50 mg of Carbon S before cartridge packing. In the third configuration, 200 mg of PFAS WAX and 10 mg of Carbon S were mixed before cartridge packing. All three configurations were evaluated under identical protocols using automated SPE and were compared to results obtained using the manual addition of carbon and separate WAX extraction. The blended sorbent containing 200 mg of PFAS WAX and 10 mg of Carbon S was selected for validation and further evaluation of several environmental matrices including groundwater from residential private wells, effluent from a wastewater storage lagoon, and a landfill monitoring well.

Experimental

Chemicals and reagents

Native PFAS were purchased as individual standards and mixed solutions, while isotopically labeled standards were acquired as mixed solutions from Wellington Laboratories, Inc. (Guelph, ON, Canada). HPLC-grade methanol (MeOH) used for cleaning the automated SPE system, and LC/MS grade MeOH and LC/MS grade acetonitrile, used for mobile phase and reagent preparation, were purchased from Honeywell (Muskegon, MI, U.S.). ACS-grade ammonium hydroxide was purchased from Millipore Sigma (Burlington, MA, U.S.). Formic acid was purchased from Tokyo Chemical Industry, Co., Ltd. (Chuo-ku, Tokyo, Japan). Sigma-Aldrich acetic acid (≥ 99.99% trace metals basis) was purchased from Millipore Sigma (Burlington, MA, U.S.). Reagent water was prepared using ELGA Purelab Chorus 1 Water Purification System (High Wycombe, Buckinghamshire, U.K.). Bulk Superclean ENVI-Carb was purchased from Millipore Sigma (Burlington, MA, U.S.) and Carbon S was provided by Agilent Technologies (Santa Clara, CA, U.S.).

Solutions and standards

Calculations for the standard and spike concentrations were based on a sample volume of 250 mL and a final extract volume was 5 mL, yielding a concentration factor of 50-fold.

All solutions required for the standard preparation and sample extraction followed the protocols listed in the method. Native standard solutions contained 40 target analytes listed in the method: 11Cl-PF3OUdS, 3:3FTCA, 4:2FTS, 5:3FTCA, 6:2FTS, 7:3FTCA, 8:2FTS, 9Cl-PF3ONS, ADONA, HFPO-DA, NEtFOSA, NEtFOSAA, NEtFOSE, NFDHA, NMeFOSA, NMeFOSAA, NMeFOSE, PFBA, PFBS, PFDA, PFDoA, PFDoS, PFDS, PFEESA, PFHpA, PFHpS, PFHxA, PFHxS, PFMBA, PFMPA, PFNA, PFNS, PFOA, PFOS, PFOSA, PFPeA, PFPeS, PFTeDA, PFTrDA, and PFUnA. For validation experiments, an additional five targets, perfluorobutanesulfonamide (PFBSA), perfluoroethylcyclohexane sulfonate (PFECHS), perfluorohexanesulfonamide (PFHxSA), perfluoropropanoic acid (PFPrA), and perfluoropropanesulfonic acid (PFPrS) were added. A stock solution containing the PFAS targets was prepared at a concentration of 100 ng/mL. The stock solution

was diluted to prepare 10 calibration levels with nominal concentrations of 10, 20, 50, 100, 200, 500, 1,000, 2,000, 5,000, and 10,000 ng/L. For target analytes in the salt form, concentrations were corrected to the acid form.

Extracted internal standards (EIS) used for target quantitation included the 24 isotopically labeled compounds listed in the method with $^{13}C_9$-PFNA, $^{13}C_6$-PFDA, $^{13}C_7$-PFUnA, $^{13}C_2$-PFDoA, and $^{13}C_2$-PFTeDA at 500 ng/L; $^{13}C_3$-PFBS, $^{13}C_3$-PFHxS, $^{13}C_8$-PFOS, $^{13}C_5$-PFHxA, $^{13}C_4$-PFHpA, $^{13}C_8$-PFOA, $^{13}C_8$-PFOSA, D_3-NMeFOSA, and D_5-NEtFOSA at 1,000 ng/L nominal concentration; $^{13}C_2$-4:2FTS, $^{13}C_2$-6:2FTS, $^{13}C_2$-8:2FTS, $^{13}C_5$-PFPeA, D_3-NMeFOSAA, and D_5-NEtFOSAA at 2,000 ng/L nominal concentration; $^{13}C_3$-HFPO-DA and $^{13}C_4$-PFBA at 4,000 ng/L; and D_7-MeFOSE and D_9-EtFOSE at 10,000 ng/L. The EIS concentrations in sample solutions were 50-fold lower. For EIS in the salt form, concentrations were corrected to the acid form.

Seven non-extracted internal standards (NIS) used for EIS recovery and instrument QC were added to the sample concentrates and standards at three levels with $^{13}C_5$-PFNA and $^{13}C_2$-PFDA at 1,250 ng/L; $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{18}O_2$-PFHxS, and $^{13}C_4$-PFOS at 2,500 ng/L nominal concentration; and $^{13}C_3$-PFBA at 5,000 ng/L. For NIS in the salt form, concentrations were corrected to the acid form.

For initial demonstration of capability (IDC) and on-going precision and recovery (OPR) samples required by the method, the low-level and mid-level sample concentrations were 4 and 40 ng/L, respectively. With the 50-fold extraction concentration factor, the final concentrations in-vial for the low-level and mid-level extraction recovery spikes were 200 and 2,000 ng/L, respectively. Method detection limit (MDL) studies were carried out with spike concentrations of 0.4 ng/L with a final extract concentration of 20 ng/L in-vial. The limit of quantitation (LOQ) was established at 2 ng/L corresponding to a concentration of 100 ng/L in-vial.

Equipment and materials

The three Agilent dual-phase cartridges used in the study are listed in Table 1. As a performance benchmark, a single-phase Bond Elut PFAS WAX sorbent cartridge (Agilent, part number 5610-2151) was used with either Carbon S bulk (Agilent, part number 5610-2095) or Superclean ENVI-Carb (Millipore Sigma, part number 57210-U).

Table 1. Agilent dual-phase SPE cartridges.

Description	Agilent Part Number
Agilent Bond Elut layered PFAS WAX (top)/ Carbon S, 200/50 mg, 6 mL	5610-2237 (30 pk) or 5610-2238 (250 pk)
Agilent Bond Elut blended PFAS WAX/ Carbon S, 200/50 mg, 6 mL	5610-2245 (30 pk) or 5610-2246 (250 pk)
Agilent Bond Elut blended PFAS WAX/ Carbon S, 200/10 mg, 6 mL	5610-2243 (30 pk) or 5610-2244 (250 pk)

Samples were extracted using the PromoChrom eight-channel automated SPE extractors with upside-down shaker racks (part number SPE-03 with MOD004), anticlogging frits (part number CF-06), high-capacity inline filters (part number F-HC-30), and anticlogging tips (part number F-T-4).

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 (G7116B). 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 6495C triple quadrupole LC/MS equipped with an Agilent Jet Stream technology ion source. Agilent MassHunter Workstation software was used for data acquisition (version 10.1) and Quantitative Analysis for QQQ (version 12.1) was used for data analysis. Instrumental conditions were determined based on detailed multiparametric optimization experiments developed in-house. The columns used for analysis are listed in Table 2.

Table 2. Agilent HPLC columns and filters.

Description	Part Number
Agilent ZORBAX Eclipse RR C18, 4.6 × 50 mm, 3.5 µm (delay column)	959943-902
Agilent ZORBAX RRHD Eclipse Plus C18, 2.1 mm, 1.8 µm (guard column)	821725-901
Agilent ZORBAX RRHD Eclipse Plus C18, 3.0 × 50 mm, 1.8 µm (analytical column)	959757-302
Agilent InfinityLab Quick Change Inline Filter (placed before the mixer)	5067-1603
Agilent 1290 Infinity II and III Inline Filter (placed between the needle seat and injection valve)	5067-6189

Methods

LC/MS/MS method: The LC parameters for the LC/MS/MS analysis are listed in Table 3. MS source parameters are listed in Table 4, and MS acquisition parameters are listed in Table 5.

Table 3. LC parameters.

Parameter	Value
Column Temperature	30 ± 5 °C
Injection Volume	5 µL
Flow Rate	0.600 mL/min
Mobile Phases	A) 5 mM ammonium acetate in 95:5 water:acetonitile B) acetonitrile
Gradient	Time (min) %A %B 0.00 98.00 2.00 0.20 98.00 2.00 4.00 70.00 30.00 7.00 45.00 55.00 9.00 25.00 75.00 10.00 0.00 100.00 11.00 0.00 100.00 11.01 98.00 2.00 14.00 98.00 2.00
Post Time	1.00 min

Table 4. MS source parameters.

Parameter	Setting
Polarity	Negative
Gas Temperature	110 °C
Gas Flow	11 L/min
Nebulizer Pressure	20 psi
Sheath Gas Temperature	380 °C
Capillary Voltage	2,500 V
Nozzle Voltage	0
iFunnel High Pressure RF	90 V
iFunnel Low Pressure RF	75 V

Table 5. MS acquisition parameters.

Parameter	Setting
Cycle Time	350 ms
Total MRMs	77
Max Concurrent MRMs	18
Minimum Dwell Time	23.12 ms
Maximum Dwell Time	247.76 ms
Delta EMV	–200 V

Automated SPE method: The automated SPE procedure closely follows the protocols given in EPA Method 1633.[2] The solvents used for automated SPE are listed in Table 6 and the extraction method is listed in Table 7.

Table 6. SPE solvents.

Solvent Number	Component
Solvent 1	Isopropyl alcohol (IPA)
Solvent 2	ELGA H_2O
Solvent 3	0.3 M formic acid in water
Solvent 4	1:1 0.1 M formic acid:MeOH
Solvent 5	1% Methanolic ammonium hydroxide
Solvent 6	HPLC-grade MeOH

Table 7. SPE protocol.

Action	Inlet 1	Inlet 2 (Ratio)	Flow	Volume (mL)
Elute W2	Solvent 5	–	8	15
Elute W1	Solvent 3	–	8	5
Add Sample W1	Sample	–	5	295
Rinse	Solvent 2	Air (20%)	80	2.5
Add Sample W1	Sample	–	5	5
Rinse	Solvent 2	Air (20%)	80	5
Add Sample W1	Sample	–	5	5
Rinse	Solvent 2	Air (20%)	80	5
Add Sample W1	Sample	–	5	5
Shake	–	Time based	–	30 s
Rinse	Solvent 4	Air (20%)	80	1.3
Add Sample W1	Sample	–	5	3
Rinse	Solvent 4	Air (20%)	80	5
Add Sample W2	Sample	–	5	5
Shake	–	Time based	–	30 s
Air-Purge W2	Air	–	5	3
Add Samp W2	Sample	–	5	5
Blow N2	–	Time based	–	15 s
Rinse	Solvent 5	Air (20%)	80	1.5
Collect 1	Sample	–	1	3
Rinse	Solvent 5	Air (20%)	80	5
Collect 1	Sample	–	1	5
Shake	–	Time based	–	15 s
Collect 1	Sample	–	1	5

* W1 and W2 are the aqueous and organic waste streams, respectively.

Quantitation: Quantitation by LC/MS/MS followed procedures described in EPA Method 1633 based on isotope dilution or extracted internal standard using isotopically labeled compounds added to the samples before extraction. Briefly, relative response calibration curves for the target analytes referenced to the appropriate EIS were generated using linear weighted (1/x) least squares regression across the 10 calibration levels (not including the origin). Goodness of fit was determined by the percent relative standard error (% RSE) of the response curves with a limit of ≤ 20%. A minimum signal-to-noise ratio (S/N) ≥ 3 was required for targets with qualifier ions and S/N ≥ 10 was required for targets without qualifier ions. Calibration was verified using low and mid-level standards with accuracy limits and qualifier ion ratios within ± 30%. Single-point relative response factors were used for EIS quantitation relative to the NIS with an RSE limit of ≤ 20%. EIS recoveries on samples post-calibration must be within accuracy limits as listed in Table 6 of EPA Method 1633. Limits of NIS recoveries must be 50 to 200% based on the average responses of the NIS in the calibration set.

Results and discussion

Protocol and SPE configuration comparison

As an initial evaluation, the recoveries for a mid-level (40 ng/L) spike in 250 mL of reagent water were compared for seven replicates using five different extraction protocols listed in Table 8. The targets included the 40 PFAS in Method 1633 with the addition of PFECHS. Protocol 1 was a control, as it followed the EPA method using 10 mg of loose ENVI-Carb. For protocol 2, the ENVI-Carb was replaced by loose Carbon S. Protocols 3, 4, and 5 used the dual-phase blended and layered cartridges in a single step extraction.

Table 8. Extraction protocols.

Protocol	Description
1	2-step extraction, single-phase 200 mg Bond Elut PFAS WAX and 10 mg loose ENVI-Carb
2	2-step extraction, single-phase 200 mg Bond Elut PFAS WAX and 10 mg loose Carbon S
3	1-step extraction, dual-phase blended 200 mg Bond Elut PFAS WAX and 10 mg Carbon S
4	1-step extraction, dual-phase blended 200 mg Bond Elut PFAS WAX and 50 mg Carbon S
5	1-step extraction, dual-phase layered 200 mg Bond Elut PFAS WAX (top) and 50 mg Carbon S (bottom)

Figure 1 shows a comparison of average target recoveries for seven replicates for the five protocols tested. For reference, the hashed lines in Figure 1 are the upper and lower acceptance limits as required for demonstration of initial precision and recovery (IPR) listed in Table 5 in Method 1633. Figure 2 shows the percent relative standard deviation (RSD) for each target with the hashed line representing the precision limits required for IPR (Table 5). Each protocol provided results within the method requirements for target recovery and precision.

The distribution of data for each protocol was further investigated. Figure 3 shows box plots for each protocol consisting of 287 data points (41 targets with seven replicates) per dataset. All protocols tested provided very similar performance. Protocols 3 and 4 had the overall highest mean and median recovery values with similar inner quartile ranges (IQR). For protocol 3, the mean and median values were 106.5 and 108.0%, respectively, with an IQR of 11.6%. For protocol 4, the mean and median values were 107.2 and 108.3%, respectively, with an IQR of 11.0%. However, protocol 3 compared to Protocol 4 had fewer outliers (8 versus 12). For this reason, in addition to the fact that 10 mg carbon is stated in the method, the Bond Elut blended 200 mg PFAS WAX/10 mg Carbon S cartridges were selected for full EPA Method 1633 validation.

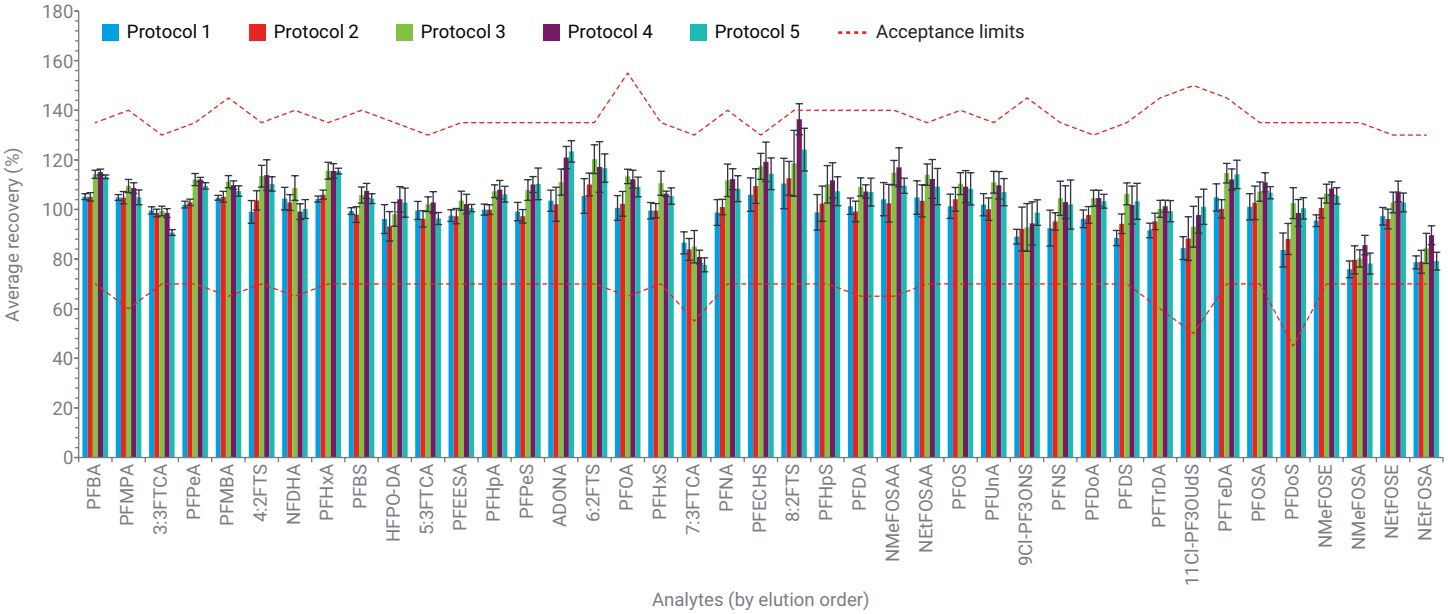

Figure 1. Average PFAS target recoveries with upper and lower IPR acceptance limits. Error bars indicate the 95% confidence intervals for seven measurements per analyte (refer to Table 8 for protocol details).

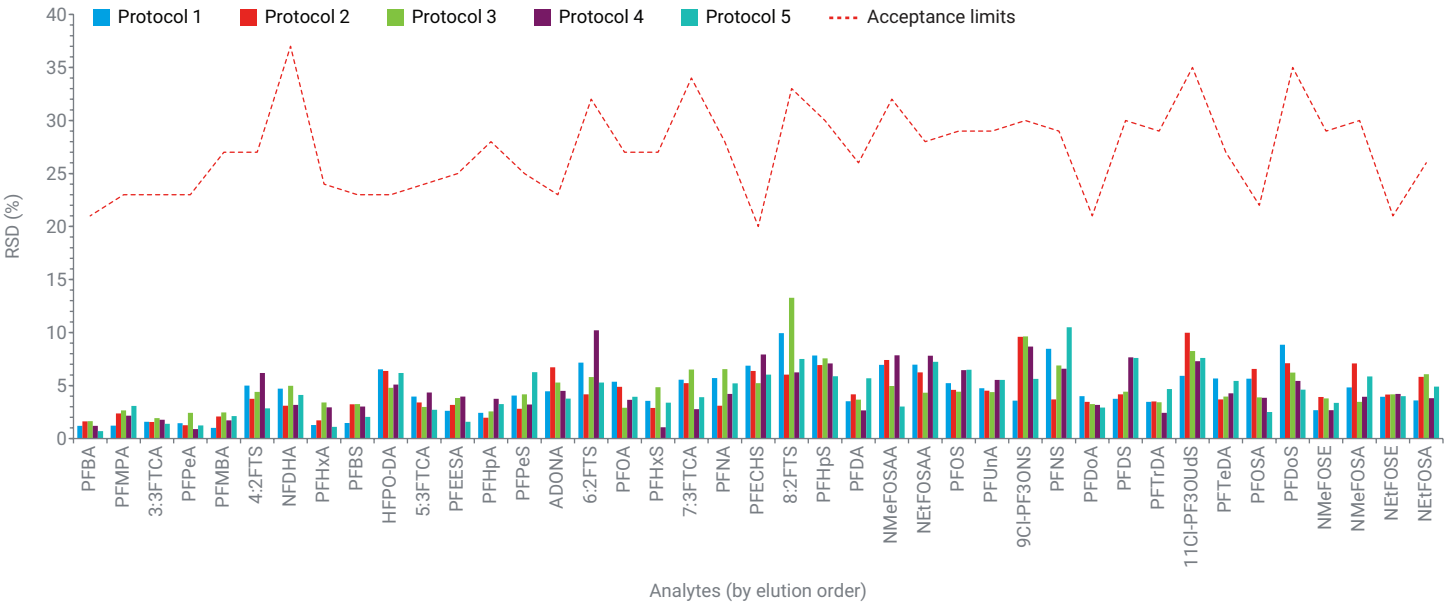

Figure 2. PFAS target recovery precision with IPR acceptance limits (refer to Table 8 for protocol details).

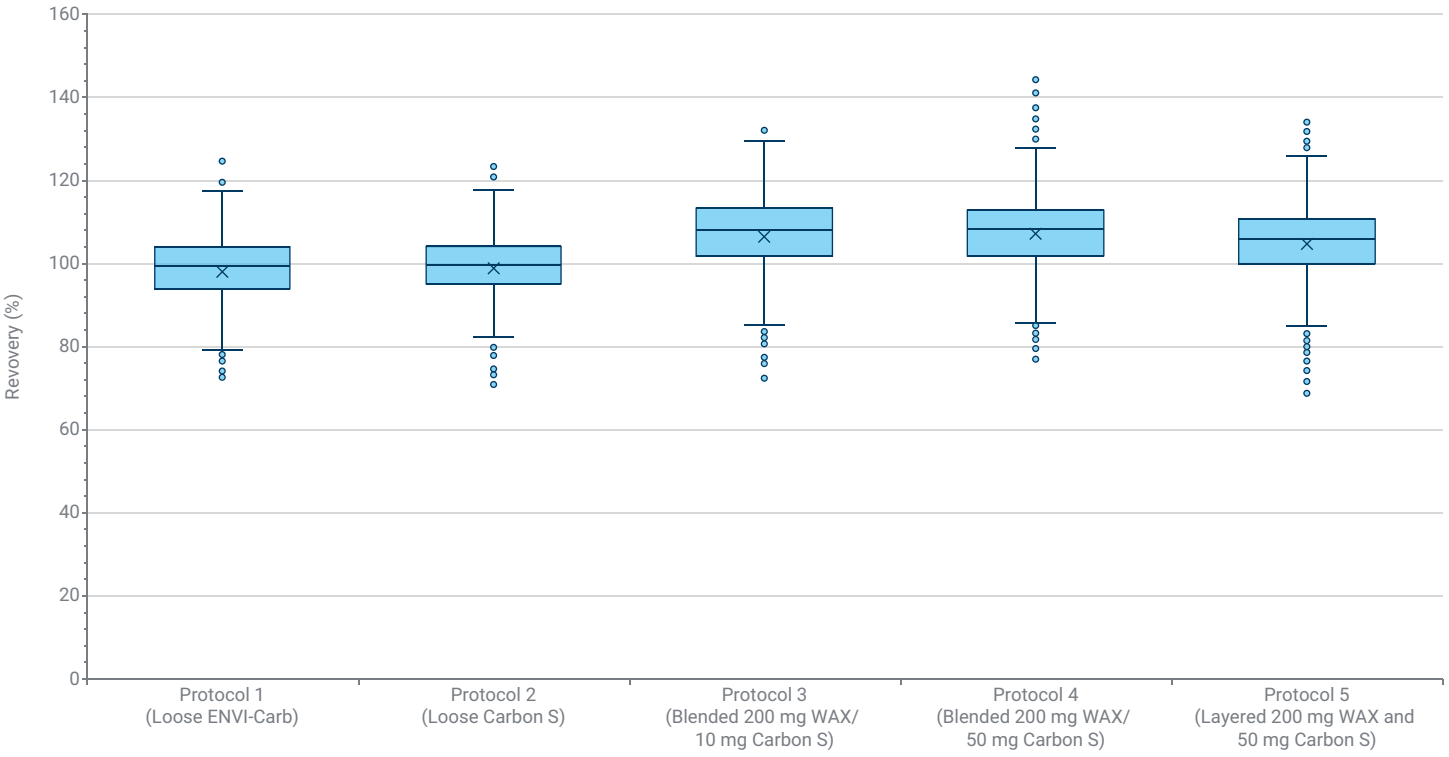

Figure 3. Box plots for protocols 1 to 5.

Initial demonstration of capability

Initial precision and recovery (IPR): For full method validation, the IPR was carried out with the Bond Elut blended 200 mg PFAS WAX/10 mg Carbon S cartridges following requirements as listed in Section 9.2 of EPA Method 1633. Recovery precision and accuracy were determined for four replicate spikes of 250 mL of reagent water with 45 PFAS targets at mid-level concentration (40 ng/L). Figure 4 shows the precision and accuracy of the reagent water spikes along with the acceptance limits listed in Table 5 of Method 1633 for 40 of method targets in aqueous matrices. For the five additional targets not included in Method 1633, recovery limits were set to 60 to 140% and an RSD limit of 20%. All recovery limits are within the acceptable ranges.

Extracted internal standards (EIS) and non-extracted internal standard (NIS) recoveries: The EIS and NIS recovery accuracies were calculated from the same four mid-level IPR extractions and are shown in Figure 5 along with the acceptance limits as listed in Table 6 of the EPA Method 1633. There are no mean recovery or precision limits for the EIS and NIS. The recovery of each EIS and NIS for each sample must be within the acceptance limits. The recovery for all EIS and NIS were within required limits.

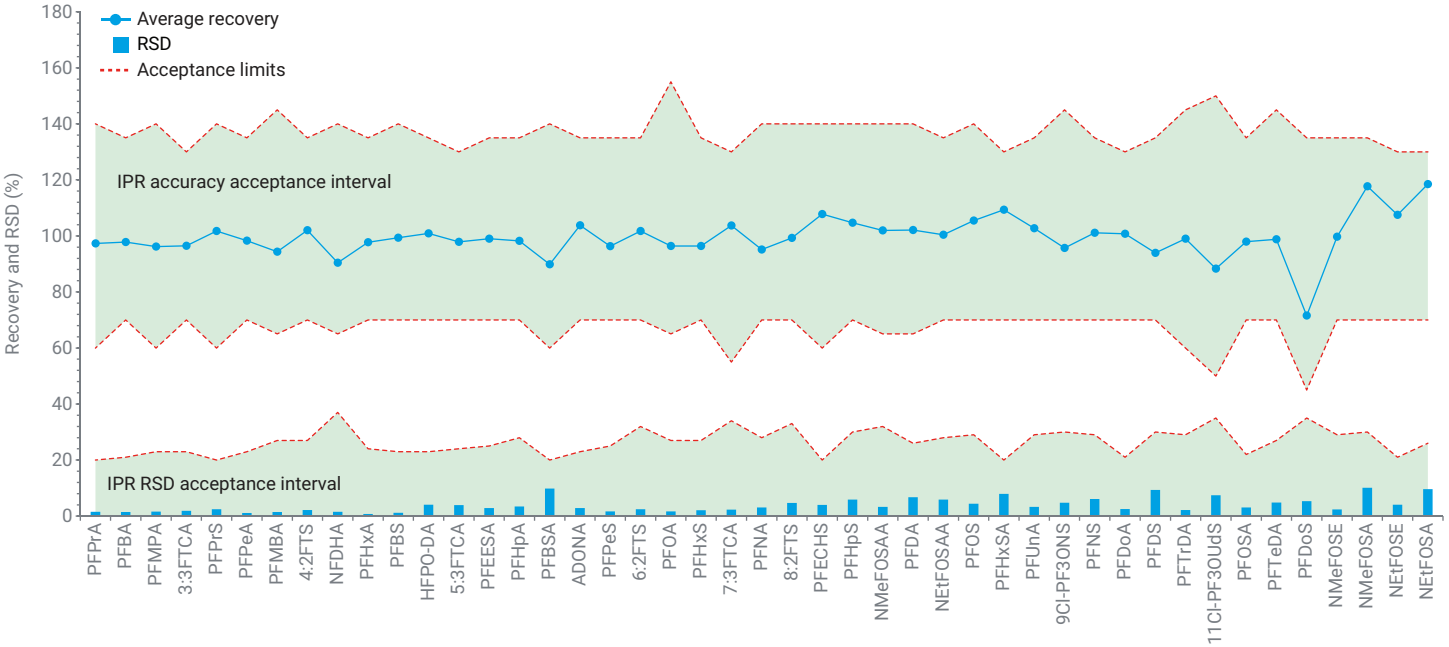

Figure 4. IPR results for average recovery and RSD with accuracy limits and precision acceptance limits shaded in green.

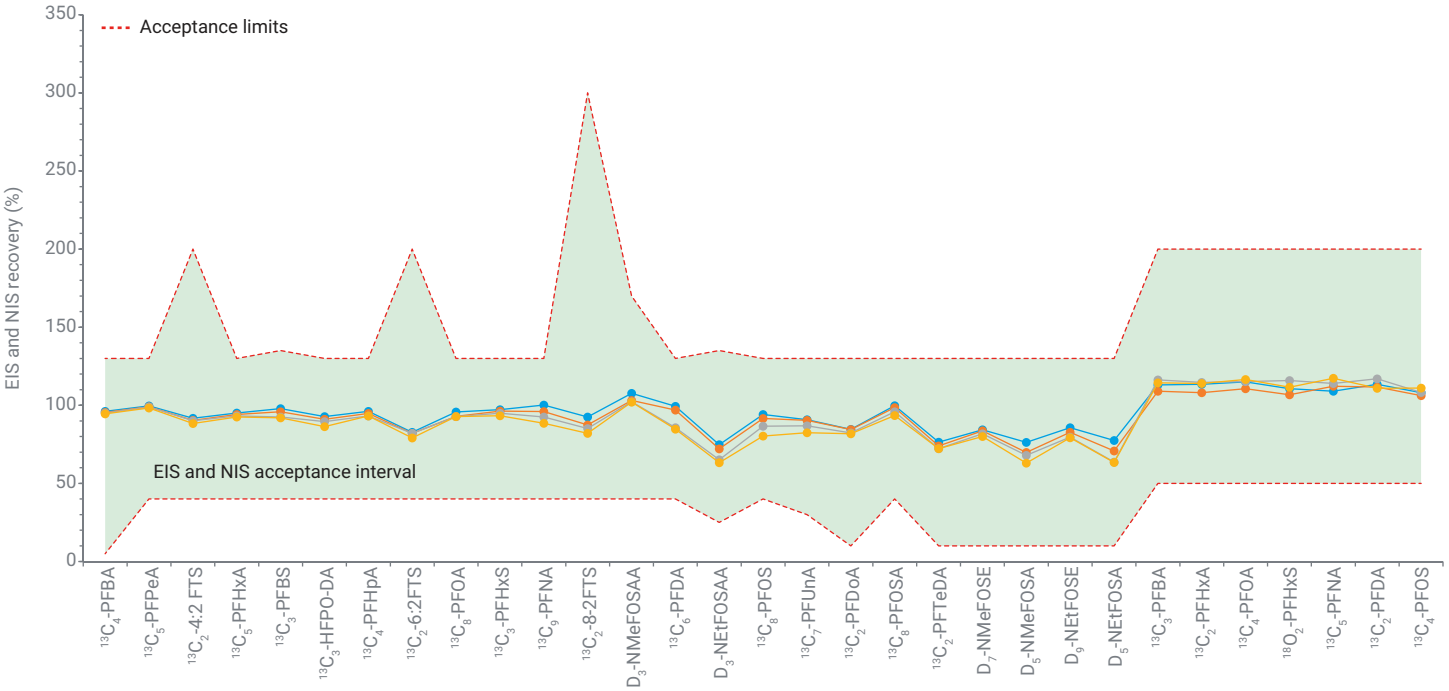

Figure 5. Overlay of EIS and NIS recoveries for four replicate IPR extractions. Hashed red lines represent the upper and lower acceptance limit for the EIS and NIS.

Method detection limits (MDLs): As required by EPA Method 1633, laboratories must establish method detection limits (MDLs) following the procedure in 40 CFR Part 136, Appendix B[6] based on seven low-level spikes and blank measurements carried out multiple days. MDLs were calculated from the standard deviation of the spike or blank measurements multiplied by 3.143, which is the Student's t critical value for seven measurements at the 99% confidence level. Table 9 lists the calculated MDLs for the 45 target PFAS. For 42 targets, the MDLs were calculated based replicate spike recoveries. For three targets, PFBA, PFHxS, and PFPrA, MDLs were calculated based on replicate blank measurements. For comparison, Table 9 lists the pooled MDLs based on the Method 1633 multi-laboratory validation study for aqueous matrices.

Method blank: The IDC mandates the analysis and reporting of at least one method blank per sample batch. The requirements for method blanks are complex and depend on the specific analysis. If any PFAS targets are detected above the LOQ, at a concentration of one-third the regulatory limit, or greater than one-tenth the concentration of a sample in a sample batch, whichever is higher, corrective action must be taken. These metrics can be impractical to implement, so a stricter standard of < 1/2 LOQ was adopted, in line with the Department of Defense and Department of Energy's Quality Systems Manual.[5] Figure 6 shows the results of the method blank analysis with the blank limit set to < 1/2 LOQ or 1 ng/L. All PFAS targets pass these criteria.

Table 9. Method detection limits (MDLs).

Analyte	Bond Elut Mixed Bed SPE (ng/L)	EPA 1633 Aq. MDL (ng/L)	Analyte	Bond Elut Mixed Bed SPE (ng/L)	EPA 1633 Aq. MDL (ng/L)	Analyte	Bond Elut Mixed Bed SPE (ng/L)	EPA 1633 Aq. MDL (ng/L)	Analyte	Bond Elut Mixed Bed SPE (ng/L)	EPA 1633 Aq. MDL (ng/L)
PFBA	0.10	0.79	PFHpA	0.09	0.37	NEtFOSAA	0.22	0.59	NMeFOSE	0.21	3.81
PFMPA	0.05	1.46	ADONA	0.10	0.50	PFOS	0.19	0.63	NMeFOSA	0.28	0.43
3:3FTCA	0.19	2.47	PFPeS	0.20	0.50	PFUnA	0.06	0.45	NEtFOSE	0.26	4.84
PFPeA	0.08	0.54	6:2FTS	0.11	2.45	9Cl-PF3ONS	0.14	1.38	NEtFOSA	0.31	0.45
PFMBA	0.06	1.41	PFOA	0.19	0.54	PFNS	0.10	0.47	PFPrA	0.09	--
4:2FTS	0.10	1.69	PFHxS	0.22	0.54	PFDoA	0.06	0.4	PFPrS	0.06	--
NFDHA	0.15	0.75	7:3FTCA	0.26	8.71	PFDS	0.12	0.6	PFBSA	0.13	--
PFHxA	0.07	0.46	PFNA	0.12	0.45	PFTrDA	0.14	0.46	PFECHS	0.09	--
PFBS	0.07	0.37	8:2FTS	0.38	2.50	11Cl-PF3OUdS	0.12	1.67	PFHxSA	0.10	--
HFPO-DA	0.22	0.51	PFHpS	0.16	0.50	PFOSA	0.11	0.32			
5:3FTCA	0.16	9.59	NMeFOSAA	0.16	0.68	PFTeDA	0.14	0.49			
PFEESA	0.04	1.17	PFDA	0.12	0.52	PFDoS	0.22	0.6			

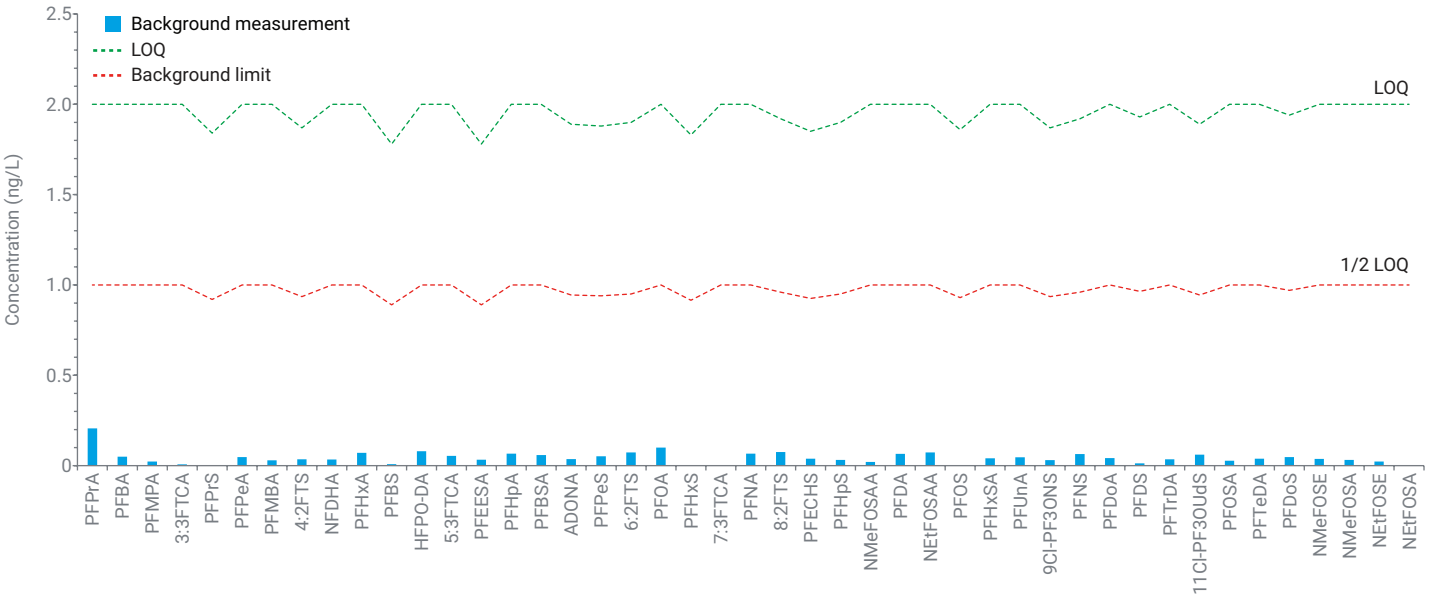

Figure 6. Method blank analysis with background measurement, LOQ, and background limit.

Sample analysis

To demonstrate method performance, PFAS analysis was carried out on different aqueous matrix samples. The first two were groundwater samples from residential private wells in different geographic locations, the third was an effluent sample from a wastewater storage lagoon, and the fourth sample was from a landfill monitoring well. Positive results are listed in Table 10. All other analytes not listed in the table were below the LOQ (note that PFPrA was not reported due to low matrix spike recoveries).

Table 10. Concentration of PFAS analytes in matrix samples.

Compound	Groundwater Sample 1 (ng/L)	Groundwater Sample 2 (ng/L)	Landfill Monitoring Well (ng/L)	Wastewater Storage Lagoon (ng/L)
PFBA	3.88	2.41	35.66	4.13
3:3FTCA	< LOQ	< LOQ	< LOQ	< LOQ
PFPeA	< LOQ	< LOQ	8.28	4.01
PFHxA	2.09	< LOQ	8.55	7.20
PFBS	4.95	< LOQ	3.41	2.42
PFOA	2.78	< LOQ	2.67	3.07
PFHxS	3.17	2.45	< LOQ	< LOQ
PFDA	< LOQ	< LOQ	< LOQ	< LOQ
PFOS	< LOQ	< LOQ	< LOQ	2.61
PFUnA	< LOQ	< LOQ	< LOQ	< LOQ

Two residential samples were spiked at mid-level concentration (40 ng/L) to prepare matrix spike (MS) and matrix spike duplicate samples (MSD) as required by DOD/DOE QSM.[5] The MS/MSD samples provide additional verification of method performance in matrix. Figure 7 shows the results of the MS and MSD samples. Acceptance intervals for recovery accuracy and relative percent deviation (RPD) of the two samples are included in Figure 7. All target recoveries were within the accuracy and precision limits (note that PFPrA was not reported due to low matrix spike recoveries).

As required by EPA Method 1633, the EIS and NIS recoveries need to be verified for all samples analyzed. Figure 8 shows the EIS and NIS recoveries for the matrix samples analyzed, including field blanks (FB) and trip blanks (TB). The hashed lines represent the EIS and NIS acceptance limits for aqueous matrices. For all EIS and NIS, recoveries are within the acceptance limits.

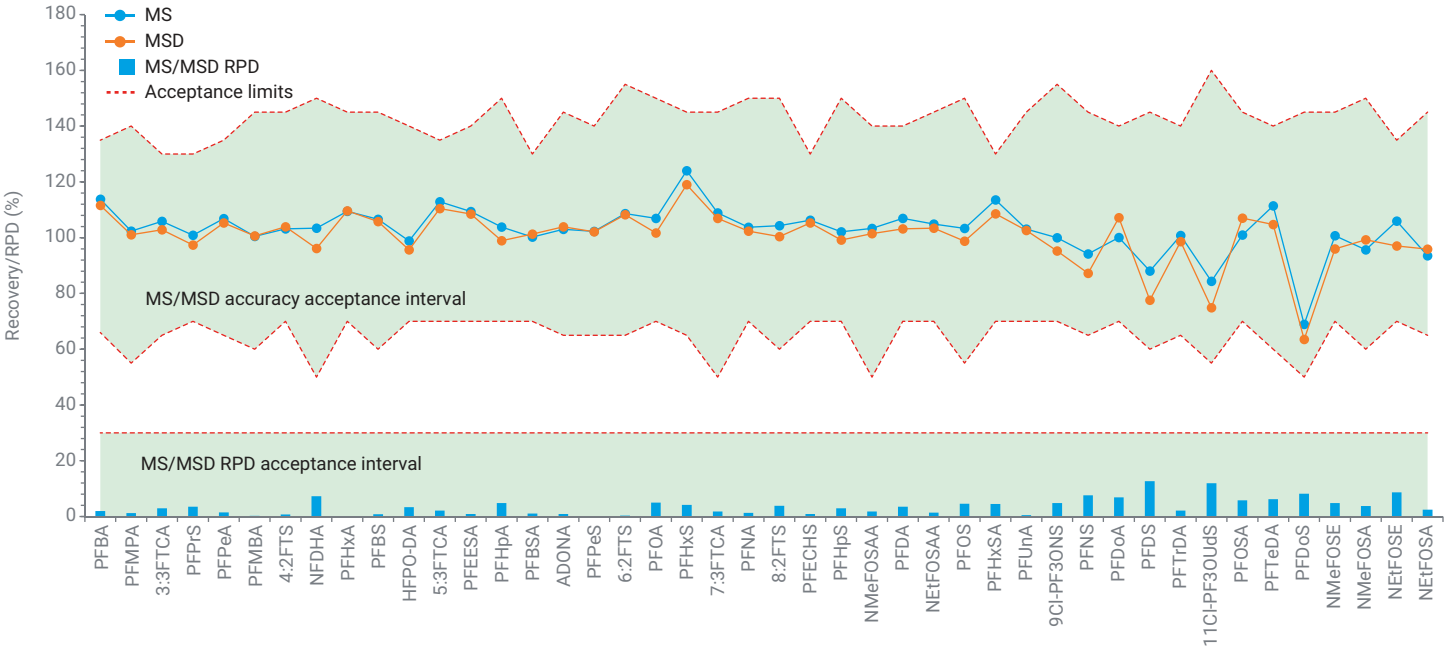

Figure 7. MS and MSD prepared from two residential groundwater samples.

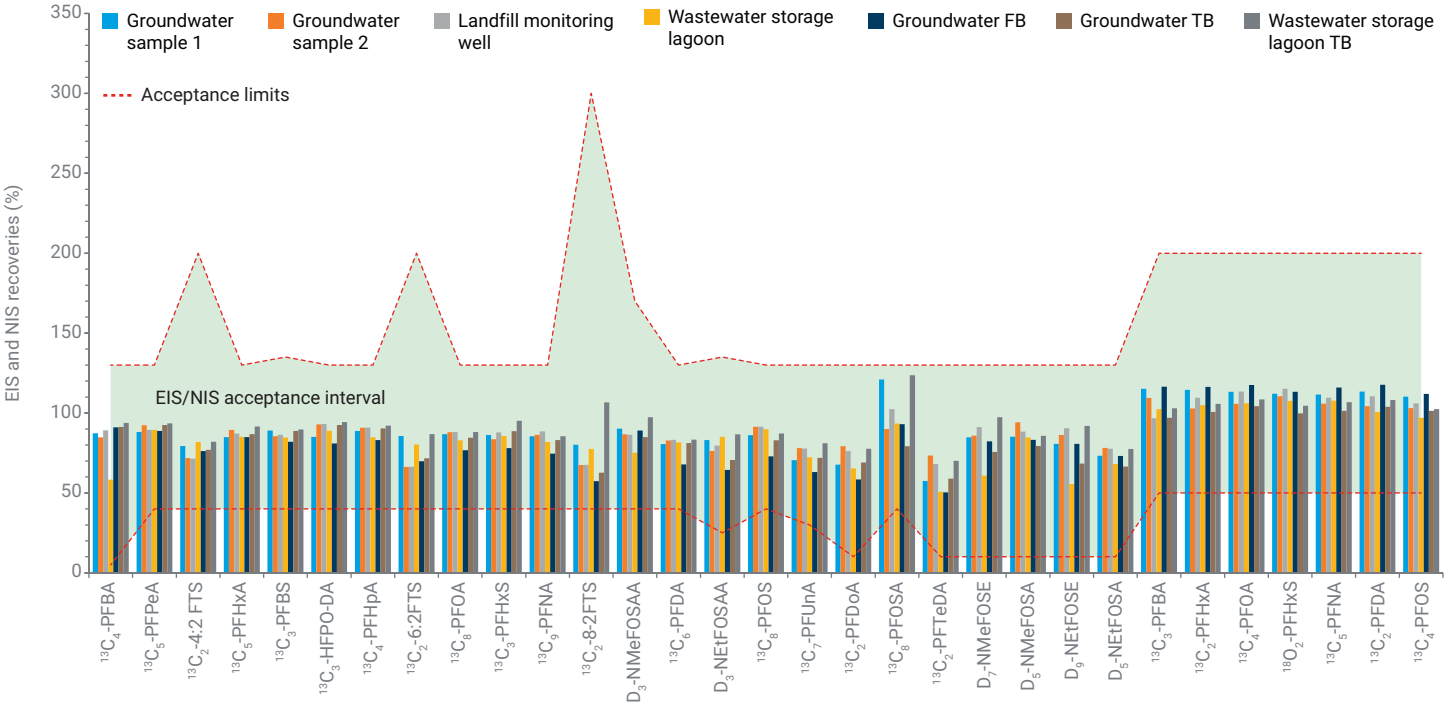

Figure 8. EIS and NIS recoveries.

Conclusion

The adoption of automated solid phase extraction (SPE) for PFAS analysis in environmental matrices significantly enhances laboratory efficiency and reduces the potential for human error. Our evaluation of five extraction protocols revealed that the blended sorbent containing 200 mg of PFAS WAX and 10 mg of Carbon S provided the best performance in terms of recovery, matrix interference reduction, and fewer outliers. This configuration was successfully applied to various environmental samples, demonstrating its versatility and reliability. The findings support the use of automated SPE with optimized sorbent cartridges as a robust method for PFAS analysis, aligning with the quality control metrics of US EPA Method 1633. Future work should focus on further refining automated SPE techniques and exploring their application to other environmental matrices.

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