Application Note

Environmental

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Analysis of Per- and Polyfluoroalkyl Substances in Soil Extracts

A workflow approach to sample preparation method development

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Abstract

Key challenges in the analysis of per and poly-fluoroalkyl substances (PFAS) are the potential of adsorption of target compounds or the introduction of interferences during sample handling. These problems may occur at any point in the sample workflow from the initial collection of field samples to sample preparation and analysis. As a result, it is common practice to avoid certain materials during sample handling and analysis. For example, the ISO and EPA methods recommend the avoidance of untreated glass and perfluorotetraethylene (PTFE) containing materials during sample preparation and instead recommend the use of polypropylene or polyethylene. Other materials may be used if they can be demonstrated to be free of interferences or adsorptions. Only recently have the performances of different materials been systematically studied and published in the scientific literature. However, there is little information published on these issues viewed within the context of a laboratory workflow. In this application note, the impact of adsorption and interference are studied in the context of a typical sample preparation workflow for the analysis of PFAS in soil during extraction, filtration, and analysis for 25 analytes representative of different classes of PFAS compounds including sulfonic acids, carboxylic acids, sulfonamides. Recommendations for best practices are discussed in detail.

Introduction

Challenges of PFAS analysis

The analysis of PFAS in environmental extracts presents many challenges. The widespread use of PTFE in laboratory equipment and supplies can lead to contamination of sample extracts.[1] In addition, it has been demonstrated that some PFAS compounds adsorb onto common materials such as glass and certain polymers, which could result in recovery losses.[2] Analysts must also be aware that film formation between the air and water interface can occur due to the surfactant nature of some PFAS compounds leading sampling bias.[3] These challenges are compounded by the low-level reporting limits in the mid to low part-per-trillion range required by regulatory agencies.

To mitigate the potential of PFAS contamination and losses, it is common practice to avoid certain materials during sample handling and analysis. For example, EPA method 8327[4,5] recommends the avoidance of untreated glass and PTFE containing materials during sample preparation and recommends the use of polypropylene or polyethylene. Other materials may be used if they are demonstrated to be free of interferences and adsorption. The performance of different materials has only recently been systematically studied and published in the scientific literature.[6] However, there is little information published on these issues viewed within the context of a laboratory workflow.

Direct analysis methods

There are several analytical methods, which rely on direct analysis of sample extracts without the use of solid-phase extraction. These include EPA method 8327[4] and ASTM methods D7968-17a[7] and D7979-19.[8] These methods follow similar sample workflow procedures involving the addition of an extraction solvent to the sample, basification, agitation, centrifugation, filtration, acidification, and analysis. Quantitation is typically performed using external calibration by LC/MS/MS.

As illustrated in Figure 1, consumables are critical in the sample workflow for these direct methods. Centrifuge tubes are used for the sample extraction and collection of the filtered supernatant. Syringes and syringe filters are used after centrifugation to remove fine suspended particulates. Volumetric containers and autosampler vials are used for standard preparation and storage. In addition, there are consumables associated with the liquid chromatograph and mass spectrometer. Each consumable must be evaluated in each step of the process to ensure that there are no losses or introduction of contaminants or interferences. In this application note, the optimization for each step in the workflow from sample storage, extraction, filtration, LC separation, and MS/MS detection are discussed in detail.

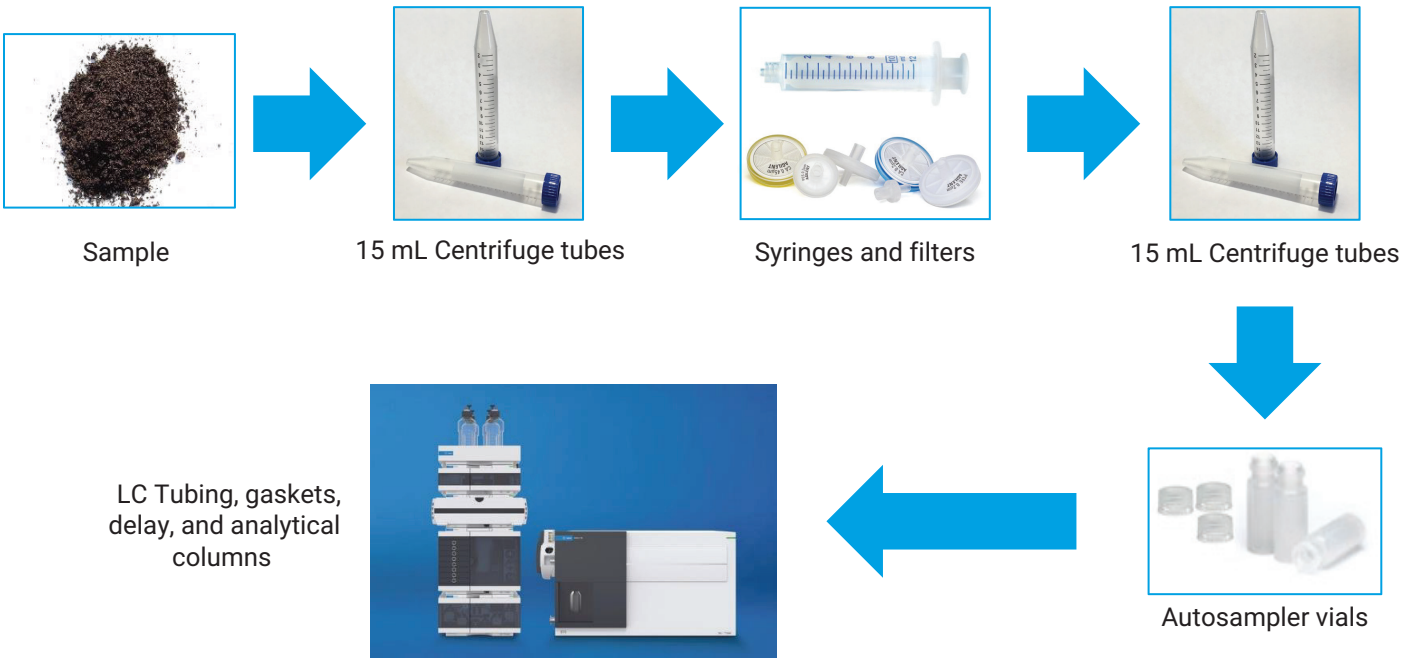

Figure 1. Consumables used in the PFAS direct analysis workflow.

Experimental

Extraction and analysis procedures closely followed those given in the ASTM and EPA methods.[4,5,7,8]

Spiking solution preparation

PFAS analytes and isotopically labeled surrogates were purchased as mixtures at a concentration of 2 µg/mL and individual components at a concentration of 50 µg/mL from Wellington Labs (Table 1). A surrogate spiking solution was prepared with the isotopically labeled surrogates in 95/5 acetonitrile/water at a concentration of 20 µg/L. An intermediate PFAS spiking solution was prepared with the target compounds in 95/5 acetonitrile/water at a concentration of 20 µg/L. The intermediate PFAS spiking solution was further diluted to prepare a lower limit of quantitation (LLOQ) spiking solution of 2 µg/L in 95/5 acetonitrile/water. The 20 µg/L surrogate and PFAS spiking solutions were prepared and stored in 50 mL polypropylene volumetric flasks. The 2 µg/L intermediate spiking solution was prepared in a 1 mL polypropylene autosampler vial (Table 2) and used immediately after preparation.

Calibration standard preparation

The highest-level calibration standard (200 ng/L) was prepared by adding 500 µL of each of the surrogate and PFAS spiking solutions to a 50 mL polypropylene volumetric flask (Table 2) and diluting with 1:1 methanol:water. The 200 ng/L calibration solution was further diluted in 1:1 methanol:water to prepare the other calibration solutions at 150, 100, 80, 60, 40, 20, 10, and 5 ng/L. The 200 ng/L calibration standard was stored in the 50 mL polypropylene volumetric flask at 6 °C. Calibration standards were used immediately after preparation.

Table 2. Sample preparation consumables.

Description	Agilent Part Number
Polypropylene autosampler vials and snap caps	5182-0567 and 5182-0542
50 mL Polypropylene volumetric flask	9301-1424
Captiva disposable syringes (10 mL)	9301-6474
Captiva premium syringe filters, regenerated cellulose, 25 mm diameter, 0.2 µm pore size	5190-5110
Centrifuge tubes and caps (15 mL)	5610-2039

Table 1. Compound list.

Targets	Surrogates
Perfluorobutyl sulfonic acid (PFBS)	Perfluoro-1-[1,2,3-^{13}C3] hexyl sulfonic acid (M3PFHxS)
Perfluorohexyl sulfonic acid (PFHxS)	Perfluoro-1-[^{13}C8] octyl sulfonic acid (M8PFOS)
Perfluorooctyl sulfonic acid (PFOS)	Perfluoro-*n*-[^{13}C4] butanoic acid (M4PFBA)
1H, 1H, 2H, 2H-Perfluorohexane sulfonic acid (4:2 FTS)	Perfluoro-*n*-[^{13}C5] pentanoic acid (M5PFPeA)
1H, 1H, 2H, 2H-Perfluorodecane sulfonic acid (8:2 FTS)	Perfluoro-*n*-[1,2,3,4,6-^{13}C5] hexanoic acid (M5PFHxA)
Perfluoro-1-pentanesulfonic acid (PFPeS)	Perfluoro-*n*-[1,2,3,4-^{13}C4] heptanoic acid (M4PFHpA)
Perfluoro-1-heptanesulfonic acid (PFHpS)	Perfluoro-*n*-[^{13}C8] octanoic acid (M8PFOA)
Perfluoro-1-nonanesulfonic acid (PFNS)	Perfluoro-*n*-[^{13}C9] nonanoic acid (M9PFNA)
Perfluoro-1-decanesulfonic acid (PFDS)	Perfluoro-*n*-[1,2,3,4,5,6-^{13}C6] decanoic acid (M6PFDA)
Perfluorobutanoic acid (PFBA)	Perfluoro-*n*-[1,2,3,4,5,6,7-^{13}C7] undecanoic acid (M7PFUnA)
Perfluoropentanoic acid (PFPeA)	Perfluoro-*n*-[1,2-^{13}C2] dodecanoic acid (MPFDoA)
Perfluorohexanoic acid (PFHxA)	Perfluoro-*n*-[1,2-^{13}C2] tetradecanoic acid (M2PFTeDA)
Perfluoroheptanoic acid (PFHpA)	1H, 1H, 2H, 2H-Perfluoro-(1,2-^{13}C2) hexyl sulfonic acid (M2-4:2 FTS)
Perfluorooctanoic acid (PFOA)	1H, 1H, 2H, 2H-Perfluoro-1(1,2-^{13}C2) decyl sulfonic acid (M2-8:2 FTS)
Perfluorononanoic acid (PFNA)	N-Methyl-d3-perfluoro-1-octanesulfonamidoacetic acid (d3-N-MeFOSAA)
Perfluorodecanoic acid (PFDA)	N-Ethyl-d5-perfluoro-1-octanesulfonamidoacetic acid (d5-N-EtFOSAA)
Perfluoroundecanoic acid (PFUdA)	Perfluoro-1-[^{13}C8] octanesulfonamide (M8FOSA)
Perfluorododecanoic acid (PFDoA)	
Perfluorotridecanoic acid (PFTrDA)	
Perfluorotetradecanoic acid (PFTeDA)	
N-Ethylperfluoro-1-octanesulfonamidoacetic acid (NEtFOSAA)	
N-Methylperfluoro-1-octanesulfonamidoacetic acid (NMeFOSAA)	
Perfluoro-1-octanesulfonamide (FOSA)	

Blanks

Double blanks were prepared to measure any potential contaminants or interferences for each component in the sample preparation workflow. For the 15 mL centrifuge tubes and disposable syringes (Table 2), 10 mL of a 1:1 methanol:water mixture was added to each tube and the pH adjusted to between 8.5 and 9.0 with an ammonium hydroxide solution. The tubes and syringes were capped and tumbled on a rotator for 1 hour. After tumbling, the solution was acidified with acetic acid to a pH between 3.5 and 4.0. Aliquots of these samples were analyzed by LC/MS/MS. For qualifying syringe filters (Table 2), syringes were filled with 10 mL of 1:1 methanol:water and the pH was adjusted to between 8.5 and 9.0. The entire 10 mL volume was pushed through the syringe filter and collected in another 15 mL centrifuge tube. The pH of the filtrate was adjusted to between 3.5 and 4.0 and an aliquot was analyzed by LC/MS/MS.

Reagent sand was analyzed as a method blank to determine the presence of any contaminants or interferences. In a 15 mL centrifuge tube, 2 g of clean sandy loam (CLNSOIL3, Supelco) was weighed to the nearest 10th of a gram and spiked with the 40 µL of the surrogate spiking solution to yield a concentration of 400 ng/kg. 10 mL of a 1:1 methanol:water solution was added to the centrifuge tube. Then the pH was adjusted to between 8.5 and 9.0 with ammonium hydroxide and the tube was tumbled on a rotator for 1 hour. After tumbling, the tubes were centrifuged at 1,900 rpm for 10 minutes. The supernatant solution was decanted into a syringe with a syringe filter and filtered into a clean 15 mL centrifuge tube. The solution was acidified with acetic acid to a pH between 3.5 and 4.0 and aliquots of these samples were analyzed by LC/MS/MS.

Low-level spikes

Low-level spikes were prepared to measure any losses that may occur for each component in the sample preparation workflow and to verify the lower level of quantitation (LLOQ). For qualifying the 15 mL centrifuge tubes, syringes, and syringe filters, the same procedure was used as described in the preparation of the double blanks with the addition of spiking the 10 mL extraction solution to produce the fortified concentration of PFAS targets and surrogates of 5 and 80 ng/L, respectively.

Reagent sand was spiked PFAS targets and surrogates to verify the LLOQ. The same extraction procedure was used as described in the preparation of the double blanks with the addition of spiking the 2 g of clean sand to produce fortified concentration of PFAS targets and surrogates of 25 ng/kg and 400 ng/kg, respectively.

Instrumental method

The optimized LC conditions are listed in Table 3 and optimized MS conditions are listed in Table 4. The fragmentor and collision energy voltages were determined using Agilent optimizer software and are listed in Table A1 in Appendix A along with the selected precursor ions, product ions, and retention times. Figure 2 shows a typical chromatogram produced at the method conditions.

Table 3. LC conditions.

Parameter	Value
LC	Agilent 1290 Infinity II LC
Analytical Column	Agilent ZORBAX RRHD Eclipse Plus C18, 2.1 × 100 mm, 1.8 µm (p/n 959758-902)
Delay Column	Agilent InfinityLab PFC Delay Column (p/n 5062-8100)
Column Temperature	30 °C
Injection Volume	30 µL
Mobile Phase	A) 20 mM ammonium acetate in 95% water and 5% acetonitrile B) 10 mM ammonium acetate in 95% acetonitrile and 5% water
Gradient	Time (min) %A %B Flow (mL/min) 0 100 0 0.3 1 70 30 0.3 6 50 50 0.3 13 15 85 0.3 14 0 100 0.4 17 0 100 0.4 18 100 0 0.4 21 100 0 0.4

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
Acquisition	
Cycle Time	500 ms
Total MRMs	61
Max Concurrent MRM	30
Min/Max Dwell	14.18 ms/247.76 ms

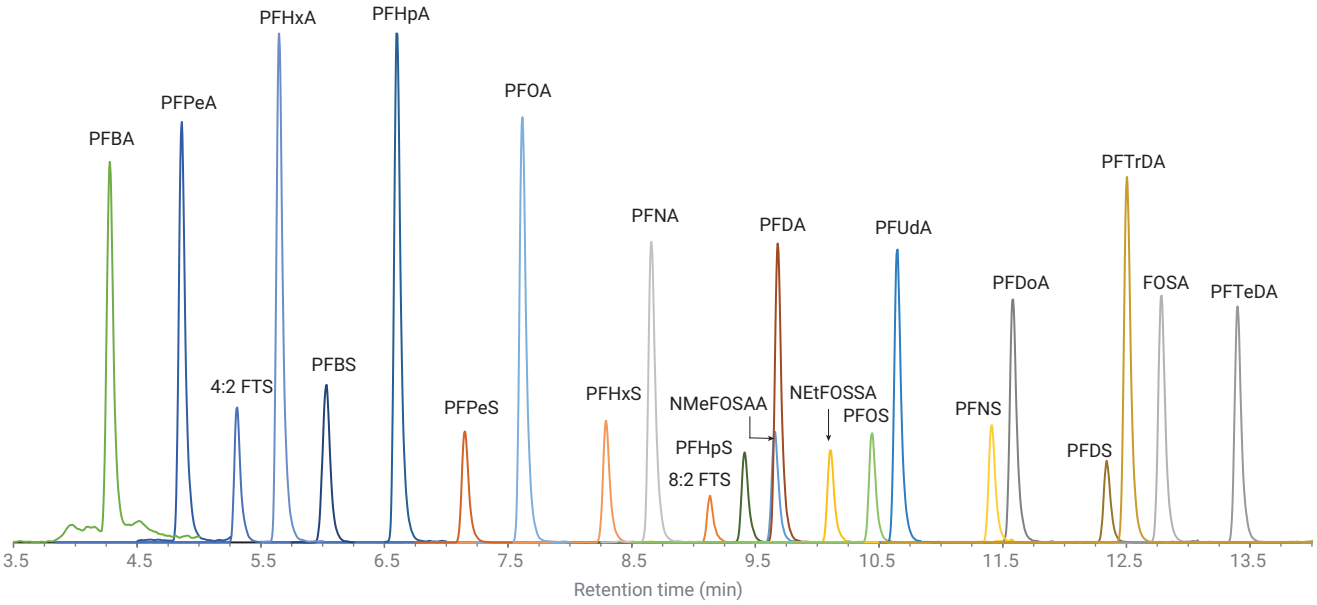

Figure 2. Chromatogram of PFAS targets in the 100 ng/L calibration standard.

Instrument calibration

A linear least-squares regression weighted by the inverse concentration (i.e. 1/x) was applied to all targets and surrogates using external calibration. According to the methods, 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. Tables A2 and A3 in Appendix A list the accuracy for each PFAS target and surrogate at each calibration level in addition to the coefficient of determination. All compounds passed the calibration criteria.

Results and discussion

Ion source sheath gas temperature

During the instrumental method optimization, it was observed that a high sheath gas temperature caused thermal degradation of the pseudomolecular precursor ions, particularly for the carboxylic acids. As an example, Figure 3 compares the spectra of PFTeDA collected with sheath gas temperatures of 350 °C and 250 °C. At 350 °C, a neutral loss of carbonyl difluoride (mass 66) from the precursor ion (*m/z* 731) produced a base peak ion of *m/z* 647. Reducing the sheath gas temperature to 250 °C yielded the desired base peak of *m/z* 713.

Thermal lability was found to increase with increasing length of the aliphatic carbon chain. In Figure 4A, the relative response of the precursor ion at sheath gas temperatures 250, 300, and 350 °C was plotted as a function of the carbon number. As indicated by the plot, loss of the precursor ion increased with carbon number and temperature. Figure 4B shows the relative response of the neutral loss product at sheath gas temperatures 250, 300, and 350 °C as a function of carbon number. Analogously, the neutral loss product increased with carbon number and temperature. A sheath gas temperature of 250 °C was found to be optimal, providing efficient ion transfer for low-level detection and reproducible quantitation while maximizing precursor ion abundance.

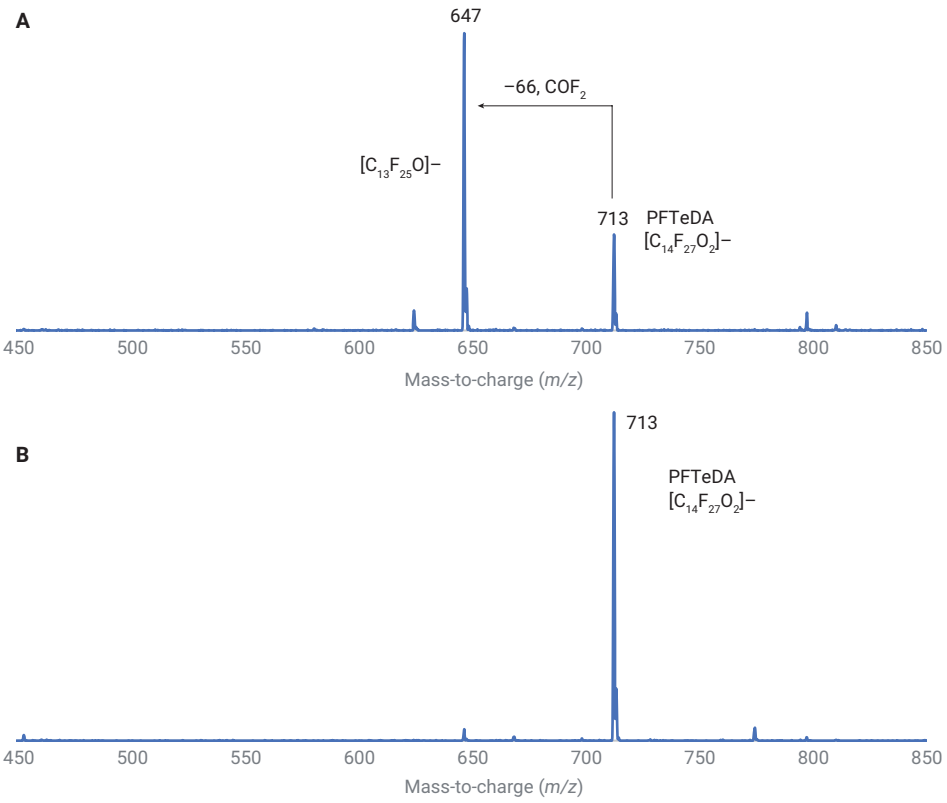

Figure 3. Spectra of PFTeDA at sheath gas temperatures of 350 °C (A) and 250 °C (B).

Storage of solutions

Standard solutions were prepared and stored in 50 mL polypropylene volumetric flasks (Table 2). As recommended in EPA method 8327, the polypropylene containers were stored at ≤6 °C and were brought to room temperature and vortexed before use. However, this protocol was not adequate for recovering the longer chain acids from the container surface. To recover these losses, heating of the polypropylene container to 50 °C for 30 minutes followed by vortex mixing was required. Figure 5 shows a comparison of a standard prepared from a stock solution brought to room temperature and a standard prepared from a stock solution heated to 50 °C. Heating brought recoveries within the method specified limits (±30%).

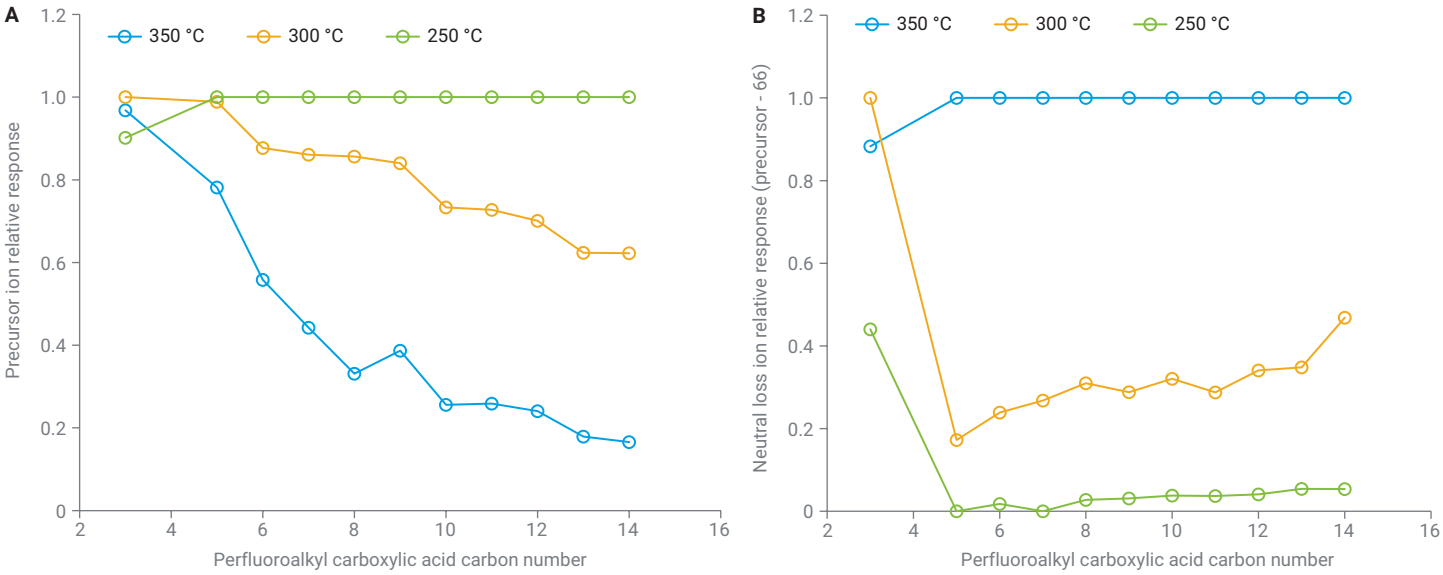

Figure 4. Relative response of precursor ions at 250, 300, and 350 °C as a function of sheath gas temperature (A). Relative response of the neutral loss product at 250, 300, and 350 °C as a function of sheath gas temperature (B).

There was concern that repeated heating cycles could cause increases in recovery over time due to solvent evaporation from the 50 mL volumetric flask. However, this was not observed. Figure 6 shows the recovery of mid-level standards prepared from both PFAS and surrogate solutions over 41 days with five heating/cooling cycles. Recoveries for all the analytes were within method specified limits (±30%).

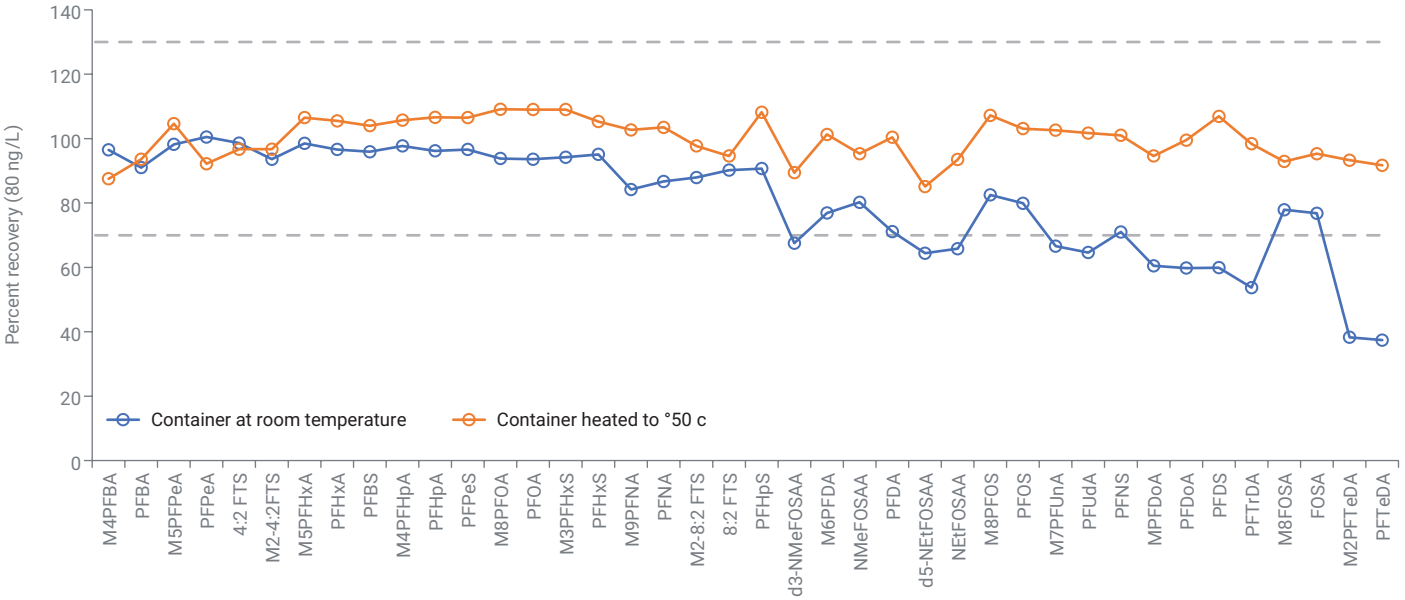

Figure 5. Recoveries of a mid-level standard (80 ng/L) prepared with a stock solution.

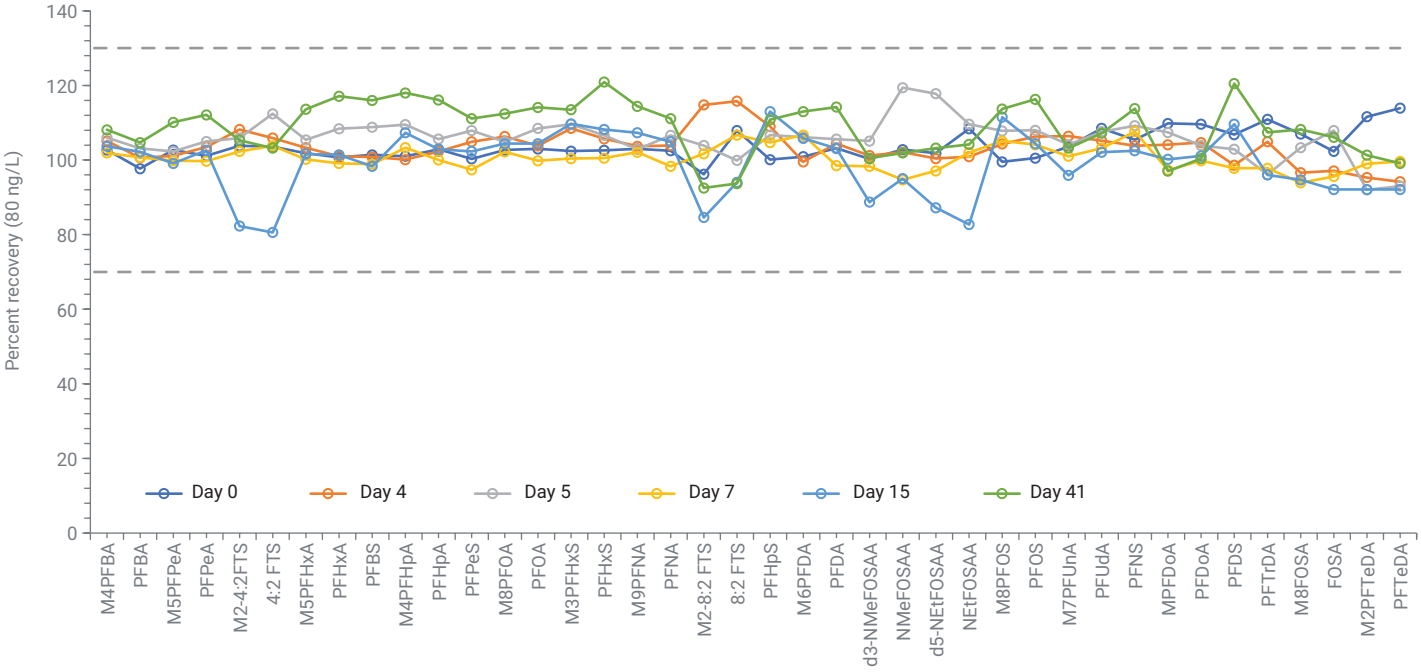

Figure 6. Recovery of standards prepared from stock solutions over 41 days with five heating/cooling cycles.

It was hypothesized that the container shape and manner of heating minimized solvent evaporation over the course of the heating cycles as illustrated in Figure 7. Submerging the lower portion of the container into the water bath with flask neck at ambient temperature allowed for solvent condensation to form and drip down into the bulk solvent. After heating, vortex mixing ensured the homogenization of the solution. The flask was allowed to cool for approximately 10 minutes before opening. No build-up of pressure was observed upon opening the flask.

Evaluation of 15 mL polypropylene centrifuge tubes

As a first experiment, the 15 mL polypropylene centrifuge tubes were tested for the presence of any PFAS residue or nominal mass isobars that could interfere with the target or surrogate responses. Figure 8 shows the results of double blank measurements for five centrifuge tubes. Indicated on the plot are the LLOQ concentration (green hashed line) and half the LLOQ (red hashed line). According to the methods[4,5,7,8], samples may be reported as blank if the measured concentrations are less than half the LLOQ. For all the targets and surrogates, the blank measurements were significantly lower than ½ LLOQ verifying that the tubes have very low background.

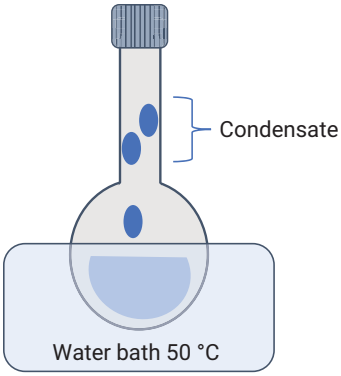

Figure 7. Illustration of the setup for heating stock solutions in a volumetric flask.

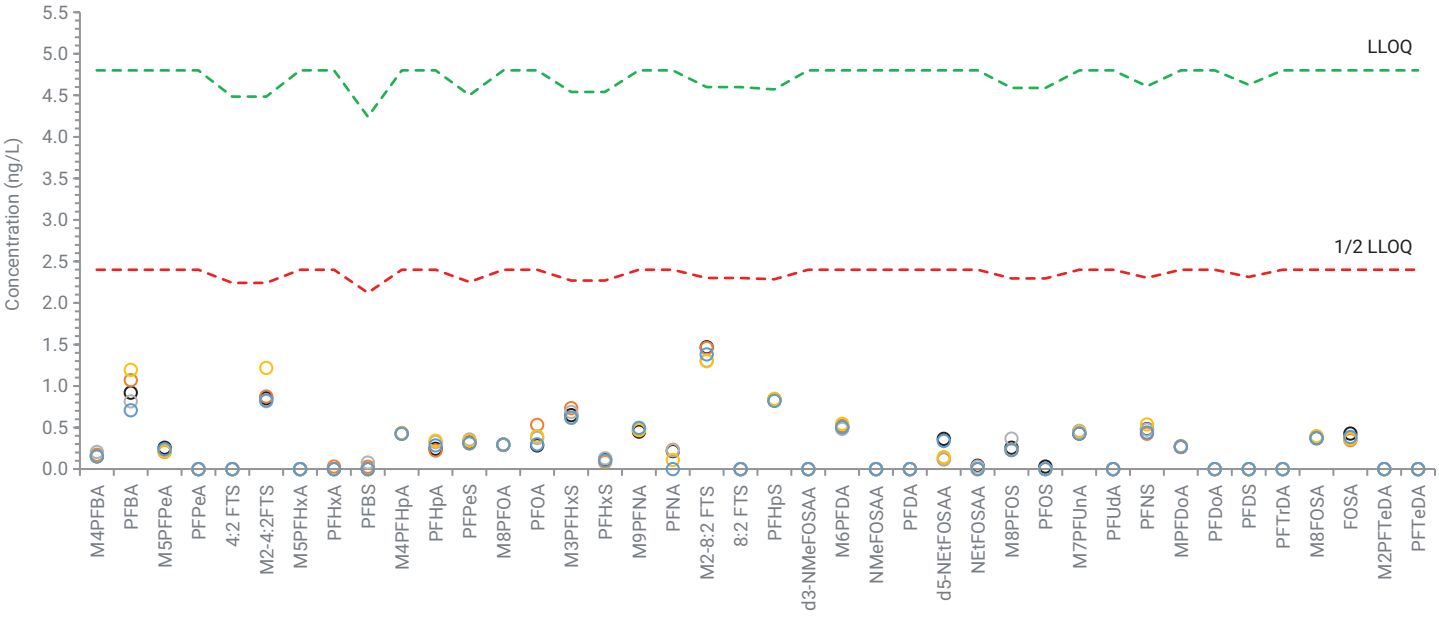

Figure 8. Double blank measurement for five centrifuge tubes. LLOQ and ½ LLOQ concentrations are indicated by the green and red hashed lines, respectively.

Surface adsorption can be problematic at low concentrations. To determine if surface adsorption affected low-level recoveries, five tubes were spiked at the LLOQ with a nominal target concentration of 5 ng/L and a surrogate concentration of 80 ng/L. The average recoveries are shown in Figure 9. For all the compounds, the target recovery at the LLOQ is within the method specified limits of between 50 and 150% for the target compounds and between 70 and 130% for the surrogates. The average recovery of the surrogate M2-8:2 FTS was high compared to the other surrogates. This compound along with the other telomer sulfonates can be problematic and are frequently susceptible to QC failure.[4]

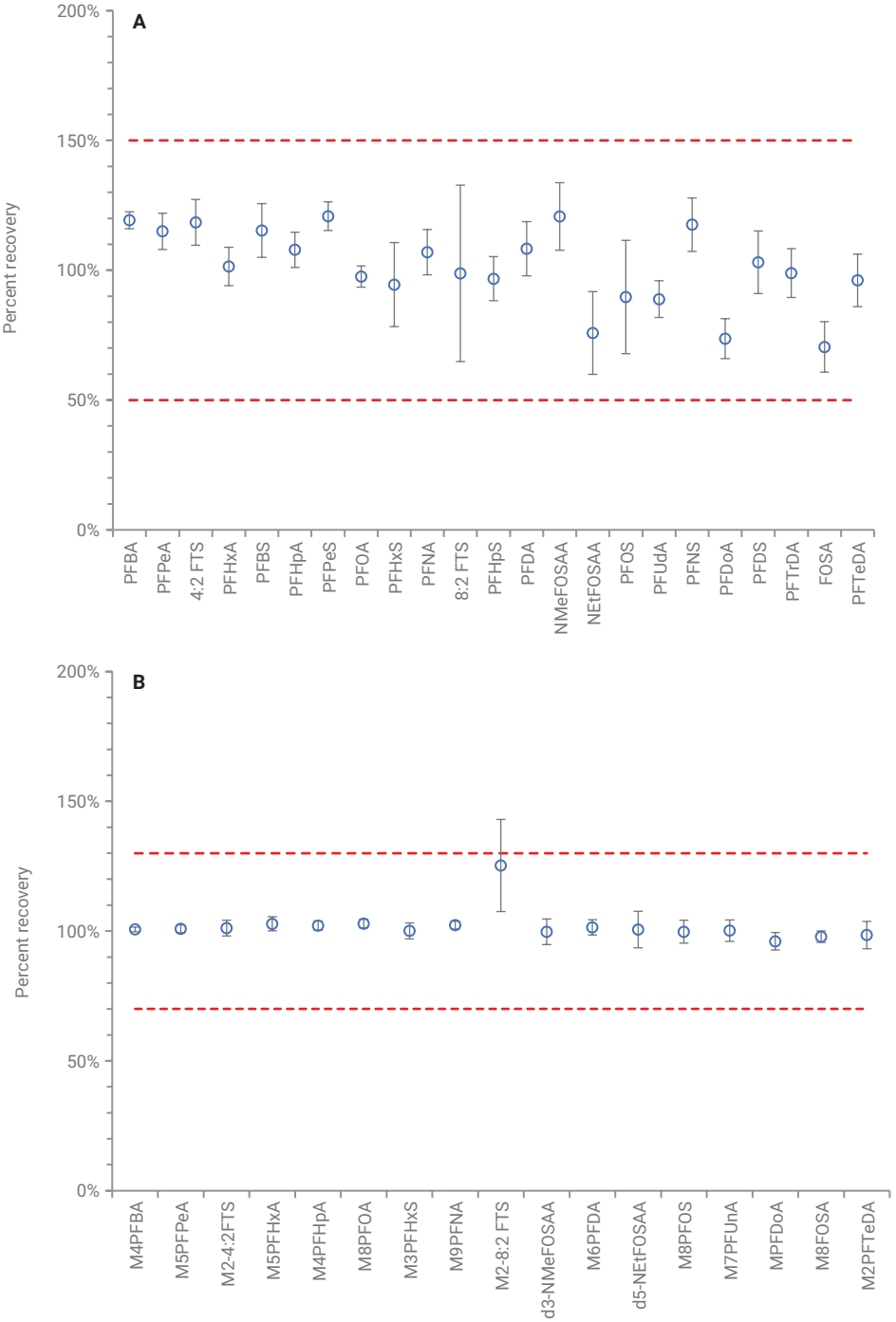

Figure 9. Average recoveries of five replicated LLOQ solvent spikes in 15 mL centrifuge tubes at 5 and 80 ng/L for PFAS targets (A) and surrogates (B), respectively. Error bars represent 1 standard deviation.

Evaluation of 10 mL polypropylene syringes

To aid with filtration, the methods specify the use of either reusable glass syringes or polymeric syringes. Reusable syringes require extensive cleaning before first use and in between each filtration. For example, EPA Method 8327 recommends soaking syringes in hot tap water followed by a 50 mL rinse with reagent water, 30 mL of acetonitrile, and 30 mL of methanol. The cleaning procedure can take a considerable amount of time and require a large volume of high purity solvent, especially when processing large numbers of samples. Disposable syringes can provide significant savings in time, solvent cost, and solvent waste disposal. However, disposable syringes must be free from background interferences and adsorptive losses.

Figure 10 shows the result of double blank measurements for five syringes directly out of the packaging, without rinsing. Indicated on the plot are the LLOQ concentration (green hashed line) and ½ LLOQ (red hashed line). For all the targets and surrogates, the blank measurements were significantly lower than half the LLOQ verifying that the syringes have very low background.

To determine if syringes caused any adsorptive losses, five syringes were spiked at the LLOQ with a nominal target concentration of 5 ng/L and a surrogate concentration of 80 ng/L. The average recoveries are shown in Figure 11. For all the compounds, the target recoveries at the LLOQ are within the method specified limits of between 50 and 150% for the target compounds and between 70 and 130% for the surrogates.

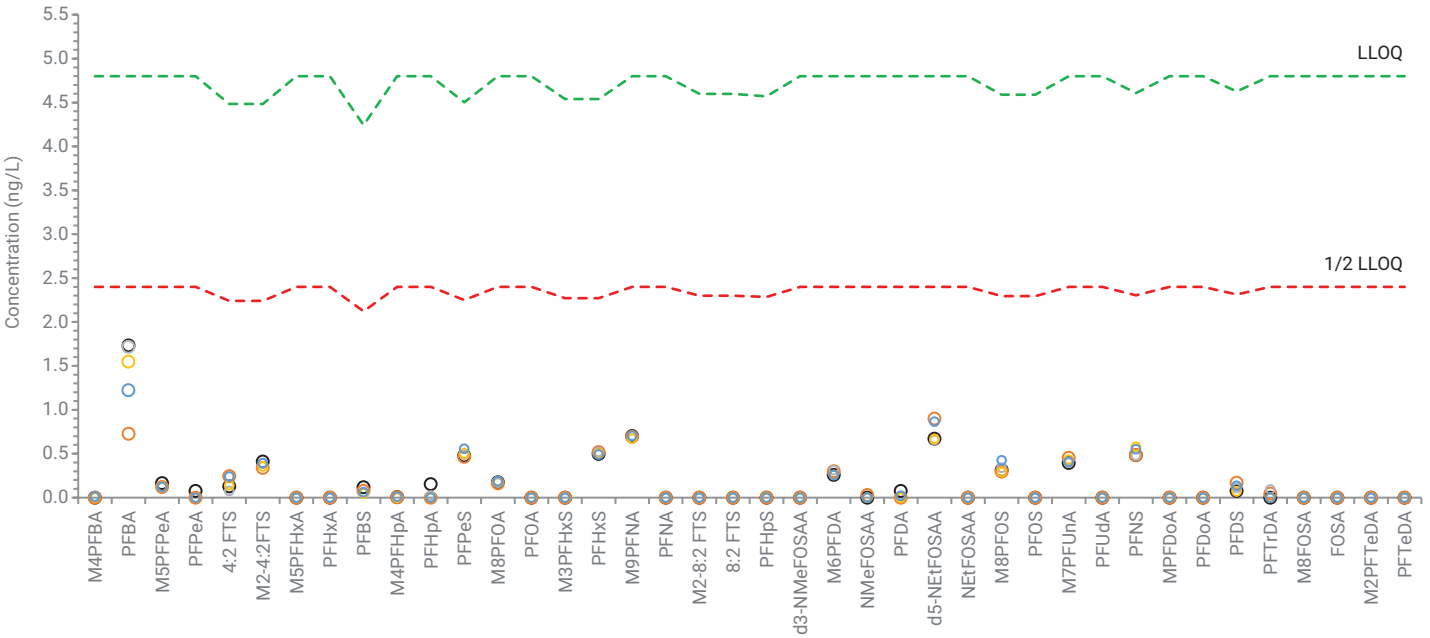

Figure 10. Double blank measurement for five centrifuge tubes. LLOQ and ½ LLOQ concentrations are indicated by the green and red hashed lines, respectively.

Evaluation of syringe filters

Perhaps the most critical step in the sample preparation procedure is filtration. Turbulent contact between the extraction solution and high surface area filtration media has the potential for sample contamination or losses. The EPA and ASTM methods were validated using a 0.2 µm dual-layer polypropylene/glass microfiber syringe filter. All methods recommend rinsing the filters before use to remove any potential contaminants. For example, EPA 8327 recommends rinsing each syringe filter with two 10 mL volumes of acetonitrile followed by two 10 mL volumes of methanol before sample filtration. The reason for this is readily apparent, Figure 12 shows a comparison between dual-layer polypropylene/glass microfiber syringes before and after rinsing for five replicate filters. As shown in the figures, significant contamination was noted for PFBA, PFHxA, PFOA, and NMeFOSSA in addition to elevated levels of PFBS, PFHpA, PFDoA, and PFTeDA.

As with the syringes, the cleaning procedure can take a considerable amount of time and solvent especially when a large number of extractions are required. As an alternative, the Agilent Captiva RC syringe filters were evaluated for intrinsic contamination. Figure 13 shows double blank extractions for five cartridges without rinsing. The concentration of PFAS targets and surrogates were less than half the LLOQ. This indicates that the filters can be used without rinsing yielding a significant improvement in sample workflow processing efficiency.Figure 13. Double blank extract of Agilent Captiva RC syringe filters.

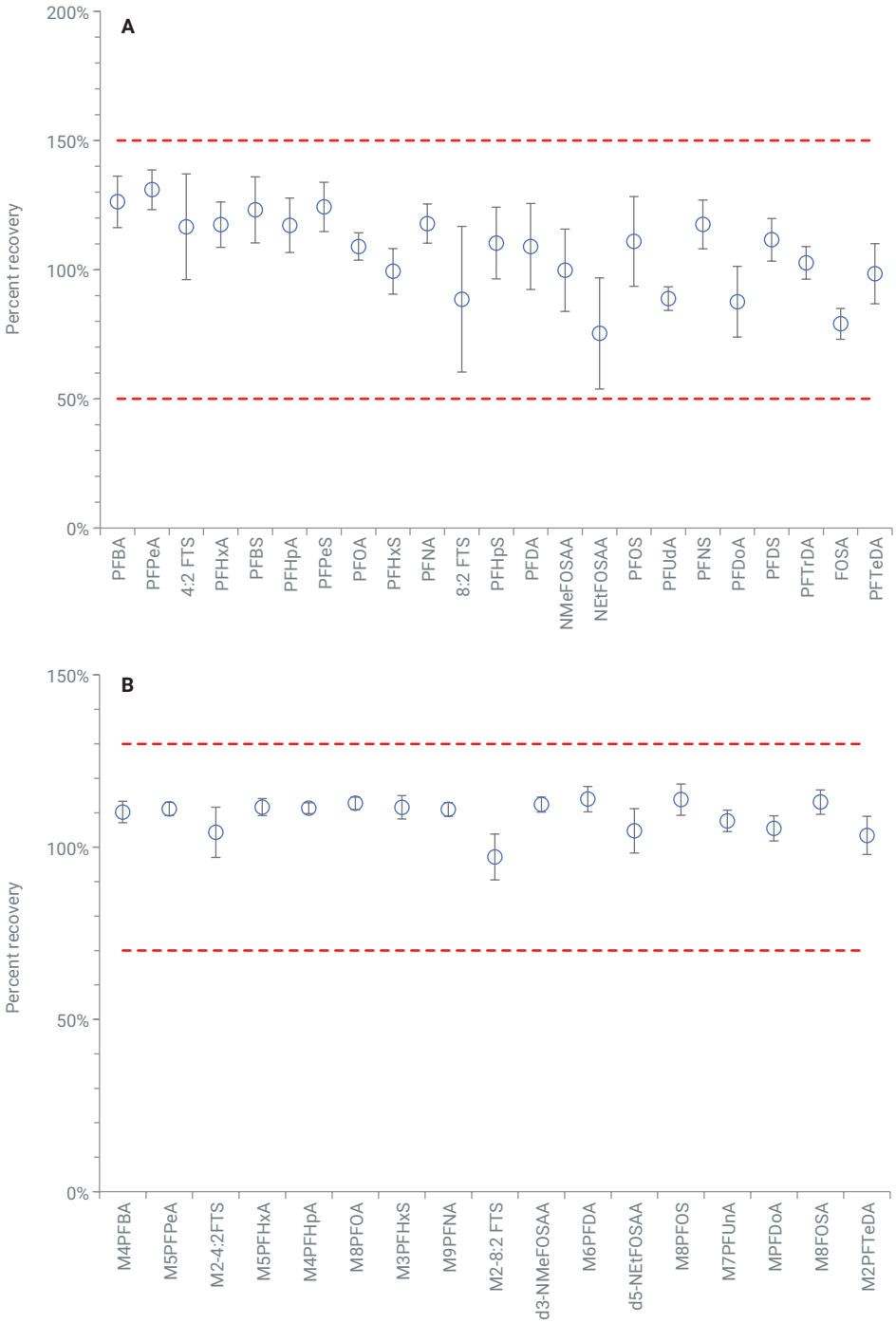

Figure 11. Average recoveries of five replicate LLOQ solvent spikes in syringes at 5 and 80 ng/L for PFAS targets (A) and surrogates (B), respectively. Error bars represent 1 standard deviation.

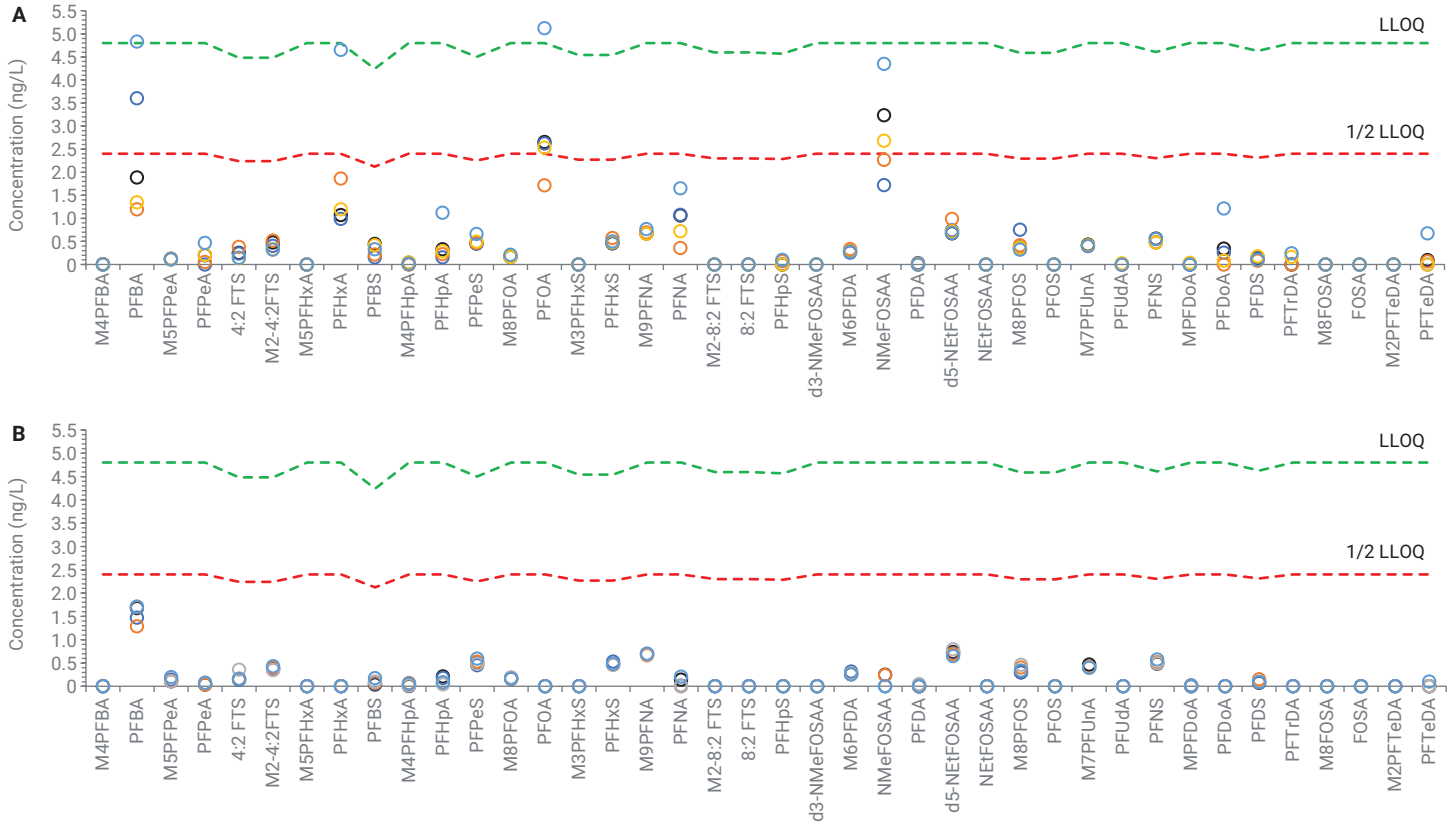

Figure 12. Comparison of dual-layer polypropylene/glass microfiber before (A) and after (B) rinsing.

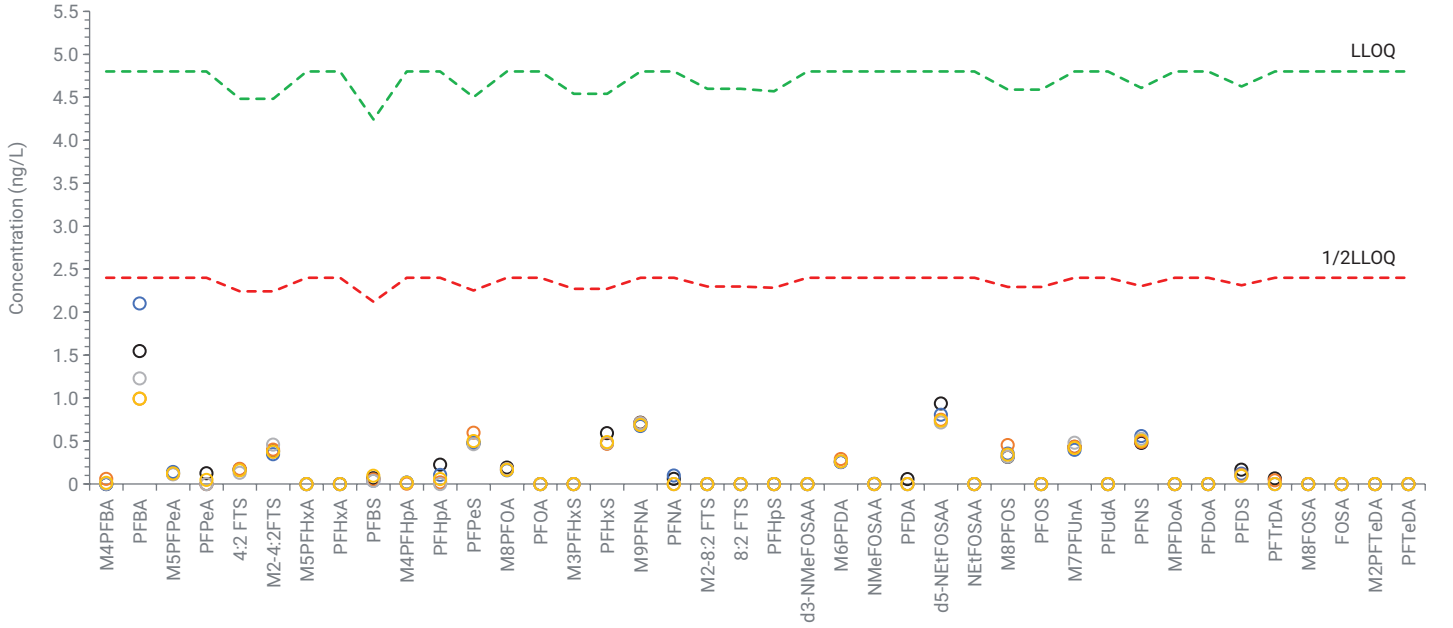

Figure 13. Double blank extract of Agilent Captiva RC syringe filters.

The next step in qualifying the syringe filters was to evaluate recovery for low level spikes to ensure the filters did not lead to adsorption losses. Figure 14 shows the recovery for five replicate spikes at the LLOQ with a nominal target concentration of 5 ng/L and surrogate concentration of 80 ng/L. For all the compounds, the target recovery at the LLOQ are within the method specified limits between 50 and 150% for the target compounds and between 70 and 130% for the surrogates.

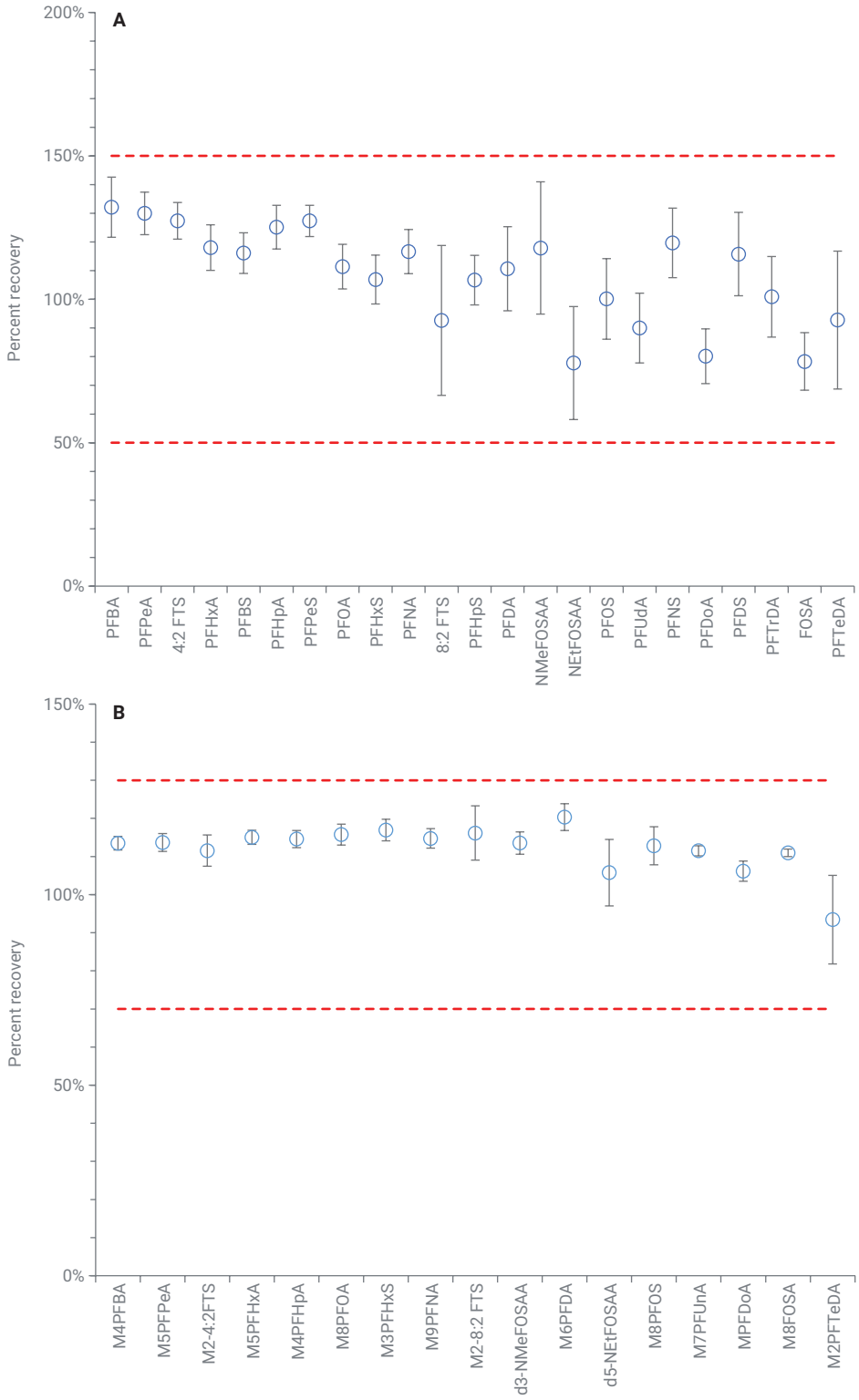

Figure 14. Average recoveries of five replicate LLOQ solvent spikes filtered through the Agilent Captiva RC filters at 5 and 80 ng/L for PFAS targets (A) and surrogates (B), respectively. Error bars represent 1 standard deviation.

Sample matrix extractions

Loamy sand was used as a method blank. The results for six replicate extractions are shown in Figure 15. It is readily apparent that the sand contained relatively high levels of PFAS with PFBA, PFHxA, and PFOA exceeding the LLOQ threshold and elevated levels of PFHpA, PFNA, 8:2 FTS, PFDoA, PFTrDA, FOSA, and PFTeDa. Interestingly, recoveries of surrogates were within 70 to 130% except for M2-8:2FTS with an approximate two-fold increase in recovery. This was thought to be due to matrixed enhanced ionization and was investigated in further detail in the next section.

Figure 16 shows the results of the background subtracted loamy sand matrix spike recovery at the LLOQ (25 ng/kg) for an average of six replicates. All recoveries are within 50 and 150% except for 8:2 FTS due to matrix induced ionization enhancement.

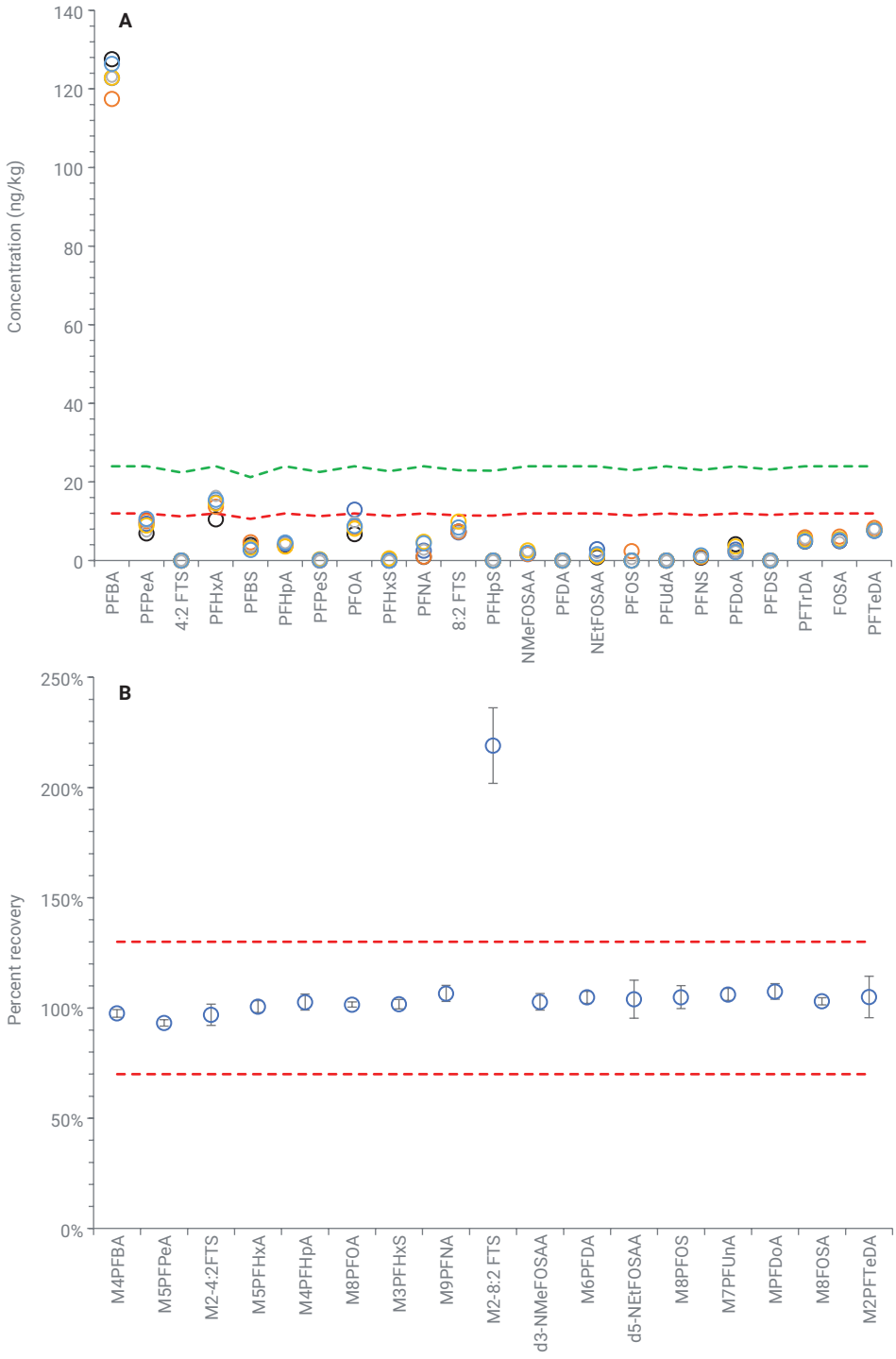

Figure 15. Results of six replicate method blank extractions from loamy sand for PFAS targets (A) and surrogate recoveries (B).

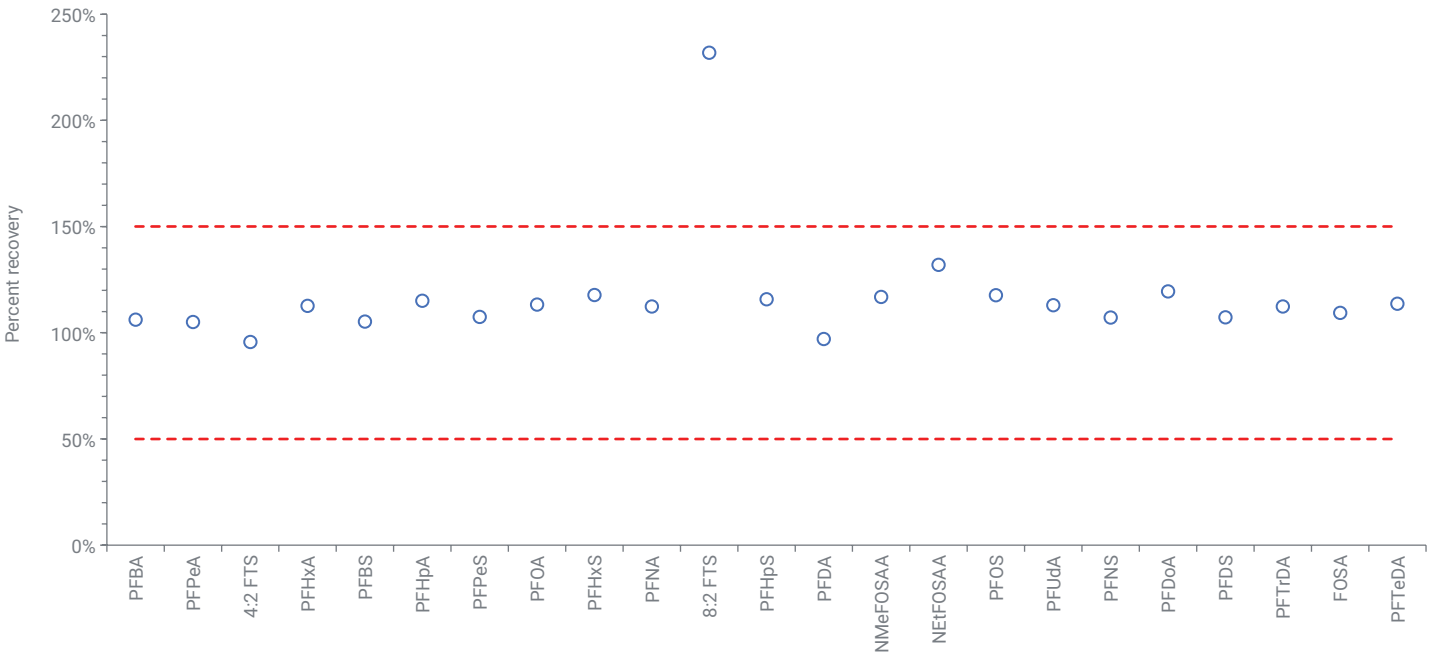

Figure 16. Loamy sand matrix spike recovery at the LLOQ (25 ng/kg).

Matrix induced ionization enhancement

It has been suggested in the literature that certain PFAS compounds are susceptible to matrix effects on ionization.[9,10] Matrix ionization enhancement can occur when coelution of an interfering component alters the spatial distribution of analytes within the fissioning electrospray droplet leading to a differentiated response between standard and extract. It was speculated that this was the cause of the high recoveries of 8:2 FTS observed in the loamy sand extracts (Figures 15 and 16). To explore this hypothesis, both the standard and extract were run in scan mode to identify any coelutions that may have occurred. Figure 17A shows an overlay of extracted ions for M2-8:2 FTS (*m/z* −529) and an unknown coeluting peak (*m/z* −445). In contrast, Figure 17B shows the response of M2-8:2 FTS in the analytical standard in which the unknown coeluting peak was not observed providing evidence for matrix induced ionization enhancement.

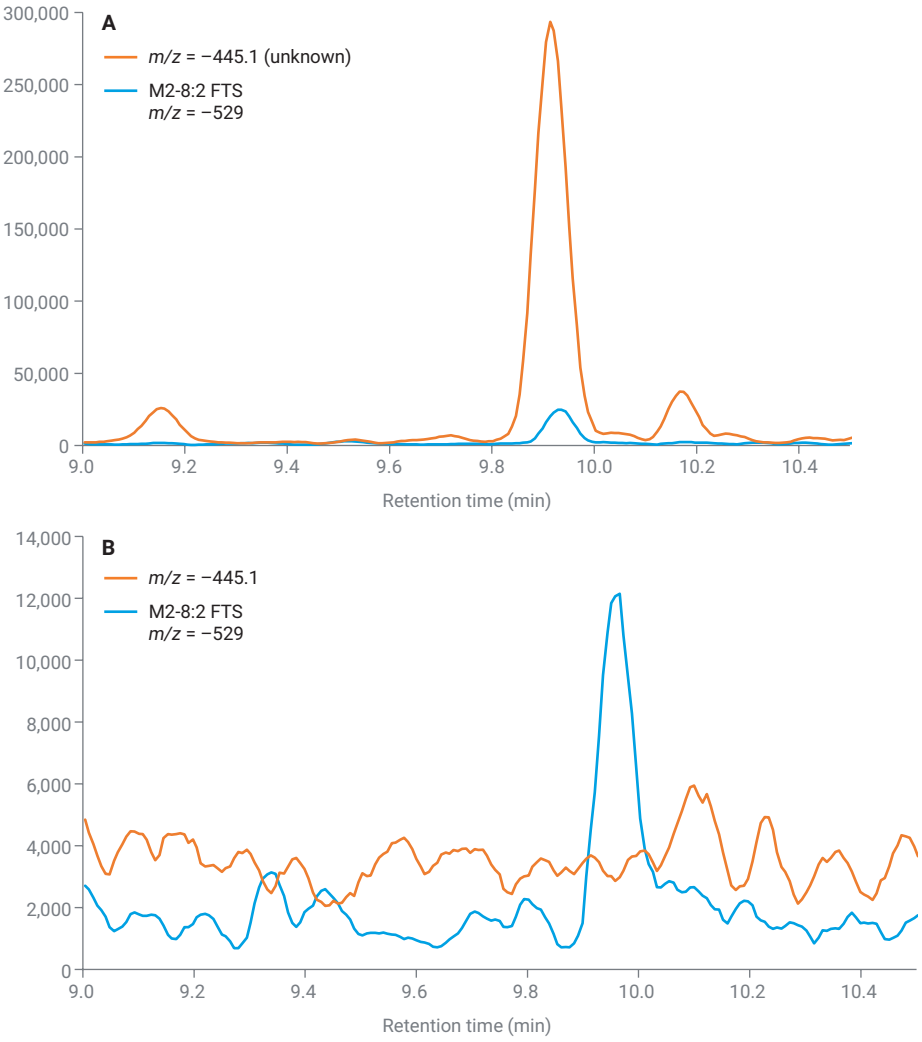

Figure 17. Coelution of an unknown peak with M2-8:2 FTS in the sandy loam extract (A) compared to the analytical standard (B).

Conclusion

Reliable consumables are critical to the success of the sample preparation workflows for the analysis of PFAS as outlined in EPA 8327, ASTM D7968-17a, and D7979-19. This application note demonstrates that Agilent 15 mL centrifuge tubes, Agilent Captiva disposable syringes, and Agilent Captiva regenerated cellulose syringe filters provide consumables free from interferences and losses that can be particularly problematic for PFAS analysis. In addition, considerable savings in time and solvent usage can be achieved by eliminating the need for rinsing before use while ensuring optimal analytical performance.

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Appendix A

Table A1. Compound MRM parameters.

Compound	Precursor Ion	Product Ion	Retention Time (min)	Fragmentor (V)	Collision Energy (V)
M4PFBA	217	172	4.333	61	8
PFBA	213	169	4.335	64	8
M5PFPeA	268	223	4.902	64	4
PFPeA	263	219	4.902	64	4
4:2 FTS	327	307	5.339	129	20
4:2 FTS	327	81	5.339	129	32
M2-4-2FTS	329	309	5.339	135	20
M5PFHxA	318	273	5.676	67	8
PFHxA	313	269	5.676	67	8
PFHxA	313	119	5.676	67	20
PFBS	299	99	6.114	141	32
PFBS	299	80	6.114	141	36
M4PFHpA	367	322	6.619	70	8
PFHpA	363	319	6.619	70	8
PFHpA	363	169	6.619	70	16
PFPeS	349	99	7.224	157	36
PFPeS	349	80	7.224	157	44
M8PFOA	421	376	7.613	76	8
PFOA	413	369	7.622	76	8
PFOA	413	169	7.622	76	20
M3PFHxS	402	80	8.369	166	48
PFHxS	399	99	8.370	166	40
PFHxS	399	80	8.370	166	48
M9PFNA	472	427	8.659	86	8
PFNA	463	419	8.660	89	8
PFNA	463	219	8.660	89	16
8:2 FTS	527	507	9.119	169	32
8:2 FTS	527	81	9.119	169	40
M2-8-2FTS	529	509	9.127	172	32
PFHpS	449	99	9.483	126	44
PFHpS	449	80	9.483	126	52
d3-NMeFOSAA	573	419	9.629	135	20
NMeFOSAA	570	483	9.638	129	16
NMeFOSAA	570	419	9.638	129	20
M6PFDA	519	474	9.674	89	8
PFDA	513	469	9.682	92	8
PFDA	513	219	9.682	92	16
d5-NEtFOSAA	589	419	10.081	132	20
NEtFOSAA	584	483	10.090	129	16
NEtFOSAA	584	419	10.090	129	20
M8PFOS	507	80	10.505	194	56
PFOS	499	99	10.506	194	48
PFOS	499	80	10.506	194	56

Compound	Precursor Ion	Product Ion	Retention Time (min)	Fragmentor (V)	Collision Energy (V)
M7PFUnA	570	525	10.643	101	8
PFUdA	563	519	10.644	95	8
PFUdA	563	269	10.644	95	20
PFNS	549	99	11.476	209	52
PFNS	549	80	11.476	209	56
MPFDoA	615	570	11.589	95	12
PFDoA	613	569	11.589	101	12
PFDoA	613	169	11.589	101	28
PFDS	599	99	12.420	209	56
PFDS	599	80	12.420	209	80
PFTrDA	663	619	12.518	110	12
PFTrDA	663	169	12.518	110	32
M8FOSA	506	78	12.858	160	36
FOSA	498	78	12.859	157	36
FOSA	498	48	12.859	157	80
M2PFTeDA	715	670	13.429	107	12
PFTeDA	713	669	13.430	110	12
PFTeDA	713	169	13.430	110	32

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

Concentration (ng/L)	Percent Accuracy																						
	PFBA	PFPeA	4:2FTS	PFHxA	PFBS	PFHpA	PFPeS	PFOA	PFHxS	PFNA	8:2 FTS	PFHpS	PFDA	NMeFOSAA	NEtFOSSA	PFOS	PFUdA	PFNA	PFDoA	PFDS	PFTrDA	FOSA	PFTeDA
5	99	95	101	99	100	92	89	99	96	94	101	73	87	95	113	94	88	91	102	90	105	107	103
10	103	103	114	101	96	106	98	94	101	106	95	107	110	105	87	105	102	98	97	105	90	92	94
20	99	99	83	95	100	99	109	102	101	92	98	114	88	96	85	94	95	98	85	93	87	95	82
40	98	99	98	102	100	99	103	101	99	103	100	103	107	100	103	104	108	106	110	107	113	103	118
60	99	103	99	101	104	102	103	102	100	102	101	104	109	102	108	100	104	106	101	101	98	102	97
80	98	101	104	101	101	103	100	103	103	103	108	100	103	103	108	101	109	105	110	107	111	102	114
100	106	101	103	103	101	101	100	101	104	103	101	104	102	101	105	107	101	101	99	103	100	101	98
150	99	100	100	101	102	102	101	101	101	99	100	97	100	103	97	100	99	99	100	100	102	101	99
200	100	98	99	97	97	97	97	97	97	98	96	97	95	96	96	96	95	96	96	95	94	97	95
R^2	0.999	1.000	0.998	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.998	0.997	0.996	0.999	0.995	0.998	0.997	0.998	0.996	0.997	0.994	0.999	0.991

Table A3. Surrogate calibration accuracy using linear least squares regression with 1/x weighting.

Concentration (ng/L)	Percent Accuracy																
	M4PFBA	M5PFPeA	M2-4:2FTS	M5PFHxA	M4PFHpA	M8PFOA	M3PFHxS	M9PFNA	M2-8:2 FTS	M6PFDA	d3-NMeFOSAA	d5-NEtFOSAA	M8PFOS	M7PFUnA	MPFDoA	M8FOSA	M2PFTeDA
5	96	98	103	99	97	95	104	109	90	91	102	101	93	96	94	111	105
10	103	101	97	101	102	104	88	94	113	101	89	99	102	96	103	87	91
20	96	95	93	97	99	98	104	88	93	99	102	94	99	96	91	94	85
40	101	104	102	100	99	101	100	105	113	108	104	107	103	108	107	103	114
60	103	100	102	102	100	101	104	100	93	102	108	102	104	104	100	102	100
80	103	103	104	102	101	103	102	103	96	101	100	102	100	104	110	107	112
100	103	102	101	101	104	103	100	103	104	101	97	97	101	101	98	99	99
150	100	101	99	101	101	99	103	102	95	102	99	99	102	99	104	100	101
200	97	97	99	98	97	98	96	97	103	96	99	100	97	97	94	98	94
R^2	0.999	0.999	0.999	1.000	0.999	0.999	0.998	0.998	0.996	0.998	0.999	0.999	0.999	0.998	0.996	0.998	0.994

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