PFAS

PERFLUOROALKYL SUBSTANCES

APPLICATION GUIDE

CHROMATOGRAPHY SOLUTIONS

- Solid Phase Extraction
- QuEChERS
- LC-MS/MS

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Perfluoroalkyl Substances (PFASs)

PFASs are a large group of compounds characterized by a linear aliphatic backbone, a high degree of fluorination and often feature a carboxylic- or sulfonic- acid functionality. These chemical characteristics make PFASs highly resistant to heat, oil and water. As a result, for many years these remarkable materials have found a multitude of uses, from components of carpeting and clothing to firefighting foams.

PFASs are unfortunately extremely resistant to degradation in the environment and also strongly bioaccumulate. Because of their strong tendency to bioaccumulate, PFAS compounds are widely found at trace levels in both humans and animals in the developed world. These same chemical properties also raise concerns about potential adverse health effects.

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Rapid Analysis of 23 Per- and Poly-Fluorinated Alkyl Substances (PFASs)

UHPLC-MS/MS

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Overview

This application describes a method for the rapid analysis of 23 PFASs by UHPLC-MS/MS using the Luna® Omega 1.6 µm PS C18 column. The high resolution and unique mixed-mode selectivity of the Luna Omega 1.6 µm PS C18 results in excellent chromatography and peak shapes for PFASs in a very short four minute run.

Acknowledgement

We would like to provide special thanks to Weck Laboratories for contributing this application.

WECK LABORATORIES, INC.

LC-MS/MS Conditions

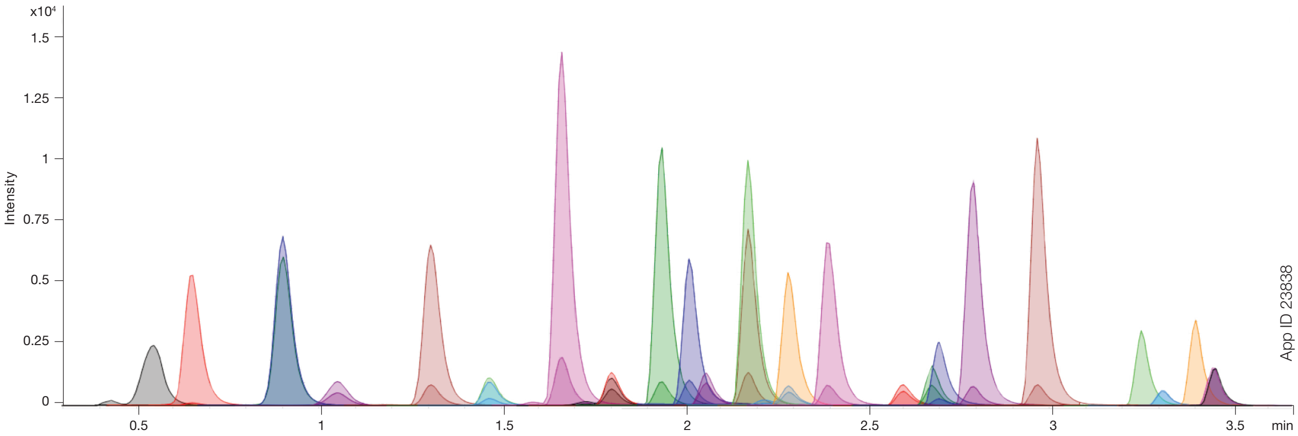
Column: Luna Omega 1.6 µm PS C18
Dimensions: 100 x 2.1 mm
Part No.: 00D-4752-AN
Mobile Phase: A: 5 mM Ammonium Acetate in Water
B: Acetonitrile

Gradient:

Time (min)	% B
0	40
0.5	40
3	90
3.1	100
4	100

Flow Rate: 0.55 mL/min
Injection: 5 µL
Temperature: 40 °C
System: Agilent® 1290
Detection: Agilent 6460 QQQ
Analytes:

1. 6:2 FTS
2. 8:2 FTS
3. EtFOSA
4. EtFOSE
5. FOSA
6. MeFOSA
7. MeFOSE
8. PFBA
9. PFBS
10. PFDA
11. PFDoA
12. PFDS
13. PFHpA
14. PFHpS
15. PFHxA
16. PFHxS
17. PFNA
18. PFOA
19. PFOS
20. PFPeA
21. PFTeDA
22. PFTrDA
23. PFUdA



App ID 23838

Determination of PFASs in Sediments

Using QuEChERS Extraction and LC-MS/MS

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Introduction

Perfluoroalkyl substances (PFASs), once released in the aquatic environment, will partition between the water phase and the sediment. To better understand the fate and transport of these compounds, it is important to measure both the solid and liquid environmental fractions.

There are several methods available for the extraction and analysis of PFASs in aqueous samples. However, very few procedures are available for extracting these compounds in solid matrices such as sediments. Typical methods used are mechanical shakers and ultrasonic-assisted Solid-Liquid Extractions (SLE).[6,7,8] The extracts are then subjected to additional clean-up steps, usually by solid phase extraction. These are generally solvent-intensive and time-consuming processes. In 2003, an extraction procedure called QuEChERS (Quick-Easy-Cheap-Effective-Rugged-and-Safe) was introduced. It was originally developed to extract pesticide residues in food matrices but has since found applications in the field of environmental analytical chemistry.

Los Angeles County Sanitation District (LACSD) previously developed and validated a QuEChERS sediment extraction procedure for emerging contaminants including: pharmaceutical and personal care products, steroids, alkylphenol ethoxylates, and pyrethroid pesticides.[2,3,4] We have successfully applied the same extraction method to determine PFASs in marine and freshwater sediments.

Materials and Methods

Reagents/Chemicals

QuEChERS Extraction – In a 50 mL plastic centrifuge tube combine 2.0 g of Anhydrous Magnesium Sulfate, and 1.5 g Sodium Acetate or use approximately 3.5 g of AOAC 2007.01 roQ™ extraction packet (Part no. AH0-9043)

QuEChERS dSPE Clean-Up — roQ 15 mL dSPE Kit (Part no. KS0-8926)

Sample Preparation Procedure

QuEChERS Extraction Protocol

1. Weigh 2.0 g of suitably dried sediment into a polypropylene container and spike with isotopically-labeled internal standards. PPCPs, Steroids, and Pyrethroids can be extracted concurrently with this method by adding the appropriate internal standard and spiking solutions to the samples and QCs.[2,3,4]
2. Add 10 mL deionized water and vortex. Add 10 mL acidified acetonitrile (1 % Acetic acid) to the slurry and vortex.
3. Add the extraction salts (1.5 g Sodium acetate and 2 g $MgSO_4$) to the sample and vortex for 1 minute.
4. Centrifuge the samples for 5 minutes at 4000 rpm.
5. Place the samples in a rack and freeze at -20 °C for 30-60 minutes. This freezing step allows for easier extraction of the supernatant.
6. Transfer 8-9 mL of the acetonitrile supernatant into a roQ QuEChERS PSA/C18 dSPE clean-up tube (Part no. KS0-8926) and vortex for one minute.
7. Centrifuge the dSPE tubes for 10 minutes at 3000 rpm.
8. Place an aliquot of the extract in a polypropylene HPLC vial and dilute 1:1 with deionized water. The sample is now ready for analysis.

LC-MS/MS Conditions

Column: Gemini® 3 µm C18
Dimensions: 100 x 3.0 mm
Part No.: 00D-4439-Y0
Inline Filter: Phenomenex KrudKatcher™ Ultra (AF0-8497)
Delay Column: Luna® 5 µm C18(2) 30 x 2.0 mm
Part No.: 00A-4252-B0
Mobile Phase: A: 20 mM Ammonium acetate in Water
B: Methanol
Gradient:

Time (min)	% B
0	10
1.5	65
8	95
8.1	99
12	99
12.5	10

Flow Rate: 0.6 mL/min
Injection: 90 µL
Temperature: 40 °C
Detector: SCIEX 5500 QTRAP®
Detection: MS/MS ESI Negative (sMRM)
Analytes:

1. PFBA
2. PFPeA
3. PFBS
4. PFHxA
5. PFPS
6. PFHxS
7. PFHpA
8. PFHpS
9. PFOA
10. PFOS
11. PFNA
12. PFOSA
13. PFNS
14. PFDA
15. PFDS
16. PFUdA
17. PFDoA
18. PFTrDA
19. PFTeDA

Mass Spectrometer Parameters

Table 1.
MRM Transitions and Compound Dependent Parameters

Compound Name	Q1	Q3	DP	CE
Perfluorobutanoic acid (PFBA)	213	169	-71	-14
Perfluoropentanoic acid (PFPeA)	263	219	-71	-12
Perfluorohexanoic acid (PFHxA)	313	269	-60	-14
Perfluoroheptanoic acid (PFHpA)	363	319	-62	-15
Perfluoroctanoic acid (PFOA)	413	369	-91	-12
Perfluorononanoic acid (PFNA)	463	419	-79	-15
Perfluorodecanoic acid (PFDA)	513	469	-83	-17
Perfluoroundecanoic acid (PFUdA)	563	519	-60	-17
Perfluorododecanoic acid (PFDoA)	613	569	-50	-21
Perfluorotridecanoic acid (PFTrDA)	663	619	-49	-18
Perfluorotetradecanoic acid (PFTeDA)	713	669	-63	-20
Perfluorobutanesulfonate (PFBS)	299	80	-94	-70
Perfluoropentantesulfonate (PFPeS)	349	80	-96	-66
Perfluorohexanesulfonate (PFHxS)	399	80	-92	-75
Perfluoroheptanesulfonate (PFHpS)	449	80	-75	-84
Perfluorooctanesulfonate (PFOS)	499	80	-78	-96
Perflluorooctanesulfonamide (PFOSA)	498	78	-60	-84
Perfluorononanesulfonate (PFNS)	549	80	-87	-100
Perfluorodecanesulfonate (PFDS)	599	80	-55	-100
Perfluoro-n-^{13}C4-butanoic acid (M4PFBA)	217	171.9	-71	-13
Perfluoro-n-^{13}C5-pentanoic acid (M5PFPeA)	268	222.7	-71	-12
Perfluoro-n-^{13}C5-hexanoic acid (M5PFHxA)	318	272.9	-60	-13
Perfluoro-n-^{13}C4-heptanoic acid (M4PFHpA)	367	321.8	-62	-14
Perfluoro-n-^{13}C8-octanoic acid (M8PFOA)	421	376	-91	-12
Perfluoro-n-^{13}C9-nonanoic acid (M9PFNA)	472	427	-79	-17
Perfluoro-n-^{13}C6-decanoic acid (M6PFDA)	519	474	-83	-21
Perfluoro-n-^{13}C7-undecanoic acid (M7PFUdA)	570	525	-60	-17
Perfluoro-n-^{13}C2-dodecanoic acid (M2PFDoA)	615	570	-50	-24
Perfluor-n-^{13}C2-tetradecanoic acid (M2PFTeDA)	715	670	-63	-25
Perfluro-^{13}C3-butanesulfonate (M3PFBS)	302	80	-94	-55
Perfluoro-^{13}C3-hexanesulfonate (M3PFHxS)	402	80	-92	-85
Perfluoro-^{13}C8-octanesulfonate (M8PFOS)	507	80	-78	-100

Note: DP = Declustering Potential
CE = Collision Energy

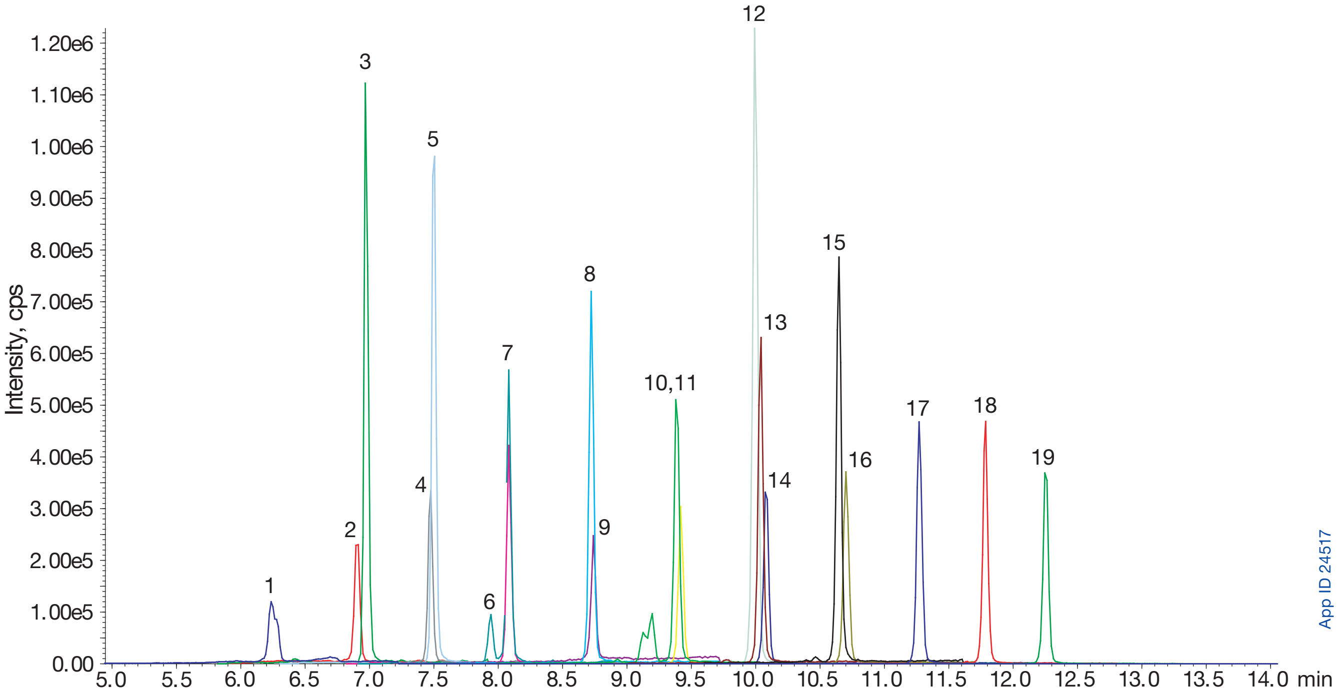
Table 2.
MS Source Parameters

Source Parameters	Settings
Temperature	400 °C
Gas 1	50
Gas 2	50
Curtain Gas	35
Ionization Energies	-4500 V
Collision Gas	High

Table 3.
Method Performance Data for Sediments Spiked at 1 ng/g of the Target Analytes (n=4)

Compound	Average % Recovery	% RSD
PFBA	91.7	0.76
PFPeA	86.3	6
PFHxA	89.4	1.2
PFHpA	93.1	2.9
PFOA	98.3	1.5
PFNA	93	1.6
PFDA	87.7	4.5
PFUdA	92.3	2.1
PFDoA	92.5	4.1
PFTrDA	88.2	2.1
PFTeDA	87.6	2.1
PFBS	86.3	2.1
PFPeS	96.2	3.2
PFHxS	81.3	5
PFHpS	92.3	2.6
PFOS	92.1	2.6
PFOSA	104.5	6.3
PFNS	89.8	6.8
PFDS	87.3	6.7

Figure 1
Sediment Spiked with 1ng/g



Results and Discussion

QuEChERS is a vortex-assisted solid-liquid extraction procedure that uses acetonitrile, salts, and buffering agents for extraction, phase-separation, and pH adjustment, respectively. Extracts are subsequently transferred to a dispersive solid phase extraction (dSPE) tube containing a drying agent ($MgSO_4$) and SPE sorbents such as C18 or PSA for sample cleanup.

The modified QuEChERS method presented here is a simple, efficient, and cost-effective method for determining PFAS levels in sediments. Accuracy and precision were assessed using four replicates of sediments spiked with the target analytes. Average % recoveries are all within the 80-120 % range and % RSDs for all analytes are below 10 % (**Table 3**). Reporting limits were set at 0.05 ng/g dry weight based on a 2.0 g initial sample weight.

Conclusion

The sediment extraction using the modified QuEChERS method is a fast, effective, and efficient way of extracting 19 PFASs from marine and river sediment matrices. The procedure significantly minimizes sample preparation time, solvent consumption, and overall cost of analysis. Only minor modifications were made to the well-established QuEChERS method to accommodate the target analytes. Excellent extraction recoveries and precision were achieved and method reporting limits are in the low ng/g range.

References

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Acknowledgements

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Quantitation of PFASs in Water

LC-MS/MS: Large-Volume Direct Injection and Solid Phase Extraction

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Overview

This application note presents two methods for the quantitation of per- and polyfluorinated alkyl substances (PFASs) in water samples. While the MS/MS detection method using the SCIEX Triple Quad™ 5500 is similar between the two methods, the sample preparation and injection volume differ significantly. The first method presented here utilizes a weak-anion exchange solid phase extraction (SPE) method to concentrate water samples for analysis using a 7.5 minute HPLC gradient. The second method utilizes dilution of a water sample in methanol and direct injection of 950 µL of the diluted sample using a 17.5 minute HPLC gradient. Special modifications to the pumps and autosampler are described to mitigate laboratory-based contamination of PFASs. Both methods achieved accurate quantitation at levels of approximately 1-10 ng/L for more than 17 PFASs.

Introduction

PFASs are unique chemicals whose physicochemical properties make them important for use in a variety of industrial and consumer products including carpets, cookware, food packaging, fire suppressants, and others[1]. Chemically, PFASs are aliphatic structures containing one or more C atoms on which H substituents have been replaced by F atoms. Classification and naming is typically by the particular functional group present, such as carboxylic acids, sulfonates, phosphonic acids, etc., as well as the length of the carbon chain. Desirable in various industrial applications for their chemical stability and low reactivity, these properties also make PFASs highly resistant to degradation in aquatic environments. Typical concentrations of PFASs found in various environmental water sources range from pg/L to µg/L levels[2].

Human exposure to PFAS residues has been implicated in the incidence of cancer, obesity, endocrine system disruption, and other adverse health effects[3-4]. In recognition of these potential risks, sources of human exposure to these chemicals (e.g., via drinking water) are receiving public and scientific attention. PFASs exhibit relatively high aqueous solubility and can be transported and bioaccumulated from contaminated water sources. The US EPA maintains health advisory limits for select PFASs (e.g., perfluorooctanoic acid (PFOA) at a limit of 70 ng/L) in water, but these levels have been exceeded in some areas experiencing extreme point source inputs of these chemicals[5].

Given the tremendous persistence of PFASs in the environment and their known presence in human populations exposed via drinking water and other environmental routes, demonstration of the capability for accurate and precise low-level quantitation is paramount for research and testing laboratories. Robust quantitative analytical methods utilize the specificity and sensitivity of LC-MS/MS with MRM monitoring. However, a primary analytical challenge to this assay is the prevention and reduction of background PFASs originating from the LC system and contamination during sample collection and preparation. The two analytical methods described here employ strategies to address PFAS contamination. These include the use of a delay column for separation of a contamination PFAS peak from the analytical peak, and a large volume injection of an aqueous sample intended to achieve method sensitivity while reducing accumulated background during sample concentration steps.

Experimental

HPLC System

Shimadzu® LC-20ADXR binary pumps with a Shimadzu DGU-20A5 degasser provided the gradient chromatographic conditions. All fluoroethylene polymer (FEP) tubing on the Shimadzu pumps and degasser was replaced with PEEK tubing with similar internal and external dimensions. A Phenomenex Luna® C18(2) column (dimensions shown in

Table 1) was installed between the pump mixing chamber and the column, outside of a Shimadzu® CTO-20AC column oven. This column served as a delay or hold-up column to isolate PFAS contamination originating from the pumps and eluents. A longer and/or larger diameter Luna® C18(2) column must be installed on heavily contaminated systems to prevent breakthrough of contamination. Outside of a Shimadzu CTO-20AC column oven. This column served as a delay or hold-up column to isolate PFAS contamination originating from the pumps and eluents. A longer and/or larger diameter Luna C18(2) column must be installed on heavily contaminated systems to prevent breakthrough of contamination.

Chromatographic separation was performed using a Phenomenex Gemini® C18 HPLC column at 0.6 mL/min (**Table 1**). The Gemini C18 column was heated to 40 °C in the column oven. A PAL® HTC-xt autosampler with dynamic load-wash (DLW) was modified by replacing all FEP tubing from the rinse solvent lines, the needle seal, and the sample holding loop with PEEK or stainless steel. The autosampler syringe and sample holding loop was rinsed with methanol and 1:1 methanol/acetonitrile between samples.

Table 1.
LC Columns for Methods 1 and 2

	Column	Dimensions
Delay Column	Phenomenex Luna C18(2)	5 µm; 30 x 2 mm
Method 1 HPLC	Phenomenex Gemini C18	3 µm; 50 x 2 mm
Method 2 HPLC	Phenomenex Gemini C18	3 µm; 100 x 3 mm

Standards and Internal Standards (IS)

The PFAS standards and internal standards were obtained from Wellington Laboratories (Guelph, Ontario) and were prepared in Baker HPLC-grade methanol. Standard stock solutions were prepared by dilution with 96% methanol and 4% water (purified using a Millipore® water purification system).

Sampling and Sample Preparation

Water samples were obtained anonymously from various sources in the United States. Samples were stored in the dark at 4°C in 250 mL high density polyethlyene bottles until analysis.

Method 1: Solid Phase Extraction and 10 µL Injection

A mixture of surrogate standards (25 ng) was added to 250 mL water samples in the sampling bottle, and the entire volume was extracted using weak anion-exchange SPE as recommended by ISO standard 251016. The empty sample container was rinsed with 10 mL of methanol with 0.3% NH_4OH, which was then added to the SPE tube to elute the PFASs. The extract was evaporated to dryness, reconstituted in 500 µL of methanol/water (80:20), and transferred to a polypropylene vial for analysis. All standards and blanks were also prepared at a final methanol concentration of 80%.

For Method 1, 10 µL injections of the standards and samples were analyzed using a 6.5 minute gradient method (**Table 2**) with a 7.5 minute total runtime, including the 1 minute autosampler injection cycle. Water with 20 mM ammonium acetate was used as the "A" solvent and methanol was the "B" solvent.

Table 2.
LC Gradient for Method 1 at a Flow Rate of 0.6 mL/min

Step	Time (min)	A (%)	B (%)
0	0.00	90	10
1	0.10	45	55
2	4.50	1	99
3	4.95	1	99
4	5.00	90	10
End	6.50		

Method 2: Dilution and Large Volume Injection

A 1 mL aliquot of a water sample was added to a 2 mL clear glass autosampler vial with a polyethylene septum cap containing 0.65 mL of methanol and a mix of surrogate standards at a final concentration of 50 ng/L. The final concentration of methanol in the diluted sample was 40%, and standards, blanks, and quality control samples were all prepared at the same concentration. A PAL HTC-xt autosampler was modified to inject 950 µL of the diluted samples and standards.

For Method 2, samples were analyzed using an extended 15.5 minute gradient method (**Table 3**) with a 17.5 minute total runtime, including the 2 minute autosampler injection cycle. Water with 20 mM ammonium acetate was used as the "A" solvent, and methanol was the "B" solvent.

Table 3. LC Gradient for Method 2 at a Flow Rate of 0.6 mL/min

Step	Time (min)	A (%)	B (%)
0	0.00	90	10
1	1.50	35	65
2	8.00	5	95
3	8.10	1	99
4	12.00	1	99
5	12.50	90	10
End	15.50		

MS/MS Detection

A SCIEX Triple Quad™ 5500 system with a Turbo V™ source and ESI probe was used for analysis in negative polarity. The ion source parameters were optimized for the LC conditions using the Compound Optimization (FIA) function in Analyst® Software (**Table 4**).

Table 4.

Parameter	Value
Curtain Gas (CUR)	35 psi
IonSpray voltage (IS)	-4500 V
Temperature (TEM)	600°C
Nebulizer Gas (GS1)	50 psi
Heater Gas (GS2)	50 psi

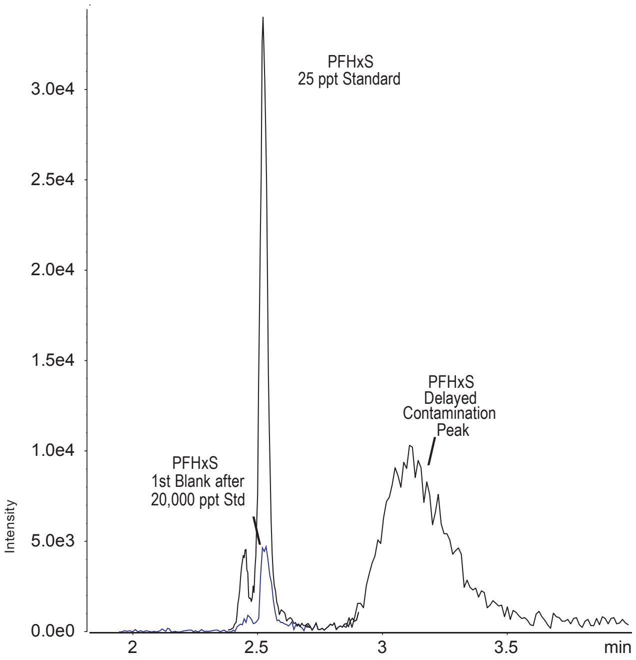
One characteristic MRM transition was monitored for each analyte and internal standard (Appendix **Table 1**). The *Scheduled* MRM™ algorithm was activated to monitor compounds only during a 60 second expected retention time window to maximize dwell times and optimize the cycle time of the method. As a result, all of the peaks in the calibration contained >12 points per peak. Calibration was performed using a 7-point curve at concentrations of 25, 50, 250, 1000, 2500, 10000, and 20000 ng/L for Method 1 and 1, 2, 5, 20, 50, 100, and 200 ng/L for Method 2. Quantitation was performed using MultiQuant™ 3.0.2 using 1.0 Gaussian smoothing and 1/x2 weighted linear regression. PFASs with matched isotopically labelled surrogate standards were quantified using isotope dilution, while PFASs without matched surrogate standards were quantified using internal standard calibration with structurally similar isotopically labeled standards (full analyte and internal standard list shown in Appendix **Figure 1**). A concentration factor of 500 was applied to samples analyzed using Method 1, and a dilution factor of 1.65 was applied to samples analyzed using Method 2.

Results and Discussion

Method 1 Chromatography

The Gemini® C18 column was selected for both methods based on its strong retention and predictable resolution of PFASs. All of the other columns tested exhibited breakthrough of the short chain acids in the column dead volume during optimization of the 950 µL injection method. The Luna® C18(2) column was selected as the delay column for both methods after initial testing indicated that it provided better separation of PFAS contamination than other columns. For PFASs, blank contamination is a major concern for analysis due to potential contamination during sample preparation or contamination originating from analytical instrumentation. **Figure 1** shows a small carryover peak at 2.5 minutes for PFHxS in a blank analyzed immediately following the injection of the highest calibration standard of 20,000 ng/L. The area of the carryover peak was only 0.078% of the highest standard and 21% of the lowest calibration standard for Method 1 (25 ng/L). The second peak at 3.2 minutes in **Figure 1** is attributed to delayed PFHxS contamination originating from the HPLC pumps. Without the delay column, this contamination would instead focus on the analytical column and elute at 2.5 minutes along with the standard and sample peak.

Figure 1.
Overlaid MRM traces for PFHxS in the lowest calibration standard (25 ng/L) and a blank injection that followed the highest concentration standard (20 µg/L). The delayed peak in the calibration standard trace represents the ambient LC system contamination retained by the delay column.

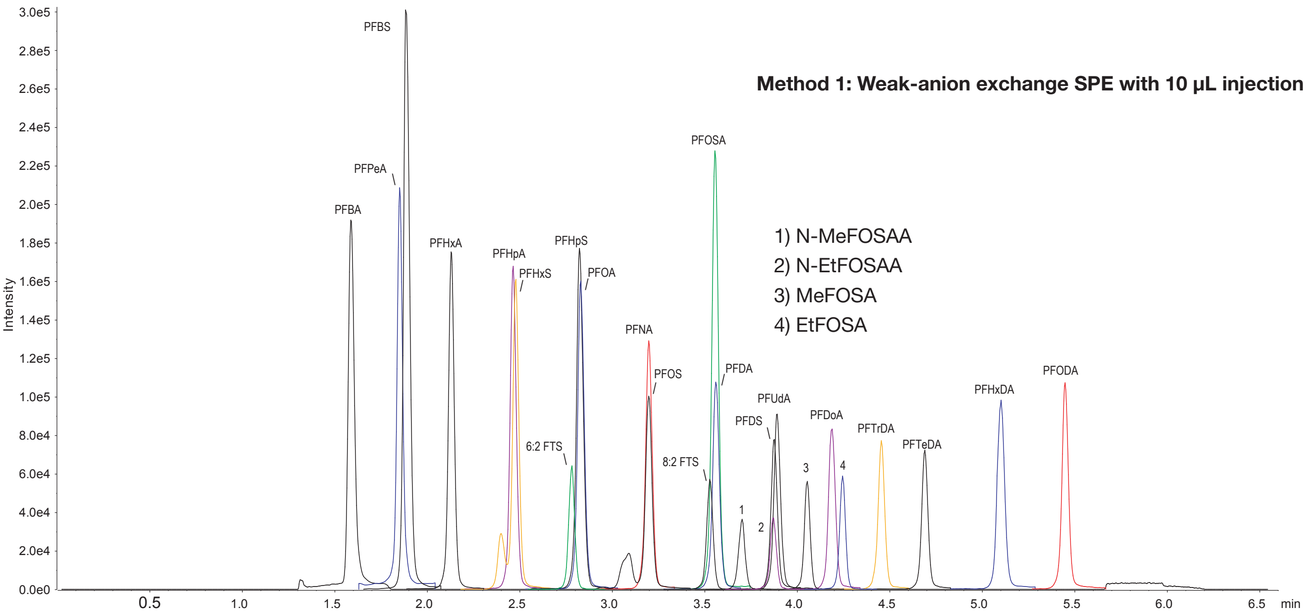


A 50 x 2.0 mm, 3 µm Gemini C18 column was selected for Method 1, which utilized a 10 µL injection volume. The chromatographic separation of 25 PFASs is shown in **Figure 2.**

The average peak asymmetry factor for the first 2 eluting peaks (PFBA and PFBS) in the initial calibration standards was calculated to be 1.3 in Method 1 using MultiQuant 3.0.2. This is within the acceptance criteria set by EPA 537 of 0.8-1.5 7.

Partial resolution of the branched and linear isotopes is necessary for PFAS analysis to distinguish between samples containing only linear isotopes or isotope mixtures. As shown in **Figure 2,** the earlier eluting branched isotopes are clearly distinguishable from the major peak corresponding to the linear isotopes for the 2 compounds that contained both branched and linear isotopes in the standards (PFHxS and PFOS). Most methods recommend that these two peaks are summed for quantitation, which was performed in this application note using MultiQuant 3.0.2.

Figure 2.
Overlaid Chromatograms of a 1 µg/L Standard Injected using Method 1.



Method 1 Calibration

The initial 7-point calibration for Method 1 exhibited good accuracy within +/- 30% of the expected values for all points, accuracy within +/- 10% for the lowest calibrator, and R^2 coefficients of >0.990, as shown in **Table 5**. Based on the S/N ratio of the low calibrator and the linearity of the curve, the calibration range could be extended on both the high and low levels to improve the dynamic range. A water sample analyzed using Method 1 exhibited concentrations of several PFASs ranging from 0.974 to 53.3 ng/L, as shown in **Figure 3.**

Method 2 Chromatography

Method 2 is a large-volume, direct aqueous injection method designed for drinking, surface, and ground water samples. After the addition of surrogate standards and a simple dilution with methanol, 950 µL of the sample was injected directly onto the Gemini® C18 column. In contrast to Method 1, a longer and larger diameter column was used to improve retention of the analytes in the large volume injection. This resulted in a longer total runtime (17.5 minutes compared with 7.5 minutes), but provided robust results for the large volume injection and minimal retention time shift (**Figure 4**). The only compound that exhibited deteriorated peak shape due to the large injection volume was PFBA. However, the broadened peak shape of PFBA did not affect quantitation accuracy or precision.

Figure 3. Overlaid Chromatograms of PFASs Quantified in a Water Sample using Method 1 (solid-phase extraction and 10 µL injection).

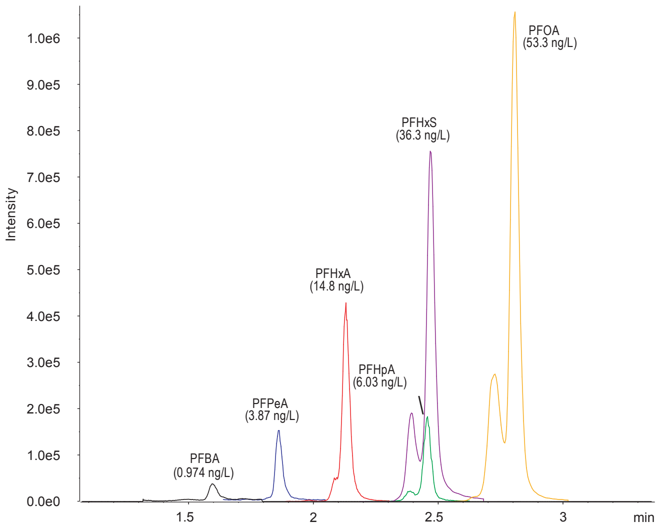
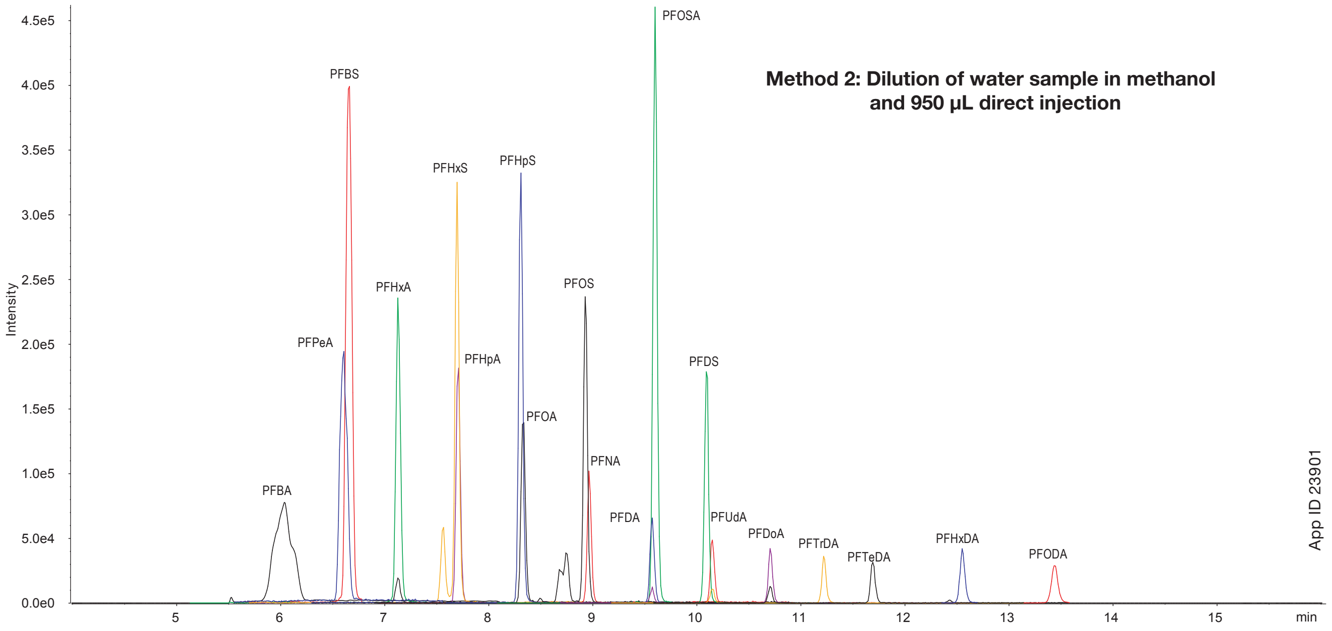


Table 5.
Sensitivity (S/N calculated using MultiQuant™ 3.0.2) and Linearity from 25 to 20,000 ng/L and 1 to 200 ng/L (coefficient of regression, R^2) using Method 1 and Method 2, respectively.

	Method 1			S/N	Method 2			
Compound	Calibration Range (ng/L)	Linear Correlation (R^2)	S/N of 25 ng/L Standard	Accuracy of 25 ng/L Standard	Calibration Range (ng/L)	Linear Correlation (R^2)	S/N of 1 ng/L Standard	Accuracy of 1 ng/L Standard
PFCAs								
PFBA	25-20,000	0.997	108	104%	1-200	0.997	328	97%
PFPeA	25-20,000	0.998	88	103%	1-200	0.999	137	101%
PFHxA	25-20,000	0.998	104	93%	1-200	0.999	284	101%
PFHpA	25-20,000	0.999	116	101%	1-200	0.993	267	96%
PFOA	25-20,000	0.999	117	106%	1-200	0.999	113	99%
PFNA	25-20,000	0.990	91	109%	1-200	0.999	137	101%
PFDA	25-20,000	0.998	103	105%	1-200	0.997	176	96%
PFUdA	25-20,000	0.995	84	101%	1-200	0.998	168	99%
PFDoA	25-20,000	0.998	60	101%	1-200	0.994	127	94%
PFTrDA	25-20,000	0.998	32	104%	1-200	0.995	125	95%
PFTeDA	25-20,000	0.994	15	107%	1-200	0.998	56	98%
PFHxDA	25-20,000	0.999	21	103%	1-200			
PFODA	25-20,000	0.999	33	102%	1-200			
PFSAs								
PFBS	25-20,000	0.995	31	92%	2-200	0.994	1178	100%
PFHxS	25-20,000	0.999	604	103%	1-200	0.998	229	96%
PFHpS	25-20,000	0.997	103	105%	1-200	0.999	327	99%
PFOS	25-20,000	0.995	312	105%	1-200	0.999	251	99%
PFDS	25-20,000	0.998	88	102%	1-200	0.999	516	98%
Other PFASs								
6:2 FTS	25-20,000	0.991	100	98%				
8:2 FTS	25-20,000	0.992	113	97%				
PFOSA	25-20,000	0.997	118	104%	1-100	0.997	1012	96%
MeFOSA	25-20,000	0.996	96	103%				
EtFOSA	25-20,000	0.994	90	101%				
N-MeFOSAA	25-20,000	0.996	109	100%				
N-EtFOSAA	25-20,000	0.994	61	103%				

Similar to Method 1, blank contamination from the instrument was minimized by using a delay column in Method 2. Blank contamination from sample preparation was also minimized in Method 2 by reducing the number of pipetting steps and testing all new batches of solvents prior to use. The integrated areas of the first blank after the highest concentration sample (200 ng/L) were less than 50% of the lowest calibrator. For example, the area of the first blank analyzed after the 200 ng/L calibration standard was 22% of the area of the 1 ng/L standard for PFOA as shown in **Figure 5**. The other blanks shown in **Figure 5** exhibited even lower response for PFOA, which could be contributed to laboratory contamination for the method blank and solvent contamination for the instrument blank.

Figure 4. Overlaid Chromatograms of a 10 ng/L Spike into Groundwater Matrix that was Diluted with Methanol and Injected According to Method 2



To be compatible with common sampling practices, Method 2 was not optimized for recovery of the longest chain PFASs, PFHxDA and PFODA, from the sample container or from the autosampler vial. Due to the stronger hydrophobicity of these compounds compared with the shorter chain PFAS, PFHxDA and PFODA appeared to bind to polypropylene containers when the methanol concentration was <40%. Modifications to this method to improve the recovery and precision of PFHxDA and PFODA analysis may include collecting smaller samples (10-20 mL), diluting the entire sample with methanol in the sampling container, and adding surrogate standard directly to the sampling container.

Direct analysis of water samples is impaired by the presence of 5g/L Trizma® in samples, which is added to drinking water samples as a requirement by EPA Method 537. Trizma suppresses ionization of the PFASs and elutes slowly from the column for minutes after the injection. Therefore, Trizma should not be added to samples that will be analyzed using direct aqueous injection, but is fully compatible with SPE as performed in Method 1.

Method 2 Calibration

Similar to Method 1, the initial calibration results for Method 2 exhibited good accuracy within +/- 30% of the expected values for all points, accuracy within +/- 10% for the lowest calibrator, and R^2 coefficients >0.990, as shown in **Table 5**. In the development of Method 2, calibration standards for 6:2 and 8:2 FTS, MeFOSA, EtFOSA, MeFOSAA, and EtFOSAA were not analyzed in the full calibration curve.

Figure 5. Overlaid PFOA Traces in a 1 ng/L Calibration Standard and a Series of Blank Injections Analyzed using Method 2: a blank injection following a high concentration standard, a method blank, and an instrument blank analyzed before the calibration standards.

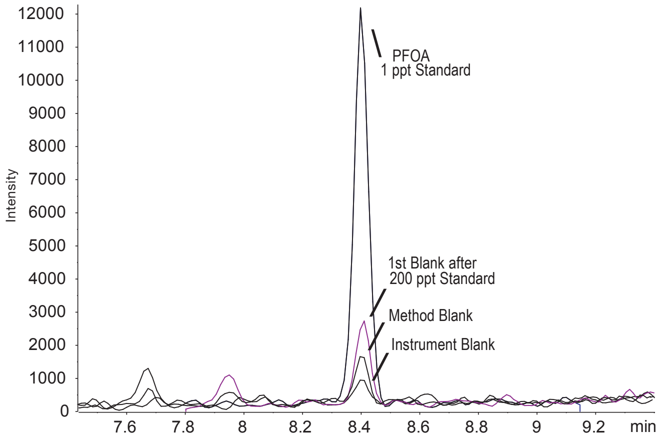
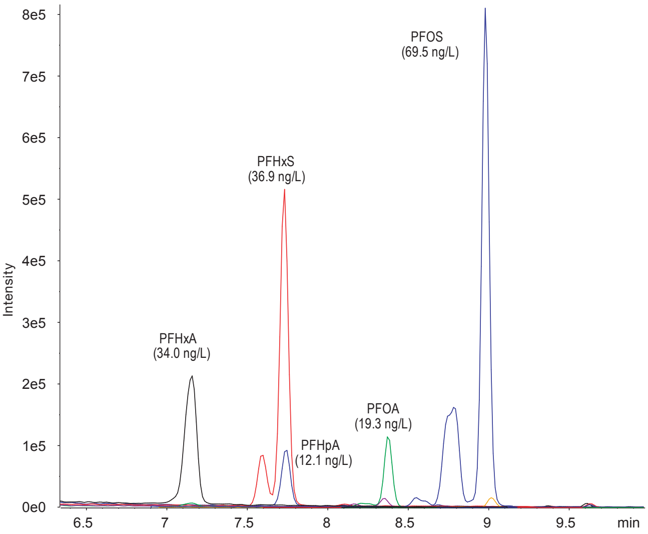


Figure 6. Overlaid MRM Traces of PFASs Detected in a Groundwater sample with the calculated concentrations of each PFAS. The sample was prepared and analyzed using Method 2.



Method 2 Performance

Because large-volume injection methods are less common for PFASs compared with offline extraction methods, this application note reports the recovery and precision of continuing calibration standards over 1 week of continuous water sample analysis to demonstrate the robustness and accuracy of Method 2. The chromatogram and quantitated values for several PFASs in one of these water samples are shown **Figure 6**.

As shown in **Table 6**, a continuing calibration standard at 20 ng/L analyzed 1 week after the initial calibration exhibited quantitative accuracy of 92-99% for all compounds with the exception of PFTrDA (81%) and PFBS (84%). Due to limited availability of surrogate standards, PFBS was analyzed using 18C2 PFHxS as an internal standard, and PFTrDA was analyzed using 13C2 PFDoA. The absence of an exact isotope-labelled surrogate for these two compounds likely contributed to the decreased accuracy of the ongoing calibration standard.

During the 1 week period of full-time water sample analysis, 9 replicates of the 20 ng/L continuing calibration verification (CCV) were analyzed as shown in **Table 6**. The precision (%CV) for all of the PFASs was <5%, which indicates excellent precision for the large volume injections. The surrogate recovery, calculated as the response of the surrogate standard in the 20 ng/L ongoing calibration standard divided by the response of the surrogate standard during the initial calibration, was within 73-120% for all of the PFASs analyzed.

Conclusion

The 2 methods reported in this application note were designed for optimum robustness using the SCIEX Triple Quad™ 5500 system as the analytical platform. Both methods may be expanded to include soil, sediment, and biological extracts. Minimum and maximum reporting limits of approximately 1 ng/L to 400 µg/L could be achieved using both methods. These ranges could be expanded by increasing the extracted volume in Method 1 or by further dilutions in Method 2. The example chromatograms shown in this application note also demonstrate that lower calibration levels than the levels analyzed here could be included in initial calibration curves to further improve the sensitivity of the method.

Method 1 has the advantage of compatibility with EPA Method 537 and allows for sample concentration using solid phase extraction. Method 2 has the advantages of minimal sample preparation and fewer steps to introduce lab-based PFAS contamination. With the growing need for PFAS analysis of environmental samples, these versatile methods are useful for labs aiming to evaluate growing lists of PFASs.

Table 6. Accuracy of a 20 ng/L CCV analyzed 1 week after the initial calibration and precision of 9 replicates of a 20 ng/L CCV analyzed between 5 and 7 days after the initial calibration using Method 2.

Compound	Calculated Conc. of 20 ng/L CCV	Accuracy of 20 ng/L CCV	Surrogate Standard Recovery	Precision of 9 20 ng/L CCVs (%CV)
PFCAs				
PFBA	19.4	96%	107%	1.50%
PFPeA	19.7	98%	107%	1.40%
PFHxA	19.7	99%	108%	2.26%
PFHpA*	18.5	92%	103%	3.11%
PFOA	19.2	96%	105%	2.07%
PFNA	19.3	97%	107%	1.11%
PFDA	19.4	97%	107%	2.62%
PFUdA	18.8	94%	109%	2.90%
PFDoA	18.7	94%	99%	1.90%
PFTrDA	16.3	81%	99%	4.77%
PFTeDA	18.9	95%	73%	1.43%
PFBS	16.8	84%	112%	2.65%
PFHxS	19.2	96%	112%	1.94%
PFHpS	19.4	97%	112%	3.85%
PFOS	18.8	94%	120%	2.62%
PFDS	18.6	93%	120%	2.69%
Other PFASs				
PFOSA	19.0	95%	112%	0.98%

Appendix Table 1. MRM masses for Methods 1 and 2. *Analytes are shown in bold font, and internal standards are shown in italic font.*

Compound	Q1	Q3	DP	CE
PFBA	212.9	169	-25	-12
PFPeA	262.9	219	-20	-12
PFHxA	313	269	-25	-12
PFHpA	363	319	-25	-12
PFOA	413	369	-25	-14
PFNA	463	419	-25	-14
PFDA	513	469	-25	-16
PFUdA	563	519	-25	-18
PFDoA	613	569	-25	-18
PFTrDA	663	619	-25	-20
PFTeDA	713	669	-25	-22
PFHxDA	813	769	-25	-24
PFODA	913	869	-25	-26
PFBS	298.9	80	-55	-58
PFHxS	399	80	-60	-74
PFHpS	449	80	-65	-88
PFOS	449	80	-65	-108
PFDS	599	80	-85	-118
6:2 FTS	427	407	-50	-32
8:2 FTS	527	507	-50	-40
PFOSA	498	78	-60	-85
MeFOSA	512	169	-75	-37
EtFOSA	526	169	-75	-37
N-MeFOSAA	570	419	-40	-36
N-EtFOSAA	584	419	-50	-36
13C4_PFBA	217	172	-25	-12
13C5_PFPeA	268	223	-20	-12
13C2_PFHxA	315	270	-25	-12
13C4_PFHpA	367	322	-25	-12
13C2_PFOA	415	370	-25	-14
13C4_PFOA	417	372	-25	-14
13C5_PFNA	468	423	-25	-14
13C2_PFDA	515	470	-25	-16
13C2_PFUdA	565	520	-25	-18
13C2_PFDoA	615	570	-25	-18
13C2_PFTeDA	715	670	-25	-22
13C2_PFHxDA	815	770	-25	-24
1802_PFHxS	403	84	-65	-74
13C4_PFOS	503	80	-65	-108
13C8_PFOSA	506	78	-65	-85
M2-6:2FTS	429	409	-50	-32
M2-8:2FTS	529	509	-50	-40
d3MeFOSA	515	169	-75	-37
d5EtFOSA	531	169	-75	-37
d3-MeFOSAA	573	419	-40	-36
d3-EtFOSAA	589	419	-50	-36

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SCIEX acknowledges TestAmerica (Sacramento, CA) for collaborating with SCIEX by providing and conducting the analysis of standards for this application note. SCIEX also acknowledges Phenomenex (Torrance, CA) for providing HPLC columns and expertise for this application note and other method development efforts.

Analysis of Perfluorinated Compounds (PFCs) by LC-MS/MS

Evaluating Various On-line SPE Sorbents

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Introduction

On-line SPE has been shown to be an excellent technique for analyzing aqueous matrices because it bypasses the "off-line" SPE time mentioned previously, increases sample throughput significantly[4], and requires a much smaller sample volume. Additionally, it can be just as sensitive due to the larger injection volume. The performance of three different on-line SPE sorbents was evaluated for this application; Strata® C18-E, Strata-X, and Strata-X-AW. Four PFC analyte classes were evaluated; Perfluoroalkyl acids (PFAAs), Perfluorosulfonates (PFSAs), Perfluorosulfonamidoacetic acids (FOSAAs), and Fluorotelomersulfonates (FTSs). We present data on the pros and cons of each sorbent as well as sensitivity, accuracy, and precision.

Materials and Methods

Materials

LC Column:	Kinetex® 5 µm EVO C18 100A
Dimensions:	100 x 2.1 mm
Part No.:	00D-4633-AN
Guard Column:	SecurityGuard™ ULTRA Cartridges
Part No.:	AJ0-9298
On-line SPE:	Strata-X-AW 33 µm Polymeric Weak Anion-Exchange
Dimensions:	20 x 2.0 mm
Part No.:	00M-S038-B0-CB
Online SPE Cartridge Holder:	20 mm Cartridge Holder
Part No.:	CH0-5845
Sample Filters:	Phenex™ Glass Fiber 1.2 µm 28 mm
Part No.:	AF0-8515-12

Sample Preparation Procedure

1. Samples are collected in polypropylene bottles and preserved with 0.5 g/L Trizma®.
2. A 10 mL aliquot is spiked with surrogates at a concentration of 50 ng/L.
3. If necessary, filter using a 10 mL syringe fitted to a 1.2 µm glass fiber syringe filter.
4. The filtered sample is spiked with internal standard at 50 ng/L.
5. The filtered sample is loaded and analyzed using a 5.0 mL injection volume.
6. The on-line SPE is completely automated; it includes a sample wash step (2.1 to 4.1 min) to wash Trizma preservative from the media.

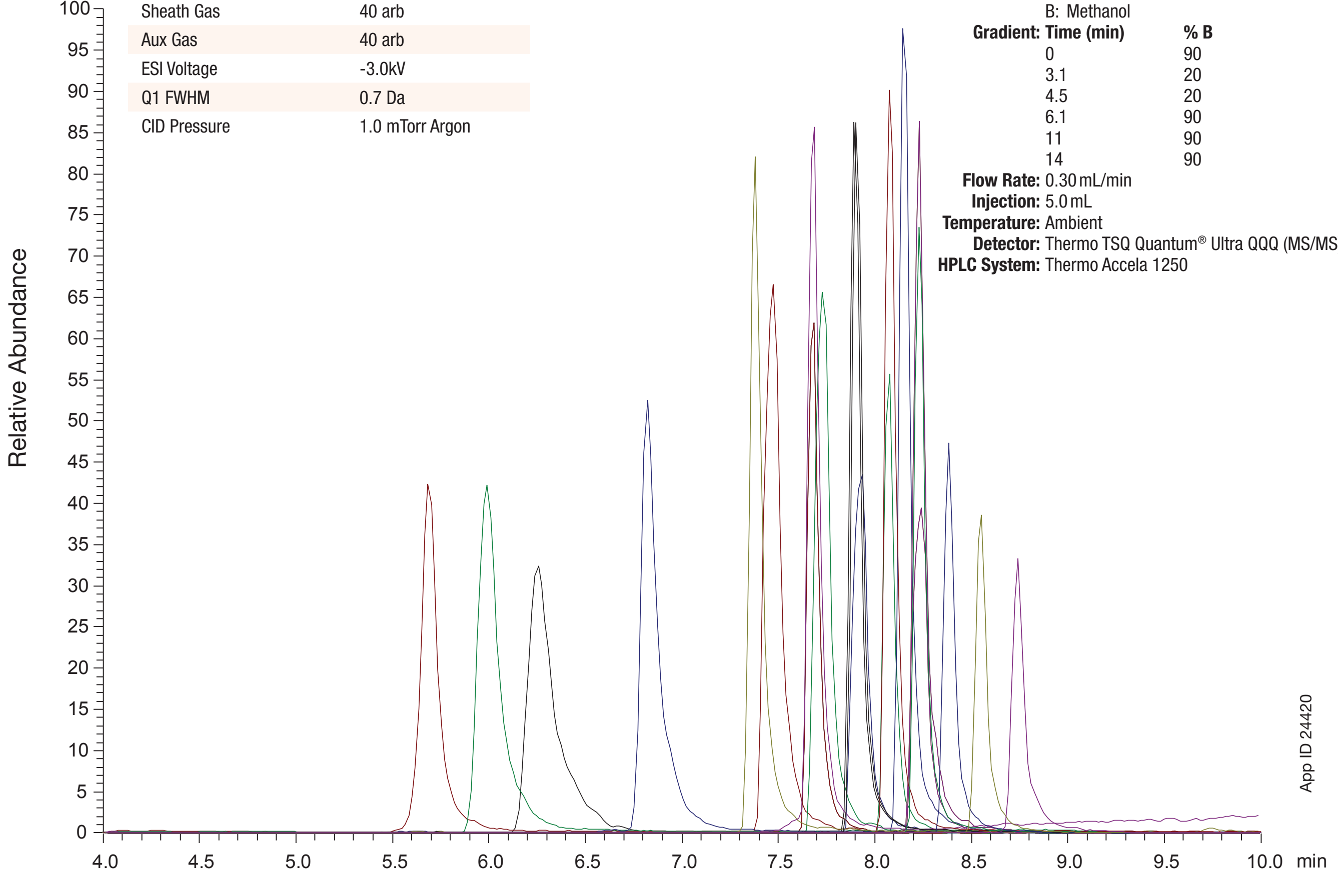
Instrumentation

LC Pump 1: Thermo Accela® 1200, Flow 300 µL/min
LC Pump 2: Thermo Accela 600 (see table for flow rates)
Autosampler Parameters: Transfer Time 250 sec, Elution Time 290 sec

Mass Spectrometer: Thermo TSQ Quantum Ultra

LC-MS/MS Conditions

Column:	Kinetex® 5 µm EVO C18 100Å	
Dimensions:	100 x 2.1 mm	
Part No.:	00D-4633-AN	
Mobile Phase:	A: 0.4 % v/v Ammonium hydroxide in Water B: Methanol	
Gradient:	**Time (min)**	**% B**
	0	90
	3.1	20
	4.5	20
	6.1	90
	11	90
	14	90
Flow Rate:	0.3 mL/min	
Injection:	5.0 mL	
Temperature:	Ambient	
Detector:	Thermo TSQ Quantum® Ultra QQQ (MS/MS)	
HPLC System:	Thermo Accela 1250	



MS Source Parameters:

Capillary Temp	150 °C
Vaporizer Temp	250 °C
Sheath Gas	40 arb
Aux Gas	40 arb
ESI Voltage	-3.0kV
Q1 FWHM	0.7 Da
CID Pressure	1.0 mTorr Argon

LC-MS/MS Conditions

Column: Kinetex® 5 µm EVO C18 100Å
Dimensions: 100 x 2.1 mm
Part No.: 00D-4633-AN
Mobile Phase: A: 0.4 % v/v Ammonium Hydroxide in Water
B: Methanol

Gradient:

Time (min)	% B
0	90
3.1	20
4.5	20
6.1	90
11	90
14	90

Flow Rate: 0.30 mL/min
Injection: 5.0 mL
Temperature: Ambient
Detector: Thermo TSQ Quantum® Ultra QQQ (MS/MS)
HPLC System: Thermo Accela 1250

LC Gradient (pump 1)

Time	Water	MeOH	0.4 % NH_3
0.00	0	90	10
3.10	20	20	60
4.50	20	20	60
6.10	0	90	10
11.00	0	90	10
14.00	0	90	10

Note: To decrease PFOA contributed by the eluent system, MeOH is kept at 90 % while loading the on-line SPE with sample and subsequently brought down to 20 % 1 min prior to on-line SPE elution.

On-line SPE Program (pump 2)

Time	Water	MeOH	ACN	Flow mL/min	Comments
0.00	100	0	0	2.5	Sample Loading
2.00	100	0	0	2.5	Sample Loading
2.10	100	0	0	2.5	SPE Wash
4.10	100	0	0	2.5	SPE Wash
4.11	30	70	0	0	Idle (Elution in to LC)
9.00	30	70	0	0	Idle (Elution in to LC)
9.01	0	0	100	2.0	ACN Wash
9.49	0	0	100	2.0	ACN Wash
9.50	2.0	98	0	3.0	MeOH Wash
11.50	2.0	98	0	3.0	MeOH Wash
11.51	100	0	0	3.0	Cond: Water
14.00	100	0	0	3.0	Cond: Water

Chemical Abbreviations: Methanol (MeOH); Acetonitrile (ACN); Ammonia (NH_3); Ammonium Hydroxide (NH_4OH); Ammonium Acetate (NH_4OAc)

On-line SPE is available in

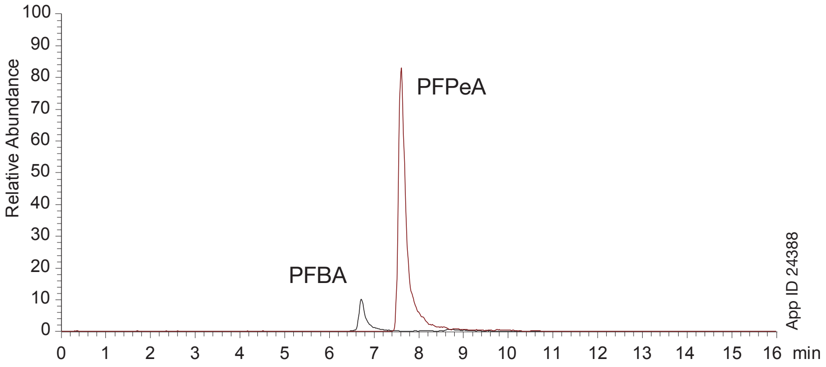
- Strata C18, C8
- Strata-X, X-C, X-CW, X-A, X-AW

Table 1.
Performance of Evaluated On-line SPE and HPLC Conditions

Options	Column	Strata® SPE Sorbent Phase	Sample pH	SPE Conditioning pH	Eluent*	PFBA / PFPeA %	Shape
1	Kinetex® EVO C18 5 µm 100 x 2.1 mm	X-AW	Trizma® (pH=7)	neutral	0.24-0.04 % NH_3	100	excellent
2	Kinetex EVO C18 5 µm 50 x 2.1 mm	X-AW	neutral	neutral	0.04 % NH_3	106	very poor
3	Kinetex EVO C18 5 µm 50 x 2.1 mm	X-AW	neutral	neutral	0.24-0.04 % NH_3	76	OK
4	Kinetex EVO C18 5 µm 50 x 2.1 mm	X-AW	acidic	neutral	0.02 % Formic Acid	13	OK
5	Luna® Omega C18 1.6 µm 50 x 2.1 mm	C18	neutral	neutral	2 mM NH_4OAc	<1	—
6	Luna Omega C18 1.6 µm 50 x 2.1 mm	C18	acidic (pH=2)	acidic (pH=2)	0.02 % Formic Acid	22	very poor
7	Luna Omega C18 1.6 µm 50 x 2.1 mm	C18	acidic (pH=2)	acidic (pH=2)	2 mM NH_4OAc	11	OK
8	Luna Omega C18 1.6 µm 50 x 2.1 mm	C18	neutral	acidic (pH=2)	2 mM NH_4OAc	11	OK
9	Luna Omega C18 1.6 µm 50 x 2.1 mm	X	neutral	neutral	2 mM NH_4OAc	5.9	poor
10	Luna Omega C18 1.6 µm 50 x 2.1 mm	X	acidic	neutral	2 mM NH_4OAc	5.1	poor

* Note: All eluents used a gradient of increasing methanol for elution.

Figure 1.
On-line SPE using C18-E Sorbent and 2.0 mM Ammonium Acetate Mobile Phase Modifier on a Luna Omega C18 LC Column



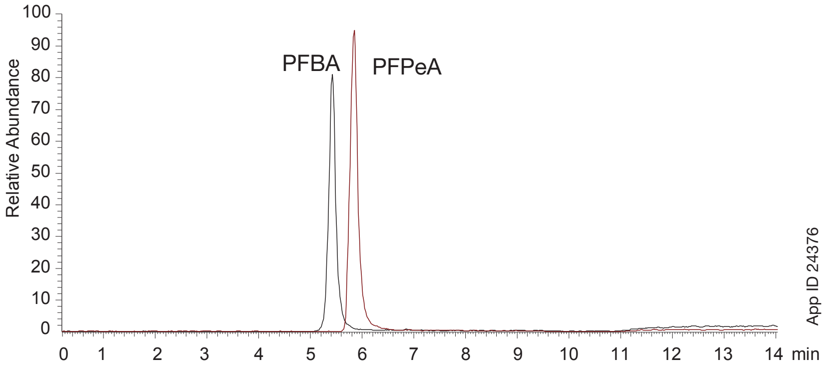
LC-MS/MS Conditions

Column: Luna Omega 1.6 µm C18 100Å
Dimensions: 50 x 2.1 mm
Part No.: 00B-4742-AN
Mobile Phase: A: 2 mM Ammonium acetate in Water
B: Methanol
Gradient:

Time (min)	% B
0	40
4.1	40
6.1	90
13	90
13.01	40
16	40

Flow Rate: 0.2 mL/min
Injection: 5 mL
Detector: Thermo TSQ Quantum® Ultra QQQ (ms/ms)
HPLC System: Thermo Accela® 1250

Figure 2.
On-line SPE using Strata-X-AW Sorbent and 0.4-0.8 % Ammonia Mobile Phase Modifier on a Kinetex C18 EVO LC Column (final conditions)



LC-MS/MS Conditions

Column: Kinetex 5 µm EVO C18 100Å
Dimensions: 100 x 2.1 mm
Part No.: 00D-4633-AN
Mobile Phase: A: 0.4 % v/v Ammonium hydroxide in Water
B: Methanol
Gradient:

Time (min)	% B
0	90
3.1	20
4.5	20
6.1	90
11	90
14	90

Flow Rate: 0.3 mL/min
Injection: 5 mL
Temperature: Ambient
Detector: Thermo TSQ Quantum Ultra QQQ (ms/ms)
HPLC System: Thermo Accela 1250

Figure 3.
Elution Strength of 0.04 % NH_3 (left) and 0.24 % NH_3 (Right) Illustrating More Efficient Elution of Analytes (PFBA and PFPeA) with Increased Base Concentration in the Mobile Phase.

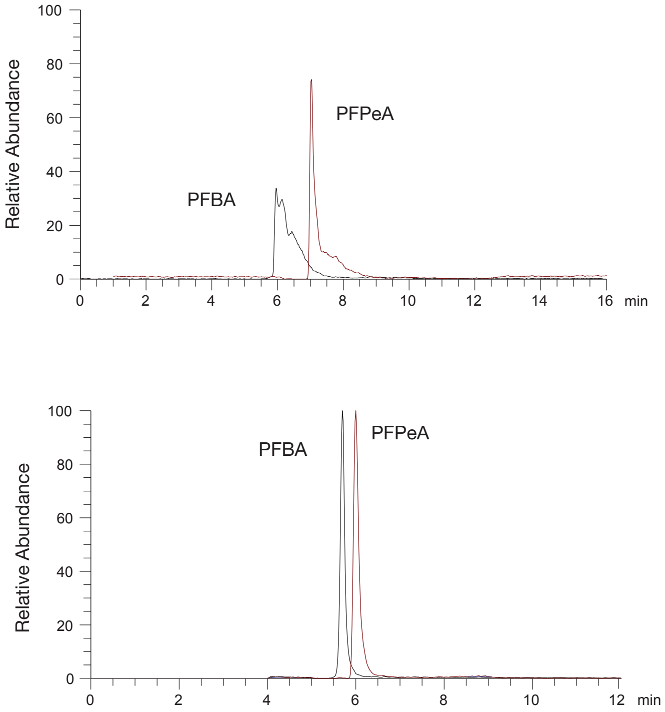


Figure 4.
Effect of Filtering on Recovery of Long Chain PFCs.

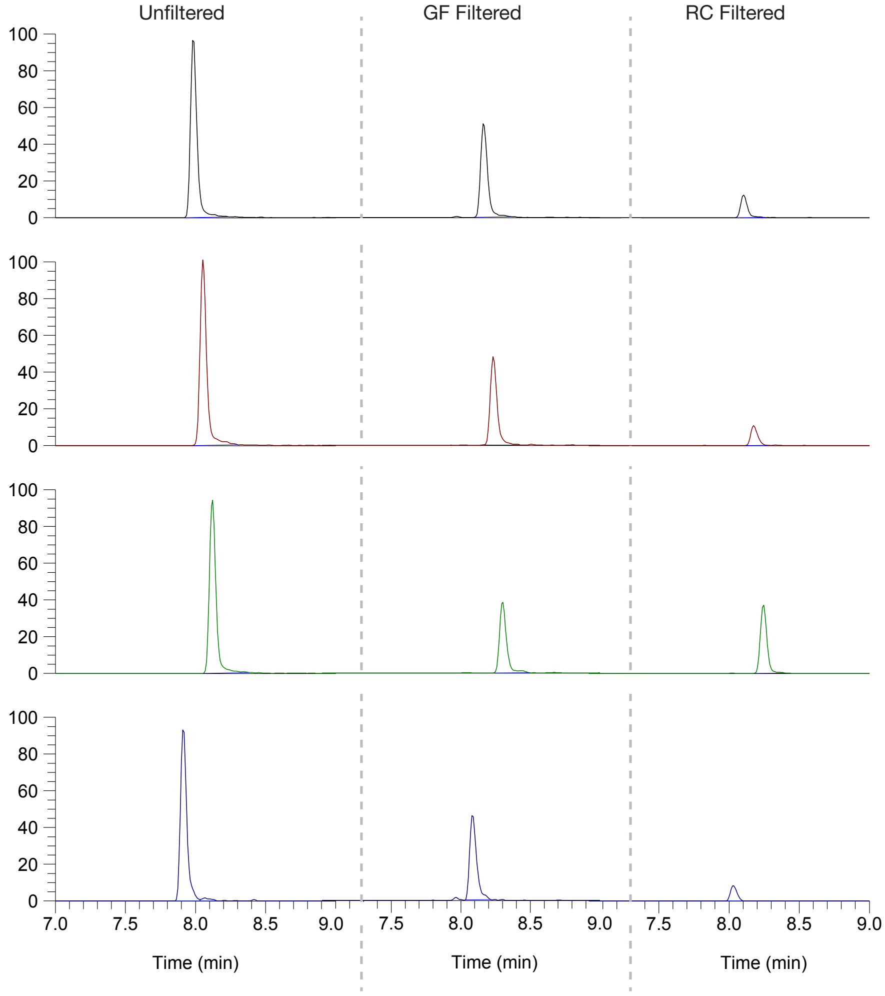
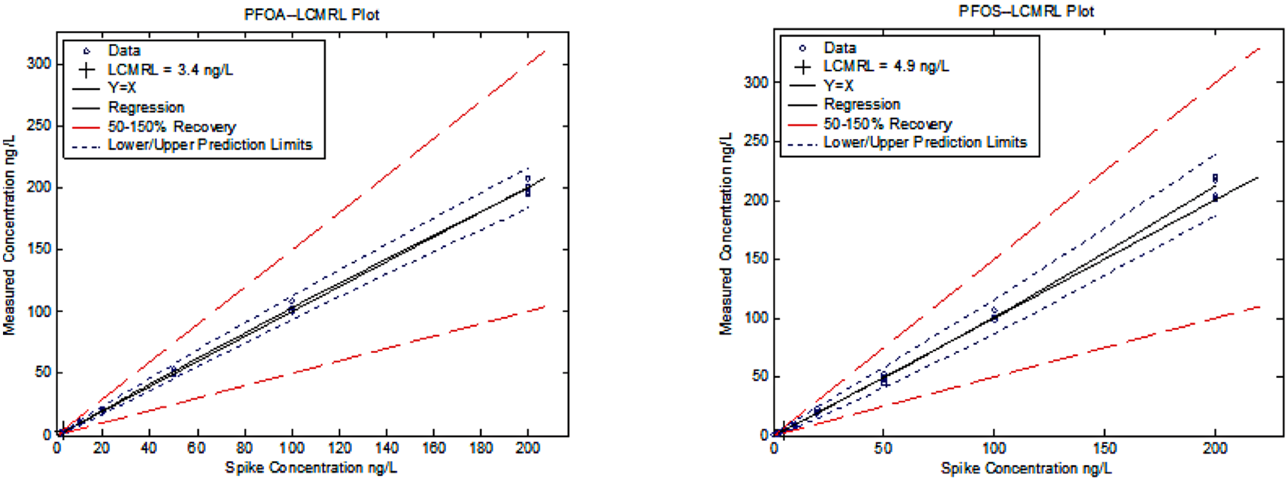


Figure 5.
LCMRL Plot of PFOA and PFOS Showing the Relationship of the Data to the Predicted Limits. The LCMRL is the Highest Value of the Upper and Lower Prediction Limit Intersection Points with the 50-150 % Criteria.



Results & Discussion

One of the first objectives was to find the best SPE sorbent that would cover the target analytes. **Table 1** summarizes the options that were investigated. It quickly became apparent during development that the earliest eluter (lowest molecular weight) analyte was to be the indicator of SPE performance. As such the relative responses of PFBA and PFPeA were tabulated as well as the peak shape in order to meet data quality objectives similar to EPA Method 537. The peak shape of the first 2 eluting peaks is addressed in EPA Method 537 with a requirement for peak asymmetry factor. It should be noted (lines 1 and 3 in the table) that the Trizma® preservative marginally improved the PFBA relative to PFPeA.

It was experimentally determined that the same elution conditions (Methanol and 2.0 mM NH_4OAc) used Strata® for C18 or Strata-X on-line SPE could not work on the Strata-X-AW. Incidentally the mechanism used in weak anion-exchange (high pH elution) is quite different than the one employed using C18. Due to limitations on standard silica C18 analytical columns and online SPE, which typically cannot operate at high pH, a different approach was chosen. The analytical column chosen was a Kinetex® EVO C18 50 x 2.1 mm due to its extended pH operability range. This does result in some retention time differences when comparing the analytical systems. For this reason and due to variability associated with electrospray ionization, response was evaluated relative to other analytes to evaluate performance.

The Strata-X-AW provided a significant improvement in trapping smaller chain PFCs. **Figure 1** shows a chromatogram of PFBA (6.71 min) and PFPeA (7.61 min) using a C18 on-line SPE cartridge and 2.0 mM ammonium acetate. Note that the response of PFBA is 11 % of the PFPeA response using C18 however this value rises noticeably to 76 % when using Strata-X-AW (**Figure 2**). This seems to be a simple limitation of using C18 for small organic acids even if the sample is acidified. The same effect was observed for the sulfonates PFBS and PFHxS, but to a lesser degree.

Another aspect of this analysis that was investigated was the ability to filter aqueous samples. This has a direct effect on whether the method could be adapted to aqueous soil extracts. Two types of filters were evaluated; glass fiber (Phenex™ GF) and regenerated cellulose (Phenex RC). The biggest impact filtering has on analytes is with longer chain PFCs like PFDoDA, PFTrDA, PFTeDA, and PFDS. **Figure 4** is a comparison between unfiltered, glass fiber filtration, and regenerated cellulose filtration (left to right).

Conclusion

Balancing the performance across the wide range of analytes, the Strata-X-AW provides the most robust on-line SPE, especially if short chain PFCs are of interest. To assess performance as compared to EPA Method 537 methodology using the Strata-X-AW, a LCMRL (lowest concentration minimum reporting level) study was performed in Trizma® preserved water to determine the lowest concentration at which an accuracy of 50-150 % can be achieved with a confidence of 99 %. Additionally, a DL (detection limit) study was performed to determine the lowest concentration at which an analyte can be detected at 99 % confidence without an accuracy limit. The results of this study are listed in **Table 2** along with results from EPA Method 537.

While all 3 SPE sorbents evaluated could be used for PFC analysis, the Strata-X-AW shows markedly improved recoveries for the widest analyte class. This is not surprising considering off-line SPE using weak anion-exchange is fairly robust in other matrices[2,3]. However, if only certain priority PFCs are required such as PFOA and PFOS, C18 would provide adequate peak shape and recovery. One caveat with this system is that the sample pH should be adjusted to 2 using formic acid and the sorbent should be conditioned using 0.2 % formic acid. This provides sufficient strength to protonate and trap analytes.

Table 2.
Performance Comparison of the On-line SPE (Strata®-X-AW) Method with EPA Method 537

Analyte	On-line SPE LCMRL	On-line SPE DL	EPA 537 LCMRL*	EPA 537 DL**
PFBA	9.8	1.4	-	-
PFPeA	5.9	0.9	-	-
PFHxA	1.4	0.9	2.9	1.6
PFHpA	5.0	0.5	3.8	0.5
PFOA	3.4	2.0	5.1	1.7
PFNA	3.5	0.8	5.5	0.7
PFDA	11	1.2	3.8	0.7
PFUnDA	14	1.2	6.9	2.8
PFDoA	17	2.5	3.5	1.1
PFTrDA	12	3.3	3.8	2.2
PFTeDA	12	2.1	4.7	1.7
PFBS	6.3	1.6	3.7	3.1
PFHxS	5.5	1.5	8.0	2.0
PFHpS	6.5	1.8	-	-
PFOS	4.9	3.2	6.5	1.4
PFDS	11	4.5	-	-
6:2-FTS	4.1	0.8	-	-
8:2-FTS	5.1	1.7	-	-
N-MeFOSAA	14	2.7	14	6.5
N-EtFOSAA	12	3.2	14	4.2

* LCMRL is the lowest concentration minimum reporting level[6]
** DL is the detection limit[6]

With the advent of analytical LC columns like the Kinetex® EVO C18 core-shell that can support a higher pH, it's possible to couple weak anion-exchange on-line SPE to a suitable analytical column. Additionally, the use of aqueous ammonia in the eluent has no limiting factors when coupled to MS due to its volatility, and preliminary data show that ammonia provides better ionization than ammonium acetate. Glass fiber filters can allow samples to be filtered without detrimentally affecting performance. This makes it possible to further expand the applicability of the method. For example, one method of extracting PFCs from soil uses methanol followed by SPE cleanup[5]. It's quite possible that a large volume (0.5-1.0 mL) of methanol could be filtered using glass fiber, diluted with water, and pre-concentrated using a Strata-X-AW as described above. Preliminary tests show that up to 10 % methanol can be injected onto Strata-X-AW before the high organic starts affecting the smallest acids (i.e.: PFBA).

References

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4. Bersuker, I.B. *Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory;* Wiley & Sons: New York, **1996**; Chapter

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5\. Strynar, Mark J., Andrew B. Lindstrom, Shoji F. Nakayama, Peter P. Egeghy, and Laurence J. Helfant. “Pilot Scale Application of a Method for the Analysis of Perfluorinated Compounds in Surface Soils.” Chemosphere 86, no. 3 (January 2012): 252–57. doi:10.1016/j.chemosphere.2011.09.036.

6\. Martin, John J., Stephen D. Winslow, and David J. Munch. “A New Approach to Drinking-Water-Quality Data: Lowest-Concentration Minimum Reporting Level.” Environmental Science & Technology 41, no. 3 (February 2007): 677–81. doi:10.1021/es072456n

Acknowledgements

We would especially like to thank David Schiessel and BABCOCK Laboratories for developing and contributing this application.

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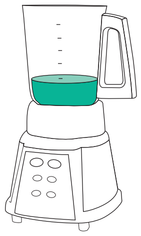
Step 1

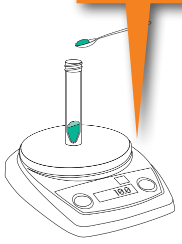
Extraction

Easily Weigh Out Samples

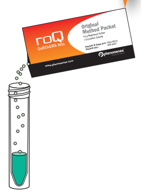
No Mess Salt Packets



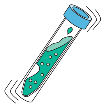
Blend fruits or vegetables to be analyzed.



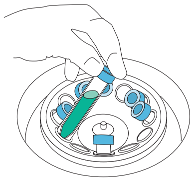
Weigh blended sample.



Add salts and acetonitrile.



Shake tube for 1 minute.

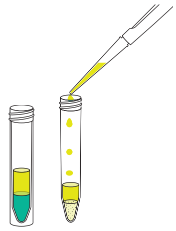


Centrifuge tube for 5 minutes.

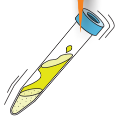
Step 2

Clean Up/dSPE

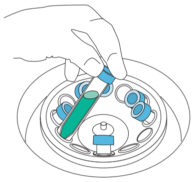
Avoid Leaky Tubes! Our tubes are designed to seal completely



Add supernatant from extraction procedure into a roQ dSPE tube.



Shake dSPE tube for 30 seconds.



Centrifuge dSPE tube for 5 minutes.

roQ Extraction Kits

Extraction kits contain fifty easy-pour salt packets and fifty 50 mL stand-alone centrifuge tubes

Description	Unit	Part No.
AOAC 2007.01 Method Extraction Kits		
6.0 g MgSO$_4$, 1.5 g NaOAc	50/pk	KS0-8911*
EN 15662 Method Extraction Kits		
4.0 g MgSO$_4$, 1.0 g NaCl, 1.0 g SCTD, 0.5 g SCDS	50/pk	KS0-8909*
Original Non-buffered Method Extraction Kits		
4.0 g MgSO$_4$, 1.0 g NaCl	50/pk	KS0-8910
6.0 g MgSO$_4$, 1.5 g NaCl	50/pk	KS0-8912

*AOAC and EN Extraction Kits also available in traditional non-collared 50 mL centrifuge tubes, Part No.: KS0-8911-NC and KS0-8909-NC

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dSPE kits contain pre-weighed sorbents/salts inside 2 mL or 15 mL centrifuge tubes

Description	Unit	Part No.
2 mL dSPE Kits		
150 mg MgSO$_4$, 25 mg PSA, 25 mg C18E	100/pk	KS0-8913
150 mg MgSO$_4$, 25 mg PSA, 2.5 mg GCB	100/pk	KS0-8914
150 mg, MgSO$_4$, 25 mg PSA, 7.5 mg GCB	100/pk	KS0-8915
150 mg MgSO$_4$, 25 mg PSA	100/pk	KS0-8916
150 mg MgSO$_4$, 50 mg PSA, 50 mg C18E, 50 mg GCB	100/pk	KS0-8917
150 mg MgSO$_4$, 50 mg PSA, 50 mg C18E	100/pk	KS0-8918
150 mg MgSO$_4$, 50 mg PSA, 50 mg GCB	100/pk	KS0-8919
150 mg MgSO$_4$, 50 mg PSA	100/pk	KS0-8920
15 mL dSPE Kits		
900 mg MgSO$_4$, 150 mg PSA, 150 mg C18E	50/pk	KS0-8921
900 mg MgSO$_4$, 150 mg PSA, 15 mg GCB	50/pk	KS0-8922
900 mg MgSO$_4$, 150 mg PSA, 45 mg GCB	50/pk	KS0-8923
900 mg MgSO$_4$, 150 mg PSA	50/pk	KS0-8924
1200 mg MgSO$_4$, 400 mg PSA, 400 mg C18E, 400 mg GCB	50/pk	KS0-8925
1200 mg MgSO$_4$, 400 mg PSA, 400 mg C18E	50/pk	KS0-8926
1200 mg MgSO$_4$, 400 mg PSA, 400 mg GCB	50/pk	KS0-8927
1200 mg MgSO$_4$, 400 mg PSA	50/pk	KS0-8928

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Tubes	1 mL (100/box)		3 mL (50/box)			6 mL (30/box)		
Phase	**50 mg**	**100 mg**	**100 mg**	**200 mg**	**500 mg**	**200 mg**	**500 mg**	**1 g**
C18-E	8B-S001-DAK	8B-S001-EAK	8B-S001-EBJ	8B-S001-FBJ	8B-S001-HBJ	8B-S001-FCH	8B-S001-HCH	8B-S001-JCH
C18-U	—	8B-S002-EAK	—	8B-S002-FBJ	8B-S002-HBJ	—	8B-S002-HCH	8B-S002-JCH
C18-T	—	8B-S004-EAK	—	8B-S004-FBJ	8B-S004-HBJ	—	8B-S004-HCH	8B-S004-JCH
C8	—	8B-S005-EAK	—	8B-S005-FBJ	8B-S005-HBJ	—	8B-S005-HCH	8B-S005-JCH
Phenyl	—	8B-S006-EAK	—	8B-S006-FBJ	8B-S006-HBJ	—	8B-S006-HCH	8B-S006-JCH
SCX	—	8B-S010-EAK	8B-S010-EBJ	8B-S010-FBJ	8B-S010-HBJ	—	8B-S010-HCH	8B-S010-JCH
WCX	—	8B-S027-EAK	—	8B-S027-FBJ	8B-S027-HBJ	—	8B-S027-HCH	8B-S027-JCH
SAX	—	8B-S008-EAK	8B-S008-EBJ	8B-S008-FBJ	8B-S008-HBJ	—	8B-S008-HCH	8B-S008-JCH
NH_2	—	8B-S009-EAK	—	8B-S009-FBJ	8B-S009-HBJ	—	8B-S009-HCH	8B-S009-JCH
CN	—	8B-S007-EAK	—	8B-S007-FBJ	8B-S007-HBJ	—	8B-S007-HCH	8B-S007-JCH
Si-1	—	8B-S012-EAK	—	8B-S012-FBJ	8B-S012-HBJ	—	8B-S012-HCH	8B-S012-JCH
Florisil®	—	—	—	—	8B-S013-HBJ	—	8B-S013-HCH	8B-S013-JCH
EPH	—	—	—	—	8B-S031-HBJ	—	—	—
AL-N	—	—	—	—	8B-S313-HBJ	—	—	8B-S313-JCH
SDB-L (Polymeric)	8B-S014-DAK	8B-S014-EAK	—	8B-S014-FBJ	8B-S014-HBJ	8B-S014-FCH	8B-S014-HCH	8B-S014-JCH

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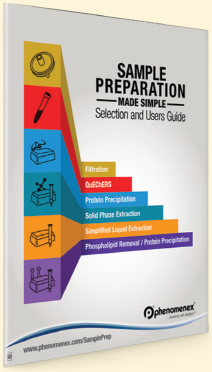
Tubes	1 mL (100/box)		3 mL (50/box)			6 mL (30/box)		
Phase	**30 mg**	**60 mg**	**60 mg**	**200 mg**	**500 mg**	**100 mg**	**200 mg**	**500 mg**
Strata-X	8B-S100-TAK	8B-S100-UAK	8B-S100-UBJ	8B-S100-FBJ	8B-S100-HBJ	8B-S100-ECH	8B-S100-FCH	8B-S100-HCH
Strata-X-C	8B-S029-TAK	—	8B-S029-UBJ	8B-S029-FBJ	8B-S029-HBJ	8B-S029-ECH	8B-S029-FCH	8B-S029-HCH
Strata-X-CW	8B-S035-TAK	—	8B-S035-UBJ	8B-S035-FBJ	8B-S035-HBJ	8B-S035-ECH	8B-S035-FCH	8B-S035-HCH
Strata-X-A	8B-S123-TAK	—	8B-S123-UBJ	8B-S123-FBJ	8B-S123-HBJ	8B-S123-ECH	8B-S123-FCH	8B-S123-HCH
Strata-X-AW	8B-S038-TAK	—	8B-S038-UBJ	8B-S038-FBJ	8B-S038-HBJ	8B-S038-ECH	8B-S038-FCH	8B-S038-HCH
Strata-XL	8B-S043-TAK	—	8B-S043-UBJ	8B-S043-FBJ	8B-S043-HBJ	8B-S043-ECH	8B-S043-FCH	8B-S043-HCH
Strata-XL-C	8B-S044-TAK	—	8B-S044-UBJ	8B-S044-FBJ	8B-S044-HBJ	8B-S044-ECH	8B-S044-FCH	8B-S044-HCH
Strata-XL-CW	8B-S052-TAK	—	8B-S052-UBJ	8B-S052-FBJ	8B-S052-HBJ	8B-S052-ECH	8B-S052-FCH	8B-S052-HCH
Strata-XL-A	8B-S053-TAK	—	8B-S053-UBJ	8B-S053-FBJ	8B-S053-HBJ	8B-S053-ECH	8B-S053-FCH	8B-S053-HCH
Strata-XL-AW	8B-S051-TAK	—	8B-S051-UBJ	8B-S051-FBJ	8B-S051-HBJ	8B-S051-ECH	8B-S051-FCH	8B-S051-HCH

Strata On-line SPE

On-line Extraction Cartridge	Dimensions	Part No.
Strata C18	20 x 2.0 mm	00M-S039-B0-CB
Strata C8	20 x 2.0 mm	00M-S101-B0-CB
Strata-X	20 x 2.0 mm	00M-S033-B0-CB
Strata-X-A	20 x 2.0 mm	00M-S132-B0-CB
Strata-X-AW	20 x 2.0 mm	00M-S038-B0-CB
Strata-X-C	20 x 2.0 mm	00M-S048-B0-CB
Strata-X-CW	20 x 2.0 mm	00M-S036-B0-CB
Cartridge Holder	20 mm	CH0-5845



HPLC/UHPLC Columns

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3 µm Microbore, Minibore and MidBore™ Columns (mm)										SecurityGuard™ Cartridges (mm)
Phases	**50 x 1.0**	**20 x 2.0**	**30 x 2.0**	**50 x 2.0**	**100 x 2.0**	**150 x 2.0**	**50 x 3.0**	**100 x 3.0**	**150 x 3.0**	**4 x 2.0* (10/pk)**
Gemini C18	00B-4439-A0	00M-4439-B0	00A-4439-B0	00B-4439-B0	00D-4439-B0	00F-4439-B0	00B-4439-Y0	00D-4439-Y0	00F-4439-Y0	AJ0-7596
										for ID: 2.0-3.0 mm

Luna®

5 µm Microbore and Minibore Columns (mm)								SecurityGuard™ Cartridges (mm)
Phases	**50 x 1.0**	**150 x 1.0**	**250 x 1.0**	**30 x 2.0**	**50 x 2.0**	**150 x 2.0**	**250 x 2.0**	**4 x 2.0* (10/pk)**
Luna C18(2)	00B-4252-A0	00F-4252-A0	00G-4252-A0	00A-4252-B0	00B-4252-B0	00F-4252-B0	00G-4252-B0	AJ0-4286
								for ID: 2.0-3.0 mm

Luna Omega

1.6 µm Minibore Columns (mm)					SecurityGuard™ ULTRA Cartridges‡
Phases	**30 x 2.1**	**50 x 2.1**	**100 x 2.1**	**150 x 2.1**	**3/pk**
Polar C18	00A-4748-AN	00B-4748-AN	00D-4748-AN	00F-4748-AN	AJ0-9505
C18	00A-4742-AN	00B-4742-AN	00D-4742-AN	00F-4742-AN	AJ0-9502
					for 2.1 mm ID

5 µm Minibore Columns (mm)					SecurityGuard Cartridges (mm)
Phases	**30 x 2.1**	**50 x 2.1**	**100 x 2.1**	**150 x 2.1**	**4 x 2.0* (10/pk)**
Polar C18	00A-4754-AN	00B-4754-AN	00D-4754-AN	00F-4754-AN	AJ0-7600
				for ID:	2.0 - 3.0 mm

5 µm Minibore Columns (mm)				SecurityGuard Cartridges (mm)
Phases	**50 x 3.0**	**100 x 3.0**	**150 x 3.0**	**4 x 2.0* (10/pk)**
Polar C18	00B-4754-Y0	00D-4754-Y0	00F-4754-Y0	AJ0-7600
			for ID:	2.0 - 3.0 mm

5 µm Analytical Columns (mm)					SecurityGuard Cartridges (mm)
Phases	**50 x 4.6**	**100 x 4.6**	**150 x 4.6**	**250 x 4.6**	**4 x 3.0* (10/pk)**
Polar C18	00B-4754-E0	00D-4754-E0	00F-4754-E0	00G-4754-E0	AJ0-7601
				for ID:	3.1-8.0 mm

Kinetex® EVO C18 Core-Shell LC Columns

5 µm Minibore Columns (mm)				SecurityGuard™ ULTRA Cartridges‡
30 x 2.1	**50 x 2.1**	**100 x 2.1**	**150 x 2.1**	**3/pk**
00A-4633-AN	00B-4633-AN	00D-4633-AN	00F-4633-AN	AJ0-9298
				for 2.1 mm ID

5 µm MidBore™ Columns (mm)			SecurityGuard ULTRA Cartridges‡
50 x 3.0	**100 x 3.0**	**150 x 3.0**	**3/pk**
00B-4633-Y0	00D-4633-Y0	00F-4633-Y0	AJ0-9297
			for 3.0 mm ID

5 µm Analytical Columns (mm)				SecurityGuard ULTRA Cartridges‡
50 x 4.6	**100 x 4.6**	**150 x 4.6**	**250 x 4.6**	**3/pk**
00B-4633-E0	00D-4633-E0	00F-4633-E0	00G-4633-E0	AJ0-9296
				for 4.6 mm ID

2.6 µm Minibore Columns (mm)				SecurityGuard ULTRA Cartridges‡
30 x 2.1	**50 x 2.1**	**100 x 2.1**	**150 x 2.1**	**3/pk**
00A-4725-AN	00B-4725-AN	00D-4725-AN	00F-4725-AN	AJ0-9298
				for 2.1 mm ID

2.6 µm MidBore Columns (mm)			SecurityGuard ULTRA Cartridges‡
50 x 3.0	**100 x 3.0**	**150 x 3.0**	**3/pk**
00B-4725-Y0	00D-4725-Y0	00F-4725-Y0	AJ0-9297
			for 3.0 mm ID

2.6 µm Analytical Columns (mm)			SecurityGuard ULTRA Cartridges‡
50 x 4.6	**100 x 4.6**	**150 x 4.6**	**3/pk**
00B-4725-E0	00D-4725-E0	00F-4725-E0	AJ0-9296
			for 4.6 mm ID

1.7 µm Minibore Columns (mm)			SecurityGuard ULTRA Cartridges‡
50 x 2.1	**100 x 2.1**	**150 x 2.1**	**3/pk**
00B-4726-AN	00D-4726-AN	00F-4726-AN	AJ0-9298
			for 2.1 mm ID

‡ SecurityGuard ULTRA Cartridges require holder, Part No.: AJ0-9000

* SecurityGuard Analytical cartridges require holder, Part No.: KJ0-4282

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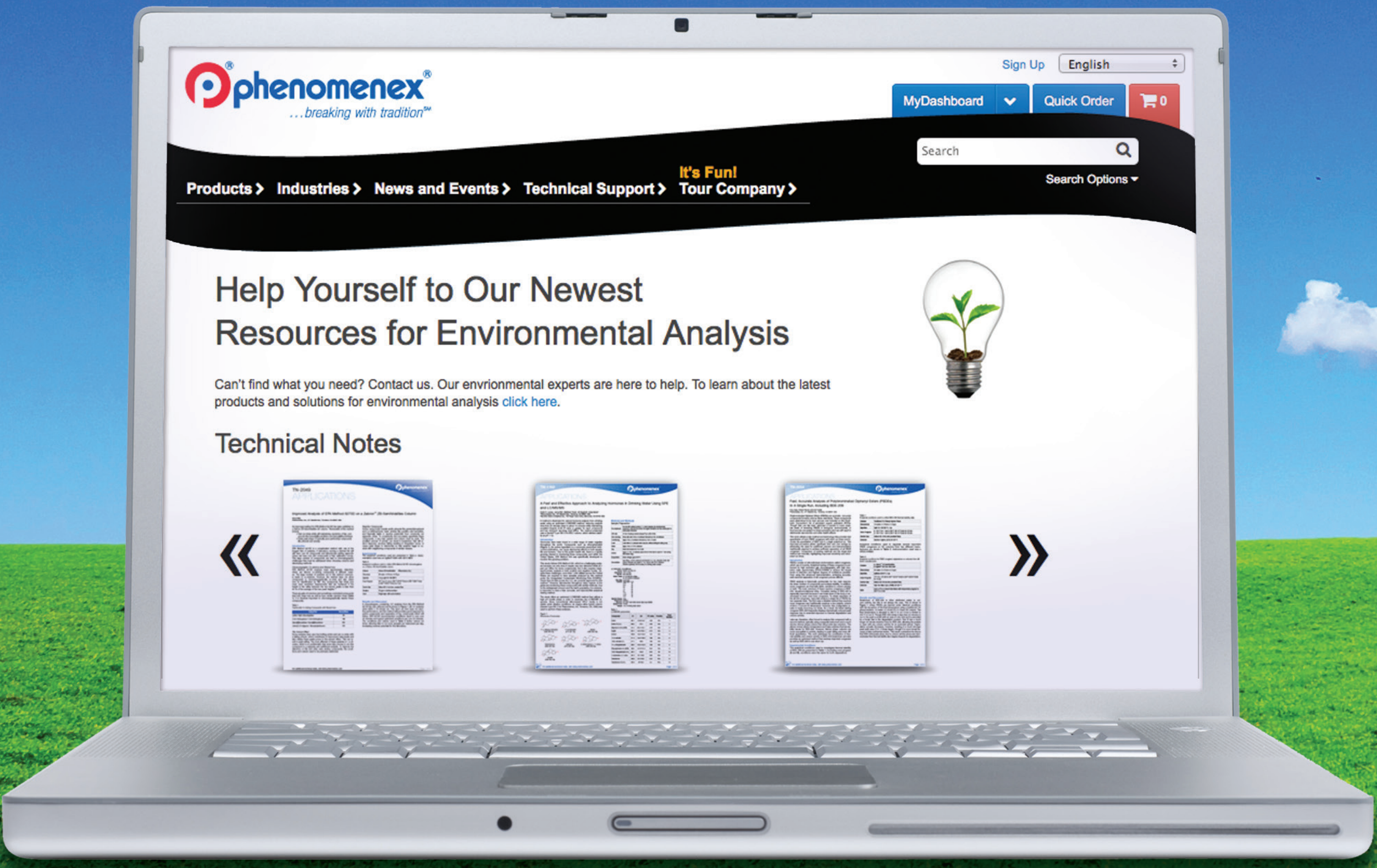

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Strata-X is patented by Phenomenex. U.S. Patent No. 7,119,145

Gemini and Kinetex EVO are patented by Phenomenex. U.S. Patent Nos. 7,563,367 and 8,658,038
and foreign counterparts.

SecurityGuard is patented by Phenomenex. U.S. Patent No. 6,162,362
Caution: this patent only applies to the analytical-sized guard cartridge holder, and does not apply to SemiPrep, PREP or ULTRA holders, or to any cartridges.

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APPLICATION GUIDE

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- Solid Phase Extraction
- QuEChERS
- LC-MS/MS

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