

# Evaluation of Online SPE Sorbents for the Analysis of Perfluorinated Compounds in Aqueous Matrices

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## Abstract

The analysis of perfluorinated compounds (PFCs) in aqueous matrices, especially finished drinking water and ground water, has received much attention in recent years. The US EPA has issued health advisories specifically for PFOA and PFOS and the occurrence data from the third Unregulated Contaminant Monitoring Rule (UCMR3) indicate a continuing need for this specific analysis. Using EPA method 537, a 250 mL water sample is fortified with surrogates and passed through a solid phase extraction (SPE) cartridge containing polystyrenedivinylbenzene (SDVB)<sup>1</sup>. This extraction is very robust and very sensitive to the low ng/L levels using only 2-10 µL injections. However, method 537 does take a considerable amount of time to perform the SPE and because the methanol extract has to be evaporated to dryness and then reconstituted. Online SPE has been shown to be an excellent technique for analyzing aqueous matrices because it

bypasses the "offline" SPE time mentioned previously, increasing sample throughput significantly<sup>2</sup>. Additionally, it can be just as sensitive due to the larger injection volume. The performance of three different online SPE sorbents was evaluated for this application; Strata<sup>®</sup> 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<sup>®</sup> 5 µm EVO C18 100Å  
**Dimension:** 100 x 2.1 mm  
**Part No:** 00D-4633-AN  
**Guard Column:** SecurityGuard<sup>™</sup> ULTRA Cartridges  
**Part No:** AJ0-9296

**Online SPE:** Strata<sup>®</sup>-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<sup>™</sup> 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<sup>®</sup>
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 online SPE is completely automated; it includes a sample wash step (2.1 to 4.1min) to wash Trizma preservative from the media.

### Instrumentation

LC Pump 1: Thermo Accela<sup>®</sup> 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<sup>®</sup> Ultra

#### LC Gradient (pump 1):

Time	Water	MeOH	0.4 % NH <sub>3</sub>
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 online SPE with sample and subsequently brought down to 20% 1 min prior to online SPE elution.

#### Online 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
9.00	30	70	0	0	Idle
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<sub>3</sub>), Ammonium Hydroxide (NH<sub>4</sub>OH), Ammonium Acetate (NH<sub>4</sub>OAc)

## Results

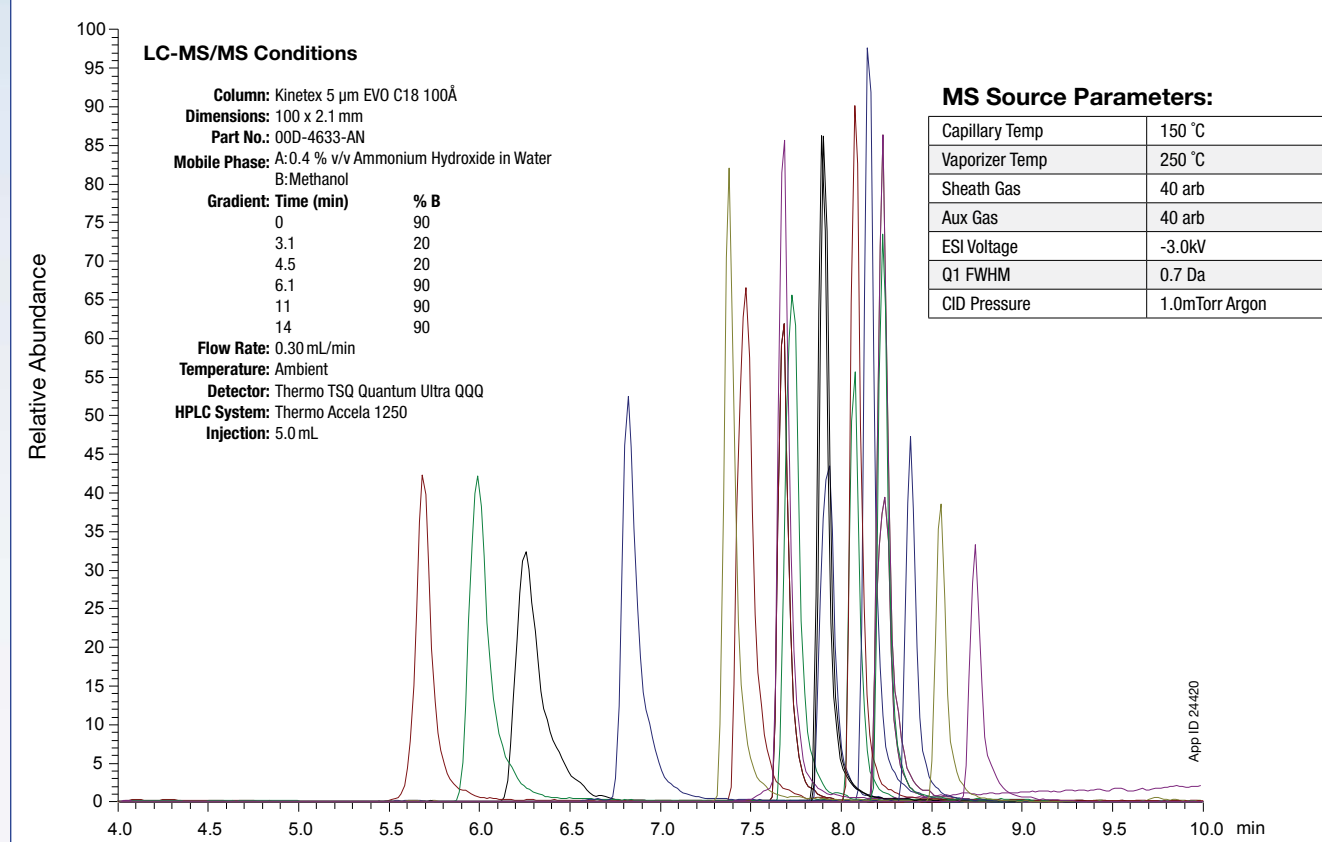


Table 1. Summary of Online SPE, HPLC conditions that were investigated and their performance

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

<sup>a</sup>Note: All eluents used a gradient of increasing methanol for elution.

Figure 1. Online SPE using C18-E sorbent and 2.0 mM ammonium acetate mobile phase modifier on a Luna Omega C18 50 mm column.

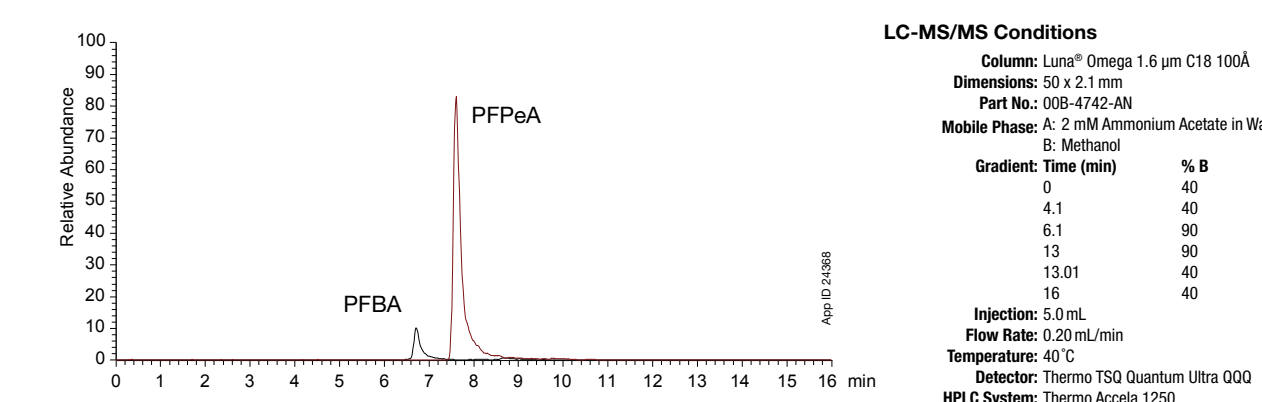


Figure 2. Online SPE using Strata-X-AW sorbent and 0.4-0.8% ammonia mobile phase modifier on a Kinetex C18 EVO column (final conditions).

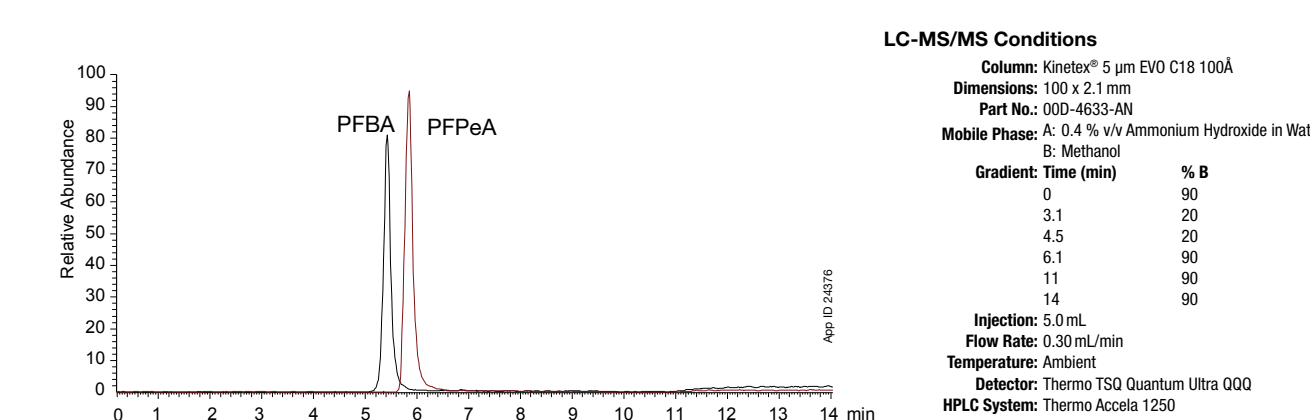


Figure 3. Elution strength of 0.04% NH<sub>3</sub> (top) and 0.24% NH<sub>3</sub> (bottom) illustrating more efficient elution of analytes (PFBA and PFPeA) with increased base concentration in the mobile phase.

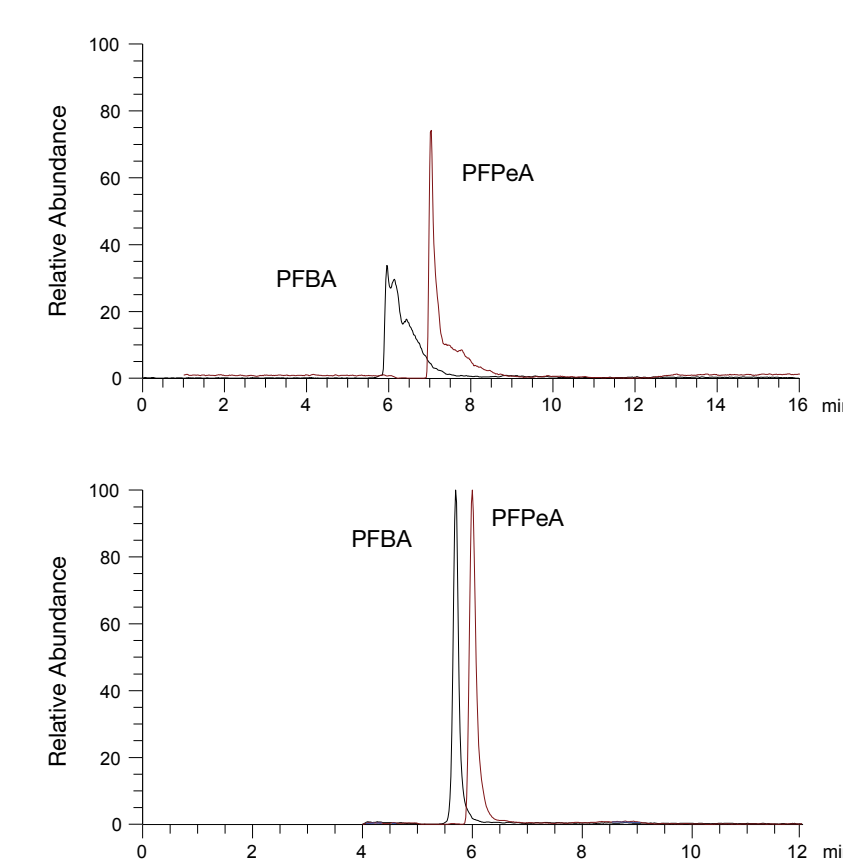


Figure 4. Effect of filtering on recovery of long chain PFCs.

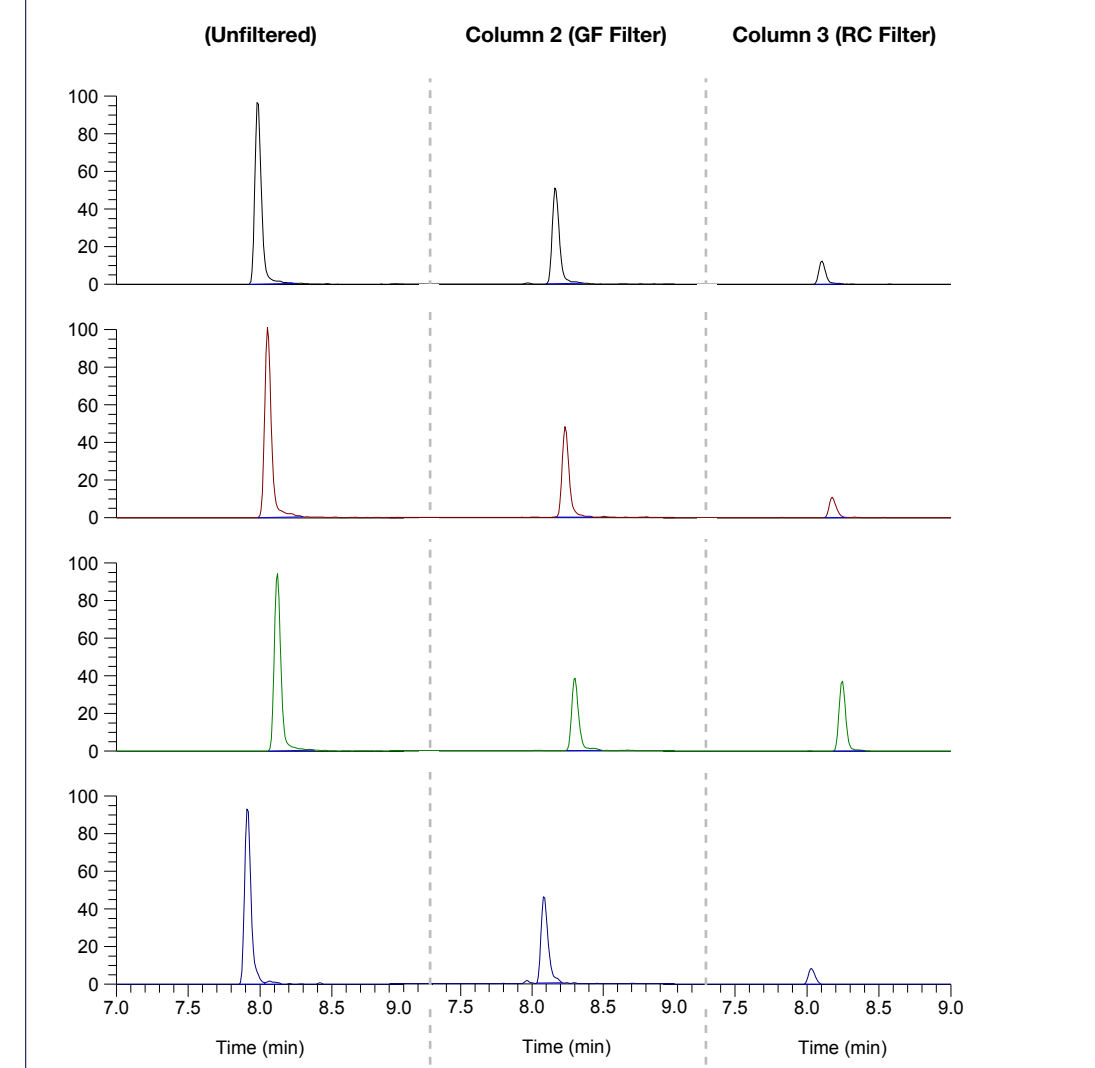


Figure 5. LCMRL plot of PFOA and PFOS showing the relationship of the data to the predicted limits. The LCMRL is the highest value of the upper and lower prediction limit intersection points with the 50-150% criteria.

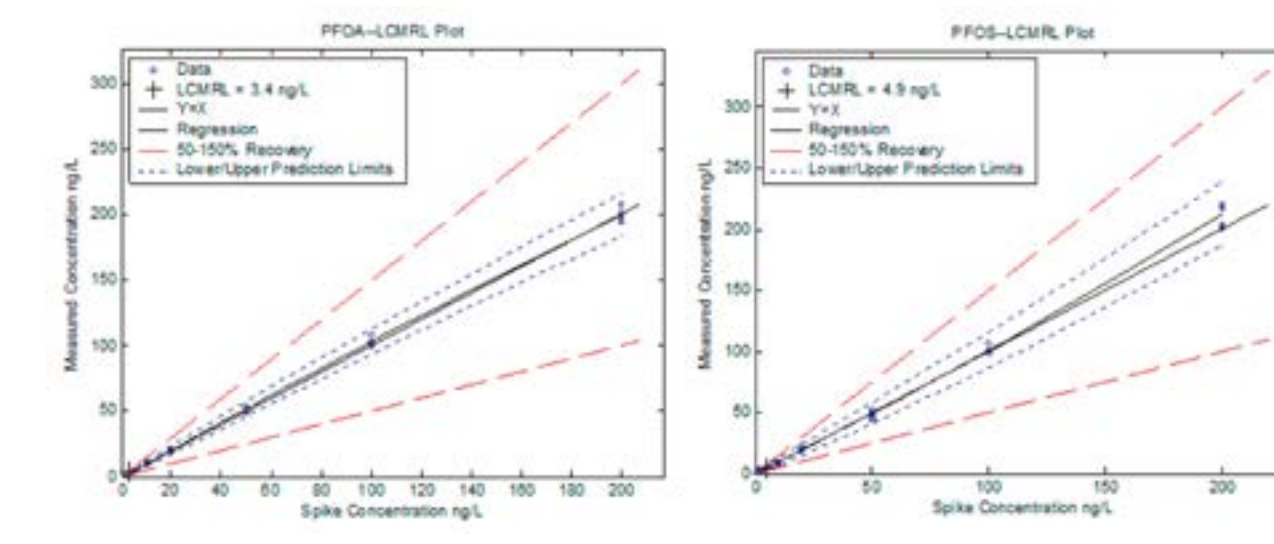


Table 2. Performance comparison of the online SPE (Strata-X-AW) method with EPA 537.

Analyte	Online SPE LCMRL	Online SPE DL	EPA537 LCMRL*	EPA537 DL**
PFBA	9.8	1.4	-	-
PFPeA	5.9	0.9	-	-
PFHxA	1.4	0.9	2.9	1.6
PFHxA	5.0	0.5	3.8	0.5
PFGA	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
PFDA	17	2.5	3.5	1.1
PFTDA	12	3.3	3.8	2.2
PFTDA	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-EFOSAA	12	3.2	14	4.2

\* LCMRL is the lowest concentration minimum reporting level<sup>3</sup>  
\*\* DL is the detection limit<sup>4</sup>

## 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<sub>4</sub>OAc) used for C18 or Strata-X online 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 online 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, PFTDA, PFTeDA, and PFDS. Figure 4 is a comparison between unfiltered, glass fiber filtration, and regenerated cellulose filtration (left to right).

## Performance

Balancing the performance across the wide range of analytes, the Strata-X-AW provides the most robust online SPE, especially if short chain PFCs are of interest. To assess performance as compared to EPA 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 with a 99% confidence without an accuracy limit. The results of this study are listed in Table 2 along with results from EPA method 537.

## Conclusions

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 offline SPE using weak anion-exchange is fairly robust in other matrices<sup>2,3</sup>. 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.

With the advent of analytical columns like the core-shell Kinetex EVO C18 that can support a higher pH, it's possible to couple weak anion-exchange online SPE to a suitable analytical column. Addi-

tionally, 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<sup>5</sup>. 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).

## Acknowledgement

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## References

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