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

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Outline

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- What is Online SPE briefly
- Application Specific Challenges
- Summary of Sorbents/Conditions Investigated
- Optimizations
- Performance
- Conclusions/Summary

What is Online SPE

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- Sample prep by the auto-sampler
- Uses 2 valves
  - Sample injection using 5.0mL loop
  - Solid Phase Extraction - backflush
- Practically Eliminates Sample Prep time
  - 5 minute prep time (filtering and loading)
- EPA Method 543

Challenges

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- Background PFOA contamination
- Range of analytes – C_4 to C_{14}
  - LogP range 2-8
- Direct injection limited to 1.0mL
  - Must be aqueous
- Extraction Mechanisms
  - Polystyrenedivinylbenzene[1] – can't do PFBA
  - C18 Reverse Phase[2] – low sample pH
  - Weak anion exchange (WAX)[3] – elute at high pH

First Attempts

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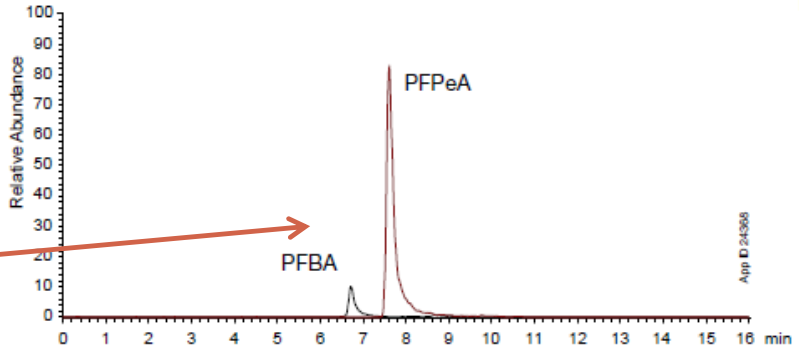
Identical results observed with offline SPE using SDVB

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.



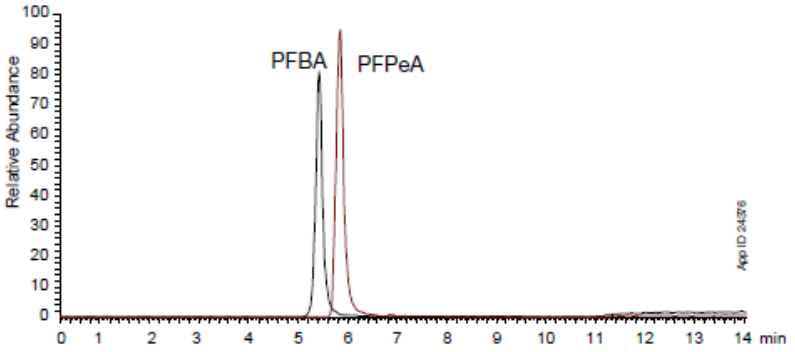
LC-MS/MS Conditions

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

Injection: 5.0 mL
Flow Rate: 0.20 mL/min
Temperature: 40°C
Detector: Thermo TSQ Quantum Ultra QQQ
HPLC System: Thermo Accela 1250

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).



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

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

First Attempts

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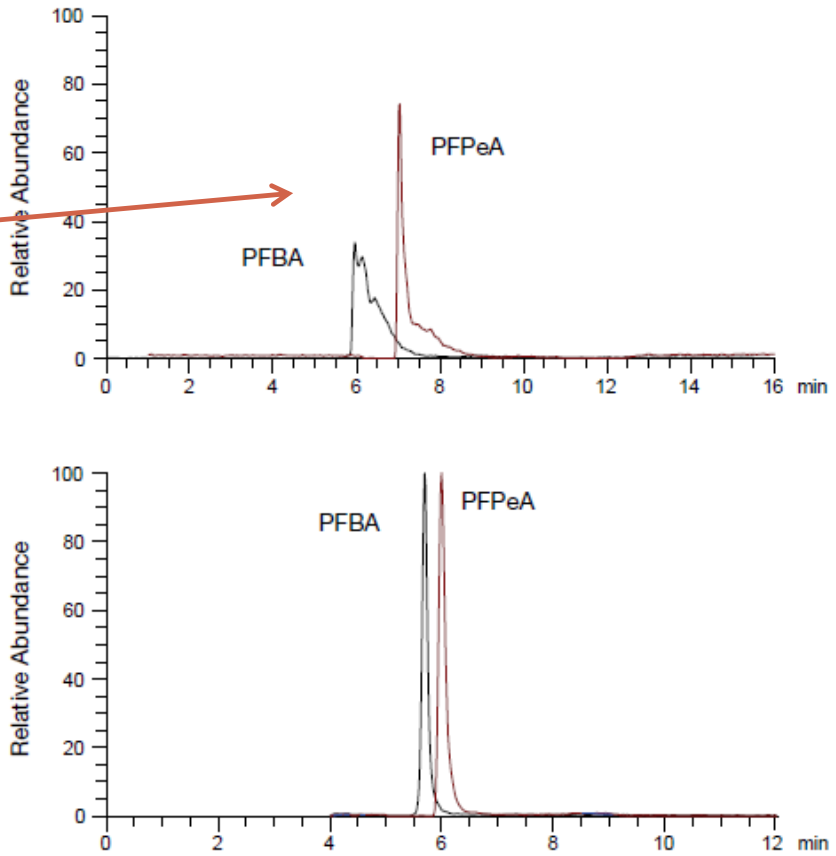
SPE chemistry still matters

Figure 3. Elution strength of 0.04% NH_3 (top) and 0.24% NH_3 (bottom) illustrating more efficient elution of analytes (PFBA and PFPeA) with increased base concentration in the mobile phase.



Results Summary

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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*	PFBA / PFPeA %	Shape
1	Kinetex EVO C18 5 µm 100 x 2.1mm	X-AW	Trizma (pH=7)	neutral	0.24-0.04 % NH_3	100	excellent
2	Kinetex EVO C18 5 µm 50 x 2.1mm	X-AW	neutral	neutral	0.04 % NH_3	106	very poor
3	Kinetex EVO C18 5 µm 50 x 2.1mm	X-AW	neutral	neutral	0.24-0.04 % NH_3	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_4OAc	<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_4OAc	11	OK
8	Luna Omega C18 1.6 µm 50 x 2.1mm	C18	neutral	acidic (pH=2)	2 mM NH_4OAc	11	OK
9	Luna Omega C18 1.6 µm 50 x 2.1mm	X	neutral	neutral	2 mM NH_4OAc	5.9	poor
10	Luna Omega C18 1.6 µm 50 x 2.1mm	X	acidic	neutral	2 mM NH_4OAc	5.1	poor

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

Filtering

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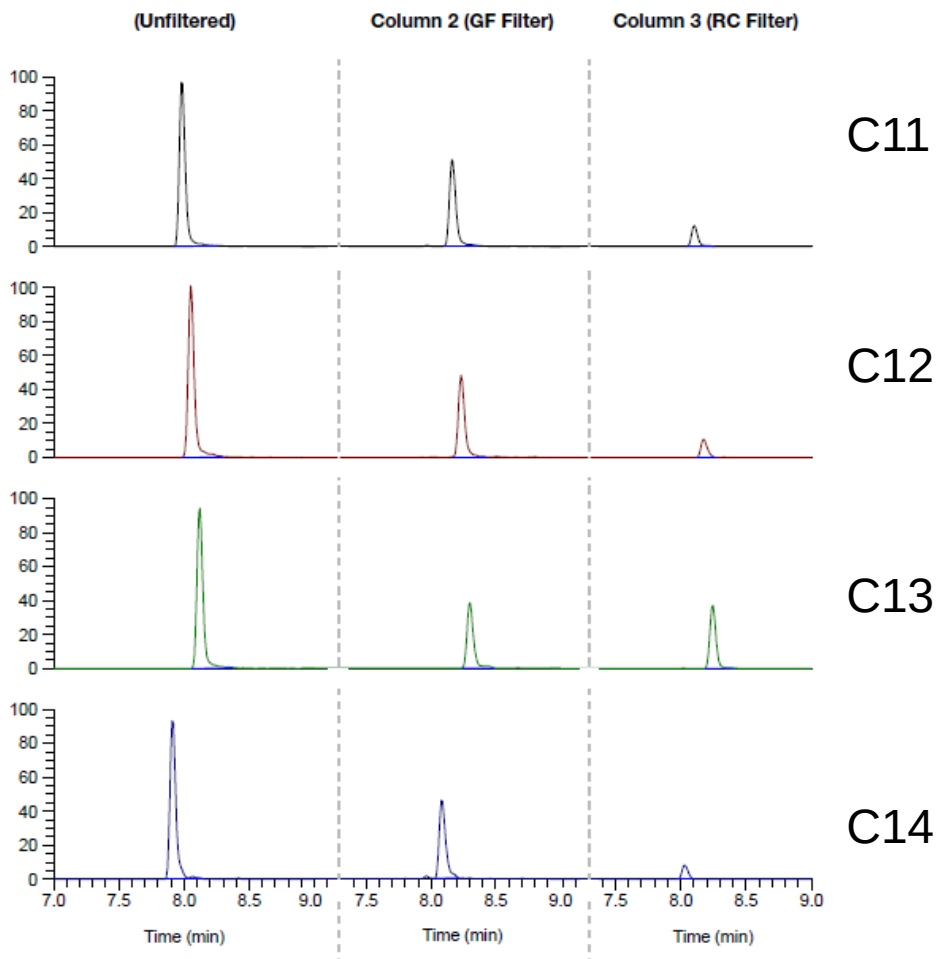
Figure 4. Effect of filtering on recovery of long chain PFCs.



Conditions

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LC Gradient (pump 1):

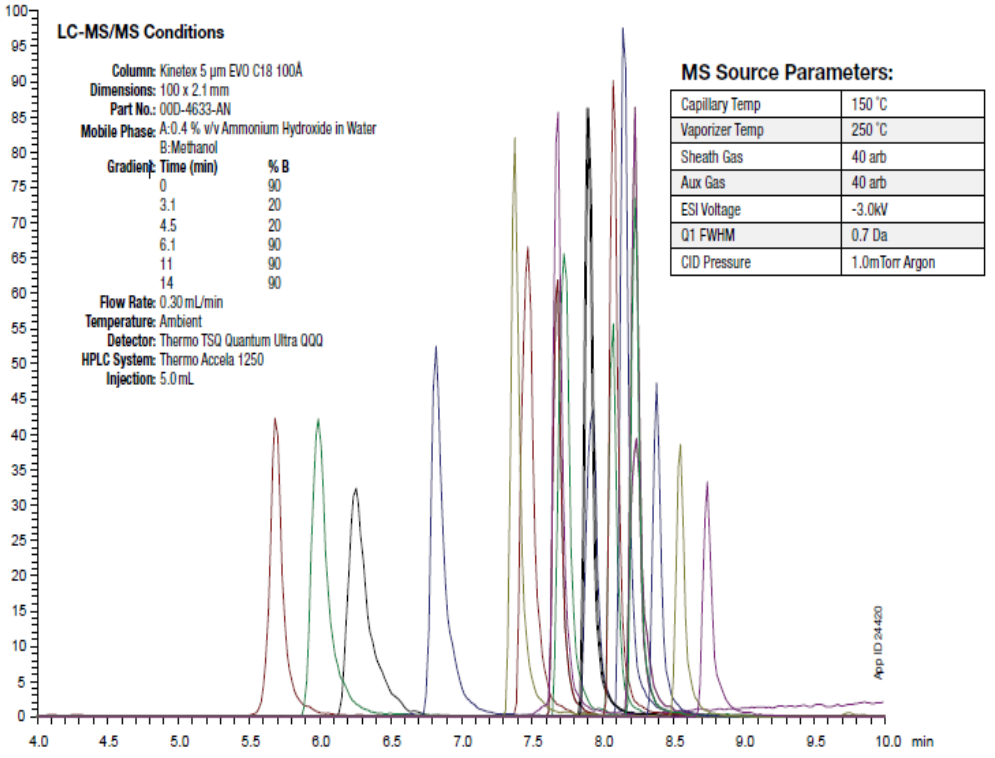
Time	Water	MeOH	0.4 % NH_3
0.00	0	90	10
3.10	20	20	60
4.50	20	20	60
6.10	0	90	10
11.00	0	90	10
14.00	0	90	10

Note: To decrease PFOA contributed by the eluent system, MeOH is kept at 90% while loading the 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_3); Ammonium Hydroxide (NH_4OH); Ammonium Acetate (NH_4OAc)



Sensitivity Performance

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Table 2. Performance comparison of the online SPE (Strata-X-AW) method with EPA 537. Units are ng/L

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
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]

LCMRL Study Plots[4]

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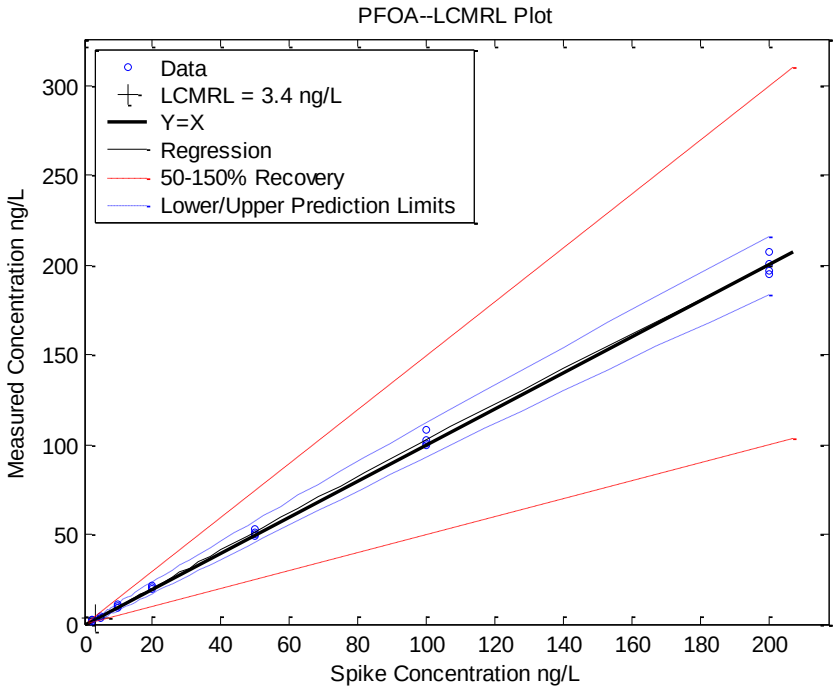

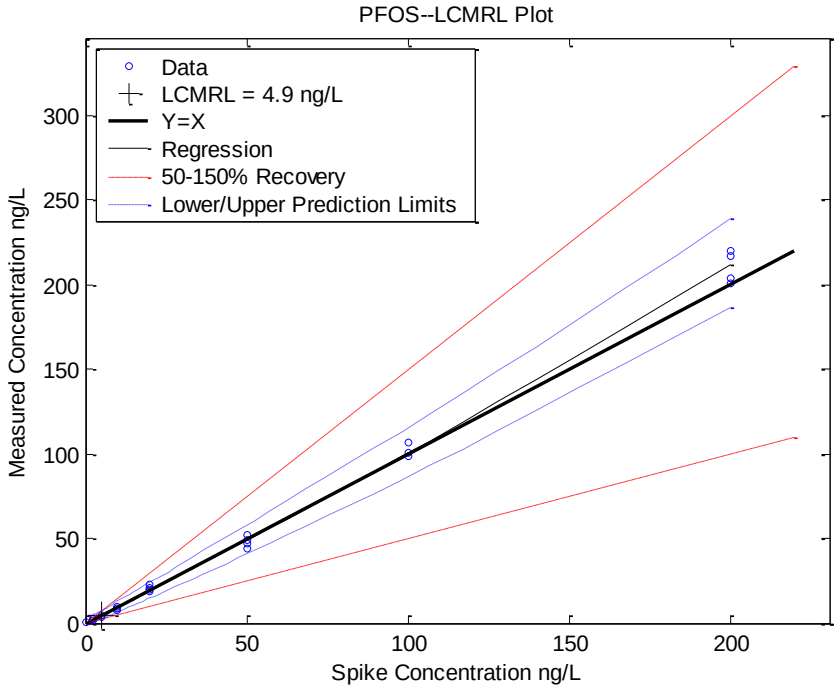

Advantages to WAX

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- Weak anion exchange extraction mechanisms may be most appropriate to capture the widest range of PFCs (C_4 – C_{18}).
- Weak anion exchange offers the advantage of being adaptable to extracts containing significant amounts of methanol or acetonitrile
- Modern stationary phases like Kinetex EVO allow high pH elution
- Ammonia fully compatible with ESI MS
- Reportedly used to extract PFCs from seawater[3]

Conclusions

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- Online SPE provides comparable sensitivity to current methodology
- Online SPE is robust enough to meet strict Data Quality Objectives.
- Weak anion exchange is the best sorbent choice
- Other SPE sorbents can be used with caveats
  - When using C18, sample pH must be adjusted to 2
  - SDVB will miss shortest chain PFCs

References

1) EPA Method 537 v1.1, Determination Of Selected Perfluorinated Alkyl Acids In Drinking Water By Solid Phase Extraction And Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), September 2009
2) Mazzoni, Michela, Marianna Rusconi, Sara Valsecchi, Claudia P. B. Martins, and Stefano Polesello. "An On-Line Solid Phase Extraction-Liquid Chromatography-Tandem Mass Spectrometry Method for the Determination of Perfluoroalkyl Acids in Drinking and Surface Waters." *Journal of Analytical Methods in Chemistry* 2015 (2015): 1–13. doi:10.1155/2015/942016.
3) Yamazaki, Eriko, Sachi Taniyasu, Kodai Shimamura, Shunya Sasaki, and Nobuyoshi Yamashita. "Development of a Solid-Phase Extraction Method for the Trace Analysis of Perfluoroalkyl Substances in Open-Ocean Water." *Bunseki Kagaku* 64, no. 10 (2015): 759–68. doi:10.2116/bunsekikagaku.64.759.
4) 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.