

# Method Validation for the California Expanded List of PFAS Compounds

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## Introduction

Recently, the state of California has expanded the required list of PFAS for analysis in wastewaters for up to 42 PFAS compounds from C4 to C18 including carboxylic and sulfonic acids, sulfonamide derivatives, telomers, and ethers. Recently, facilities with bulk fuel storage also require analysis of this expanded PFAS panel.

The US Department of Defense (DOD) quality assurance manual suggests using a two-step SPE approach using WAX followed by a graphitized carbon black (GCB) clean-up. We have previously demonstrated the utility of a WAX and GCB in a stacked SPE format for EPA 533 and 537.1 for a variety of water matrices, known as Strata® PFAS. Strata PFAS<sup>®</sup> saves time and cost by combining two phases into one cartridge. The goal of this study was to validate method performance using Strata PFAS for an expanded list of PFAS compounds recently required for wastewater discharges and bulk fuel storage facilities by the California Water Resources Board.

## **Materials and Methods**

#### Sample Preparation

This section shows the items and steps for the conditioning of the SPE phase, load, extraction and concentration are shown below.

- Cartridge: Strata PFAS (WAX/GCB), 200 mg/50 mg Part No.: CS0-9207 Sample pH adjusted to pH 6-7 using 1M phosphate **Condition:** 10 mL 0.1% NH<sub>4</sub>OH in Methanol 10 mL MeOH 10 mL Phosphate Buffer pH=7 Load: 250 mL Wash: 5 mL 0.1% Formic Acid in 50:50 Water: Methanol Dry: 2 mins Elute: 4 mL 0.1% NH, OH in Methanol Soak: 2 mins Elute: 4 mL 0.1% NH, OH in Methanol
- **Dry:** Using N<sub>2</sub> adjust to below 2 mL adjust to 2 mL final volume using 100% Methanol

#### LC-MS/MS Sample Analysis Conditions

Two MRM transitions for each analyte and one for each deuterated internal standard were monitored.

#### **HPLC Conditions**

Delay Column Kinetex EVO C18 50 x 2.1mm (00B-4633-AN)   Column Temp: 350°C   Injection Volume: 10 μL   Mobile Phase: A: 20 mM Acetic Acid   Mobile Phase: B: 25 mM Ammonium Hydroxide in Methanol   Gradient: Time (min) % A % B   0 95 5   1.2 55 45   3.6 35 65   11 10 90   13 10 90   13.01 95 5   17 95 5	Column:	Kinetex EVO C18 100 x 2.1mm (00D-4633-AN)				
Column Temp:   350°C     Injection Volume:   10 μL     Mobile Phase: A:   20 mM Acetic Acid     Mobile Phase: B:   25 mM Ammonium Hydroxide in Methanol     Gradient: Time (min)   % A   % B     0   95   5     1.2   55   45     3.6   35   65     11   10   90     13.01   95   5     17   95   5	<b>Delay Column:</b>	Kinetex EVO C18 50 x 2.1mm (00B-4633-AN)				
Injection Volume: 10 μL   Mobile Phase: A: 20 mM Acetic Acid   Mobile Phase: B: 25 mM Ammonium Hydroxide in Methanol   Gradient: Time (min) % A % B   0 95 5   1.2 55 45   3.6 35 65   11 10 90   13 10 90   14 95 5   15 5 5   16 95 5   17 95 5	<b>Column Temp:</b>	350°C				
Mobile Phase: A: 20 mM Acetic Acid   Mobile Phase: B: 25 mM Ammonium Hydroxide in Methanol   Gradient: Time (min) % A % B   0 95 5   1.2 55 45   3.6 35 65   11 10 90   13.01 95 5   17 95 5	<b>Injection Volume:</b>	10 µL				
Mobile Phase: B: 25 mM Ammonium Hydroxide in Methanol   Gradient: Time (min) % A % B   0 95 5   1.2 55 45   3.6 35 65   11 10 90   13 10 90   13.01 95 5   17 95 5	Mobile Phase: A:	20 mM Acetic Acid				
Gradient: Time (min) % A % B   0 95 5   1.2 55 45   3.6 35 65   11 10 90   13 10 90   13.01 95 5   17 95 5	Mobile Phase: B:	25 mM Ammonium Hydroxide in Methanol				
0 95 5   1.2 55 45   3.6 35 65   11 10 90   13 10 90   13.01 95 5   17 95 5	Gradient: Time (min)	% <b>A</b>	% B			
1.2 55 45   3.6 35 65   11 10 90   13 10 90   13.01 95 5   17 95 5	0	95	5			
3.6 35 65   11 10 90   13 10 90   13.01 95 5   17 95 5	1.2	55	45			
11 10 90   13 10 90   13.01 95 5   17 95 5	3.6	35	65			
13 10 90   13.01 95 5   17 95 5	11	10	90			
13.01 95 5   17 95 5	13	10	90			
<b>17</b> 95 5	13.01	95	5			
	17	95	5			

HPLC System: Agilent<sup>®</sup> 1100

#### **MS Conditions**

MS	Thermo <sup>®</sup> TS	Q Vantage
<b>Capillary Temp:</b>	250	°C
Vapor Temp:	300	°C
Sheath Gas	40	arb
Aux Gas	15	arb
Sweep Gas	0	arb
CID	1.0	mTorr Argon
Q1 FWHM	0.4	Da



#### Matrix Studies

Chromatographic Separation of Spiked PFAS compounds in a Wastewater sample. Note the peak interference for PFBS in this waste water sample. This resulted in signal enhancement when using M/Z 80.



## Discussion

The data shows the extraction of C4-C18 PFAS compounds using Strata PFAS, a weak anion-exchange SPE phase. Fig. 1 shows excellent peak shape and good chromatographic resolution for the majority of compounds, especially the early eluting PFBA. Most of the PFAS compounds showed a MDL in the 1-2 ng/L range, LODs in the 1-2.5 ng/L range, and LOQs at 5 or 8 ng/L. The LOQs are the required reporting limit set forth in the California Water Resources Board order WQ 2020-0015-DWQ. The percent recoveries were well within the range required by EPA drinking water standards. Most RSD were below 10%. The recoveries for the C16 PFHxDA and C18 PFOcDA show that a WAX based SPE can bind long chain PFAS compounds as well as for the sulfanomide PFAS compounds, PFOSA, MeFOSA, EtFOSE, MeFOSE, EtFOSA, EtFOSSA. In addition, the use of 50 mg GCB did not interfere with recoveries of any of the PFAS compounds.

#### **Precision and Accuracy**

Spike recoveries of PFAS compounds from various water matrices

WW Effluent 1WW Discharge<br/>PondStormwater<br/>RunoffWW Effluent 2 MS MSD MS MSD MS MSD MS MSD **N-EtFOSAA** 86% 92% 94% 92% **N-MeFOSAA** 112% 115% 100% **PFBSa** 209% 219% 239% 218% 162% 2040% 2003% 182% 111% PFBSb 106% **PFBA** 104% 79% 123% 123% **PFPeA** 107% 70% 133% 139% 106% **PFHxA** 163% 76% 166% 102% **PFHpA** 106% 107% 93% 82% **PFHxS** 103% 145% 160% 96% 117% 88% **PFOA** 96% 114% 93% PFNS 87% 104% **PFNA** 109% 108% **PFDA** 113% **PFUnDA PFDoDA** PFOS **PFTrDA** 104% 83% 71% 74% 89% 88% 95% 96% **PFPeS** 78% 92% 82% 93% 86% **PFTeDA** 107% 67% 94% **PFHxDA** 104% 110% 54% 56% 100% **PFOcDA** 90% 101% 54% 55% 65% 63% **5:3-FTCA** 114% 76% 134% 124% 126% **7:3-FTCA** 122% 131% 144% HFPO-DA 109% 104% 86% 99% 87% DONA 106% 9CI-PF3ONS 83% 11CI-PF3OUdS **EtFOSE** 92% 72% 120% 142% 100% MeFOSE 83% **EtFOSA** 124% 112% 54% MeFOSA 12% **PFOSA** 127% 114% 101% 120% 95% **4:2-FTS** 117% 109% 109% 98% 118% **PFHpS** 115% 111% 68% PFDS 96% 96% 95% 69% 82% 51% 83% **8:2-FTS** 119% 93% 109% 111% 107% 104% **6:2-FTS** 114% 97% 106% 134% 129% 104% **10:2-FTS** 107% 105% 70% 69% 47% 80% 54% 87% **3:3-FTCA** 101% **PFEESA** 108% 120% PFMPA PFMBA 117% 103% 116% 114% 112% **NFDHA** 111% 111% 96% 108% 103% 117% 120% 104%

a PFBS MS 299-80 used as quantifier ion b PFBS MS 299 – 99 used as quantifier ion

### **Precision and Accuracy**

Initial Demonstration of Capability from spike extracts in reagent water. Spike concentration of 20 ng/L were used.

Analyte	MDLa	LODb	<b>RL/LOQc</b>
PFBA	0.65	1.0	5.0
PFPeA	2.1	2.5	5.0
PFHxA	0.76	1.0	5.0
PFHpA	0.76	1.0	5.0
PFOA	1.2	2.5	5.0
PFNA	0.64	1.0	5.0
PFDA	0.68	1.0	5.0
PFUnDA	0.98	1.0	5.0
PFDoDA	0.85	1.0	5.0
PFTrA	0.94	1.0	5.0
PFTeDA	0.90	1.0	5.0
PFHxDA	0.94	1.0	5.0
PFOcDA	0.88	1.0	5.0
PFBS	1.1	2.5	5.0
PFPeS	1.3	2.5	5.0
PFHxS	1.5	2.5	5.0
PFHpS	0.87	1.0	5.0
PFOS	3.2	4.5	5.0
PFNS	1.8	2.5	5.0
PFDS	2.4	2.5	5.0
4:2-FTS	0.93	1.0	5.0
6:2-FTS	2.1	2.5	5.0
8:2-FTS	2.5	2.5	5.0
10:2FTS	1.9	2.5	8.0
N-MeFOSAA	2.3	2.5	8.0
N-EtFOSAA	2.3	2.5	8.0
PFOSA	2.7	2.5	8.0
HFPO-DA	2.2	2.5	5.0
ADONA	0.71	1.0	5.0
9CI-PF3ONS	1.5	2.5	5.0
11CI-PF3OUdS	1.4	2.5	5.0
3:3FTCA	4.7	4.5	5.0
5:3FTCA	1.4	2.5	8.0
7:3FTCA	2.6	2.5	8.0
EtFOSA	1.8	2.5	8.0
EtFOSE	2.7	2.5	8.0
MeFOSA	2.5	2.5	8.0
MeFOSE	2.5	2.5	8.0
NFDHA	2.0	2.5	5.0
PFEESA	0.90	1.0	8.0
PFMPA	0.93	1.0	8.0
PFMBA	1.5	2.5	8.0
PFEChS	1.0	1.0	8.0

## Conclusion

The data shows that WAX / GCB stacked dual SPE phase can be used to extract for short and long chain PFAS compounds, for carboxylic, sulfonic, sulfonamides and derivatives, Fluorotelomer sulfonates, Fluorotelomer carboxylic acids, Perfluoroalkyl ether carboxylic acids, Chlorinated Polyfluoroalkyl Ether Sulfonic Acids from a wide variety of water matrices. The use of the Kinetex EVO C18 column and its stability at high pH allows the use of a pH gradient to effectively separate water and organic soluble PFAS compounds while maintaining excellent peak shape. Finally, the flexibility to use alternate transitions is crucial to overcome matrix interferences.

**Terms and Conditions** 

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

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