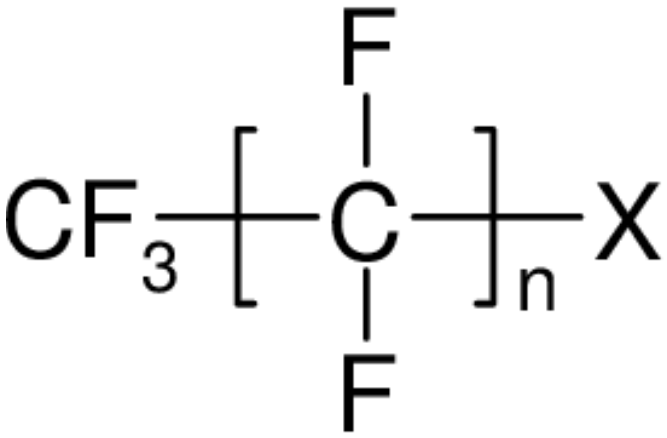
EPA Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)



UCT Part Numbers

ECDVB156P
ENVIRO-CLEAN® DVB
500 mg, 6 mL cartridge,
PE frits

Or

ECHLD156-P
ENVIRO-CLEAN® Highly
Cross-Linked HLD 500 mg,
6 mL cartridge, PE frits

SLC-18100ID21-3UM
Selectra® C18 HPLC column
(50 × 2.1 mm, 3 µm)

CLTTP050
Polypropylene Clean-Thru Tips

SLGRDHLDR
Guard cartridge holder

SLC-1850ID46-5UM
Selectra® C18 Delay Column
(50 x 4.6 mm, 5 µm)

Summary:

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of synthetic organofluorine compounds widely used in industrial applications and consumer products. PFAS are persistent in the environment, resistant to degradation, and are known to bioaccumulate in humans and wildlife. PFAS have historically been analyzed in drinking water according to EPA Method 537 (14 compounds) and 537.1 (18 compounds) [1,2]. An updated EPA Method 533, has been validated to analyze multiple short-chain PFAS, including telomers and precursor compounds, which cannot be measured by EPA 537.1 [3]. EPA 537.1 extracts PFAS using styrene-divinylbenzene (SDVB) single polymer solid-phase extraction (SPE) and liquid chromatography/tandem mass spectrometry (LC-MS/MS).

This application note outlines the analysis of PFAS in drinking water according to EPA 537.1 using UCT's Enviro-Clean® polymeric styrene-divinylbenzene (DVB and High-Load DVB (HLD)) SPE cartridges (**ECDVB156P/ ECHLD156-P**). LC-MS/MS analysis was conducted using a Selectra® C18 HPLC analytical column (**SLC-18100ID21-3UM**), while a short (5 cm) C18 delay column (**SLC-1850ID46-5UM**) was used to reduce potential PFAS contamination from the HPLC system. A seven-point calibration (0.5-25 ng/mL) was performed, and all compounds were linear with R^2 values > 0.99. The extraction method was evaluated by spiking reagent water samples with PFAS at 2.5 and 20 ng/L. Recoveries of all analytes were within a 70-110% range, and RSD values were <10%. Because fluorochemicals exist in lab equipment, removing PTFE containing labware throughout the sampling and analytical processes (including HPLC solvent inlet tubing) is essential for accurate analysis.

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Sample Pretreatment:

Collect samples in a 250-mL polypropylene bottle fitted with a polypropylene screw cap. All Field and QC Samples, including the LRB, LFB and FRB, must contain the dechlorinating agent listed in Section 8.1.2 of Method 537.1 (Trizma 5g/L).

SPE Procedure:

1. SPE Conditioning

a) Rinse each cartridge with 15 mL of methanol.

b) Rinse the cartridge with 18 mL of reagent water, being sure not to allow the water to drop below the top edge of the packing. Add 4-5 mL of reagent water to the cartridge reservoir.

2. Sample Extraction/Drying

a) Attach a large volume sample transfer tube to the top of each SPE cartridge and place the stainless-steel end of the transfer tube directly into the sample bottle.

* Ensure transfer tubes are adequately rinsed with methanol prior to use.

b) Adjust the vacuum so that the flow rate is approximately 10-15 mL/min.

c) After the entire sample has passed through the cartridge, rinse the sample bottle with 2 x 7.5 mL of reagent water; draw the rinsate through the sample transfer tubes and the cartridges.

d) Dry the cartridge under high vacuum (15-20 in Hg) for 5 minutes to remove any residual water.

3. Elution

a) Insert a collection rack containing 15 mL polypropylene collection tubes into the extraction manifold.

b) Add 4 mL of methanol to the sample container, cap and thoroughly rinse the sides of the container.

Note: Rinsing the sides of the container is important for obtaining good recovery of the long-chain hydrophobic PFAS.

c) Elute the analytes from the cartridges by pulling the elution solvent through the sample transfer tubes and the cartridges. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion

d) Repeat sample bottle rinse and cartridge elution with a second 4 mL aliquot of methanol.

4. Concentration

a) Concentrate the extract to just dryness under a gentle stream of nitrogen in a heated water bath (60–65 °C).

b) Reconstitute the extract with 1.0 mL of 96:4 methanol: reagent water (v/v) and IS PDS.

c) Vortex.

d) Transfer an aliquot of the final extract to a polypropylene autosampler vial (PTFE free).

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LC-MS/MS Parameters:

To avoid background in LC-MS/MS analysis, all PTFE solvent lines should be replaced with PEEK tubing. PFAS contamination is difficult to eliminate, and depending on the analytical conditions used, any PFAS present in the mobile phase, solvent lines, and online degasser can become concentrated in the analytical column and be detected simultaneously as the injected sample analyte. To overcome this, a short C18 "delay column" is commonly installed after the solvent mixer and before the sample injector to separate the contaminant peaks from any PFAS present in the sample. Alterations to existing HPLC systems can be readily performed, although checking with your HPLC's manufacturer before proceeding is recommended. Additional information can also be found in EPA Method 533 [3].

HPLC Conditions	
HPLC system	Shimadzu Nexara LC-30AD
Delay column	UCT Selectra® C18, 50 × 4.6 mm, 5 µm (**p/n: SLC-1850ID46-5UM**)
HPLC column	UCT Selectra® C18, 100 × 2.1 mm, 3 µm (**p/n: SLC-18100ID21-3UM**)
Guard column	UCT Selectra® C18, 10 × 2.0 mm, 3 µm (**p/n: SLC-18GDC20-3UM**)
Guard column holder	**p/n: SLGRDHLDR**
Column temperature	45°C
Flow rate	300 µL/min
Injection volume	10 µL

Time (min)	Mobile Phase A (%): 20 mM Ammonium Acetate	Mobile Phase B (%): Methanol
0.0	95	5
0.5	50	50
7.5	5	95
8.5	5	95
8.6	95	5
11.0	95	5

MS Conditions	
MS/MS system	Shimadzu LCMS-8050
Ionization Mode	Electrospray Ionization in negative mode (ESI-)
Interface Temperature	125°C
DL Temperature	200°C
Heat Block Temperature	250°C
Nebulizing Gas Flow	3 L/min
Heating Gas Flow	15 L/min
Drying Gas Flow	10 L/min

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MRM Transitions:

Analyte	R.T.	Precursor	Fragment Ion 1	Fragment Ion 2	R^2
PFBS	2.13	299.0	79.9	99.0	0.9989
PFHxA	2.67	313.0	269.1	118.9	0.9971
HFPO-DA	2.89	285.0	169.0	185.1	0.9986
PFHpA	3.42	362.8	319.1	169.1	0.9987
PFHxS	3.47	399.0	80.0	99.0	0.9979
ADONA	3.52	377.1	251.0	85.0	0.9982
PFOA	4.21	412.8	369.1	169.2	0.9976
PFOS	4.95	499.1	80.0	99.0	0.9979
PFNA	4.95	463.1	419.0	219.2	0.9978
9Cl-PF3ONS	5.33	530.9	351.0	-	0.9980
PFDA	5.61	513.1	468.9	219.1	0.9988
PFUnA	6.19	563.1	518.9	268.8	0.9984
11Cl-PF3OUdS	6.45	631.1	451.0	-	0.9977
PFDoA	6.70	612.9	569.0	319.1	0.9980
NEtFOSAA	6.20	584.1	419.1	526.1	0.9967
NMeFOSAA	5.90	569.7	418.9	482.9	0.9989
PFTrDA	7.14	662.9	618.9	162.2	0.9918
PFTA	7.53	713.0	668.9	169.1	0.9981
Isotope Performance Standards					
$^{12}C2$-PFOA	4.21	414.8	370.0	169.0	
$^{13}C4$-PFOS	4.95	502.5	80.0	99.0	
d_3-NMeFOSAA	5.90	572.8	419.0	483.0	
Isotope Dilution Standards					
$^{13}C_2$-PFHxA	2.67	314.9	270.0	120.1	
$^{13}C_2$-PFDA	5.61	514.8	470.1	269.1	
d_5-NEtFOSAA	6.19	588.9	419.1	531.1	
$^{13}C_3$-HFPO-DA	2.89	287.0	169.0	185.1	
Isotope Dilution Standards					
$^{13}C_4$-PFBA	4.11	217.1	172.1	-	
$^{13}C_5$-PFPeA	6.09	268	223.2	70.1	
$^{13}C_3$-PFBS	6.47	302.1	79.9	99.0	
$^{13}C_2$-4:2FTS	7.96	328.9	309	80.9	
$^{13}C_5$-PFHxA	8.13	318.1	273	121.1	
$^{13}C_3$-HFPO-DA	8.67	287	169	185.1	
$^{13}C_4$-PFHPA	9.90	367.1	322.1	-	
$^{13}C_3$-PFHxS	10.01	401.9	80	99.0	
$^{13}C_2$-6:2FTS	11.31	429.1	409	81.0	
$^{13}C_8$-PFOA	11.36	421.1	376.1	172.2	
$^{13}C_8$-PFOS	12.61	507.1	80	98.9	
$^{13}C_9$-PFNA	12.62	471.5	427	-	
$^{13}C_6$-PFDA	13.68	519	474	-	
$^{13}C_2$-8:2FTS	13.68	529	508.9	81.0	
$^{13}C_7$-PFUnA	14.61	570	525	-	
$^{13}C_2$-PFDoA	15.40	612.9	569	319.1	

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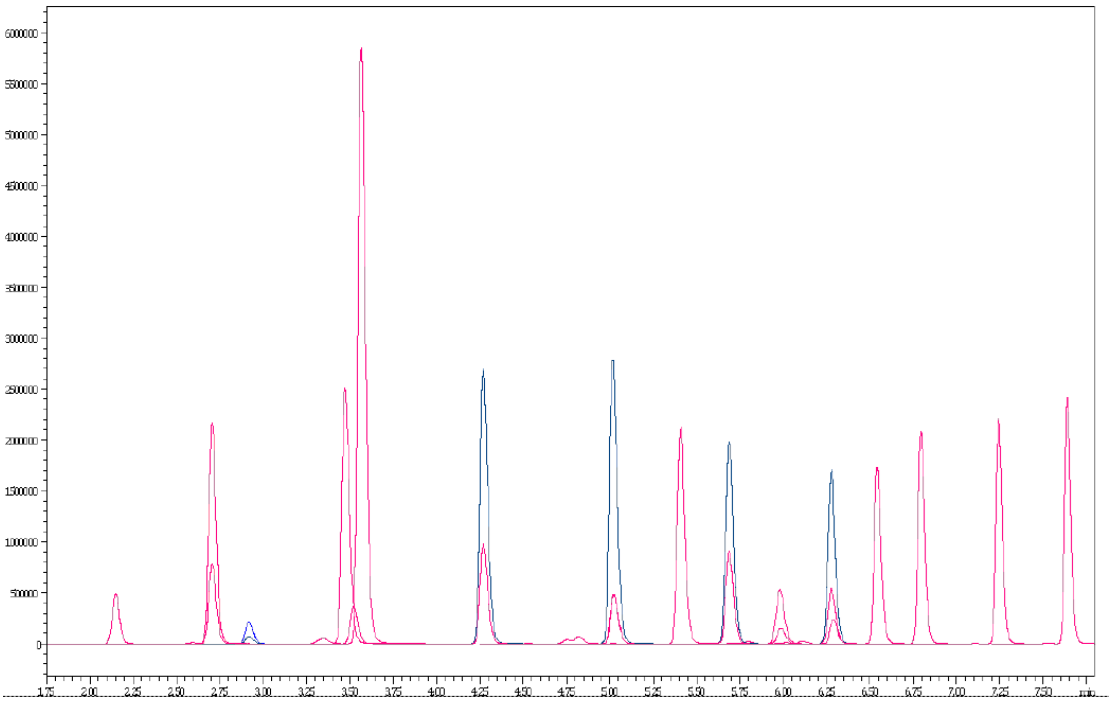


Figure 1: PFAS fortified at low fortification level 5 ng/L in reagent water (5 ng/mL in vial).

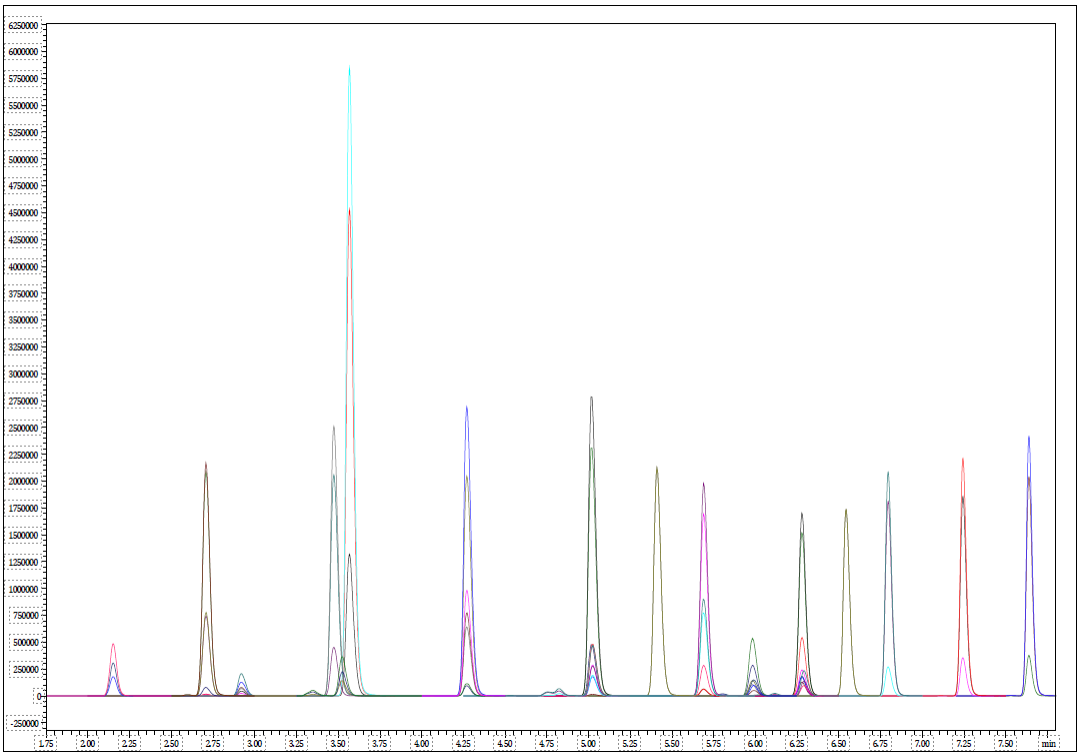


Figure 2: PFAS fortified at high fortification level 10 ng/L in reagent water (10 ng/mL in vial).

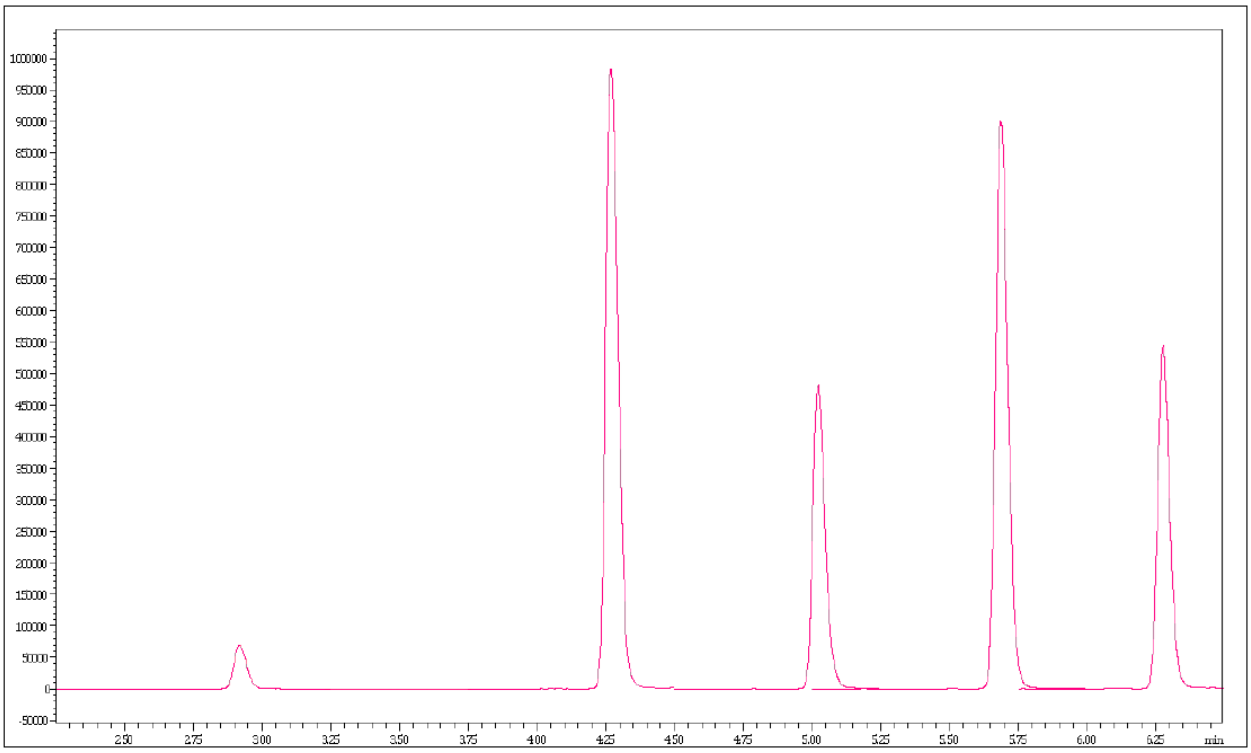


Figure 3: Chromatogram of a LRB sample containing Isotope Dilution and Isotope Performance Standards

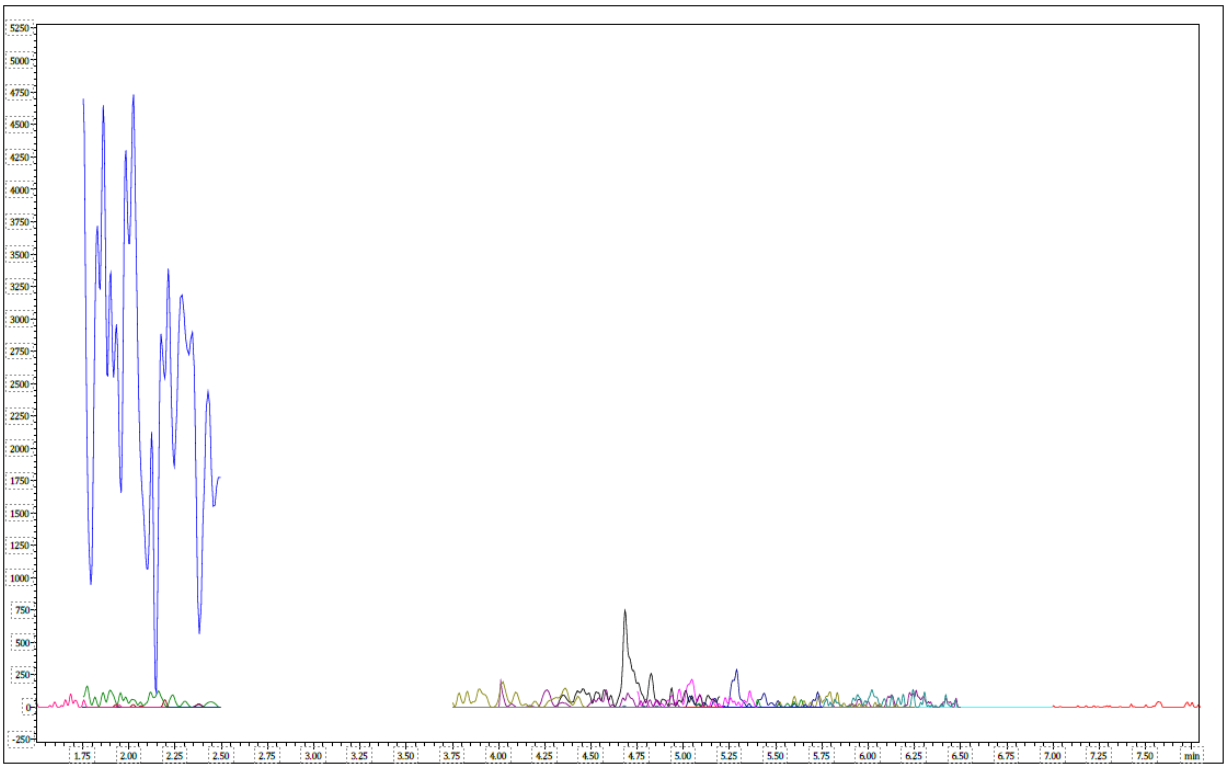
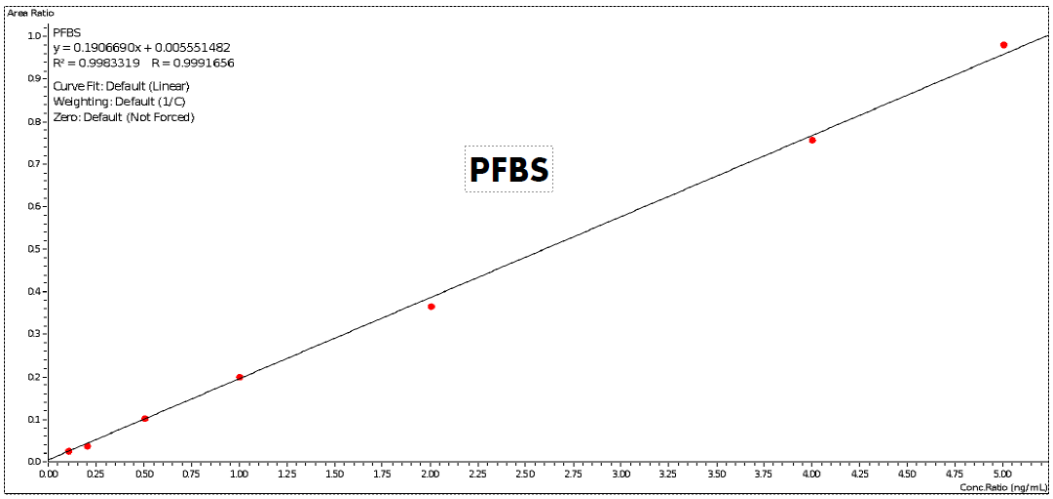
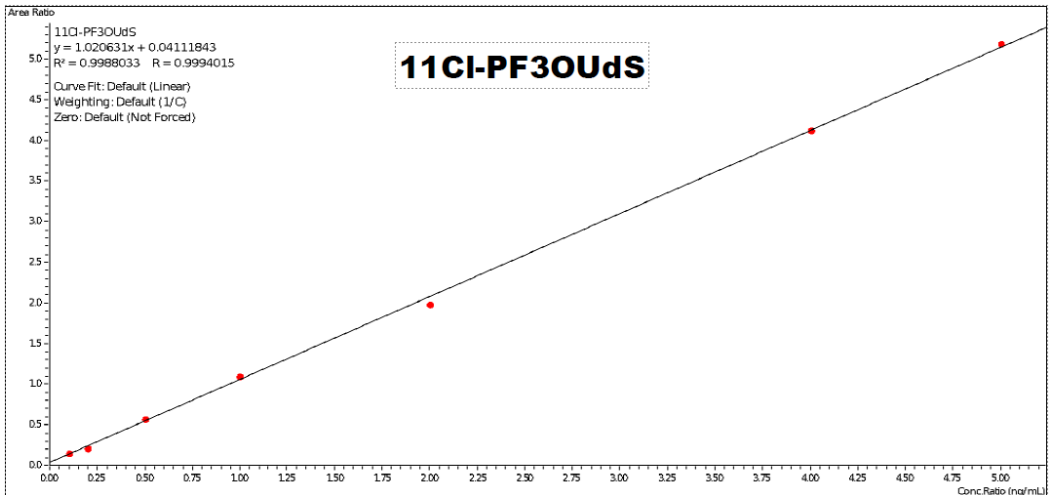
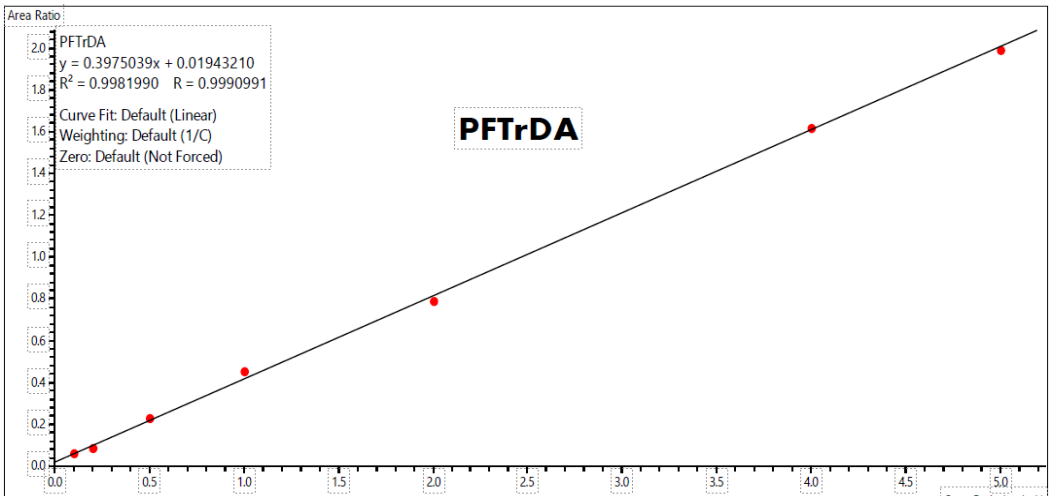


Figure 4: Chromatogram of a blank solvent injection demonstrating low system background levels

Calibration Curves:







SPE Results:

Results in Reagent Water - ECHLD156-P				
	Low Fortification (2.5 ng/L; n=4)		High Fortification (10 ng/L; n=4)	
Analyte	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
PFBS	93%	5%	97%	2%
PFHxA	82%	3%	89%	2%
HFPO-DA	75%	4%	72%	4%
PFHpA	81%	4%	91%	1%
PFHxS	108%	4%	96%	1%
ADONA	77%	3%	88%	1%
PFOA	85%	4%	93%	1%
PFOS	99%	4%	90%	2%
PFNA	82%	3%	101%	1%
9Cl-PF3ONS	91%	3%	98%	2%
PFDA	84%	2%	105%	1%
PFUnA	85%	1%	106%	1%
11Cl-PF3OUdS	88%	4%	95%	2%
PFDoA	81%	3%	93%	1%
N-EtFOSAA	77%	4%	81%	2%
N-MeFOSAA	108%	2%	87%	3%
PFTA	80%	2%	93%	2%
PFTrDA	79%	5%	89%	1%

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Results in Reagent Water - ECDVB156P		
Analyte	One Point Fortification (5 ng/L; n=4)	
	Recovery (%)	RSD (%)
PFBS	96%	2%
PFHxA	96%	2%
HFPO-DA	86%	4%
PFHpA	95%	3%
PFHxS	101%	2%
ADONA	93%	3%
PFOA	95%	3%
PFOS	96%	3%
PFNA	101%	3%
9Cl-PF3ONS	92%	3%
PFDA	99%	5%
PFUnA	98%	5%
11Cl-PF3OUdS	95%	3%
PFDoA	92%	3%
N-EtFOSAA	98%	2%
N-MeFOSAA	106%	4%
PFTA	87%	4%
PFTrDA	85%	3%

References:

1. Unregulated Contaminant Monitoring Rule 3 (UCMR3), accessed online November 2017, http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/.
2. EPA Method 537.1: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), November 2018, EPA/600/R-18/352.
3. Shimadzu's Parts Compatibility Guide for LCMS Analysis of PFC's; accessed from Shimadzu website on November 2017; http://www.ssi.shimadzu.com/products/literature/lcms/085_Shimadzu%E2%80%99s%20Guide%20to%20US%20DOD_DOE%20Analysis%20of%20PFCs%20using%20the%20LCMS-8060.pdf.

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UCT, LLC • 2731 Bartram Road • Bristol, PA 19007 • 800.385.3153 • 215.781.9255
www.unitedchem.com Email: methods@unitedchem.com