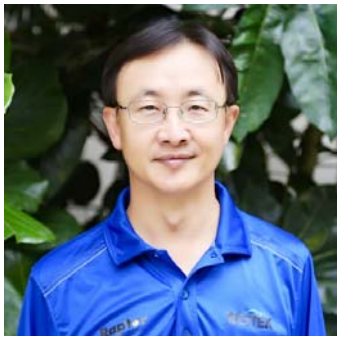
Novel Stationary Phase for Simultaneous Analysis of Ultrashort-Chain (C2, C3), Alternative, and Legacy PFAS



Shun-Hsin Liang, Ph.D

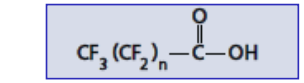
Senior Scientist, LC Applications

Shun-HsinLiang@Restek.com

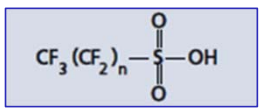
Outline

- PFAS Panel
- Ultrashort-Chain PFAS
- Direct Injection Method Evaluation for Ultrashort-Chain/Alternative/Legacy PFAS (Polar X Column)
- Comprehensive PFAS Analysis (Polar X Column)
- Conclusions

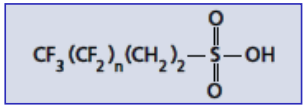
PFAS (Per- and Polyfluoroalkyl Substances)



Perfluoroalkylcarboxylic Acid (PFCA)



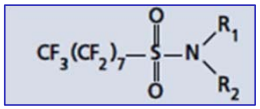
Perfluoroalkylsulfonic Acid (PFSA)



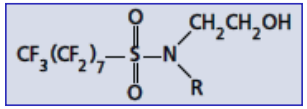
X:2 Telomer Sulfonic Acid (X:2 FTS)

Surfactant

- Processing aid
- Mist suppressant
- Fire fighting foam
- Cleaning Products

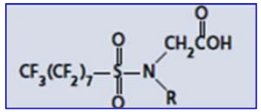


Perfluorooctanesulfonamide (FOSA)

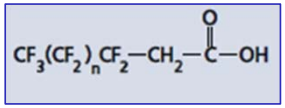


Perfluorooctanesulfonamido-ethanol (FOSE)

Raw Material



Perfluorooctanesulfonamido-acetic acid (FOSAA)



Telomer Carboxylic Acid (X:2 FTA)

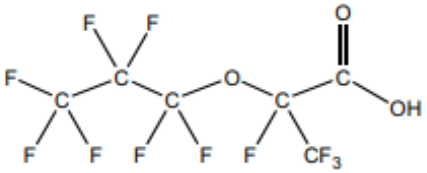
Environmental Transformation Product

PFAS Testing Standards

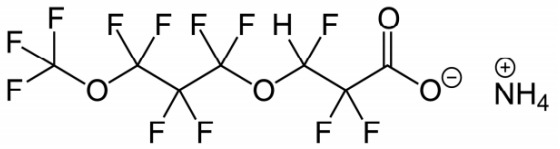
Test Method	US EPA 537.1	ISO 25101:2009	DIN 38407-42	ASTM D7968-17a	ASTM D7979-17	US EPA 533	US EPA 8327	ISO 21675
Sample Matrix	Drinking Water	All water types	All water types	soil	All water types (- drinking water)	Drinking Water	Non-potable water	All water types
# of Analytes	18	24	2	21	21	25	24	30
Sample Prep	SPE	Direct injection	SPE	Direct injection	Direct injection	SPE	Direct injection	SPE
Sample Volume	250 mL	1000 mL	50 mL	2 g	5 mL	250 mL	5 mL	50 – 1000 mL*
Detection limit	Optional	Not shown	• 0.01 ug/L • 0.025 ng/L for treated waste water	MDL (2.41 – 258.37 ng/kg)	MDL (0.7 – 106.8 ng/L)	LCMRL (1.7 – 20 ng/L)	• MDL (0.7 – 4.6 ng/L) • LLOQ is 10 ng/L	LOQ: 0.2 ng/L (loose term)

PFOA and PFOS Alternatives

Perfluoroalkyl ether carboxylic acids (PFECAs)

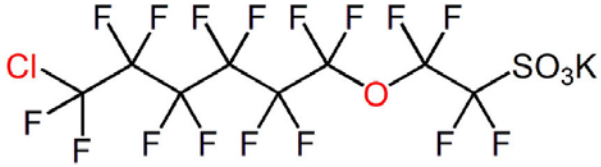


Hexafluoropropylene oxide dimer acid
(HFPO-DA) ***GenX***

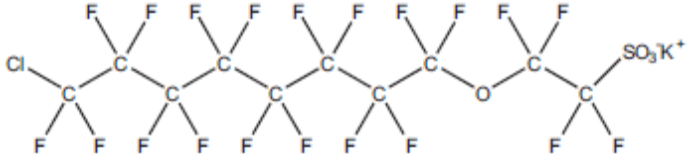


ammonium 4,8-dioxa-3H-perfluorononanoate
(ADONA)

Polyfluoroalkyl ether sulfonates (PFESAs)

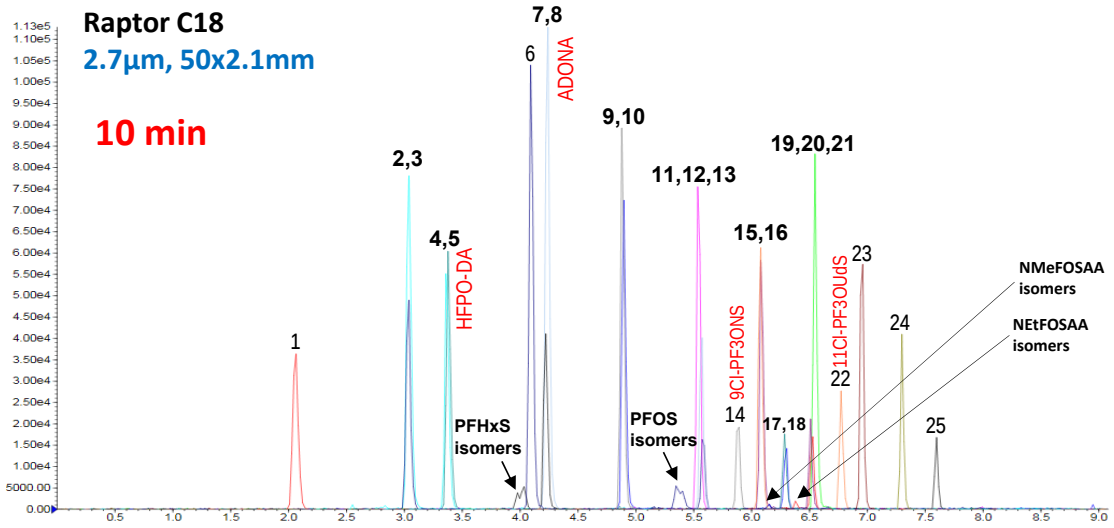


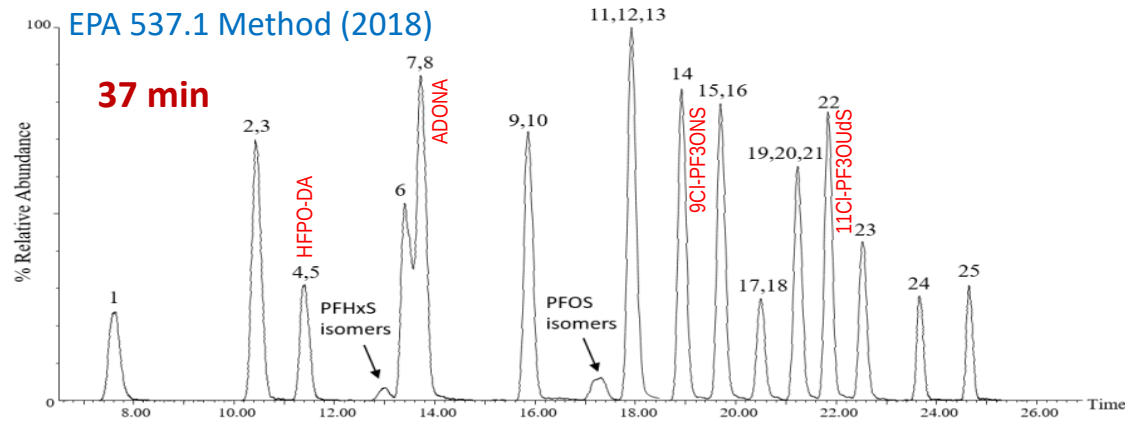
F-53B
(9-chlorohexadecafluoro-3-oxanonane-1-sulfonate)
(9Cl-PF3ONS)



F-53B
(11-chloroeicosafluoro-3-oxanonane-1-sulfonate)
(11Cl-PF3OUdS)

Updated 537.1 Method (Drinking Water)





Analyte	Peak # (Fig. 1)	RT (min)	IS# Ref
PFBS	1	7.62	2
PFHxA	2	10.42	1
HFPO-DA	4	11.38	1
PFHpA	6	13.40	1
PFHxS	7	13.58	2
ADONA	8	13.73	1
PFOA	9	15.85	1
PFOS	11	17.91	2
PFNA	13	17.92	1
9Cl-PF3ONS	14	18.91	2
PFDA	15	19.69	1
NMeFOSAA	17	20.50	3
PFUnA	19	21.21	1
NEtFOSAA	20	21.26	3
11CL-PF3OUdS	22	21.84	2
PFDoA	23	22.52	1
PFTrDA	24	23.66	1
PFTA	25	24.64	1
$^{13}C_2$-PFHxA	3	10.42	1
$^{13}C_3$-HFPO-DA	5	11.40	1
$^{13}C_2$-PFDA	16	19.69	1
d_5-NEtFOSAA	21	21.24	3
$^{13}C_2$-PFOA– IS#1	10	15.85	-
$^{13}C_4$-PFOS– IS#2	12	17.91	-
d_3-NMeFOSAA–IS#3	18	20.49	-

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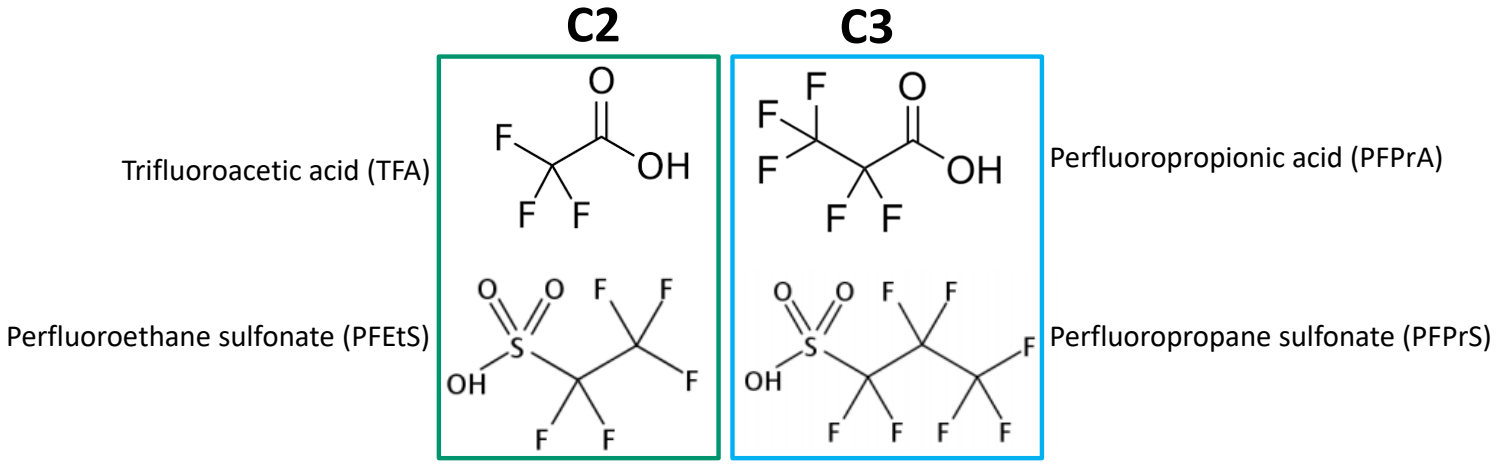
Ultrashort-Chain PFAS



Detected in different water matrices (snow, rain, river, and tap water)

1. **PFPrA is up to 45% of the total PFAS in rain and snow samples (USA, France, Japan)**
2. **C2-C3 accounted for >40% of the total PFAS in rain samples (Canada)**
3. **TFA is the most abundant PFAS in rainwater (Japan)**
4. **PFEtS and PFPrS are detected in aqueous film-formimg foam (AFFF)**

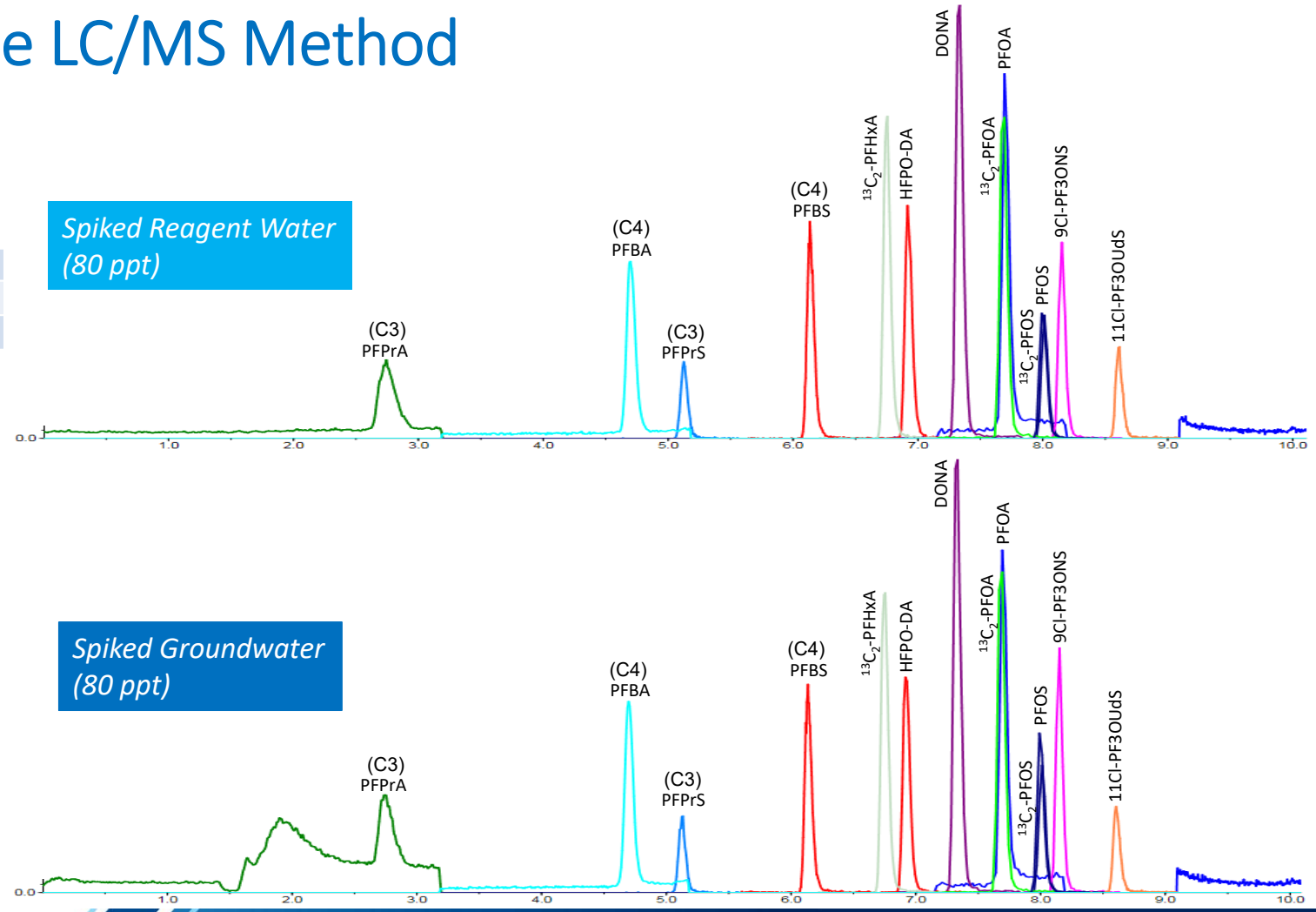
Analytical methods for investigation on the sources and environmental levels

Reversed-Phase LC/MS Method

Raptor C18
2.7µm, 100x3.0mm

LC Conditions : (Shimadzu Nexera X2)	
Mobile Phase A	5mM ammonium acetate in water
Mobile Phase B	methanol

Gradient	Time (min)	%B
	0.00	20
	7.00	95
	9.00	95
	9.01	20
	11.00	20
Injection	10 µL	
Flow Rate	0.25 mL/min	
Run Time	11 min	
Column Temp.	40°C	



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Direct Injection Method Evaluation

Raptor LC Columns

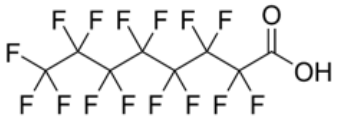
Polar X

- A Single ligand capable of **HILIC** and **Ion Exchange** retention
- Proper retention for polar compounds

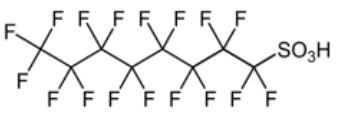
Direct Injection Method Evaluation

Legacy PFAS

C8



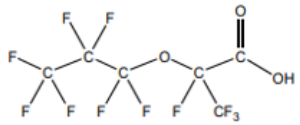
Perfluorooctanoic acid (PFOA)



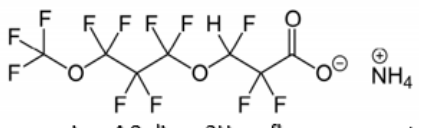
Perfluorooctanesulfonic acid (PFOS)

PFOA and PFOS Alternatives

Perfluoroalkyl ether carboxylic acids (PFECAs)

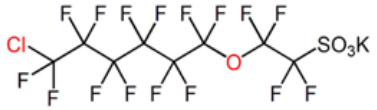


Hexafluoropropylene oxide dimer acid
(HFPO-DA)



ammonium 4,8-dioxa-3H-perfluorononanoate
(ADONA)

Polyfluoroalkyl ether Sulfonates (PFESAs)

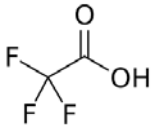


F53-B
(9-chlorohexadecafluoro-3-oxanonane-1-sulfonate)
(9Cl-PF3ONS)

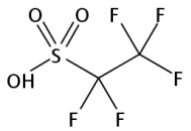
F53-B
(11-chloroeicosafluoro-3-oxanonane-1-sulfonate)
(11Cl-PF3OUdS)

UltraShort & Short-Chain PFAS

C2

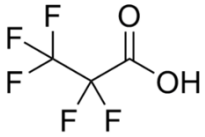


Trifluoroacetic acid (TFA)

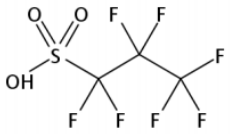


Perfluoroethane sulfonate (PFEtS)

C3

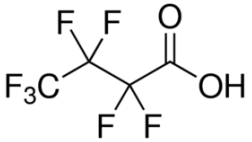


Perfluoropropionic acid (PFPrA)

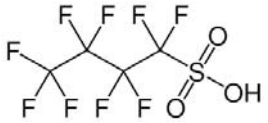


Perfluoropropane sulfonate (PFPrS)

C4

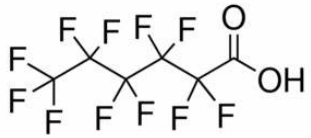


Perfluorobutanoic acid (PFBA)

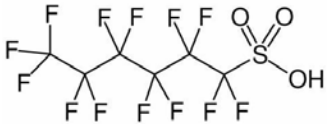


Perfluorobutane sulfonate (PFBS)

C6

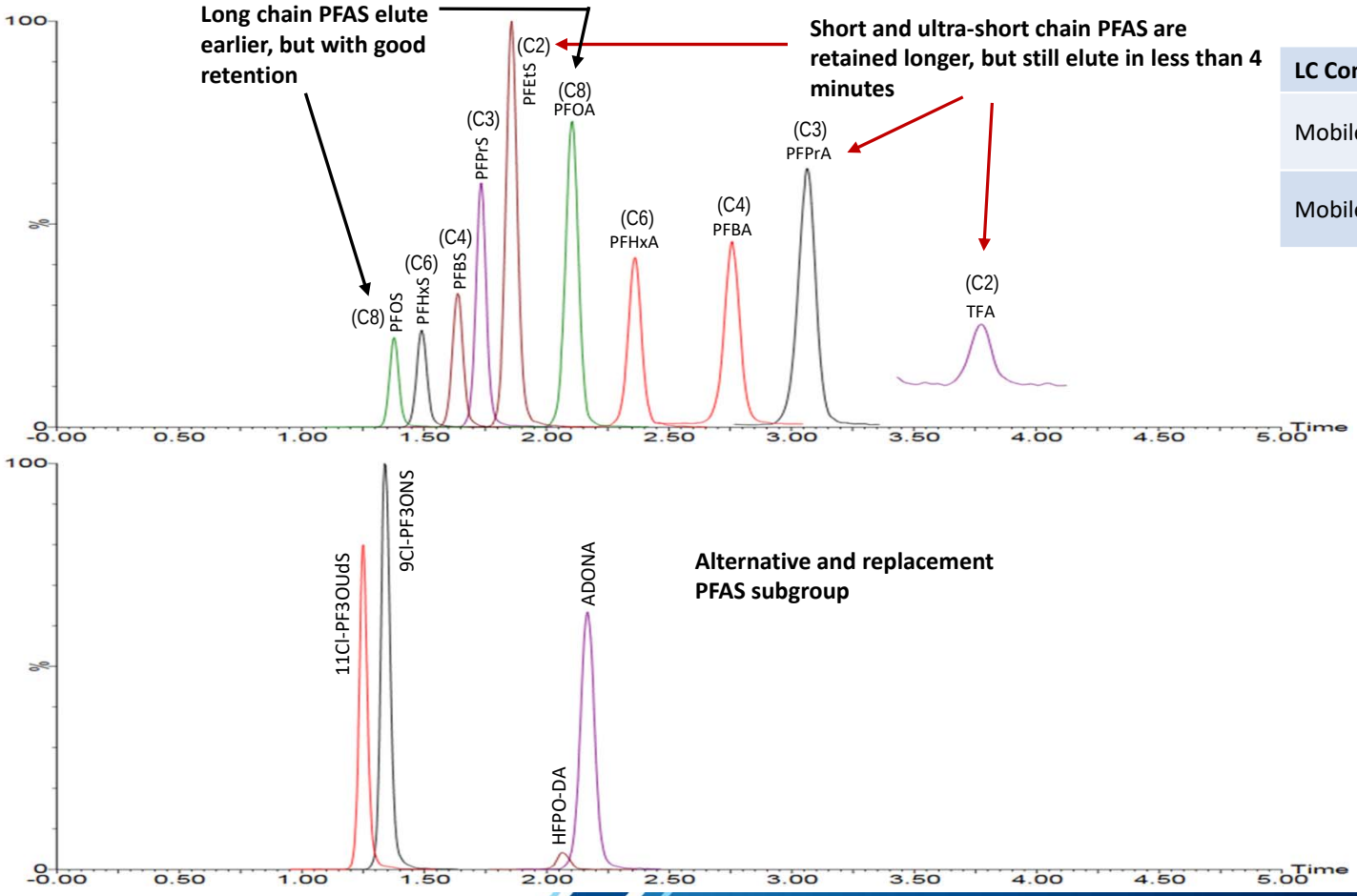


Perfluorohexanoic acid (PFHxA)



Perfluorohexane sulfonate (PFHxS)

Direct Injection Method Evaluation



Polar X: 2.7µm 50x2.1 mm

LC Conditions : (Waters Acquity UPLC)	
Mobile Phase A	10mM ammonium formate, 0.05% formic acid in water
Mobile Phase B	0.05% formic acid in 60:40 acetonitrile:methanol

Gradient	Time (min)	%B
	0.00	85
	5.00	85
Injection	10 µL	
Flow Rate	0.5 mL/min	
Run Time	8 min	
Column Temp.	40°C	

400 ppt in 50:50 water:methanol

Direct Injection Method Evaluation

Precision & Accuracy of Fortified Water Samples:

1. **Tap water**
2. **River water (Chicago)**
3. **Groundwater**
4. **POTW water (Effluent)**




Direct Injection Method Evaluation

Analyte	Precursor Ion	Product Ion	IS for Quantification
TFA	113.03	69.01	$^{13}C_2$-PFHxA
PFPrA	163.03	119.01	$^{13}C_2$-PFHxA
PFBA	212.97	168.97	$^{13}C_2$-PFHxA
PFHxA	312.97	268.90	$^{13}C_2$-PFHxA
PFOA	412.90	368.91	$^{13}C_2$-PFOA
HFPO-DA	284.97	168.92	$^{13}C_2$-PFOA
ADONA	376.90	250.93	$^{13}C_2$-PFOA
PFEtS	198.87	79.92	$^{13}C_3$-PFBS
PFPrS	248.97	79.98	$^{13}C_3$-PFBS
PFBS	298.97	79.97	$^{13}C_3$-PFBS
PFHxS	398.90	79.97	$^{13}C_3$-PFBS
PFOS	498.84	79.97	$^{13}C_4$-PFOS
9Cl-PF3ONS	530.78	350.85	$^{13}C_4$-PFOS
11Cl-PF3OUdS	630.78	450.80	$^{13}C_4$-PFOS
$^{13}C_2$-PFHxA	314.97	269.93	-
$^{13}C_2$-PFOA	414.90	369.87	-
$^{13}C_3$-PFBS	301.90	79.97	-
$^{13}C_4$-PFOS	502.84	79.97	-

Direct Injection Method Evaluation

Polar X Column
2.7µm, 50x2.1mm

Sample Preparation:

(polypropylene vial)

250 µL water sample or standard

+

250 µL methanol

+

5 µL internal standard

(10 ng/mL $^{13}C_2$-*PFHxA*, $^{13}C_2$-*PFOA*, $^{13}C_3$-*PFBS*, $^{13}C_4$-*PFOS* in methanol)

Direct Injection Method Evaluation

Quadratic regression (1/x weighted)

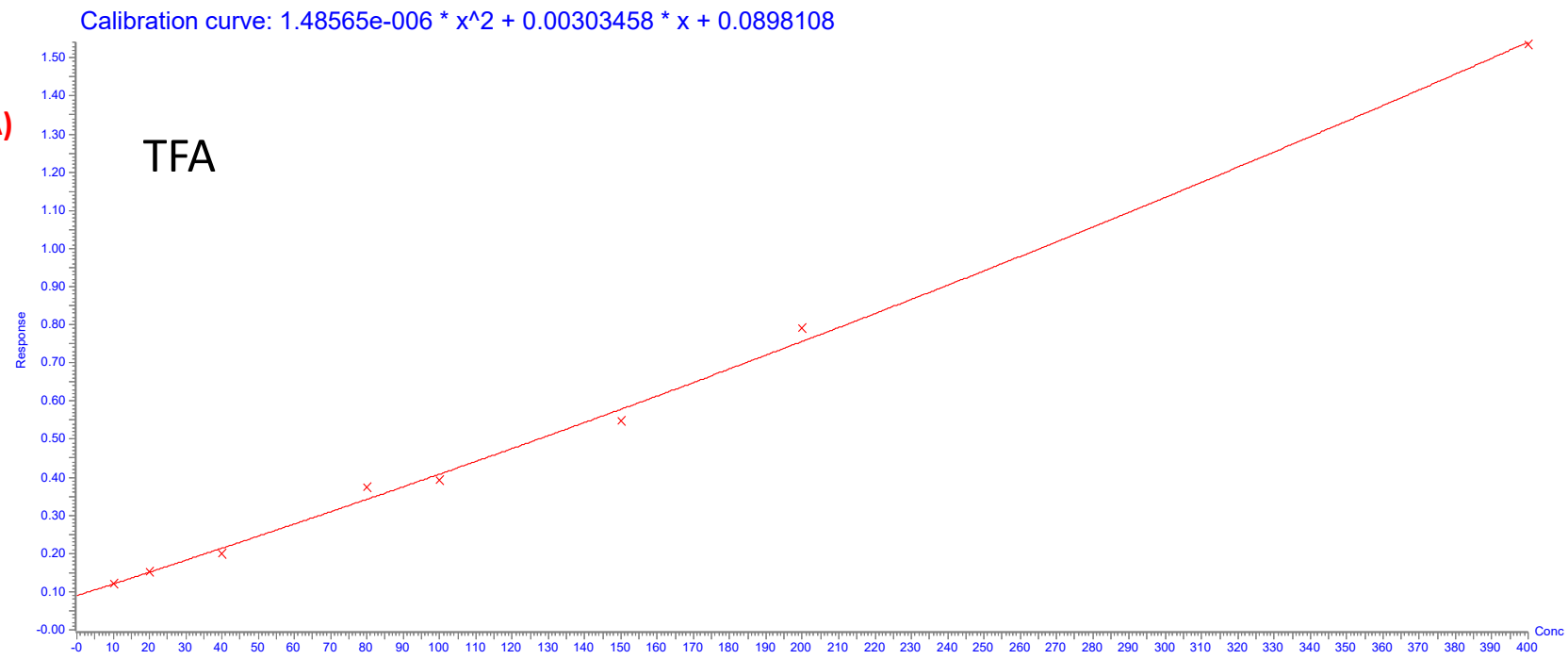
Calibration Range:

10 – 800 ng/L

20 – 800 ng/L (for TFA)

r^2 value > 0.996

deviations <20%



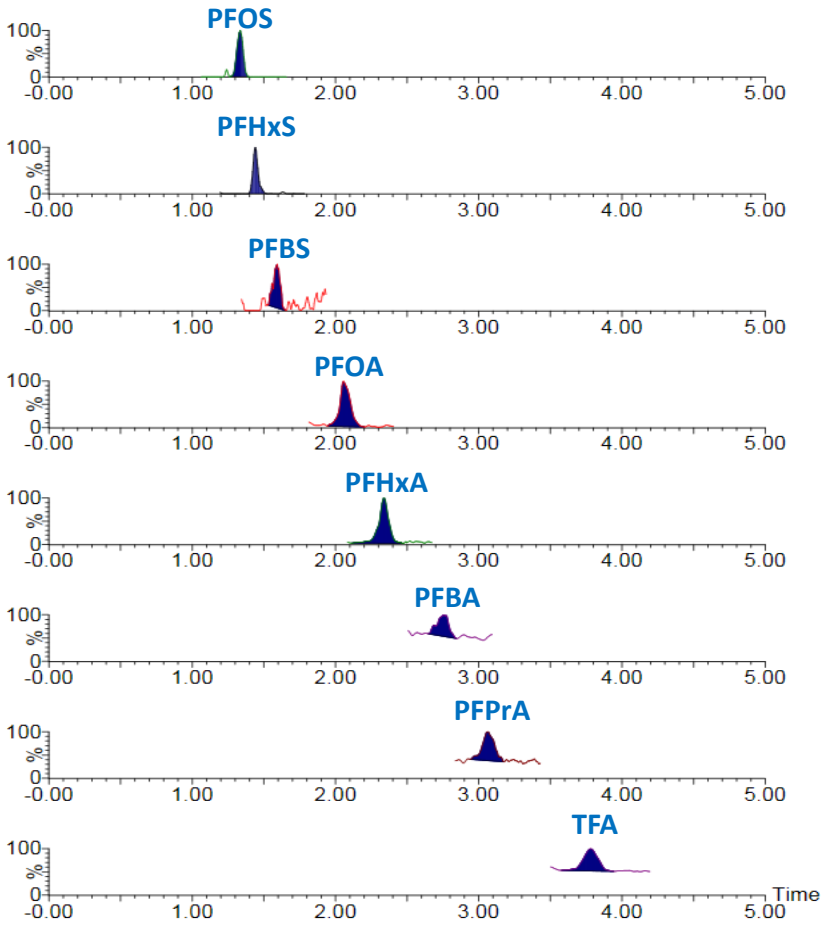
Direct Injection Method Evaluation

Analytes in Blank Water Samples

Samples	Detected Concentration (ng/L)													
	TFA	PFPrA	PFBA	PFHxA	PFOA	HFPO-DA	ADONA	PFEtS	PFPrS	PFBS	PFHxS	PFOS	9Cl-PF3ONS	11Cl-PF3OUdS
Tap Water	164.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
River Water	193.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Groundwater	1425.2	ND	ND	ND	5.4	ND	ND	ND	ND	6.7	3.9	ND	ND	ND
POTW Water	352.8	9.6	15.3	93.5	20.4	ND	ND	ND	ND	6.8	6.7	9.6	ND	ND

Direct Injection Method Evaluation

PFAS in Blank POTW Water

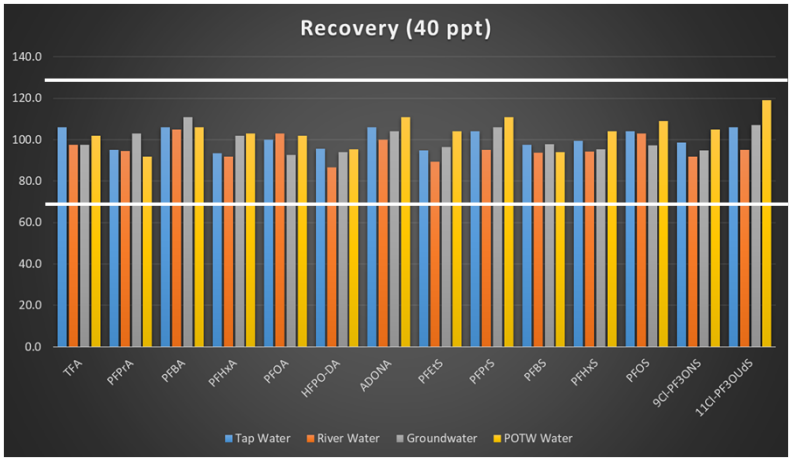


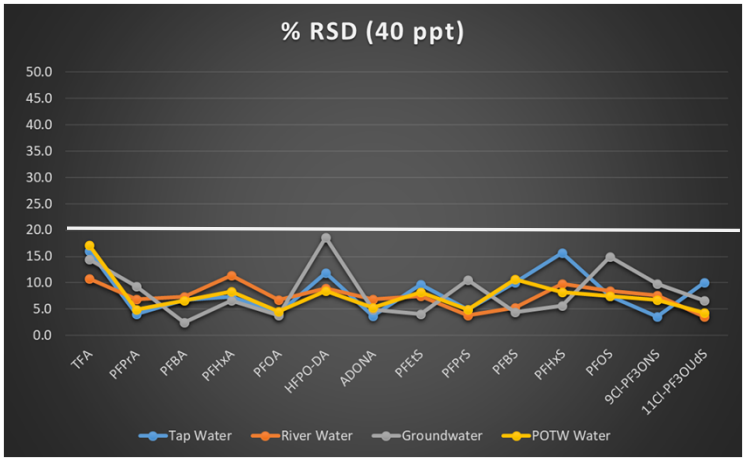
Direct Injection Method Evaluation

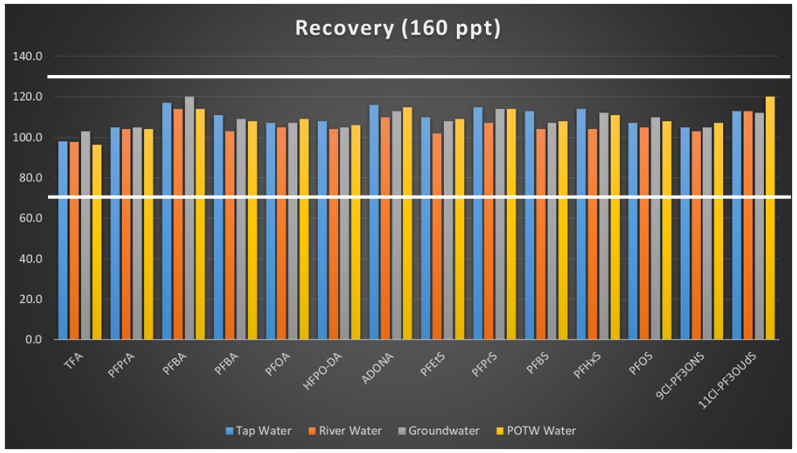
Accuracy

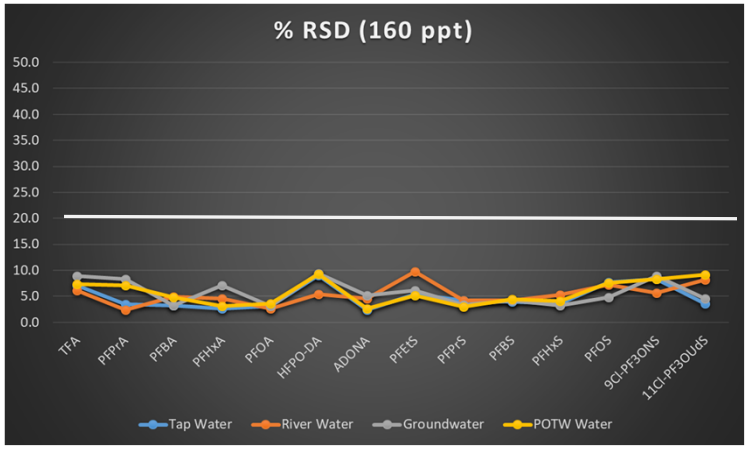
% Recovery:

70 – 130 %







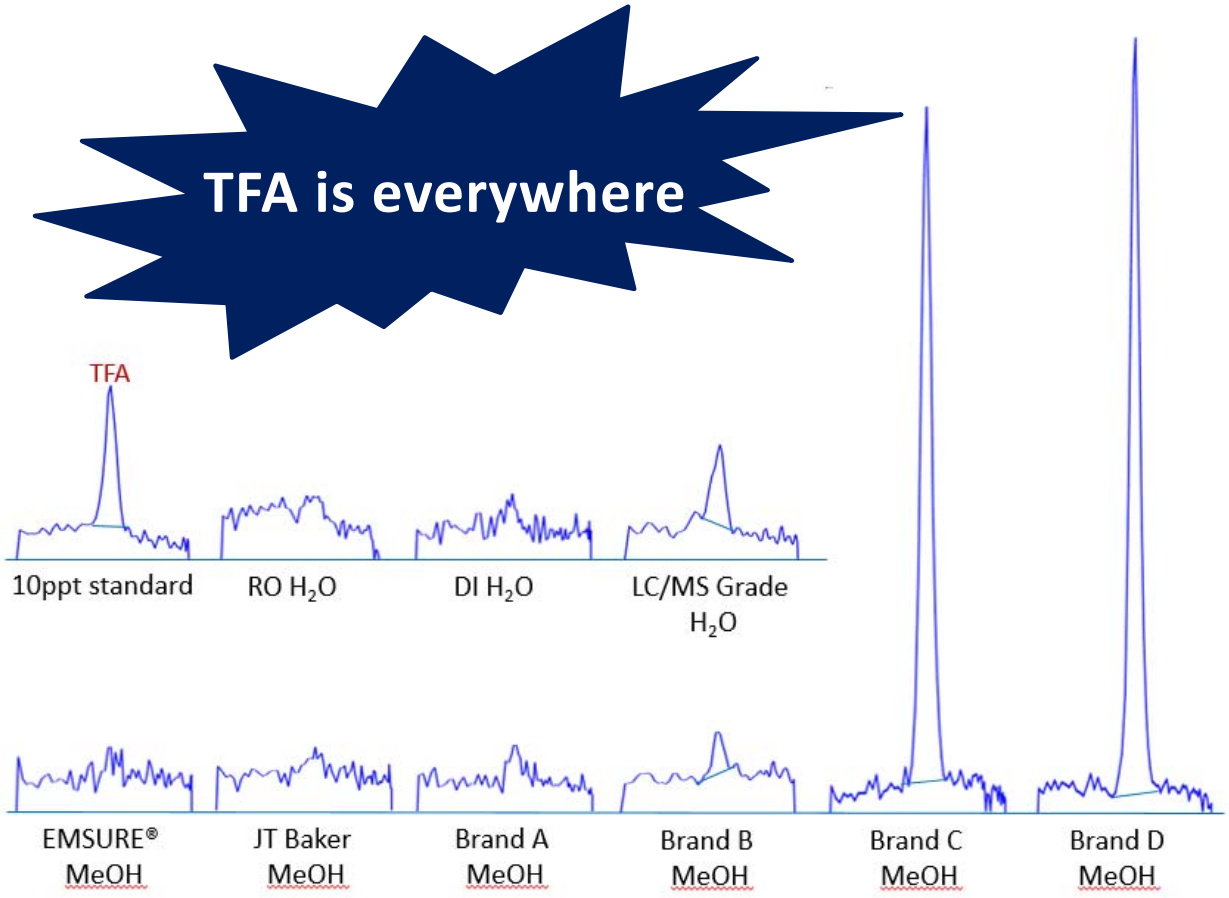


Precision

% RSD:

<20 %

TFA Contamination in Reagent Solvent



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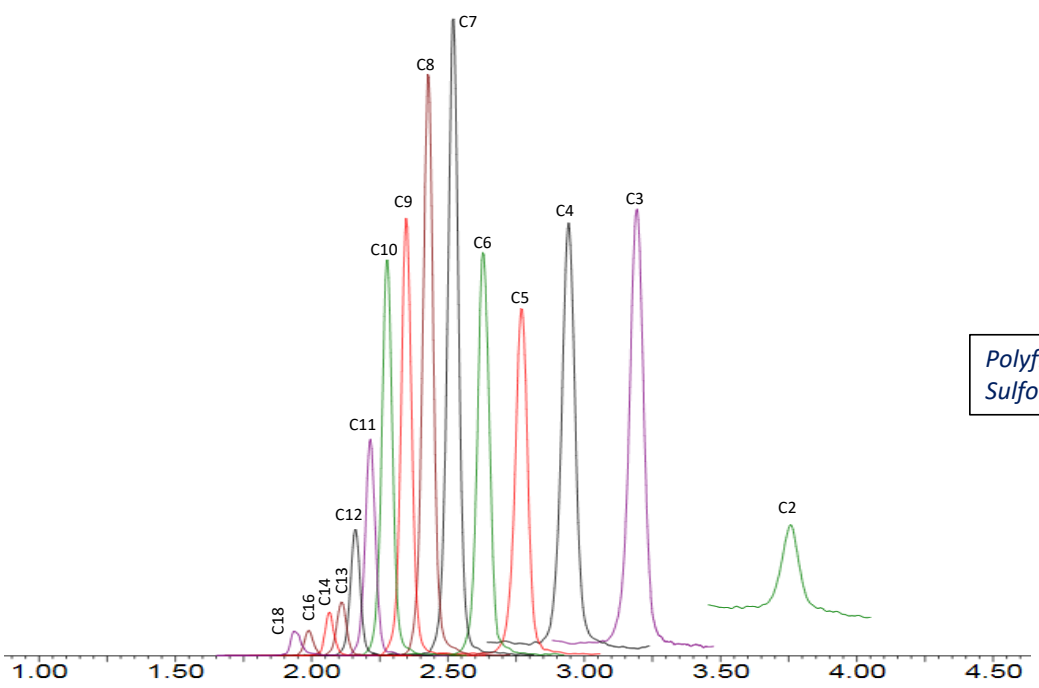
Comprehensive & Simultaneous Analysis of Different Classes of PFAS on the Raptor Polar X

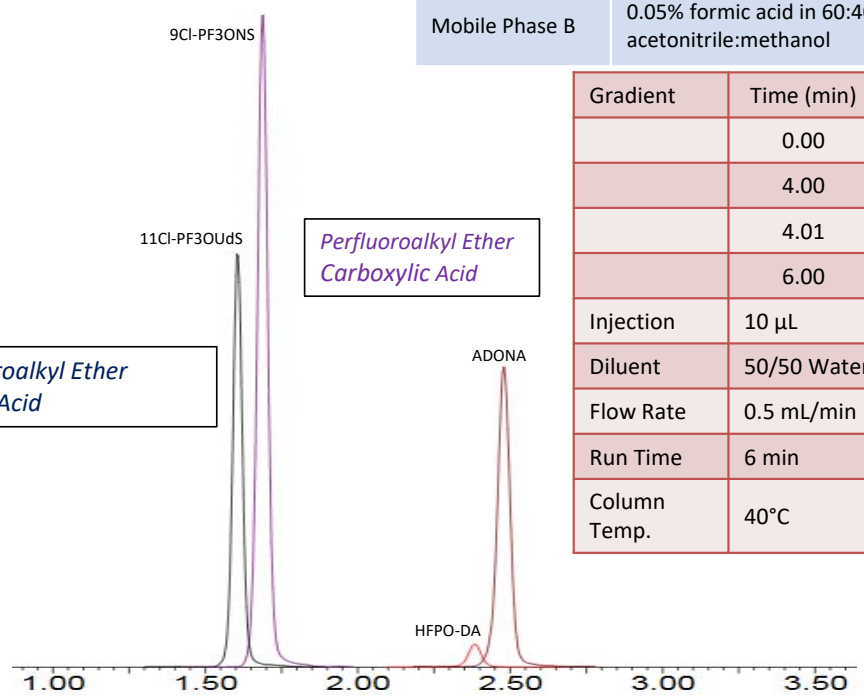
Polar X: 2.7µm 50 x 2.1 mm

Perfluoroalkylcarboxylic Acid



Polyfluoroalkyl Ether Sulfonic Acid

Perfluoroalkyl Ether Carboxylic Acid

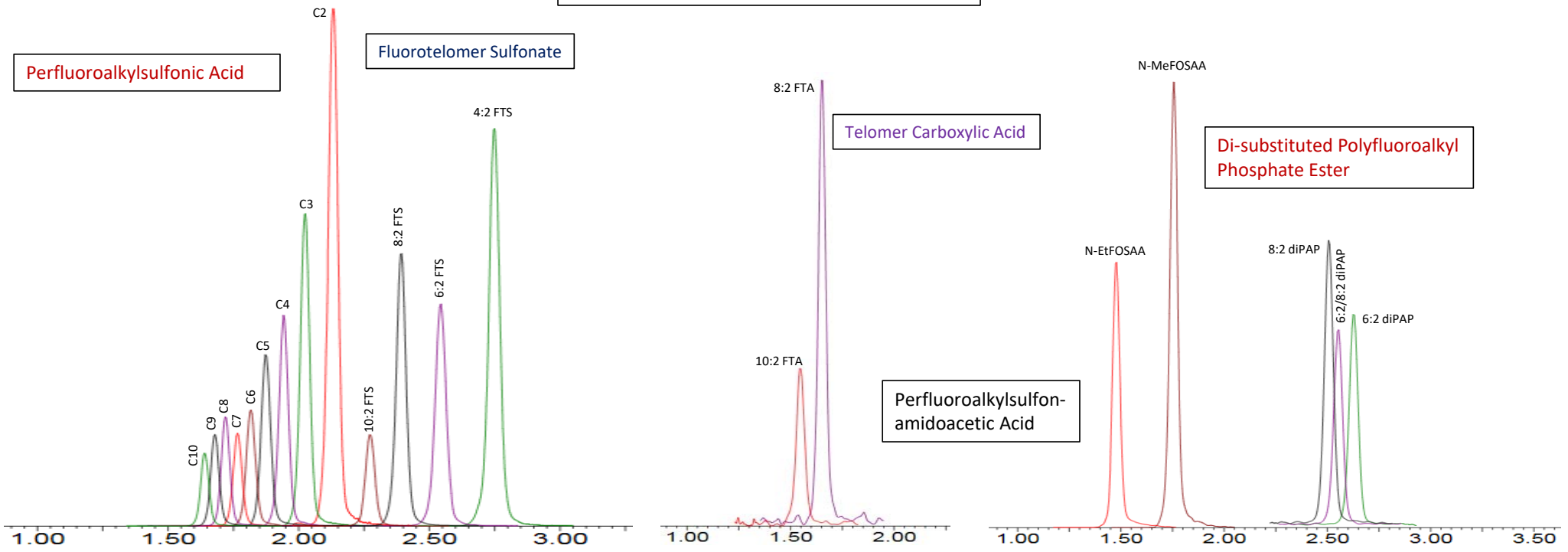


LC Conditions : (Waters Acquity UPLC)	
Mobile Phase A	10mM ammonium formate, 0.05% formic acid in water
Mobile Phase B	0.05% formic acid in 60:40 acetonitrile:methanol

Gradient	Time (min)	%B
	0.00	95
	4.00	65
	4.01	95
	6.00	95
Injection	10 µL	
Diluent	50/50 Water/MeOH	
Flow Rate	0.5 mL/min	
Run Time	6 min	
Column Temp.	40°C	

Comprehensive & Simultaneous Analysis of Different Classes of PFAS on the Raptor Polar X

Polar X: 2.7µm 50 x 2.1 mm



Conclusions

- Unique stationary phase provides proper chromatographic retention of small, polar ultrashort-chain PFAS.
- Fast and simple isocratic LC-MS/MS method allows high-throughput PFAS analysis in potable and non-potable waters.
- This method is suitable for labs interested in adding ultrashort-chain compounds to an existing PFAS assay.
- Multi-classes of PFAS can be simultaneously analyzed on the Polar X column.

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Thanks for Your Attention

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