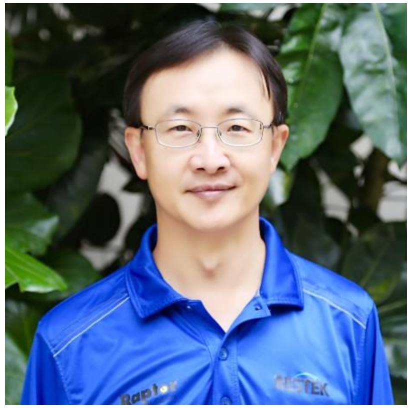
Method Development for Ultrashort-Chain and Short-Chain PFAS Analysis in Potable and Non-Potable Waters



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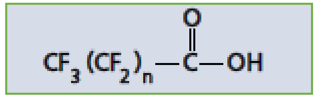
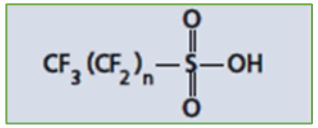
Outline

- PFAS Panel
- Ultrashort-Chain PFAS Analysis
- Direct Injection Method for Ultrashort-Chain/Alternative/Legacy PFAS Analysis
- ASTM WK80687 Method Development for Ultrashort-Chain and Short-Chain PFAS Analysis
- Conclusions

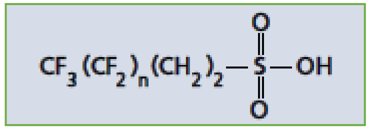
PFAS (Per- and Polyfluoroalkyl Substances)



Perfluoroalkylcarboxylic Acid (PFCA)



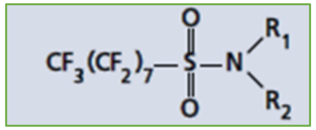
Perfluoroalkylsulfonic Acid (PFSA)



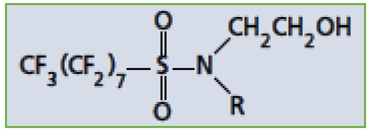
X:2 Telomer Sulfonic Acid (X:2 FTS)

Surfactant

Processing aid
Mist suppressant
Fire fighting foam
Cleaning Products

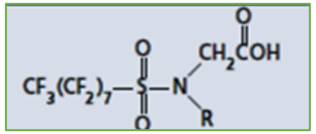


Perfluorooctanesulfonamide (FOSA)

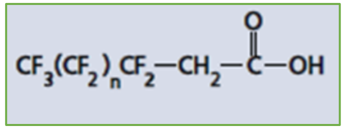


Perfluorooctanesulfonamido-ethanol (FOSE)

Raw Material



Perfluorooctanesulfonamido-acetic acid (FOSAA)



Telomer Carboxylic Acid (X:2 FTA)

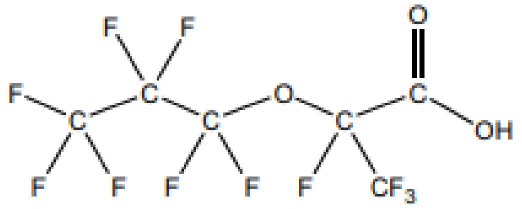
Environmental Transformation Product

PFAS Testing Standards

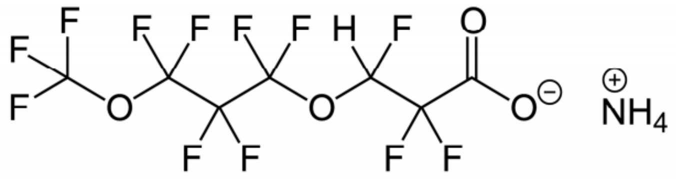
Test Method	US EPA 537.1	ISO 25101:2009	DIN 38407-42	ASTM D7968-17a	ASTM D7979-17	US EPA 533	US EPA 8327	ISO 21675
Sample Matrix	Drinking Water	All water types	All water types	soil	All water types (- drinking water)	Drinking Water	Non-potable water	All water types
# of Analytes	18	24	2	21	21	25	24	30
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)

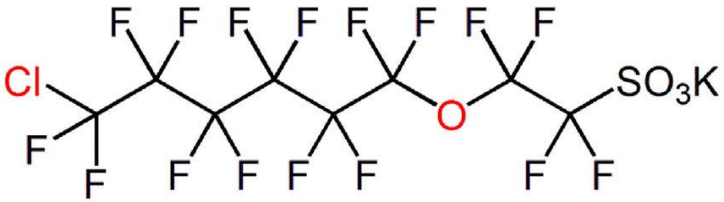


Hexafluoropropylene oxide dimer acid
(HFPO-DA) ***GenX***

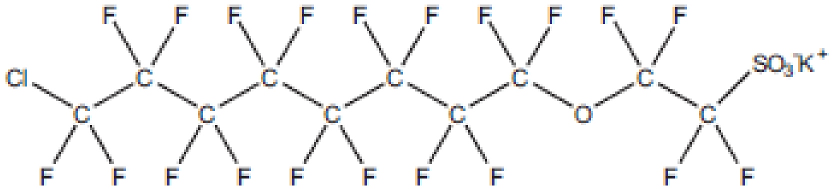


ammonium 4,8-dioxa-3H-perfluorononanoate
(ADONA)

Polyfluoroalkyl ether sulfonates (PFESAs)



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



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

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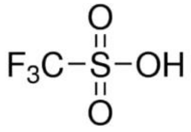
Ultrashort-Chain PFAS

Carboxylic Acid PFAS

Sulfonic Acid PFAS

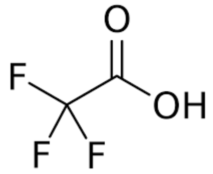
C1



Trifluoromethanesulfonic acid (TFMS)

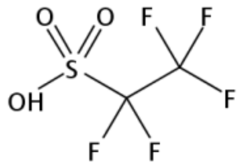
- **A strong acid**
- **Catalyst in chemical reactions - production of pharmaceuticals & electrochemical devices**
- **Firefighting training sites and hazardous waste management facilities – water sources**

C2



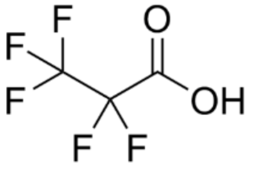
Trifluoroacetic acid (TFA)

- **Atmospheric degradation of hydrofluorocarbons (HFCs) & hydrochlorofluorocarbons (HCFCs) – refrigerants**
- **Breakdown of pharmaceuticls, pesticides, and polymers**
- **Stable in the environment & persist in water, soil, air**



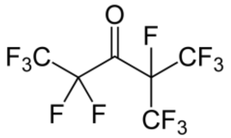
Perfluoroethane sulfonate (PFEtS)

C3

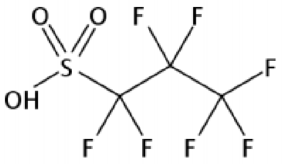


Perfluoropropionic acid (PFPrA)

- **Atmospheric degradation of HFCs & HCFCs – refrigerants**
- **Degradation of perfluoro-2-methyl-3-pentanone (used in firefighting fluid)**



- **Predominant PFAS - 45% of total detectable PFAS in rain & snow collected from the US, France, and Japan**



Perfluoropropane sulfonate (PFPrS)

- **Present in aqueous film-forming foams**
- **Detected in groundwaters collected from military bases in US**

Levels of USC PFAS are trending higher in aquatic environments and drinking waters

Measurement of Ultrashort-Chain PFAS

Reversed-phase liquid chromatography – insufficient retention/matrix effects

GC-MS for TFA and C4 – C6 carboxylic acid PFAS analysis – needs derivatization and is unable for simultaneous analysis of sulfonic acid PFAS

Anionic exchange LC column – extended retention (>20 minutes) and broader peak shapes for USC PFAS

Supercritical fluid chromatography – efficient analysis but needs to invest in SFC instrument

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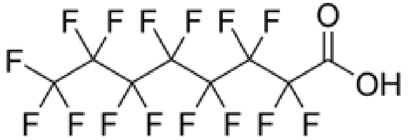
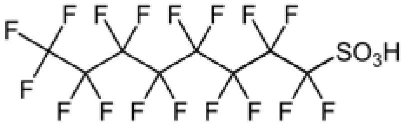
Ultrashort-Chain/Legacy/Alternative PFAS

Legacy PFAS

C8



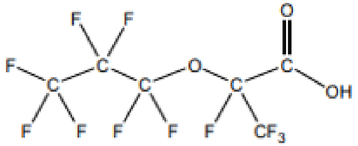
Perfluorooctanoic acid (PFOA)



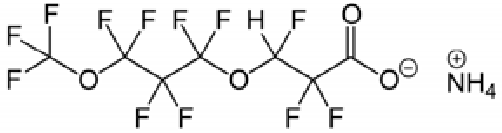
Perfluorooctanesulfonic acid (PFOS)

PFOA and PFOS Alternatives

Perfluoroalkyl ether carboxylic acids (PFECAs)

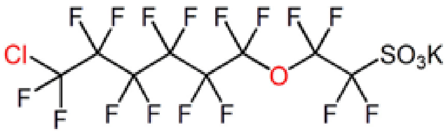


Hexafluoropropylene oxide dimer acid (HFPO-DA)

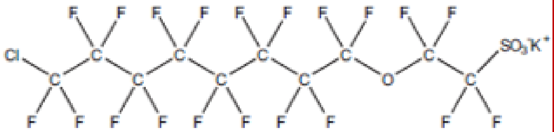


ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA)

Polyfluoroalkyl ether Sulfonates (PFESAs)



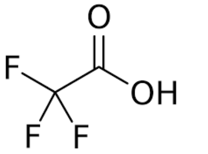
F53-B
(9-chlorohexadecafluoro-3-oxanonane-1-sulfonate)
(9Cl-PF3ONS)



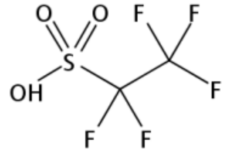
F53-B
(11-chloroeicosafluoro-3-oxanonane-1-sulfonate)
(11Cl-PF3OUdS)

UltraShort & Short-Chain PFAS

C2

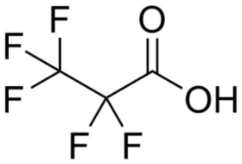


Trifluoroacetic acid (TFA)

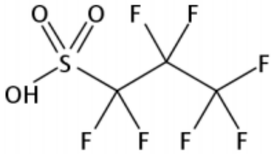


Perfluoroethane sulfonate (PFEtS)

C3

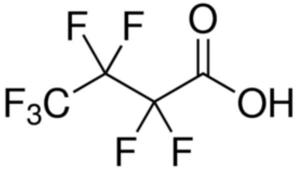


Perfluoropropionic acid (PFPrA)

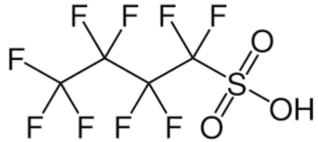


Perfluoropropane sulfonate (PFPrS)

C4

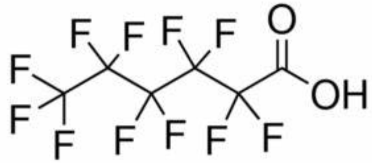


Perfluorobutanoic acid (PFBA)

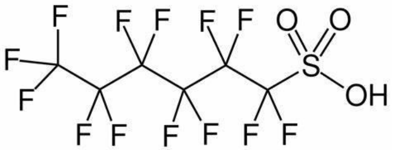


Perfluorobutane sulfonate (PFBS)

C6



Perfluorohexanoic acid (PFHxA)



Perfluorohexane sulfonate (PFHxS)

Novel Solution for Ultrashort-Chain PFAS Analysis

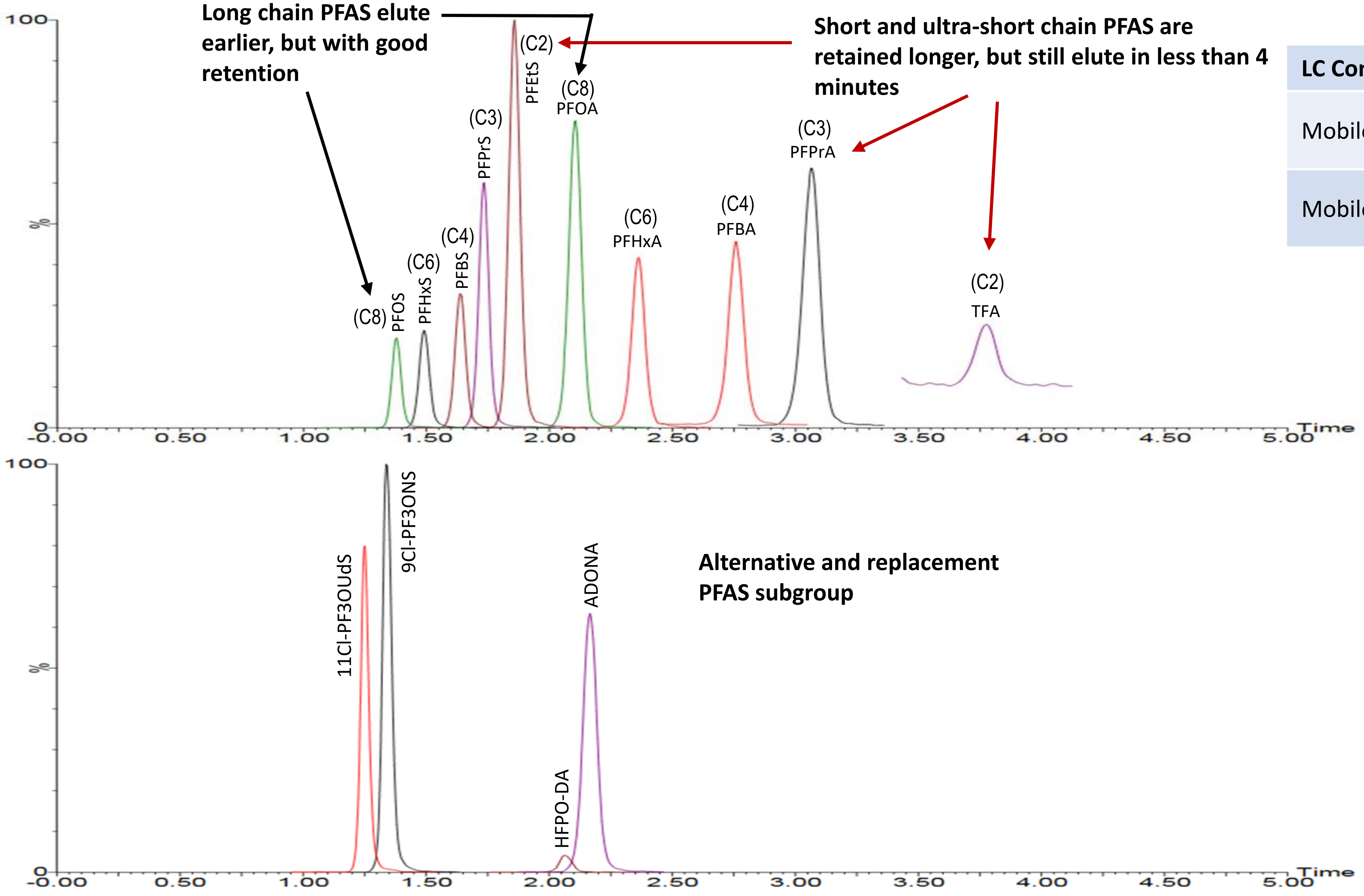
Raptor LC Columns

Polar X

- A single ligand capable of **HILIC** and **Ion Exchange** retention

- Proper retention for polar compounds

Analysis of Ultrashort-Chain/Legacy/Alternative PFAS



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

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

Accuracy & Precision of Fortified Water Samples:
(40 & 160 ppt)

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

Calibration Range:

10 – 800 ng/L

20 – 800 ng/L (for TFA)

r^2 value > 0.996

deviations <20%

Accuracy	***Precision***
% Recovery:	% RSD:
92 – 120 %	<20 %

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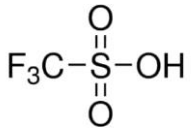
ASTM WK80687 Method Development

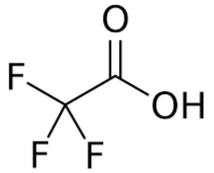
(C1 to C4 PFAS in Potable and Non-Potable Waters)

Carboxylic Acid PFAS | **Sulfonic Acid PFAS**

C1

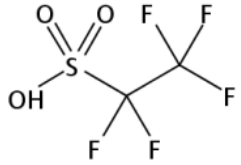


Trifluoromethanesulfonic acid (TFMS)

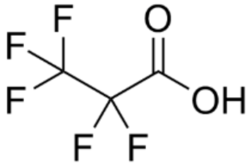


Trifluoroacetic acid (TFA)

C2

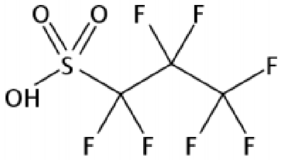


Perfluoroethane sulfonate (PFEtS)

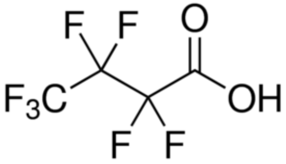


Perfluoropropionic acid (PFPrA)

C3

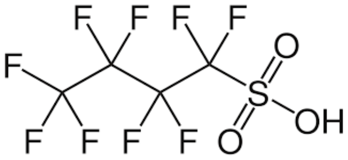


Perfluoropropane sulfonate (PFPrS)



Perfluorobutanoic acid (PFBA)

C4



Perfluorobutane sulfonate (PFBS)

ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)

TFA contamination:

Reagent waters and solvents (methanol & acetonitrile)

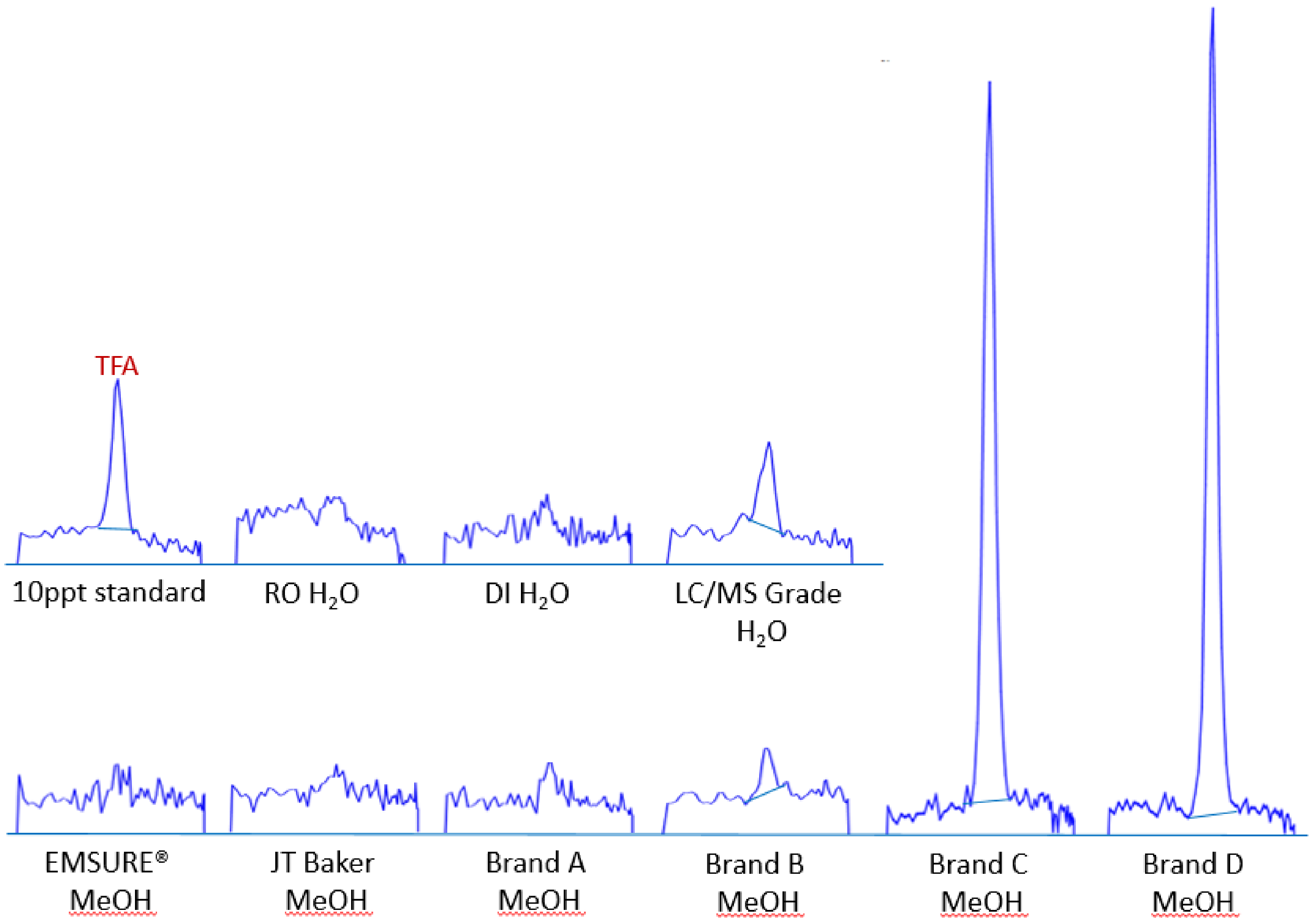
Pipette tips

Vials (glass & polypropylene)

Syringe filters

Glass wool

TFA Contamination in Reagent Solvent



ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)

TFA contamination:

Reagent waters and solvents (methanol & acetonitrile)

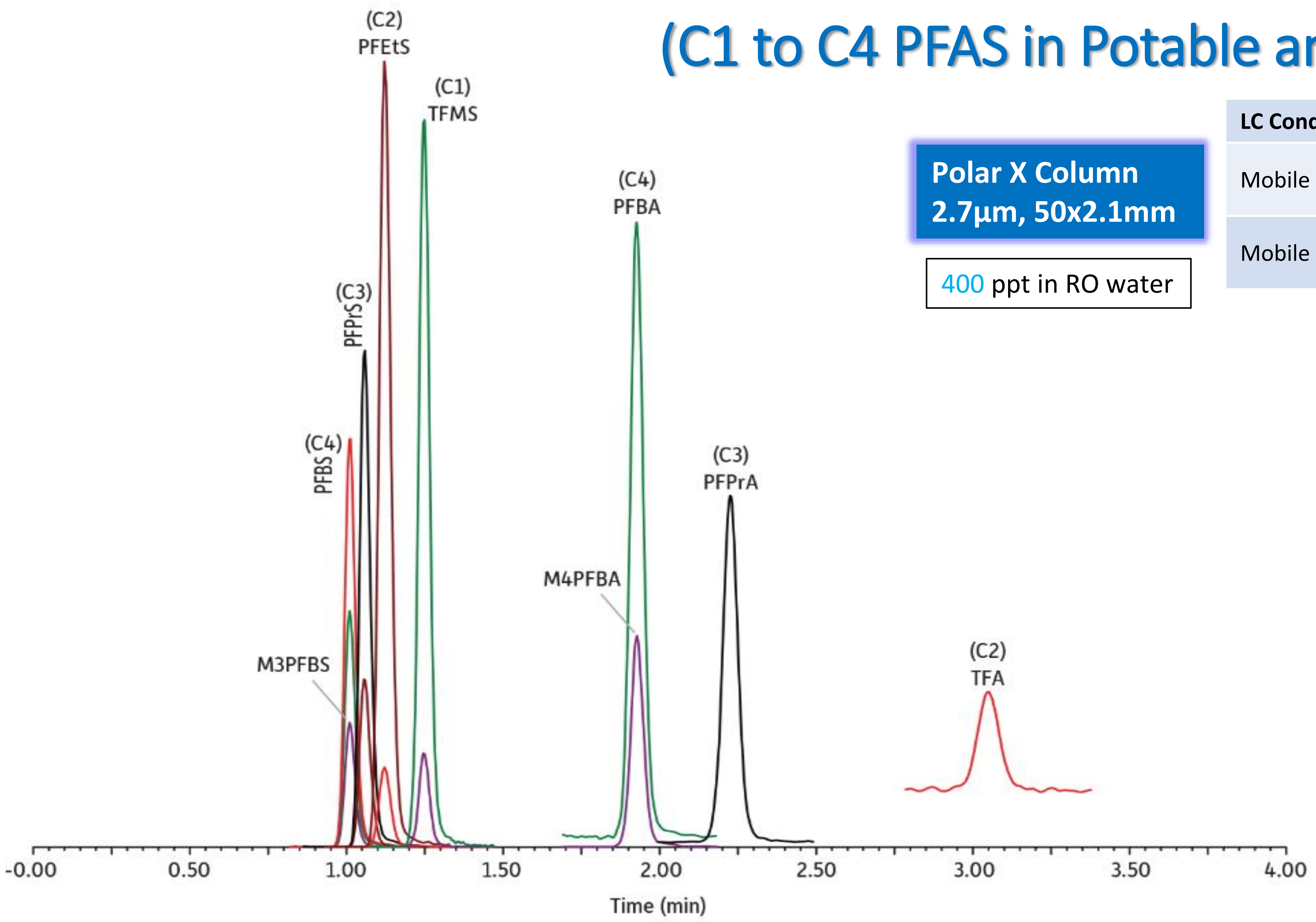
Pipette tips

Vials (glass & polypropylene)

Syringe filters

Glass wool

ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)



Polar X Column
2.7µm, 50x2.1mm

400 ppt in RO water

LC Conditions : (Waters Acquity UPLC)	
Mobile Phase A	10mM ammonium formate, 0.1% formic acid in water
Mobile Phase B	0.1% formic acid in 95:5 acetonitrile:isopropanol

Gradient	**Time (min)**	**%B**
	0.00	85
	7.00	85
Injection	10 µL	
Flow Rate	0.3 mL/min	
Run Time	7 min	
Column Temp.	40°C	

ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)

Accuracy & Precision
of Fortified Water Samples:
(25, 50, 175 ppt)

1. **Tap water**
2. **Bottled spring water**
3. **POTW water (Effluent)**

ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)

Sample Preparation:

(polypropylene vial)

Direct injection of drinking waters (no filtration)

Direct injection of wastewaters (filtration with syringe filter)

Internal standard : $^{13}C_3$-PFBS, $^{13}C_4$-PFBA

<u>Standard solutions were prepared in RO water</u>

ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)

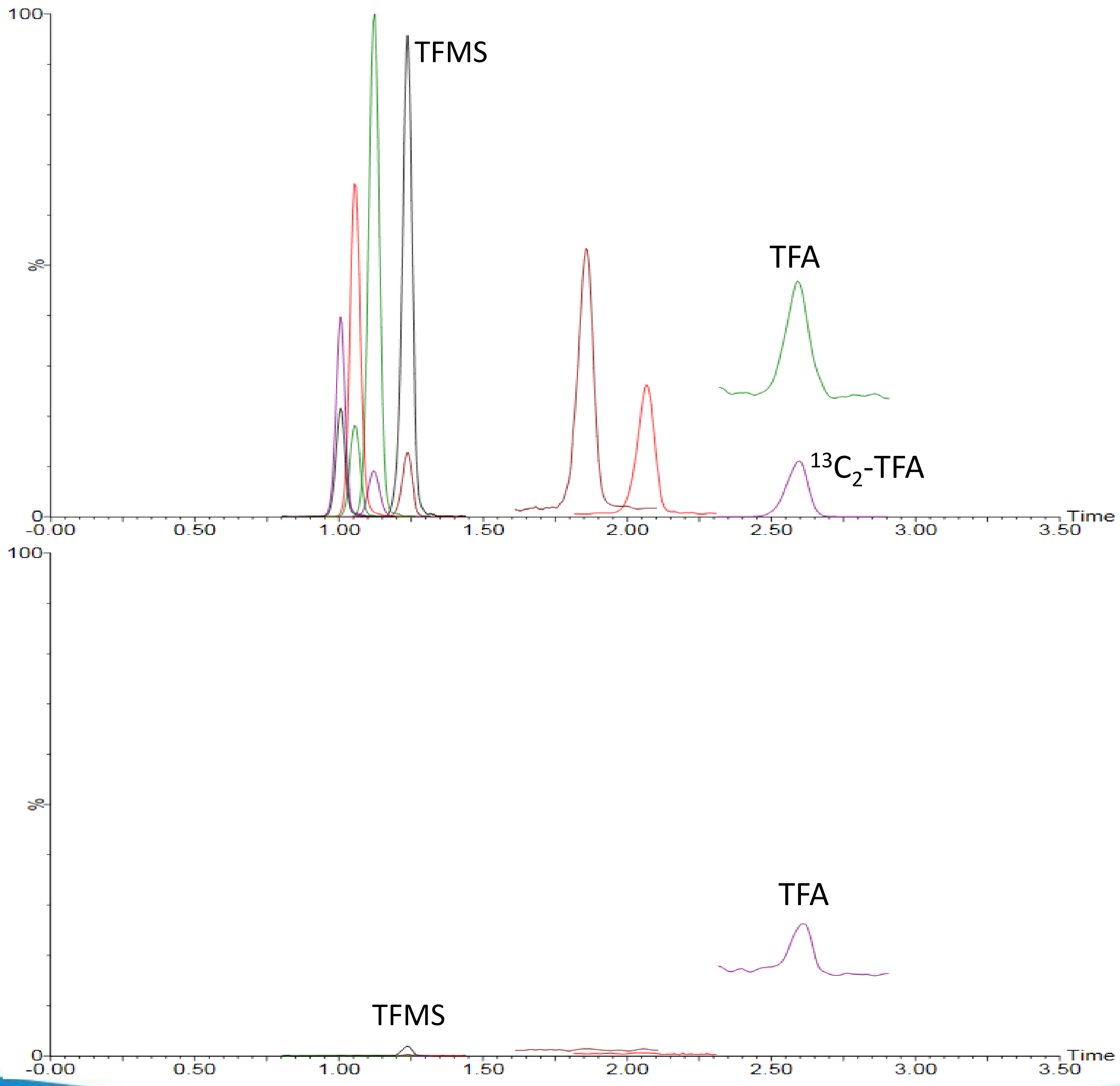
Quantification with Internal Standards

Analytes	Precursor Ion	Product Ion 1	Product Ion 2	IS for Quantification
TFA (C2)	113.03	69.01	-	$^{13}C_4$-PFBA
PFPrA (C3)	162.97	119.02	-	$^{13}C_4$-PFBA
PFBA (C4)	213.03	168.98	-	$^{13}C_4$-PFBA
TFMS (C1)	148.97	79.93	98.92	$^{13}C_3$-PFBS
PFEtS (C2)	198.90	79.92	98.91	$^{13}C_3$-PFBS
PFPrS (C3)	248.97	79.92	98.91	$^{13}C_3$-PFBS
PFBS (C4)	298.97	79.97	98.89	$^{13}C_3$-PFBS
$^{13}C_3$-PFBS	301.97	79.97	-	-
$^{13}C_4$-PFBA	217.03	171.98	-	-

Incurred TFA and TFMS in tap water

175 ppt fortified tap water

Blank tap water



ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)

Linear regression
(1/x weighted)

Calibration Range:

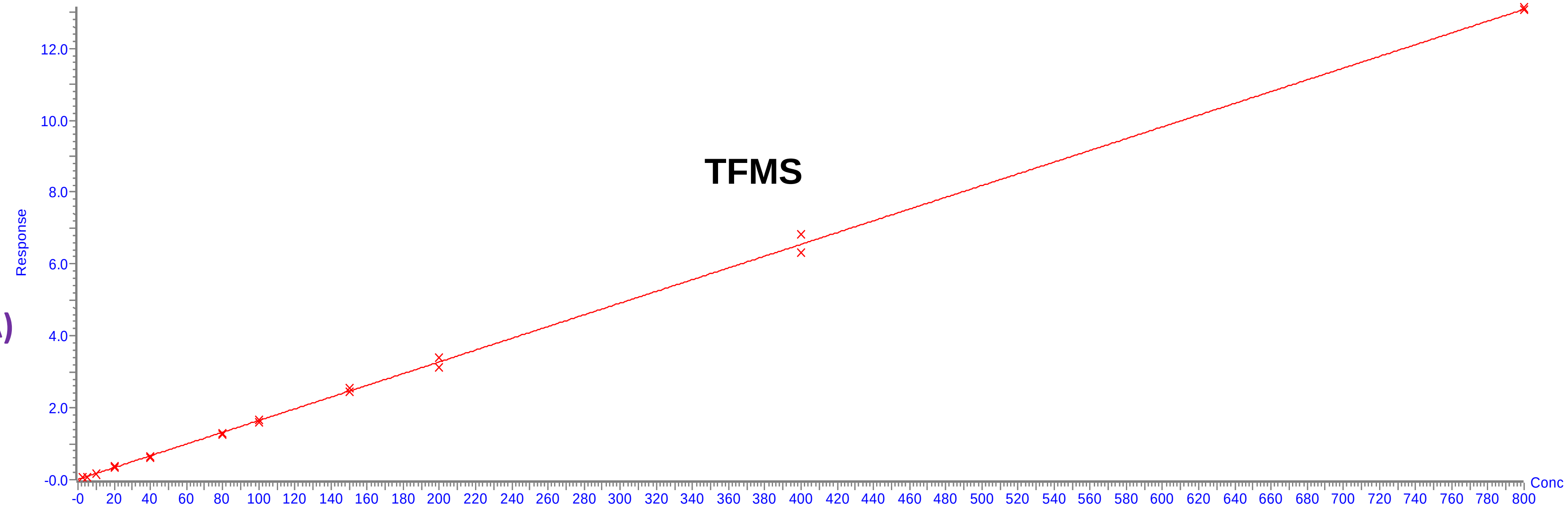
2.5 – 800 ng/L (for PFSA)

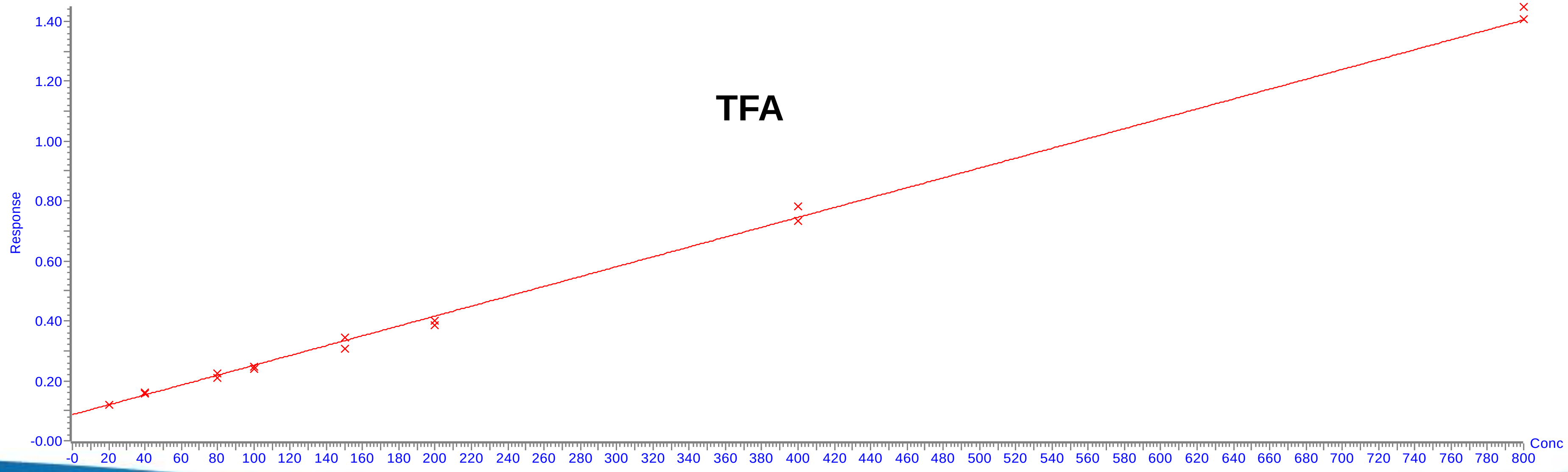
5.0 – 800 ng/L (for PFPrA & PFBA)

20 – 800 ng/L (for TFA)

r^2 value > 0.995

deviations <20%





ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)

Analytes in Unspiked Water Samples

Samples	Detected Concentration (ng/L)						
	TFA	PFPrA	PFBA	TFMS	PFEtS	PFPrS	PFBS
Tap Water	230	ND	ND	5.58	ND	ND	ND
Bottled Spring Water	102	ND	ND	ND	ND	ND	ND
POTW Water	1113	36.6	<5.00	8.53	ND	ND	4.35

ASTM WK80687 Method Development
(C1 to C4 PFAS in Potable and Non-Potable Waters)

Accuracy % Recovery: 86.6 – 107 %

Precision % RSD: 1.62 – 10.7 %

	Average Recovery (RSD, %)								
Samples	Tap Water			Spring Bottled Water			POTW Water		
Concentration (ng/L)	25	50	175	25	50	175	25	50	175
TFA	-	98.2 (7.63)	97.4 (6.68)	-	107 (5.92)	97.1 (4.27)	-	96.7 (10.7)	106 (4.02)
PFPrA	106 (3.49)	107 (2.26)	103 (2.19)	96.6 (4.10)	107 (4.29)	102 (2.19)	102 (3.08)	102 (3.02)	101 (1.71)
PFBA	99.5 (4.61)	100 (5.09)	101 (1.72)	94.4 (9.17)	101 (5.08)	99.6 (3.12)	100 (6.36)	95.2 (5.25)	97.4 (1.62)
TFMS	87.5 (1.62)	95.8 (5.66)	96.4 (3.02)	86.6 (5.99)	95.5 (5.74)	94.6 (3.99)	92.6 (7.42)	94.5 (7.94)	93.8 (5.25)
PFEtS	96.2 (5.68)	100 (7.62)	96.9 (3.93)	92.0 (6.18)	101 (6.24)	95.1 (6.77)	93.8 (6.54)	97.2 (7.75)	95.7 (7.48)
PFPrS	94.2 (4.80)	99.8 (5.38)	97.3 (3.60)	92.5 (7.94)	99.4 (6.31)	96.1 (4.50)	97.6 (4.47)	97.6 (6.52)	96.8 (5.78)
PFBS	98.7 (4.02)	102 (4.92)	101 (3.79)	95.5 (8.10)	104 (7.03)	98.6 (5.09)	99.8 (6.97)	103 (5.99)	100 (3.58)

Measurement of C1 to C4 PFAS in Potable and Non-Potable Waters

Water Samples	Averaged Concentration (ng/L; ppt)						
	TFA	PFPrA	PFBA	TFMS	PFEtS	PFPrS	PFBS
Potable Waters							
Tap Water #1	230	nd*	nd	5.58	nd	nd	nd
Tap Water #2	520	nd	nd	6.88	nd	nd	nd
Tap Water #3	450	< 5.00	nd	3.20	nd	nd	nd
Tap Water #4 (filtrated well water)	267	nd	nd	nd	nd	nd	nd
Tap Water #5	297	< 5.00	nd	4.68	nd	nd	nd
Tap Water #6	428	< 5.00	nd	< 2.5	nd	nd	nd
Tap Water #7 (RO filtrated tap water #6)	nd	nd	nd	nd	nd	nd	nd
Tap Water #8	400	< 5.00	nd	nd	nd	nd	nd
Tap Water #9	228	nd	nd	5.22	nd	nd	nd
Tap Water #10	117	nd	nd	nd	nd	nd	nd
Bottled Water #1 (RO purified)	nd	nd	nd	nd	nd	nd	nd
Bottled Water #2 (spring water)	102	nd	nd	nd	nd	nd	nd
Bottled Water #3 (spring water)	368	nd	nd	< 2.5	nd	nd	nd
Natural Spring Water	527	<5.00	nd	<2.5	nd	nd	nd
Well Water (non-filtrated)	342	nd	nd	15.6	nd	nd	nd
Non-Potable Waters							
POTW water (treated seweage wastewater, effluent)	1113	36.6	< 5.00	8.53	nd	nd	4.35
Hospital Effluent	1363	24.6	< 5.00	4.67	nd	nd	nd
Metal Finisher	741	11.4	< 5.00	5.16	nd	nd	2.77
Chemical Manufacturer Effluent	131200	11084	52.0	4.02	nd	nd	nd

*non-detected

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 workflow is suitable for labs interested in adding ultrashort-chain compounds to an existing PFAS assay.
- We will be recruiting labs for the multi-lab validation study of ASTM WK80687 for ultrashort-chain and short-chain PFAS analysis

Acknowledgement

General Dynamics Information Technology:

Harry McCarty

Thanks for Your Attention

Questions?

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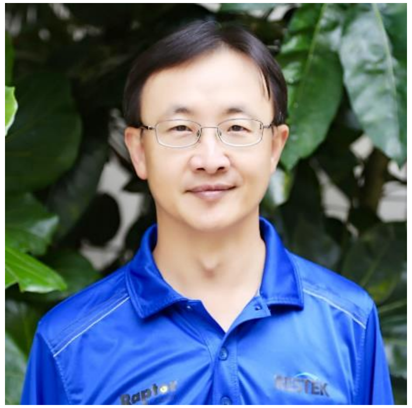
Principal Scientist



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