Development of a New Standardized Method for the Analysis of PFAS in Consumer Products

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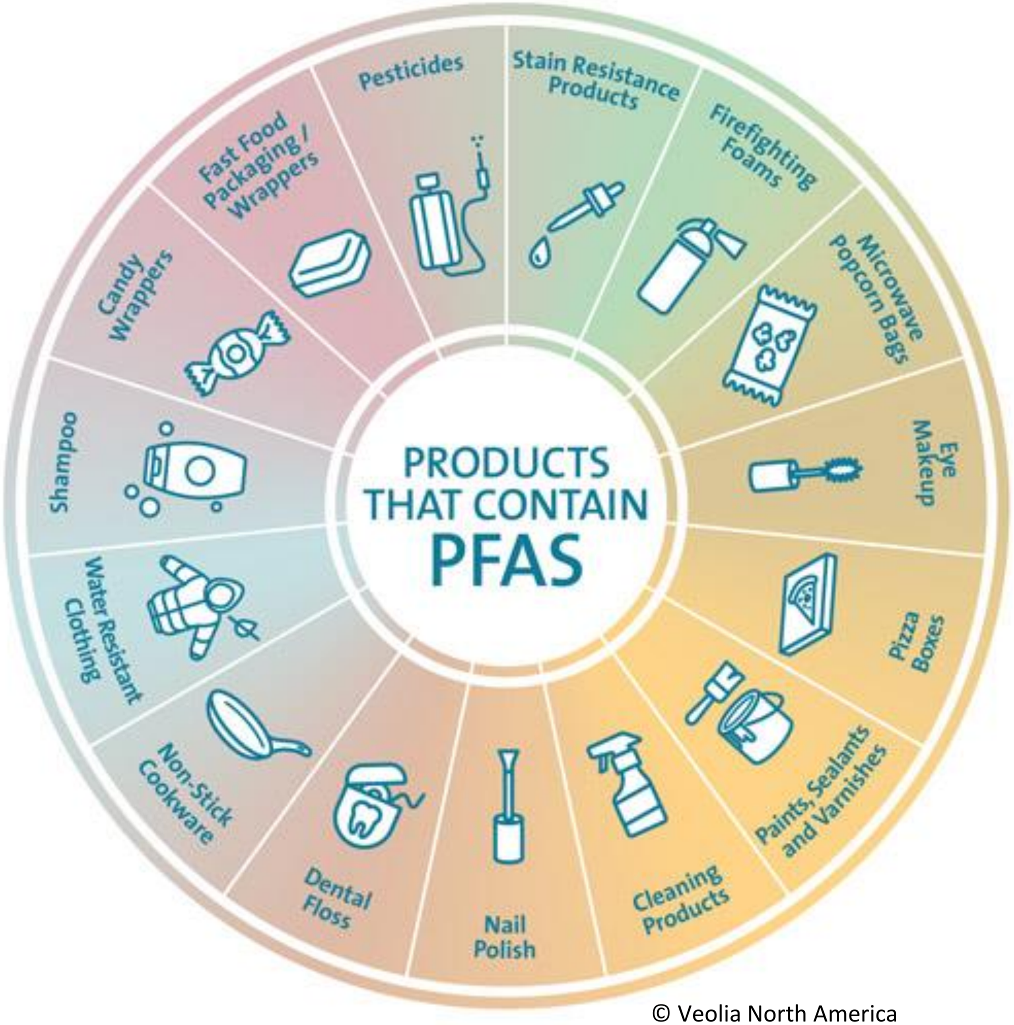
August 8, 2024

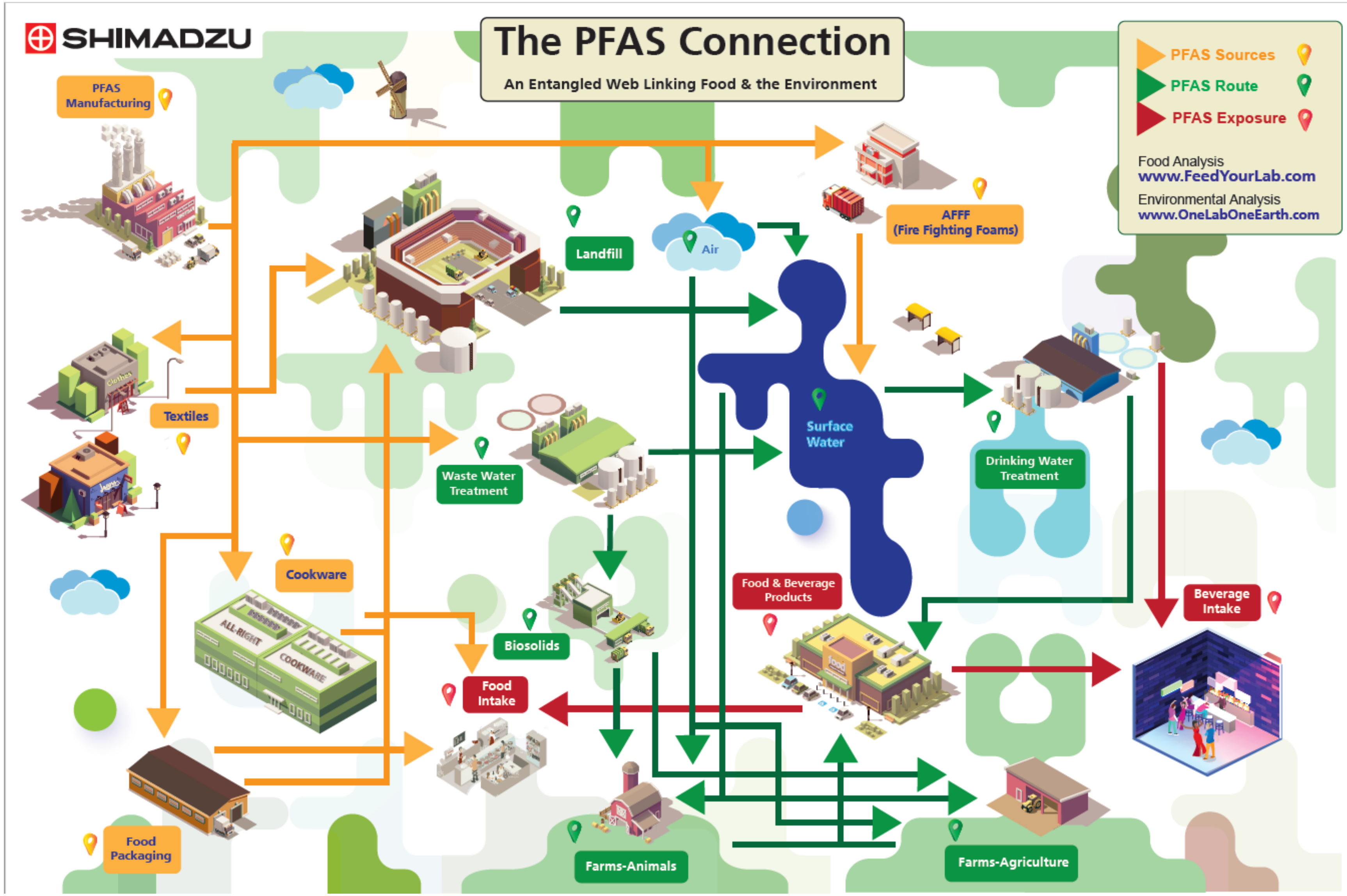
PFAS Use in Manufacturing

- Per-and Polyfluorinated alkyl substances (PFAS) are a broad class of thousands of chemicals with a varied global definition that include carbon-fluorine bonds
- PFAS was manufactured for desirable water resistant, oil resistant, and heat resistant properties
- Since the 1940's, industries have integrated PFAS in products such as food packaging, textiles, and household products due to their unique properties
- Characteristic of PFAS of concern is their slow breakdown rate, leading to potential accumulation in people, animals, and the environment [1]
- In response to growing concerns regarding consumer exposure to PFAS, many states have initiated bans of PFAS uses in various consumer products and food packaging materials
- This led to a need for analytical testing to determine the amount of PFAS in consumer products, however, the lack of standardized methods present challenges in ensuring reliability and reproducibility between labs



1 https://www.atsdr.cdc.gov/pfas/

PFAS Connection from Source to Exposure



Collaboration Between RJ Lee Group and Shimadzu Scientific Instruments

- Joint collaboration between two companies to develop first ASTM standard for the analysis of extractable PFAS in consumer products
- ASTM F15.81; Consumer Products Subcommittee on PFAS
  - Michael Deible is technical contact for the standard development
- Goal is to develop a method applicable to various categories of consumer products using a simple co-solvation sample preparation coupled with large volume LCMS injection to achieve 100 ng/kg reporting limit
- Method currently has 46 target analytes and 25 surrogates with quantitation based on external standard calibration

PFAS Target Analyte List

Analyte Name	Acronym	CAS Number	Reporting Range (ng/kg)
Perfluorotetradecanoic acid	PFTreA	376-06-7	100-4000
Perfluorotridecanoic acid	PFTriA	72629-94-8	100-4000
Perfluorododecanoic acid	PFDoA	307-55-1	100-4000
Perfluoroundecanoic acid	PFUnA	2058-94-8	100-4000
Perfluorodecanoic acid	PFDA	335-76-2	100-4000
Perfluorononanoic acid	PFNA	375-95-1	100-4000
Perfluorooctanoic acid	PFOA	335-67-1	100-4000
Perfluoroheptanoic acid	PFHpA	375-85-9	100-4000
Perfluorohexanoic acid	PFHxA	307-24-4	100-4000
Perfluoropentanoic acid	PFPeA	2706-90-3	500-20000
Perfluorobutanoic acid	PFBA	375-22-4	1000-20000
Perfluorodecanesulfonic acid	PFDS	335-77-3	100-4000
Perfluorononanesulfonic acid	PFNS	68259-12-1	100-4000
Perfluorooctanesulfonic acid	PFOS	1763-23-1	100-4000
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	100-4000
Perfluorohexanesulfonic acid	PFHxS	355-46-4	100-4000
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	100-4000
Perfluorobutanesulfonic acid	PFBS	375-73-5	100-4000
Perfluorooctanesulfonamide	PFOSA	754-91-6	100-4000
8:2 Fluorotelomer sulfonic acid	8:2 FTS	39108-34-4	200-4000
6:2 Fluorotelomer sulfonic acid	6:2 FTS	27619-97-2	100-4000
4:2 Fluorotelomer sulfonic acid	4:2 FTS	757124-72-4	200-4000
N-Ethylperfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6	100-4000
N-Methylperfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9	100-4000
Perfluorododecanesulfonic acid	PFDoS	79780-39-5	100-4000
N-Methylperfluorooctanesulfonamide	NMeFOSA	31506-32-8	100-4000
N-Ethylperfluorooctanesulfonamide	NEtFOSA	4151-50-2	100-4000
N-Methylperfluorooctanesulfonamidoethanol	NMeFOSE	24448-09-7	100-4000
N-Ethylperfluorooctanesulfonamidoethanol	NEtFOSE	1691-99-2	100-4000
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	100-4000
4,8-dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	100-4000
9-chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	100-4000

Analyte Name	Acronym	CAS Number	Reporting Range (ng/kg)
11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	100-4000
Pentafluorpropanoic acid	PFPrA	422-64-0	1000-20000
Perfluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	100-4000
Perfluoro(2-ethoxyethane) sulfonic acid	PFEESA	113507-82-7	100-4000
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	100-4000
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	100-4000
2H,2H,3H,3H-Perfluorohexanoic Acid	3:3 FTCA	356-02-05	400-4000
2H,2H,3H,3H-Perfluorooctanoic Acid	5:3 FTCA	914637-49-3	100-4000
2H,2H,3H,3H-Perfluorodecanoic acid	7:3 FTCA	812-70-4	100-4000
2H-perfluoro-2-octenoic acid	FHUEA	70887-88-6	100-4000
2H-perfluoro-2-decenoic acid	FOUEA	70887-84-2	100-4000
Lithium Bis(trifluoromethane)sulfonimide	HQ-115	90076-65-6	100-4000
Bis[2-(perfluorohexyl)ethyl]phosphate	6:2-diPAP	57677-95-9	500-20000
Bis[2-(perfluorooctyl)ethyl]phosphate	8:2-diPAP	678-41-1	500-20000

PFAS Surrogate List

Surrogates	Acronym	CAS Number	Range (ng/kg)
Perfluoro-n-[^{13}C4] butanoic acid	MPFBA	1017281-29-6	1000-20000
Perfluoro-n-[$^{13}C_5$] pentanoic acid	M5PFPeA	2283397-79-3	500-20000
Perfluoro-n-[1,2,3,4,6-$^{13}C_5$] hexanoic acid	M5PFHxA	2328024-54-8	100-4000
Perfluoro-n-[1,2,3,4-$^{13}C_4$] heptanoic acid	M4PFHpA	2328024-55-9	100-4000
Perfluoro-n-[$^{13}C_8$] octanoic acid	M8PFOA	1350614-84-4	100-4000
Perfluoro-n-[$^{13}C_9$] nonanoic acid	M9PFNA	2283397-80-6	100-4000
Perfluoro-n-[1,2,3,4,5,6-$^{13}C_6$] decanoic acid	M6PFDA	2328024-56-0	100-4000
Perfluoro-n-[1,2,3,4,5,6,7-$^{13}C_7$] undecanoic acid	M7PFUnA	N/A	100-4000
Perfluoro-n-[1,2-$^{13}C_2$] dodecanoic acid	MPFDoA	960315-52-0	100-4000
Perfluoro-n-[1,2-$^{13}C_2$] tetradecanoic acid	M2PFTreA	N/A	100-4000
Perfluoro-1-[$^{13}C_8$] octanesulfonamide	M8FOSA	N/A	100-4000
N-methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid	D3-N-MeFOSAA	N/A	100-4000
N-ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid	D5-N-EtFOSAA	N/A	100-4000
N-methyl-d_3-perfluoro-1-octanesulfanamide	D3-N-MeFOSA	N/A	100-4000
N-ethyl-d_5-perfluoro-1-octanesulfanamide	D5-N-EtFOSA	1265205-97-7	100-4000
2-(N-methyl-d_3-perfluoro-1-octanesulfonamido) ethan-d_4-ol	d7-N-MeFOSE	1265205-95-5	100-4000
2-(N-ethyl-d_5-perfluoro-1-octanesulfonamido) ethan-d_4-ol	D9-N-EtFOSE	1265205-96-6	100-4000
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy-$^{13}C_3$-propanoic acid	MHFPO-DA	N/A	100-4000
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$] hexane sulfonate	M4:2FTS	2708218-88-4	200-4000
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-octane sulfonate	M6:2FTS	2708218-89-5	100-4000
1H,1H,2H,2H-perfluoro-1-[1,2-$^{13}C_2$]-decane sulfonate	M8:2FTS	2708218-90-8	100-4000
Perfluoro-1-[$^{13}C_8$] octanesulfonate	M8PFOS	2522762-16-7	100-4000
Perfluoro-1-[2,3,4-$^{13}C_3$] butanesulfonate	M3PFBS	2708218-84-0	100-4000
Perfluoro-1-[1,2,3-$^{13}C_3$] hexanesulfonate	M3PFHxS	2708218-86-2	100-4000
($^{13}C_2$)$_2$ Bis[2-(perfluorohexyl)ethyl]phosphate	M4-6:2-diPAP	N/A	500-20000

Materials and Methods: Calibration Curve

- Stocks made from Accustandard and Wellington Laboratories purchased standards and were diluted using 95:5 (vol:vol) methanol:water into HDPE bottles and stored at 4^{o}C
- The stocks were used to prepare a 7-9 point calibration curve in 50:50 (vol:vol) methanol:water with 0.1% acetic acid at the concentration listed in **Table 1**.

Table 1. *In-vial* Native and Surrogate Calibration Curve Concentrations (ng/L)

Analyte/Surrogate	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7	Cal 8	Cal 9
All Analytes not Specified Below	5	10	20	40	60	80	100	150	200
3:3 FTCA	--	--	20	40	60	80	100	150	200
8:2 FTS, 4:2 FTS	--	10	20	40	60	80	100	150	200
PFPeA, 6:2-diPAP, 8:2-diPAP	25	50	100	200	300	400	500	750	1000
PFPrA, PFBA	--	50	100	200	300	400	500	750	1000

In-Vial to Product Range Concentration

- The curve is established at low ng/L concentrations in vial consideration that the method sample preparation procedure effectively dilutes the original consumer product by approximately 20 times
- Equation 1 shows in-vial (ng/L) to in consumer product (ng/kg) conversion

$$Cs\left(\frac{ng}{kg}\right) = \frac{\left[Ci\left(\frac{ng}{L}\right)\right] \times [Vs(L)]}{[Wd(kg)]}$$

where:

C_s = concentration of target analyte in sample,

C_i = concentration of target analyte in sample from instrument

V_s = volume of sample

W_d = dry weight of sample

Materials and Methods: Sample Preparation

1. Weigh 0.5 g test portion into 50mL centrifuge tube

2. Add SSS, mix, equilibrate for 15 min
3. Add 10ml 50:50 MeOH:H_2O, vortex
4. Add NH_4OH to pH 9-10, vortex

5. Tumble for 2 hrs

6. Filter through preconditioned 0.2µm PP syringe into 15mL centrifuge tube

7. Add acetic acid to pH 3-4, vortex

8. Centrifuge at 8°C, 3000 rpm, 15 min

9. Aliquot to silanized glass vial with PE/silicone septa/cap

Materials and Methods: Analytical Method

- Standard analysis was performed using a Shimadzu Nexera UHPLC consisting of 2 pumps (LC-40D X3, 130 MPa), autosampler (SIL-40C X3), system controller (SCL-40), and column oven (CTO-40C). The LC was coupled to a Shimadzu LCMS-8060NX with IonFocus ESI source.

[LC] Nexera	
Mobile Phase (LCMS Grades)	A: 2 mmol/L Ammonium Acetate in H_2O/ Acetonitrile = 95/5
	B: Acetonitrile
Delay Column	Shimadzu Nexcol PFAS Delay
	3.0 mm x 50 mm, 5 µm (P/N: 220-91394-09)
Analytical Column	Shim-pack Scepter C18-120
	2.1 mm x 100 mm, 3 µm (P/N: 227-31014-05)
Gradient (%B)	10% (0.5 min) ⇒22% (2.3-3.0 min) ⇒45% (6.0 min) ⇒ 75% (12.0 min) ⇒95% (12.1-14.0 min) ⇒10% (14.1-17.0 min)
Interface	IonFocus ESI (-)
Column Oven Temp.	45 ℃
Flow rate	0.45 mL/min
Injection volume	40 µL
Multiple draw injection program	Co-injection 20 µL Sample → 25 µL 0.1% Acetic acid in H_2O → Co-injection 20 µL Sample → 25 µL 0.1% Acetic acid in H_2O
Autosampler Rinsing	60/40 Acetonitrile/2-propanol, Before/After Aspiration 5 seconds

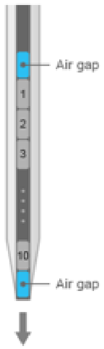
[MS] LCMS-8060NX	
Interface Temp.	170℃
Probe position	+3 mm
Nebulizer gas flow	3 L/min
Heating gas flow	15 L/min
Interface Voltage	-0.5 kV (same value for all compounds)
DL Temp.	200 ℃
Heatblock Temp.	300 ℃
Drying gas flow	8 L/min
Focus bias	-2 kV (same value for all compounds)
CID Cell Pressure	270 kPa; 350 kPa 6.6 - 7.6 min and 11.6 - 12.6 min

Materials and Methods: Autosampler Pretreatment

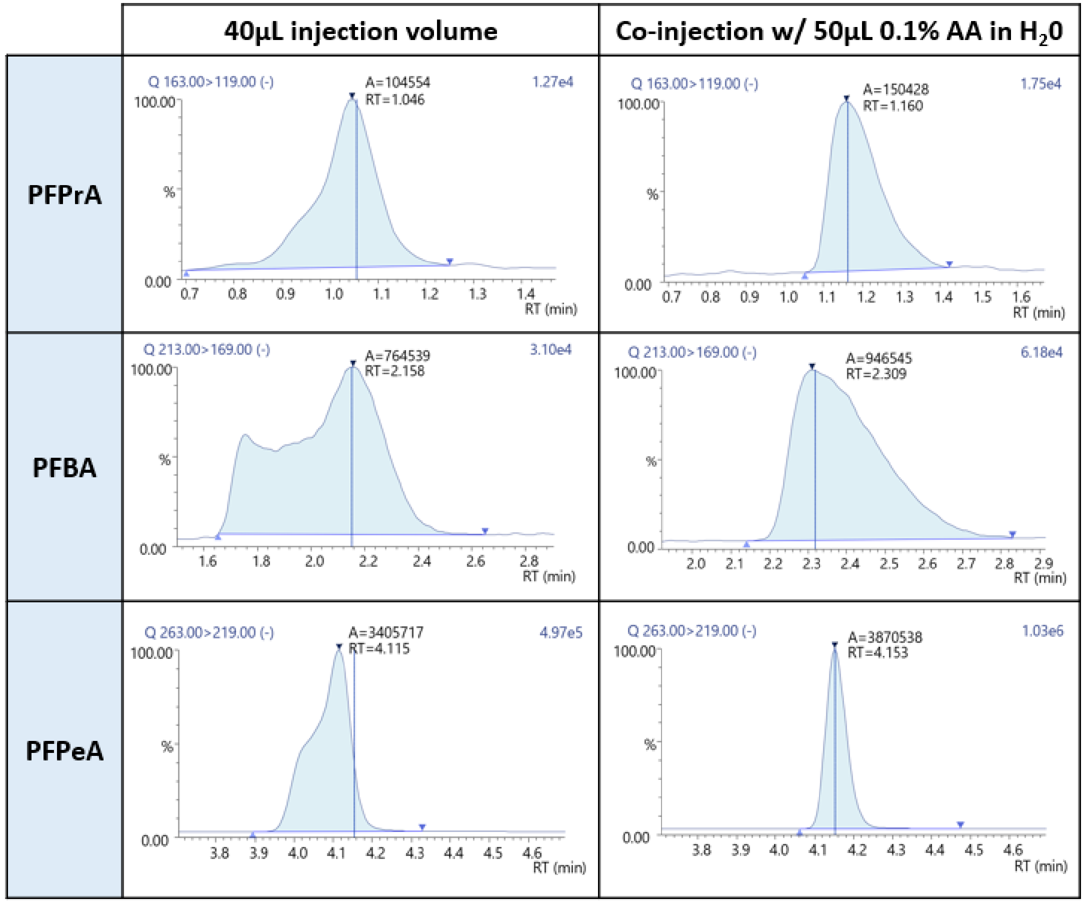
- Co-injection function provides the ability to inject samples in higher elution strength solvents than the initial mobile phase conditions.
- Injecting a weaker strength solvent, such as water, lowers the overall elution strength of the injection, improving early eluter peak shapes and the reliability of quantitative results

Aspiration settings

Order	Tray number	Vial number	Volume (µL)
1	Analytical sample		
2	3	53	25.0
3	Analytical sample		
4	3	54	25.0



- Final solvent composition for method is 50% methanol, starting mobile phase composition is 10%, impact of co-injection can be seen to right



Results: Linearity Study

Compound	Quantitation Ion	Confirmation Ion	RT (min)	% RSD RF
PFTreA	712.95>668.95	712.95>169.00	10.84	9.3
PFTriA	662.95>618.95	662.95>169.00	10.19	8.0
PFDoA	612.95>568.95	612.95>319.00	9.55	9.7
PFUnA	562.95>518.95	562.95>269.00	8.91	6.2
PFDA	512.95>468.95	512.95>219.00	8.29	14.5
PFNA	462.95>418.95	462.95>219.00	7.72	12.7
PFOA	412.95>369.00	412.95>169.00	7.16	4.8
PFHpA	362.95>319.00	362.95>169.00	6.51	7.9
PFHxA	312.95>269.00	312.95>119.00	5.64	2.9
PFPeA	263.00>219.00	263.00>69.00	4.15	1.6
PFBA	213.00>169.00	----	2.32	7.6
PFDS	598.90>79.95	598.90>98.95	9.91	4.3
PFNS	548.95>79.95	548.95>98.95	9.24	2.8
PFOS	498.95>79.95	498.95>98.95	8.59	7.9
PFHpS	448.95>79.95	448.95>98.95	7.96	12.5
PFHxS	398.95>79.95	398.95>98.95	7.35	7.9
PFPeS	348.95>79.95	348.95>98.95	6.64	6.8
PFBS	298.95>79.95	298.95>98.95	5.63	9.6
PFOSA	497.95>77.95	497.95>477.95	10.45	3.7
8:2FTS	526.95>506.95	526.95>80.90	8.00	19.0
6:2FTS	426.95>406.95	426.95>80.90	6.90	12.9
4:2FTS	326.95>306.95	326.95>80.90	5.23	19.8
NEtFOSAA	584.00>418.95	584.00>526.00	8.55	9.4
NMeFOSAA	569.95>418.95	569.95>482.95	8.28	4.7
PFDoS	698.90>79.95	698.90>98.95	11.21	7.6
NMeFOSA	511.95>219.00	511.95>169.00	12.75	4.8
NEtFOSA	526.00>219.00	526.00>169.00	13.36	4.9
NMeFOSE	616.00>59.00	----	12.45	4.9
NEtFOSE	630.00>59.00	----	13.07	14.5
HFPO-DA	285.00>169.00	285.00>185.00	6.01	3.7
ADONA	376.95>251.00	376.95>85.00	6.77	6.2
9Cl-PF3ONS	530.90>350.95	532.90>352.95	9.07	3.4

Compound	Quantitation Ion	Confirmation Ion	RT (min)	% RSD RF
11Cl-PF3OUdS	630.90>450.95	632.90>452.95	10.40	4.1
PFPrA	163.00>119.00	----	1.16	6.8
NFDHA	294.95>201.00	294.95>85.00	5.51	5.5
PFEESA	314.95>135.00	314.95>82.95	6.16	6.2
PFMPA	228.95>85.00	----	3.21	8.1
PFMBA	278.95>85.00	----	4.61	6.3
3:3 FTCA	241.00>177.00	241.00>117.00	3.55	14.6
5:3 FTCA	341.00>237.00	341.00>217.00	6.16	13.3
7:3 FTCA	441.00>317.00	441.00>337.00	7.57	9.5
FHUEA	357.00>293.00	----	6.23	2.4
FOUEA	456.95>393.00	----	7.44	3.5
HQ-115	279.90>146.95	279.90>210.90	6.57	3.6
6:2-diPAP	789.00>442.90	789.00>97.00	9.99	8.3
8:2-diPAP	989.00>543.00	989.00>97.00	12.07	9.8
11Cl-PF3OUdS	630.90>450.95	632.90>452.95	10.40	4.1
PFPrA	163.00>119.00	----	1.16	6.8
NFDHA	294.95>201.00	294.95>85.00	5.51	5.5
PFEESA	314.95>135.00	314.95>82.95	6.16	6.2
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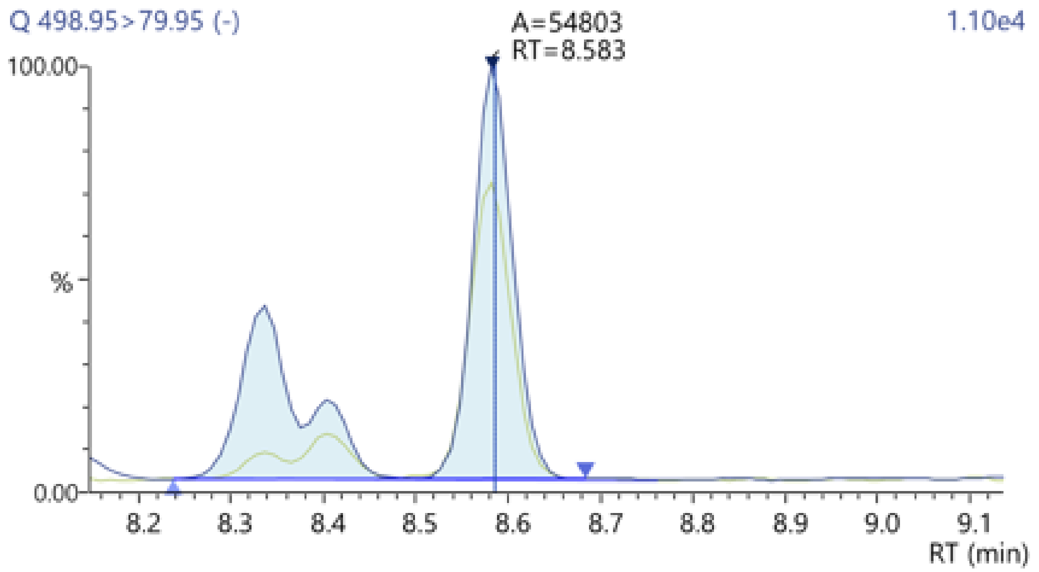
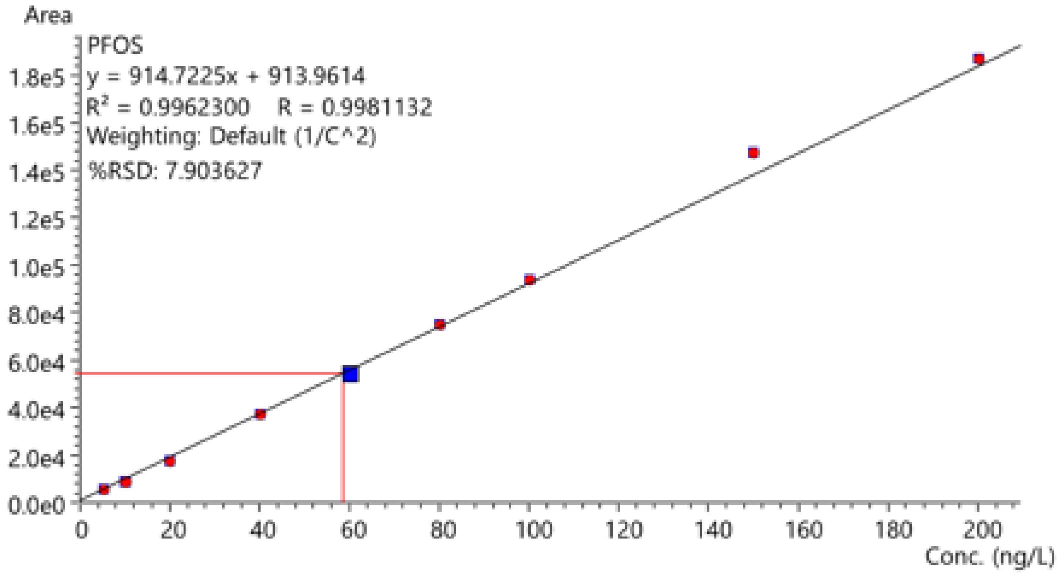
6:2-diPAP	789.00>442.90	789.00>97.00	9.99	8.3
8:2-diPAP	989.00>543.00	989.00>97.00	12.07	9.8

* All surrogate % RSD RF within 20% as well

Results: Example Chromatogram and Calibration

- PFOS example chromatogram (branched and linear integrated as one peak for total measurement), external calibration





Results: Surrogate Recovery (n=3)

Compound	Spike Conc. ng/kg	Sand Matrix % Recovery	Sand %RSD	Plastic Product % Recovery	Plastic Product %RSD	Non-stick Foil % Recovery	Non-stick Foil %RSD
13C4-PFBA_Surr	8000	104.6	9.7	102.6	2.4	100.5	1.4
13C5-PFPeA_Surr	8000	99.8	6.3	103.4	0.5	101.5	0.6
13C5-PFHxA_Surr	1600	95.7	5.6	98.2	1.4	99.3	0.4
13C4-PFHpA_Surr	1600	96.2	2.1	100.4	2.9	105.3	2.5
13C8-PFOA_Surr	1600	96.4	1.9	96.7	0.8	102.9	3.3
13C9-PFNA_Surr	1600	95.9	2.1	98.1	3.6	95.3	7.1
13C6-PFDA_Surr	1600	95.9	1.6	102.1	2.4	101.4	4.3
13C7-PFUnA_Surr	1600	95.0	4.6	96.7	1.0	103.7	0.5
13C2-PFDoA_Surr	1600	97.0	3.8	119.2	1.6	118.4	2.9
13C2-PFTreA_Surr	1600	92.0	8.6	116.4	0.9	104.1	4.7
13C8-PFOSA_Surr	1600	96.0	7.0	90.8	3.1	93.2	2.0
D3-NMeFOSAA_Surr	1600	97.7	2.5	105.3	1.7	112.0	12.5
D5-NEtFOSAA_Surr	1600	102.2	4.1	98.5	4.1	88.2	12.7
D3-NMeFOSA_Surr	1600	91.2	13.2	97.3	2.5	93.5	4.1
D5-NEtFOSA_Surr	1600	93.4	5.4	88.1	3.5	90.8	3.5
D7-NMeFOSE_Surr	1600	91.5	0.8	99.0	1.5	93.9	1.7
D9-NEtFOSE_Surr	1600	85.1	5.0	91.0	0.5	90.1	3.3
13C3-HFPO-DA_Surr	1600	95.1	3.6	104.5	1.0	103.1	2.9
13C2-4:2FTS_Surr	1600	97.1	6.7	102.7	8.2	104.4	8.2
13C2-6:2FTS_Surr	1600	96.0	14.8	93.4	2.5	102.7	0.2
13C2-8:2FTS_Surr	1600	94.7	12.9	102.5	15.4	101.9	9.6
13C8-PFOS_Surr	1600	99.0	10.3	102.6	1.5	102.4	4.4
13C3-PFBS_Surr	1600	103.0	3.1	100.1	3.4	98.4	1.0
13C3-PFHxS_Surr	1600	95.3	2.1	97.7	8.4	102.1	4.5
M4-6:2-diPAP_Surr	8000	128.7	3.2	117.8	3.2	102.2	6.4

Results: Initial Target Spiking Recovery (Plastic Product, n=3)

Plastic Product Low 600 ng/kg Triplicate Spike

Target Analytes	Spike Recovery	% RSD
PFTeDA	135%	10.0
PFTrDA	114%	9.5
PFDoA	118%	11.9
PFUnA	103%	9.5
PFDA	133%	16.9
PFNA	117%	28.0
PFOA	102%	8.1
PFHpA	106%	5.0
PFHxA	123%	7.1
PFPeA	103%	0.5
PFBA	94%	1.6
PFDS	128%	14.3
PFNS	113%	10.4
PFOS	99%	3.2
PFHpS	115%	27.2
PFHxS	96%	13.7
PFPeS	120%	6.6
PFBS	116%	9.9
PFOSA	102%	10.0
8:2 FTS	118%	6.7
6:2 FTS	95%	9.5
4:2 FTS	117%	13.4
NEtFOSAA	125%	36.0
NMeFOSAA	131%	19.8
PFDoS	113%	11.9
NMeFOSA	105%	9.9
NEtFOSA	99%	13.9

Target Analytes	Spike Recovery	% RSD
NMeFOSE	95%	7.4
NEtFOSE	109%	7.7
HFPO-DA	107%	11.8
ADONA	95%	12.1
9Cl-PF3ONS	102%	11.0
11Cl-PF3OUdS	100%	14.2
PFPrA	116%	7.2
NFDHA	106%	12.3
PFEESA	105%	14.7
PFMPA	108%	10.1
PFMBA	119%	17.6
3:3 FTCA	ND	ND
5:3 FTCA	95%	9.7
7:3 FTCA	81%	26.2
FHUEA	101%	17.1
FOUEA	109%	22.9
HQ-115	121%	15.1
6:2 diPAP	140%	6.2

Plastic Product Mid 1,800 ng/kg Triplicate Spike

Target Analytes	Spike Recovery	% RSD
PFTeDA	121%	2.5
PFTrDA	105%	3.0
PFDoA	111%	0.4
PFUnA	98%	2.4
PFDA	105%	5.4
PFNA	98%	2.4
PFOA	97%	2.8
PFHpA	100%	6.1
PFHxA	107%	4.0
PFPeA	103%	2.0
PFBA	101%	0.7
PFDS	96%	2.7
PFNS	106%	2.5
PFOS	99%	2.7
PFHpS	96%	12.0
PFHxS	95%	6.7
PFPeS	103%	4.1
PFBS	101%	1.5
PFOSA	94%	4.6
8:2 FTS	92%	11.0
6:2 FTS	80%	1.8
4:2 FTS	97%	3.1
NEtFOSAA	105%	5.6
NMeFOSAA	99%	14.3
PFDoS	112%	2.7
NMeFOSA	100%	1.1
NEtFOSA	90%	1.6

Target Analytes	Spike Recovery	% RSD
NMeFOSE	89%	1.7
NEtFOSE	95%	2.9
HFPO-DA	110%	5.1
ADONA	109%	3.1
9Cl-PF3ONS	96%	2.2
11Cl-PF3OUdS	106%	1.9
PFPrA	113%	3.7
NFDHA	108%	3.6
PFEESA	103%	3.2
PFMPA	103%	3.2
PFMBA	119%	5.9
3:3 FTCA	107%	8.2
5:3 FTCA	115%	4.2
7:3 FTCA	99%	8.2
FHUEA	105%	4.5
FOUEA	102%	8.6
HQ-115	118%	5.2
6:2 diPAP	122%	3.0

*Recovery corrected for native target concentration found in product

Results: Initial Target Spiking Recovery (Plastic Product, n=3)

Plastic Product High 3,500 ng/kg Triplicate Spike

Target Analytes	Spike Recovery	% RSD
PFTeDA	104%	1.2
PFTrDA	102%	0.4
PFDoA	117%	1.3
PFUnA	94%	1.2
PFDA	93%	15.6
PFNA	91%	15.5
PFOA	96%	3.3
PFHpA	95%	4.6
PFHxA	98%	1.1
PFPeA	101%	0.5
PFBA	98%	0.3
PFDS	95%	1.6
PFNS	94%	0.6
PFOS	95%	5.8
PFHpS	99%	5.3
PFHxS	95%	6.8
PFPeS	98%	1.9
PFBS	96%	1.5
PFOSA	92%	0.9
8:2 FTS	104%	6.6
6:2 FTS	83%	1.4
4:2 FTS	97%	4.3
NEtFOSAA	100%	4.3
NMeFOSAA	102%	7.2
PFDoS	104%	0.5
NMeFOSA	93%	1.5
NEtFOSA	89%	1.2

Target Analytes	Spike Recovery	% RSD
NMeFOSE	89%	1.3
NEtFOSE	86%	1.2
HFPO-DA	100%	1.9
ADONA	95%	1.9
9Cl-PF3ONS	92%	0.7
11Cl-PF3OUdS	96%	2.5
PFPrA	100%	1.3
NFDHA	102%	1.6
PFEESA	96%	2.5
PFMPA	99%	1.7
PFMBA	103%	0.6
3:3 FTCA	95%	1.4
5:3 FTCA	103%	5.6
7:3 FTCA	104%	8.1
FHUEA	102%	0.9
FOUEA	94%	2.7
HQ-115	104%	1.0
6:2 diPAP	103%	1.5

*Recovery corrected for native target concentration found in product

Results: Initial Target Spiking Recovery (Foil Product, n=3)

Coated Foil Product Low 600 ng/kg Triplicate Spike

Target Analytes	Spike Recovery	% RSD
PFTeDA	114%	12.5
PFTrDA	117%	8.1
PFDoA	149%	3.3
PFUnA	111%	15.8
PFDA	118%	11.3
PFNA	101%	19.2
PFOA	86%	20.0
PFHpA	118%	10.7
PFHxA	136%	9.3
PFPeA	108%	6.0
PFBA	103%	8.1
PFDS	124%	7.3
PFNS	113%	6.1
PFOS	104%	11.9
PFHpS	121%	21.7
PFHxS	108%	17.4
PFPeS	125%	2.3
PFBS	130%	6.6
PFOSA	104%	13.2
8:2 FTS	114%	15.9
6:2 FTS	96%	10.4
4:2 FTS	117%	4.8
NEtFOSAA	116%	24.7
NMeFOSAA	124%	12.9
PFDoS	115%	1.6
NMeFOSA	118%	5.3
NEtFOSA	108%	7.0

Target Analytes	Spike Recovery	% RSD
NMeFOSE	101%	3.5
NEtFOSE	115%	3.7
HFPO-DA	120%	2.8
ADONA	127%	1.6
9Cl-PF3ONS	113%	4.6
11Cl-PF3OUdS	112%	4.6
PFPrA	141%	9.0
NFDHA	126%	2.7
PFEESA	123%	5.2
PFMPA	134%	3.7
PFMBA	126%	6.4
3:3 FTCA	ND	ND
5:3 FTCA	111%	11.8
7:3 FTCA	93%	12.4
FHUEA	118%	5.1
FOUEA	127%	6.5
HQ-115	137%	3.4
6:2 diPAP	108%	10.5

Coated Foil Product Mid 1,800 ng/kg Triplicate Spike

Target Analytes	Spike Recovery	% RSD
PFTeDA	111%	8.5
PFTrDA	101%	7.7
PFDoA	120%	1.4
PFUnA	101%	6.0
PFDA	94%	9.2
PFNA	92%	6.5
PFOA	90%	2.6
PFHpA	103%	2.1
PFHxA	103%	3.2
PFPeA	101%	2.3
PFBA	99%	1.0
PFDS	99%	3.4
PFNS	104%	2.4
PFOS	98%	2.5
PFHpS	107%	2.5
PFHxS	99%	6.0
PFPeS	100%	3.1
PFBS	103%	1.1
PFOSA	99%	4.1
8:2 FTS	92%	13.7
6:2 FTS	85%	4.0
4:2 FTS	92%	4.7
NEtFOSAA	97%	9.4
NMeFOSAA	108%	0.8
PFDoS	104%	2.4
NMeFOSA	95%	1.6
NEtFOSA	93%	3.1

Target Analytes	Spike Recovery	% RSD
NMeFOSE	91%	1.1
NEtFOSE	92%	0.6
HFPO-DA	104%	1.9
ADONA	103%	1.9
9Cl-PF3ONS	96%	1.4
11Cl-PF3OUdS	102%	1.7
PFPrA	117%	4.9
NFDHA	107%	1.8
PFEESA	95%	4.3
PFMPA	89%	2.3
PFMBA	105%	2.3
3:3 FTCA	97%	3.5
5:3 FTCA	109%	1.3
7:3 FTCA	87%	10.8
FHUEA	103%	1.4
FOUEA	94%	2.8
HQ-115	106%	3.2
6:2 diPAP	110%	11.4

*Recovery corrected for native target concentration found in product

Results: Initial Target Spiking Recovery (Foil Product, n=3)

Coated Foil Product High 3,500 ng/kg Triplicate Spike

Target Analytes	Spike Recovery	% RSD
PFTeDA	93%	1.8
PFTrDA	101%	3.5
PFDoA	116%	2.3
PFUnA	100%	1.8
PFDA	107%	3.6
PFNA	82%	17.0
PFOA	93%	4.1
PFHpA	99%	1.1
PFHxA	97%	0.9
PFPeA	98%	1.5
PFBA	96%	3.1
PFDS	96%	2.0
PFNS	95%	3.5
PFOS	98%	1.9
PFHpS	105%	18.0
PFHxS	94%	10.2
PFPeS	96%	1.9
PFBS	99%	0.9
PFOSA	95%	2.4
8:2 FTS	104%	7.1
6:2 FTS	97%	3.5
4:2 FTS	97%	1.8
NEtFOSAA	87%	10.3
NMeFOSAA	108%	15.0
PFDoS	100%	0.3
NMeFOSA	92%	3.0
NEtFOSA	91%	1.5

Target Analytes	Spike Recovery	% RSD
NMeFOSE	91%	3.5
NEtFOSE	83%	2.5
HFPO-DA	93%	5.0
ADONA	95%	2.0
9Cl-PF3ONS	90%	2.5
11Cl-PF3OUdS	95%	1.3
PFPrA	103%	4.0
NFDHA	98%	2.1
PFEESA	95%	2.4
PFMPA	98%	2.6
PFMBA	96%	1.1
3:3 FTCA	95%	1.9
5:3 FTCA	98%	2.6
7:3 FTCA	92%	19.0
FHUEA	101%	2.2
FOUEA	91%	5.9
HQ-115	97%	0.5
6:2 diPAP	103%	12.3

*Recovery corrected for native target concentration found in product

Ongoing Efforts Towards ASTM Method Balloting

- Summation of data for other consumer product categories and investigation of using internal standard calibration for some product categories that could improve recovery calculations (such as absorbable matrices like cardboard and fabric)
- Evaluation of cyromilling vs. product coupons (cost/benefit analysis of increased sample preparation time vs. impact of native target recovery, preliminary studies have shown modest increase in extraction efficiency)
- Preliminary studies on an exhaustive extraction technique like Soxhlet in comparison to current co-solvation extraction (results are analyte dependent with some such as PFDoA showing large improvement in extraction efficiency while others are negligible)

Conclusion:

- extraction procedure, chromatography, and mass spectrometry conditions were optimized to ensure optimal sensitivity for co-solvation sample preparation procedure
- Developed method eliminates need for solid phase extraction to simplify extraction process
- Target analytes/surrogates are quantitated using external standard method resulting in a reporting range for majority of analytes from 100-4,000 ng/kg
- Surrogate and target spike recoveries for the plastic and foil matrices were within acceptable limits as well as reasonable %RSD for the triplicate spiking experiments
- Work provides foundation for ongoing work related to the development of the first ASTM method for extractable PFAS analysis in consumer products