Detection of 40+ per- and polyfluoroalkyl substances (PFAS) in non-potable waters using liquid chromatography tandem mass spectrometry (LC-MS/MS)

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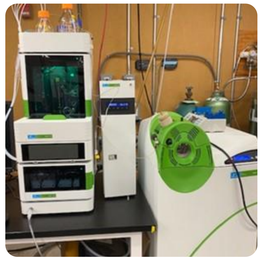
INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS), a large group of manufactured fluorinated compounds, have been used in a wide variety of applications ranging from nonstick cookware, water-repellent clothing, food packaging, firefighting foams, and even cosmetics. The prevalent use in consumer products and persistence in the environment has led to growing concern regarding PFAS exposure and human health. PFAS have leached into the air, soil, and water, making exposure widespread, with the most likely sources coming from contaminated food or water. Historically, the focus of PFAS research has been on drinking water (EPA methods 537.1 and 533), the biggest source of human exposure. PFAS have also been found in non-potable waters (e.g., wastewater, groundwater), which if not treated or properly removed will remain in the environment furthering potential exposure. There is still a need to better understand the fate and transport of PFAS within the environment. Public concern regarding the level of these compounds in environmental sources has required laboratories to develop efficient and reproducible methods for routine analysis. **Here we present an efficient, sensitive, and reproducible method for the detection of 40+ PFAS in non-potable sources.**

Instrumentation



LC Conditions	
Analytical Column	Brownlee™ SPP C18 Column, 75 x 4.6mm, 2.7 µm
Guard Column	Brownlee™ SPP C18 Column, 5mm x 4.6mm, 2.7 µm
Delay Column	Brownlee™ SPP C18 Column, 50 x 3.0mm, 2.7 µm
Mobile Phase A	10 mM ammonium acetate in water
Mobile Phase B	Methanol
Flow Rate	0.8 mL/min
Oven Temp (°C)	40
Auto Sampler Temp (°C)	15
Injection Volume	10
Gradient (B Conc.)	0 min (5%), 0.7-1 min (45%), 1-7 ,min (98%), 8-10 min (5%)

SPE METHOD

Automated System: Promochrome SPE-003
Cartridge Phase: WAX/GCB (Phenomenex)

Conditioning
i. 15 mL 1% methanolic ammonium hydroxide
ii. 5 mL 0.3M formic acid

Sample Loading
i. Flow rate 5 mL/min

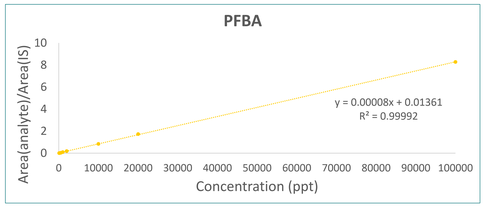
Rinse and Dry
i. 5 mL reagent water (x2)
ii. 5 mL 1:1 0.1M formic acid:Methanol
iii. Dry under high pressure for 2 min

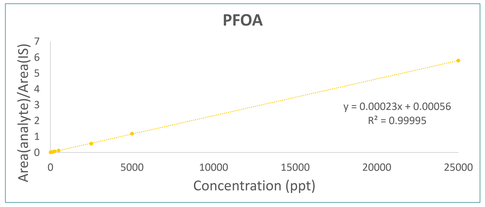
Elution
i. 5 mL of 1% methanolic ammonium hydroxide

Filter
i. 5mL syringe, filter (25-mm, 0.2µm nylon membrane)
ii. Spike Non-Extracted Internal Standard

CALIBRATION

Analyte	Correlation Coefficient (R^2)	LOD (ng/L)	LOQ (ng/L)
PFBA	0.99992	10	30
PFMPA	0.99988	1	4
PFPeA	0.999971	5	15
3:3FTCA	0.99941	50	160
PFBS	0.999906	1	4
PFMBA	0.99830	3	10
PFEESA	0.99923	2	5
NFDHA	0.999906	1	4
4:2FTS	0.99940	1	4
PFHxA	0.99980	4	10
PFPeS	0.99990	1	4
HFPO-DA	0.99918	20	60
PFHxS	0.99946	1	4
PFHpA	0.99982	0.5	2
ADONA	0.99800	0.8	3
5:3FTCA	0.99970	0.3	1
6:2FTS	0.99850	4	10
PFOA	0.99995	2	5
PFHpS	0.99970	1	3
PFOS	0.999905	0.5	2
PFNA	0.99939	6	20
7:3FTCA	0.99907	5	20
9Cl-PF3ONS	0.99954	10	30
NMeFOSAA	0.99992	6	20
PFNS	0.99976	2	6
PFDA	0.99935	20	70
8:2FTS	0.99949	4	10
NEtFOSAA	0.999957	4	10
PFDS	0.999908	1	4
PFUnA	0.99980	10	50
11-PF3OUdS	0.99976	0.5	2
PFOSA	0.99985	0.5	2
PFDoA	0.99860	20	70
PFTrDA	0.99370	10	30
PFDoS	0.99959	30	90
PFTeDA	0.99939	4	10
NMeFOSA	0.99965	10	30
NMeFOSE	0.99984	20	50
NEtFOSE	0.99870	5	20
NEtFOSA	0.99975	10	30





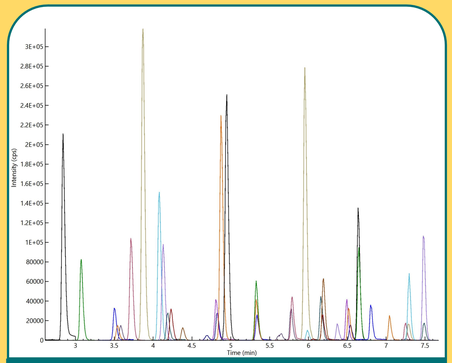


Figure 1. Target Analytes

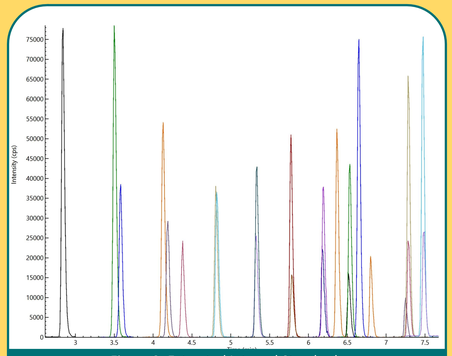


Figure 2. Extracted Internal Standards

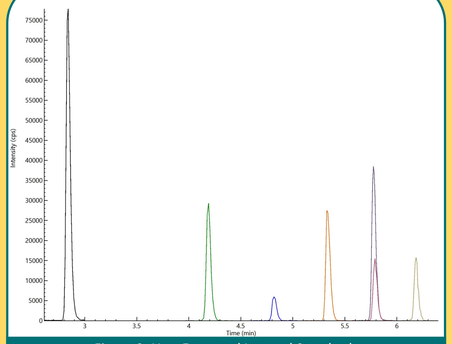
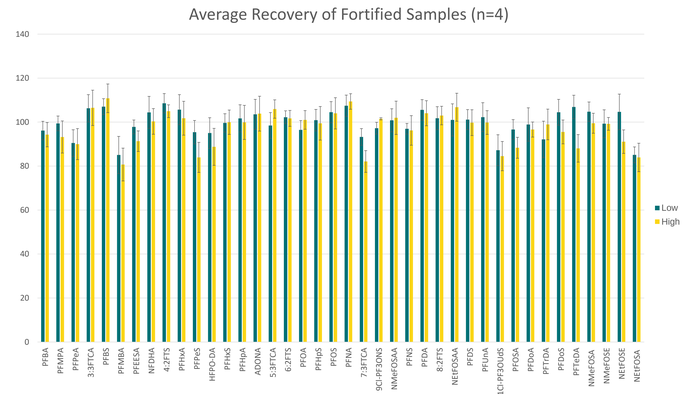


Figure 3. Non-Extracted Internal Standards

RECOVERY



SAMPLES

Non-potable water samples were collected from three different sources in the Baltimore-Metro area. (n=3)

Analyte	Concentration (ng/L) Sample 1	Sample 2	Sample 3
PFBA	BLD	12 ± 2	13 ± 1
PFMPA	BLD	BLD	BLD
PFPeA	BLD	BLD	BLD
3:3FTCA	BLD	BLD	BLD
PFBS	BLD	1.5 ± 0.5	BLD
PFMBA	BLD	BLD	BLD
PFEESA	BLD	BLD	BLD
NFDHA	BLD	BLD	BLD
4:2FTS	BLD	BLD	BLD
PFHxA	BLD	BLQ	BLQ
PFPeS	BLD	BLD	BLD
HFPO-DA	BLD	BLD	BLD
PFHxS	BLD	BLD	BLD
PFHpA	BLD	0.7 ± 0.1	0.6 ± 0.02
ADONA	BLD	BLD	BLD
5:3FTCA	BLD	BLD	BLD
6:2FTS	BLD	BLD	BLD
PFOA	BLD	BLQ	BLQ
PFHpS	BLD	BLD	BLD
PFOS	2.0 ± 0.3	8 ± 1	BLD

Analyte	Concentration (ng/L) Sample 1	Sample 2	Sample 3
PFNA	BLD	BLD	BLD
7:3FTCA	BLD	BLD	BLD
9Cl-PF3ONS	BLD	BLD	BLD
NMeFOSAA	BLD	BLD	BLD
PFNS	BLD	BLD	BLD
PFDA	BLD	BLD	BLD
8:2FTS	BLD	BLD	BLD
NEtFOSAA	BLD	BLD	BLD
PFDS	BLD	BLQ	BLD
PFUnA	BLD	BLD	BLD
11Cl-PF3OUdS	BLD	BLQ	BLD
PFOSA	BLD	BLD	BLD
PFDoA	BLD	BLD	BLD
PFTrDA	BLD	BLD	BLD
PFDoS	BLD	BLD	BLD
PFTeDA	BLD	BLD	BLD
NMeFOSA	BLD	BLD	BLD
NMeFOSE	BLD	BLQ	BLD
NEtFOSE	BLD	BLQ	BLD
NEtFOSA	BLD	BLQ	BLD

CONCLUSION

This poster reports the validation of an LC-MS/MS method for the determination of 40 targeted PFAS analytes in non-potable water sources. Initial calibration demonstrated excellent linearity for all PFAS analytes, with R^2 values greater than 0.99. LODs and LOQs show the ability for the method to reach necessary levels to stay up to date with federal and state regulations. Recoveries of all analytes fell within 70-130% with %RSDs all falling below 10%, which is comparable to current literature. Non-potable sources from the Baltimore-Metro area were sampled and reportable levels are below any current action levels. Overall, an improved analysis method was developed for the detection of 40 PFAS in non-potable sources.

References

United States Environmental Protection Agency. Per- and Polyfluoroalkyl Substances (PFAS). http://www.epa.gov/pfas.

2nd Draft Method 1633 Analysis of Per- an Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolics. And Tissue Samples by LC-MS/MS. https://www.epa.gov/system/files/documents/2021-09/method_1633_draft_aug-2021.pdf

This work was done in collaboration with PerkinElmer. The authors would like to extend a special thanks to Cole Strattman.

LaCourse Lab