Development of a Targeted LC-MS/MS Method for the Analysis of PFAS in Concrete Matrices

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS), often referred to as "forever chemicals," have gained significant attention due to their persistence in the environment, bioaccumulation potential, and adverse health effects. Concrete, widely used in construction, infrastructure, and industrial applications, can serve as both a receptor and potential source of PFAS contamination. This is relevant in scenarios where aqueous film-forming foam (AFFF) is used, which is a common source of PFAS due to its widespread application in firefighting at industrial facilities, airports, and military facilities. Concrete exposed to PFAS-containing AFFF, either through direct application or runoff, may act as a reservoir for these compounds. This application note further advances the collaborative efforts between Shimadzu Scientific Instruments and RJ Lee Inc., to develop methodology for monitoring PFAS in diverse environmental matrices. This newly developed method is specifically designed to detect and quantify PFAS in concrete, particularly focusing on contamination associated with the use of AFFF. Various concrete samples were molded with and without PFAS contaminated water, ground and analyzed on a Shimadzu triple quadrupole mass spectrometer LCMS-8060NX (**Figure 1**) in accordance with ASTM guidelines.[1]

Figure 1. Shimadzu LCMS-8060NX

2. Methods

Stock standard solutions containing native analytes and labeled isotopes (surrogates) were diluted from commercially available mixed or single stock standards using a 95:5 methanol:water mixture. An 8- or 9-point calibration curve was prepared in 50:50 (vol:vol) methanol:water with 0.1% acetic acid.

Six concrete cylinders were cast to evaluate the effects of PFAS-containing water on concrete properties. A 0.3% aqueous solution of AFFF gel was prepared to simulate PFAS-contaminated water, while PFAS-free in-house water was used as a control. Three cylinders were made using each water type, across three different concrete mixes: high strength, high early strength, and advanced pro mix. All cylinders were cast in accordance with ASTM C31.

Once the concrete cylinders were cured, they were removed from their molds, cut into sub-samples using a diamond-tip saw, then prepared for grinding. Briefly, each section was mounted into the stage of a drill press affixed with custom diamond-embedded grinder attachment. The material was further prepared through pre-rinse stainless steel sieves to a achieve a final aggregate powder size between 38-600 µm, **Figure 2**. This powder was then processed following the sample preparation procedure outlined in **Figure 3** and analyzed with conditions in **Table 1.**

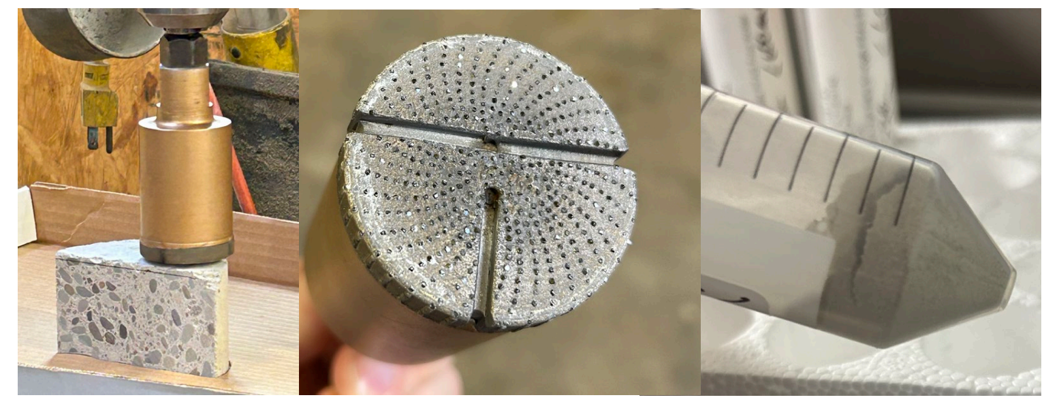

Figure 2. Concrete sample with brass/diamond drill and final sieved sample

1. Weigh 0.5 g concrete into 50mL centrifuge tube
2. Add SSS, mix, equilibrate for 15 min
3. Add 10ml 50:50 MeOH:H_2O, vortex
4. Tumble for at least 1 hour
5. Centrifuge at 8°C, 3000 rpm, 10 min
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, 10 min
9. Aliquot to silanized glass vial with PE/silicone septa/cap

Figure 3. Sample preparation procedure for concrete samples

Table 1. Analytical conditions for concrete PFAS assay

[LC] Nexera	
Mobile Phase (LCMS Grade)	A: 2 mmol/L Ammonium Acetate in H_2O/ Acetonitrile = 95/5 B: Acetonitrile
Delay Column	Shimadzu Nexcol PFAS Delay 50 mm x 3.0 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)
Column Oven Temp.	45 ℃
Flow rate	0.45 mL/min
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

3. Results

Linear calibration curves were generated for each native and surrogate compound. **Table 2** shows the in-vial calibration range for each compound/surrogate, the passing calibration criteria, and the final reporting range in the concrete.

Table 2. Summary of calibration data for native analytes

Compound	Calibration Range In-Vial (ng/L)	Calibration Curve Criteria	Reporting Range (ng/kg)
PFTreA, PFTriA, PFDoA, PFUnA, PFDA, PFNA, PFOA, PFHpA, PFHxA, PFDS, PFNS, PFOS, PFHpS, PFHxS, PFPeS, PFBS, PFOSA, 8:2FTS, 6:2FTS, 4:2FTS, NEtFOSAA, NMeFOSAA, PFDoS, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE, HFPO-DA, ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, NFDHA, PFEESA, PFMPA, PFMBA, 5:3 FTCA, 7:3 FTCA, FHUEA, FOUEA, HQ-115, SURROGATES	5-200	R2 > 0.99 RSE < 30% RF RSD < 30%	100-4000
PFBA, PFPrA, 6:2-diPAP	50-1000		1000-20000
PFPeA	25-1000		500-20000
3:3 FTCA	10-200		200-4000

It is important to note for this project it is necessary for the FTS compounds that the 80.90 MRM transition is used otherwise severe inflation of the recovery will be found. This is due to the extremely high concentration of native 6:2/8:2 FTS found within the AFFF foam used for this project. The foam used in this experiment is a second-generation foam that primarily contains fluorotelomer sulfonates compared to first-generation foam that is abundant in PFOA/PFOS.

Example chromatogram shown in **Figure 4** was achieved with the developed method. Adequate peak shape was attained for early eluting compounds using the co-injection function. All of the compounds were eluted within11.5 minutes.

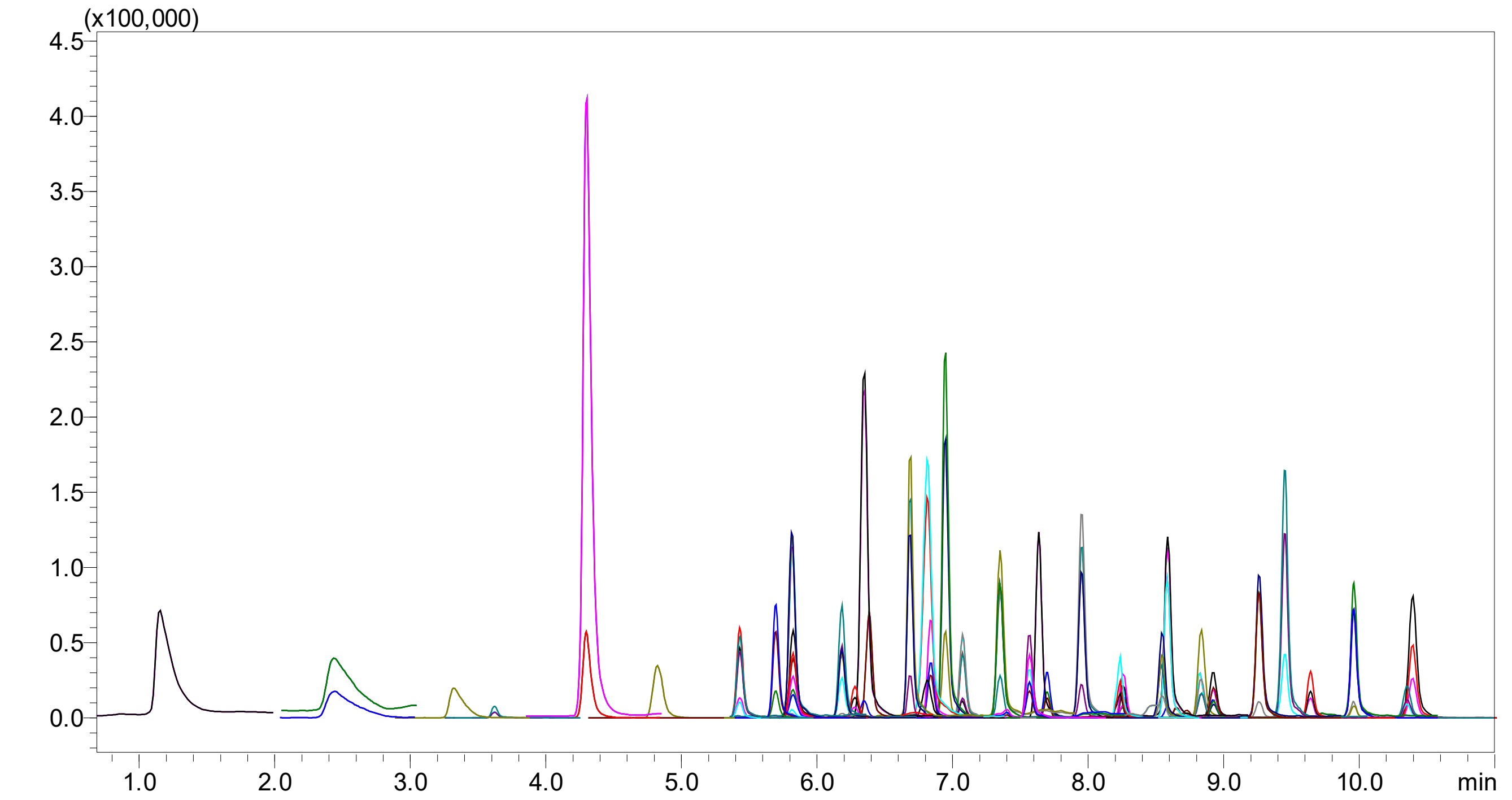

Figure 4. Chromatogram of mid-point standard

Recovery and repeatability were evaluated for the surrogates in each concrete matrix. Each matrix was spiked with surrogate spiking solution at the concentration specified in **Table 3**, based on a 0.5g sample.

Table 3. AFFF molded high strength, high early strength, and advanced pro mix concrete matrices surrogate spiking recovery (n=3)

Surrogate	Spike Conc. ng/kg	High Strength %Recovery	High Strength %RSD	High Early Strength %Recovery	High Early Strength %RSD	Adv. Pro Mix %Recovery	Adv. Pro Mix %RSD
13C4-PFBA	1600	90.1	2.6	93.0	3.7	95.1	0.9
13C5-PFPeA	1600	92.5	2.9	93.7	3.8	96.3	0.9
13C5-PFHxA	1600	90.7	4.2	96.4	3.9	97.2	2.3
13C4-PFHpA	1600	94.1	5.8	95.8	4.2	96.8	2.7
13C8-PFOA	1600	93.1	1.8	96.8	4.4	97.6	2.0
13C9-PFNA	1600	94.1	4.6	91.1	4.8	92.4	1.2
13C6-PFDA	1600	94.5	3.1	91.4	5.3	89.6	2.1
13C7-PFUnA	1600	92.2	3.6	91.2	3.1	85.8	1.3
13C2-PFDoA	1600	87.8	2.9	85.9	3.7	72.6	0.9
13C2-PFTeDA	1600	53.8	9.4	52.5	3.1	36.1	4.7
13C8-PFOSA	1600	91.9	3.5	94.0	4.8	91.5	0.7
D3-NMeFOSAA	1600	84.8	4.4	82.2	1.4	77.9	3.1
D5-NEtFOSAA	1600	84.3	3.5	85.4	4.2	76.7	2.0
D3-NMeFOSA	1600	92.8	5.6	92.4	4.2	94.3	4.2
D5-NEtFOSA	1600	94.1	6.8	93.3	2.7	91.0	8.2
D7-NMeFOSE	1600	92.6	0.5	89.9	1.0	88.7	3.5
D9-NEtFOSE	1600	91.8	1.7	89.1	3.2	86.8	5.5
13C3-HFPO-DA	1600	91.3	3.3	92.3	3.8	94.6	6.4
13C2-4:2FTS	1600	70.7	1.3	70.9	4.9	70.2	10.0
13C2-6:2FTS	1600	90.3	2.0	91.2	1.1	105.7	2.6
13C2-8:2FTS	1600	93.2	6.9	82.0	12.2	80.4	6.6
13C8-PFOS	1600	94.5	2.7	91.5	2.1	93.7	3.1
13C3-PFBS	1600	91.7	2.3	94.8	5.5	96.0	3.7
13C3-PFHxS	1600	95.2	5.2	97.6	8.2	99.8	0.7
M4-6:2 diPAP	1600	73.2	2.8	83.7	3.2	57.9	9.4

4. Conclusion

This work demonstrates the analysis of 45 PFAS and 25 surrogate compounds in concrete matrices using a newly developed method employing a Shimadzu LCMS-8060NX LC-MS/MS system. The extraction procedure, chromatography, and mass spectrometry conditions were optimized to ensure optimal sensitivity for the co-solvation sample preparation procedure. These conditions resulted in a method that eliminates the need for solid phase extraction, therefore significantly reducing cost and time associated with solid-phase extraction sample preparation methodologies. Target analytes were quantitated using either an 8- or 9-point calibration curve with a resulting reporting range between 100-20,000 ng/kg (dependent on analyte, **Table 2**). Excellent surrogate recoveries were obtained in the various concrete matrices, with recovery values typically within 70-106%. It was noted that the longer chain PFAS showed lower recoveries overall which is speculated to be caused from the higher carbon content contained within several of the concrete matrices. Triplicate extractions of the spiked concrete casts resulted in %RSD less than 10%, **Table 3.**

Reference

1) ASTM D8421-21

Conflict of Interest Statement:
(2) authors are affiliated/funded by Shimadzu Corporation, (1) authors are affiliated/funded by RJ Lee Group