SHIMADZU RJ Lee Group

WP314

Investigating the Leaching and Transformation of PFAS in AFFF Encapsulated Concrete

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1. Introduction

Aqueous Film-Forming Foams (AFFF) are specialized firefighting agents that are engineered to rapidly extinguish flammable liquid fires by creating a barrier that cools the fire and suppresses vapor release. They are widely used in high-risk environments such as airports, military bases, oil refineries, and chemical processing facilities, where quick and effective fire suppression is critical. However, the widespread use of AFFF has raised environmental concerns due to the presence of per- and polyfluoroalkyl substances (PFAS), a group of chemicals known for their persistence and potential health risks.

Early formulations of AFFF, developed in the 1960s and 1970s, are often referred to as “Legacy PFOS-based AFFF.” These foams primarily utilized long-chain PFAS such as perfluorooctanesulfonic acid (PFOS) and perfluorohexanesulfonic acid (PFHxS) in various ratios, valued for their exceptional film-forming and firefighting properties. By the 1970s, new formulations emerged under the classification of “Legacy fluorotelomer-based AFFF,” which incorporated a mixture of long-chain fluorotelomers alongside compounds including 6:2 fluorotelomer sulfonate (6:2 FTS), 8:2 fluorotelomer sulfonate (8:2 FTS), and 6:2 fluorotelomer sulfonamide betaine (6:2 FTAB). By the 2010s, responding to growing concerns, manufacturers transitioned to "modern fluorotelomer AFFF" formulations, which employed shorter-chain PFAS such as perfluorobutane sulfonate (PFBS), 6:2 FTS, and 4:2 FTS. These shorter-chain compounds are less prone to bioaccumulation in living organisms but remain highly persistent in the environment.[1]

This application demonstrates the use of the Shimadzu LCMS-9030 Quadrupole Time-of-Flight (QTOF) mass spectrometer for untargeted analysis of AFFF encapsulated concrete (**Fig. 1**). Concrete is an important matrix to study since it can be impacted by AFFF run-off and for possible remediation strategies to immobilized PFAS wastes. This high-resolution analytical technique provides a detailed chemical profile, enabling the characterization of PFAS compounds and their transformation products found in AFFF encapsulated concrete samples. Understanding how the alkaline matrix of concrete impacts PFAS break-down/transformation helps provide value information for future remediation and environmental studies.

Figure 1. Shimadzu LCMS-9030

2. Methods

A second-generation AFFF solution was prepared as a 0.3% (v/v) aqueous solution. This solution was used to cast concrete blocks, following ASTM casting guideline C31. PFAS-free laboratory water was used as the control sample for the concrete matrix. 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-rinsed stainless-steel sieves to a achieve a final aggregate powder size between 38-600 µm. The powder was then extracted with 50:50 methanol:water procedure.

Diluent was run in triplicate first with the method conditions outlined in **Table 1**. The MS data was then processed with LabSolutions Insight Explore and the top intensity hits were selected to be included within the exclusion list for all the AFFF sample runs. A prior ion list was also constructed from previous laboratory work with 56 known PFAS and their matched retention times. LabSolutions LCMS software was configured to automatically export each data file as an .mzML file which was required for FluoroMatch processing. Additional processing was accomplish utilizing Shimadzu’s new LabSolutions Insight Profiler software to investigate unique features amongst the different experimental groups.

Table 1. Analytical method conditions for untargeted PFAS experiment

[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) ⇒95% (30 min) ⇒95% (35 min) ⇒ 10% (35.1-40 min)
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 4 seconds
[MS] LCMS-9030	
Interface Temp.	170℃
Probe position	+1 mm
Nebulizer gas flow	3 L/min
Heating gas flow	15 L/min
Interface Voltage	-3 kV
DL Temp.	200 ℃
Heatblock Temp.	300 ℃
Drying gas flow	8 L/min
Ionization Mode	ESI (-) and ESI (+)
MS Acquisition Type	DDA, MS (110-1300*m/z*), MS/MS (40-1300*m/z*) 6 Dependent Events with Exclusion and Prior Ions Lists
Collision Energy	35 +/- 22

All required sample types were loaded into the FluoroMatch software (Flow version 5.72 was at the time of this analysis) and processed using the parameters summarized in **Table 2.**

Table 2. Processing parameters for FluoroMatch Flow

FluoroMatch Parameters	
Peak Picking Algorithm	Mzmine 2
MS/MS intensity threshold	25
Full-scan intensity threshold	200
Full-scan Peak Height Minimum	1500
Noise Level (MS1)	100
Full-Scan Mass Accuracy Tolerance	15 ppm/0.007 Da
MS/MS intensity threshold	25
***m/z* Search Window MS/MS**	25 ppm

3. Results

The .mzML files were processed through FluoroMatch, and the results were exported and analyzed using a customized PowerBI visualizer, enabling efficient review of the complex identified features. An example of the feature-level comparison is shown in **Figure 2**, which presents a Kendrick mass defect plot of all detected features (displaying only features with confidence scores ranging from A to C+). As illustrated in the plot, AFFF-encapsulated concrete samples can contain thousands of detected features.

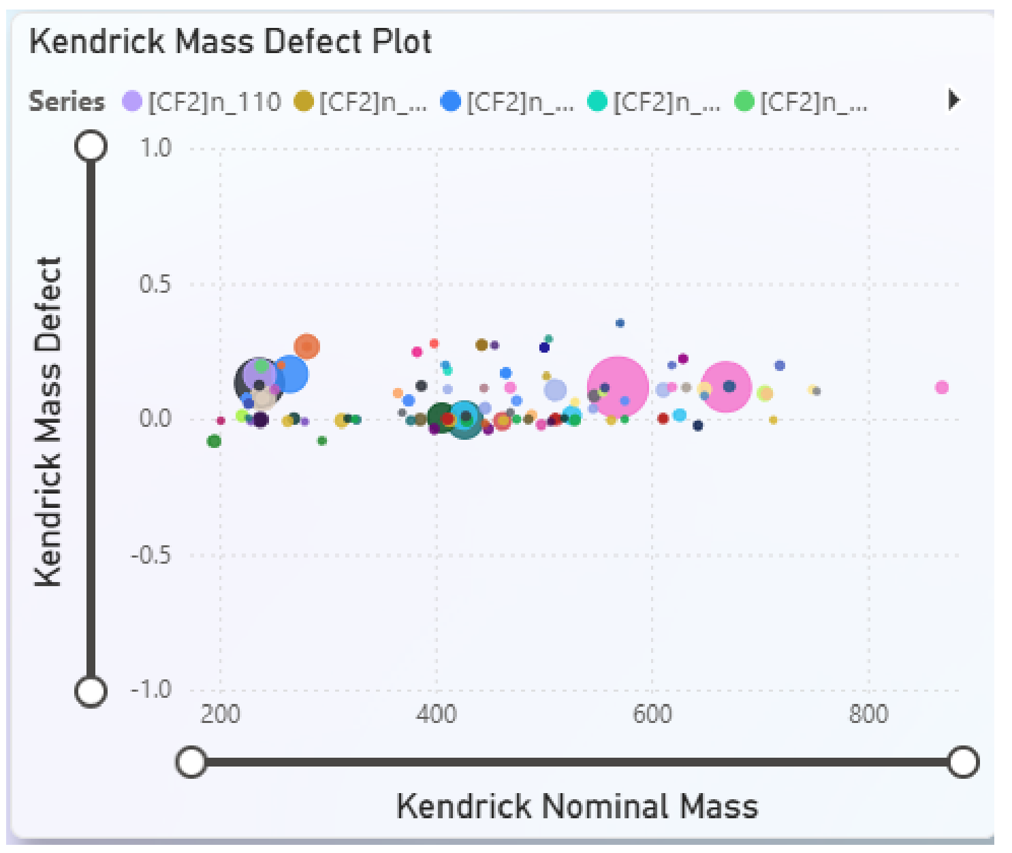

Figure 2. Kendrick mass plots of feature landscape for AFFF encapsulated concrete sample (plotting scores A-C+)

Further investigation of the feature landscape reveals generalized trends among similar series of compounds appearing across comparable mass defect and nominal mass ranges. These patterns should also correlate with the retention time versus *m/z* distribution, as shown in **Figure 3**.

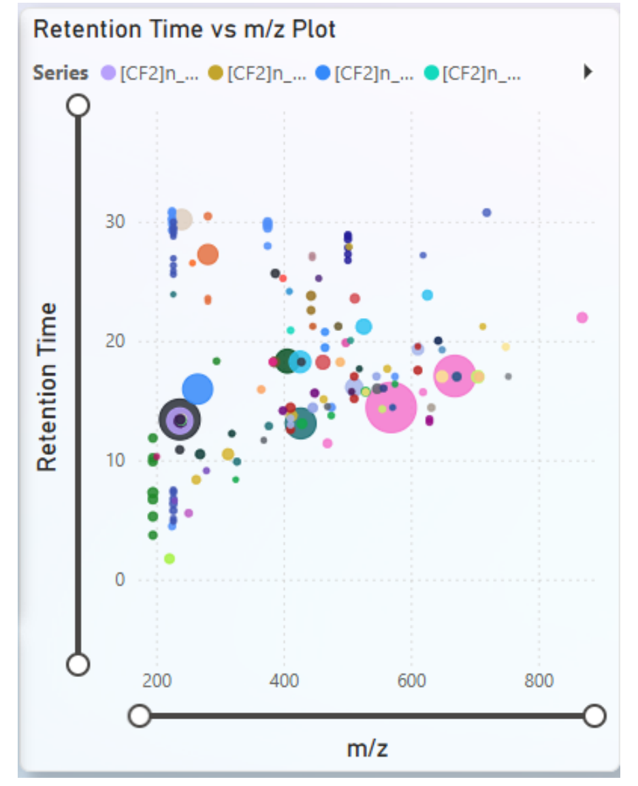

Figure 3. Retention time vs. *m/z* ratio plot where related series of compounds align along a distinct trend. Each pattern suggests a compound with the series that shares a common structural relationship or progression.

Through the investigation of the found features through FluoroMatch and Insight Profiler software unique features that are contributed to the casted concrete sample can begin to be seen. As previously noted, the AFFF used in this analysis was a second-generation foam, predominantly composed of fluorotelomer-based components. Accordingly, a high abundance of 6:2 FTS, 8:2 FTS, and 10:2 FTS was expected and observed. Beyond these dominant species, examination of lower-abundance features provided additional insight into potential transformation products within the cast concrete samples.

Figure 4 illustrates the difference in signal intensity between the cast concrete sample and a spiked AFFF blank concrete sample (serving as a comparison between AFFF in a blank matrix and AFFF that had undergone the concrete curing process) for 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane-1-sulfonamide (6:2 FTSAm). Since 6:2 FTSAm is a known oxidation product of 6:2 FTAB, a well-characterized component of AFFF formulations. The observed difference likely indicate that transformation processes occur within the concrete matrix during curing. Similar behavior was found with 10:2 FTSAm analyte as well in the encapsulated sample, possibly from the 10:2 FTAB precursor in the AFFF.

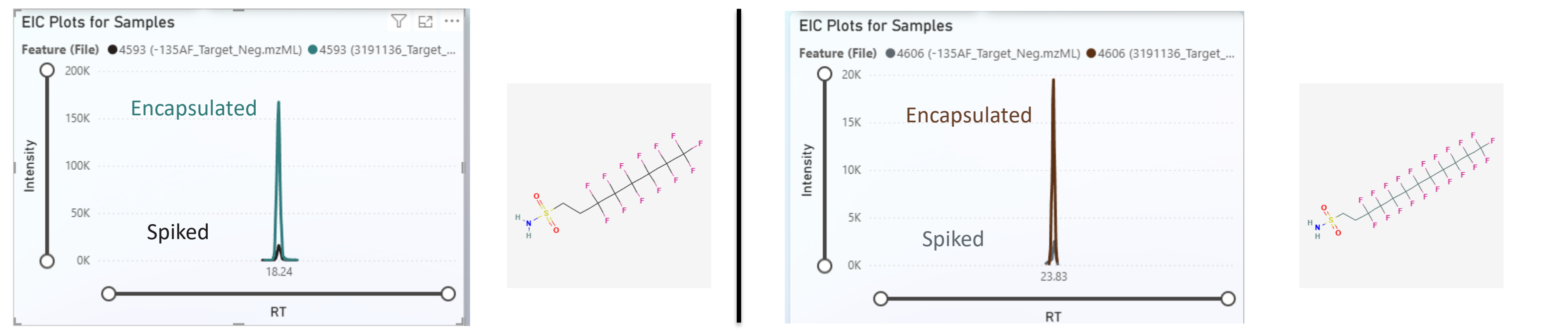

Figure 4. (Left) Extracted chromatogram for 6:2 FTSAm in spiked sample (black) and AFFF encapsulated sample (teal). **(Right)** Extracted chromatogram for 10:2 FTSAm in spiked sample (grey) and AFFF encapsulated sample (brown). The significantly higher response seen for the encapsulated sample could indicate the alkaline concrete environment had impact on degradation/transformation over the 28-day curing process.

Figure 5 presents an example PCA score plot generated from the processing of non-targeted QTOF data using LabSolutions Insight Profiler software. In combination with the aligned feature table, this workflow provides a streamlined approach for characterizing complex non-targeted datasets. When used alongside the FluoroMatch platform, it further supports the identification of unknown compounds in complex matrices.

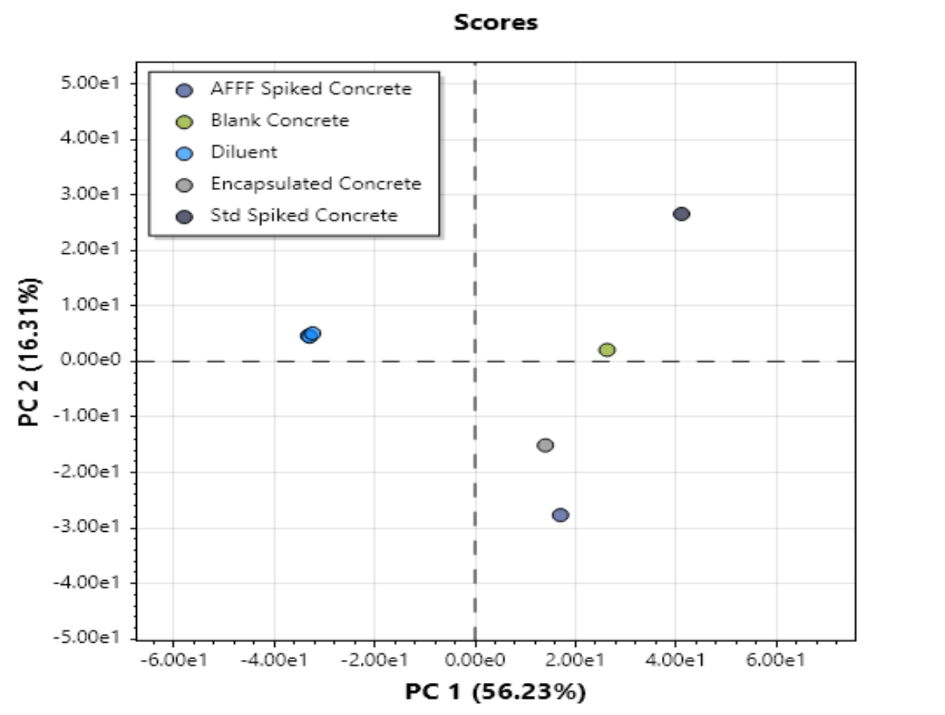

Figure 5. PCA score plot from LabSolutions Insight Profiler

4. Conclusion

The combined use of FluoroMatch and LabSolutions Insight Profiler for untargeted QTOF PFAS analysis provides a comprehensive workflow for characterizing complex AFFF-containing matrices. Together, these platforms support efficient feature detection, alignment, and multivariate statistical analysis, enabling both detailed interrogation and high-level pattern recognition in large non-targeted datasets. This integrated approach improves the resolution and interpretation of complex chemical signatures in concrete systems, capturing both dominant constituents and lower-abundance transformation products formed during curing. Overall, this workflow enables a more complete understanding of PFAS distribution, transformation, and potential degradation pathways in cementitious environments, offering a robust and practical solution for evaluating AFFF fate and supporting future remediation and encapsulation strategies.

Reference

1) Interstate Technology Regulatory Council: pfas-1.itrcweb.org/3-firefighting-foams

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