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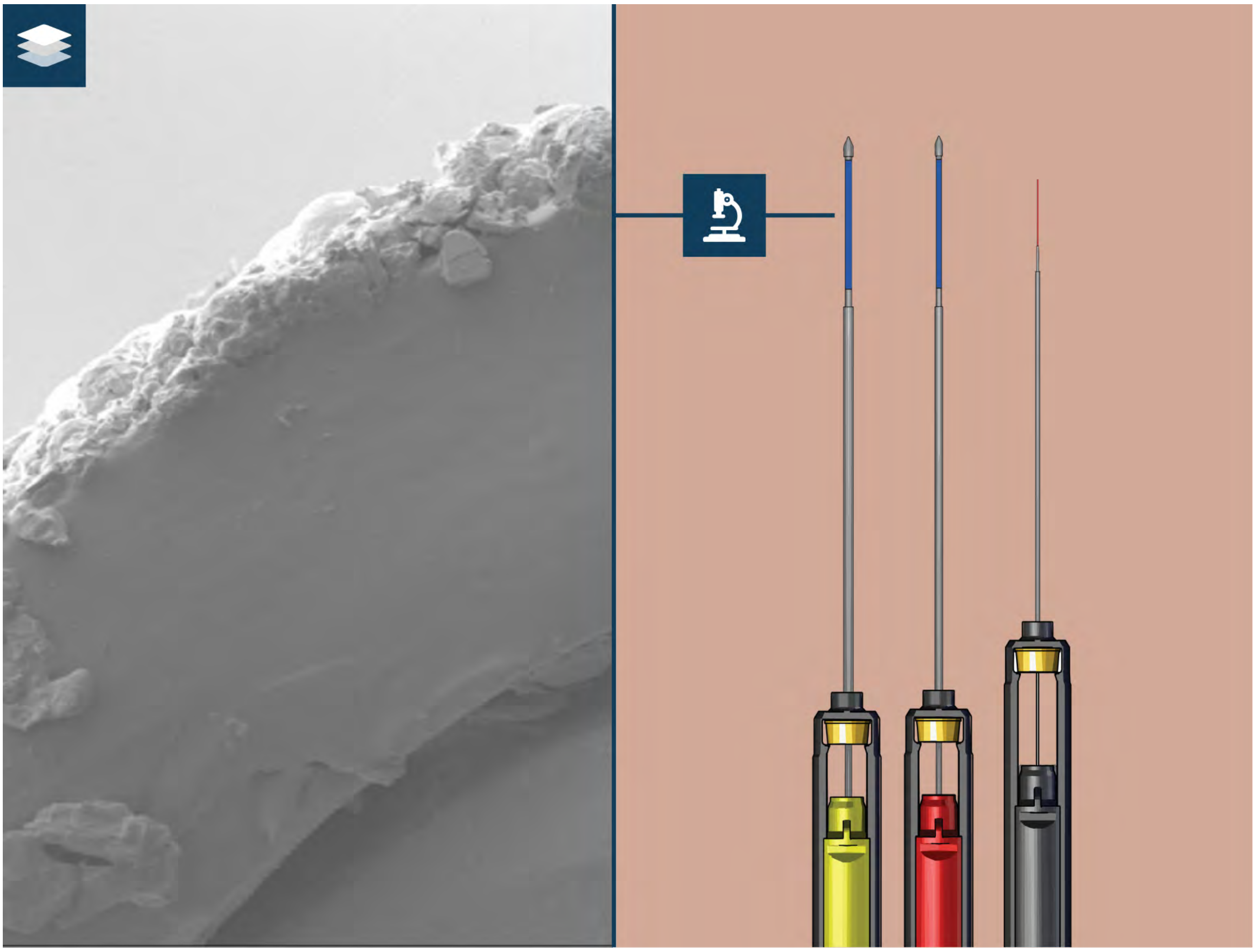
Optimizing the Preconcentration of Volatile PFAS Precursors:
A Comparative Study of SPME Geometries



Optimizing the Preconcentration of Volatile PFAS Precursors:

A Comparative Study of SPME Geometries

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Abstract

The analysis of neutral, volatile, and semi-volatile per- and polyfluoroalkyl substances (PFAS) precursors, such as fluorotelomer alcohols (FTOHs) and sulfonamidoethanols (FOSEs), is essential for understanding the full scope of PFAS sources and environmental contamination. Extracting these compounds for Gas Chromatography/Mass Spectrometry (GC/MS) analysis, however, presents a significant challenge. This Application Note summarizes a study by Williams et al. (2025) that performs a comprehensive comparison of two Solid Phase Microextraction (SPME) geometries: the traditional SPME Fiber and the robust SPME Arrow. The study systematically evaluates the impact of SPME geometry and extraction mode (Headspace vs. Direct Immersion) on extraction efficiency. The results provide a clear, data-driven basis for method development, showing how SPME configurations can be optimized for the specific physicochemical properties of different PFAS analytes.

Keywords
Automation, SPME Arrow, Micro-SPE, PFAS

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Key Take-Home Messages

- **Performance is Analyte-Dependent:** The choice of geometry is not “one-size-fits-all.” The SPME Arrow showed higher sensitivity (lower LOQ) for key volatile FTOHs (e.g., 4:2 FTOH, 8:2 FTOH), while the SPME Fiber offered a lower LOQ for the hydrophobic, semi-volatile MeFOSE.
- **SPME Arrow Provides Superior Robustness:** While performance is nuanced, the SPME Arrow’s durable stainless steel construction offers a significant advantage in automated workflows by eliminating the risk of fiber breakage, reducing instrument downtime, and ensuring long-term reliability.
- **Competitive Adsorption is a Key Factor:** When analyzing mixtures, more hydrophobic analytes (like MeFOSE) can displace less affine, volatile compounds (like 4:2 FTOH) from the sorbent over time. This highlights that extraction time must be carefully optimized to avoid under-quantification of certain analytes.

Introduction

PFAS: Overview and Volatility

Per- and polyfluoroalkyl substances (PFAS) are a large and diverse class of synthetic compounds characterized by their fully or partially fluorinated carbon chains. Their unique chemical properties, such as thermal stability and both hydro- and oleophobicity, have led to their use in a vast array of industrial and consumer products, including firefighting foams, non-stick coatings, and food packaging [10].

However, the strength of the carbon-fluorine bond makes these compounds extremely resistant to degradation, earning them the moniker "forever chemicals" [2].

This persistence leads to their accumulation in the environment, bioaccumulation in organisms, and biomagnification through food webs. For humans, the primary exposure pathways are the consumption of contaminated food and drinking water [2, 3, 11].

The broad class of PFAS can be divided into two main categories: ionic and neutral. The most well-known and regulated PFAS, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), are ionic and non-volatile.

A Guide to PFAS Sample Preparation Techniques

The vast chemical diversity of PFAS means that no single analytical method is suitable for all compounds. The choice of technique is primarily dictated by the analyte's physicochemical properties, matrix complexity, and desired sensitivity. All of these workflows, from simple dilutions to complex multi-step extractions involving centrifugation, can be fully automated on a modular platform like the PAL System.

Technique	Description	Common Workflow & Analytes
SPE /LLE	Traditional extraction methods used to concentrate ionic PFAS from aqueous samples.	Best for legacy ionic PFAS (PFOA, PFOS) from water. Followed by LC/MS [3].
QuEChERS	"Quick, Easy, Cheap, Effective, Rugged, and Safe" method adapted for extracting a wide range of PFAS from solid matrices like food and biological tissues [9].	Sample Homogenization --> Acetonitrile Extraction --> dSPE Cleanup --> LC/MS.
µSPE	A miniaturized, automated form of SPE cleanup that significantly reduces solvent and sample consumption, aligning with green chemistry principles. Ideal for high-throughput labs.	QuEChERS Extract --> µSPE Cleanup --> LC/MS or GC/MS analysis.
Dilute-and-Shoot	The simplest approach, typically used for clean samples like drinking water. It involves minimal sample preparation but can be susceptible to matrix effects.	Sample Dilution --> Filtration -->LC/MS.
SPME (HS/DI)	A solvent-free technique ideal for volatile and semi-volatile compounds. The focus of this note for analyzing precursors like FTOHs, FOSAs, and FOSEs.	Headspace (HS) or Direct Immersion (DI) Extraction --> GC/MS [1, 7].

Abbreviations: SPE (Solid Phase Extraction), LLE (Liquid-Liquid Extraction), QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe), dSPE (dispersive SPE).

However, there is growing concern over their neutral, volatile, and semi-volatile precursors. This group includes fluorotelomer alcohols (FTOHs), perfluorooctanesulfonamides (FOSAs), and N-methylperfluorooctanesulfonamidoethanol (MeFOSE).

These precursors can be transported over long distances in the atmosphere and can be transformed into the more persistent and toxic perfluorinated acids in the environment and in organisms, acting as a continuous source of legacy PFAS contamination [1, 12]. The different physicochemical properties of these PFAS classes necessitate distinct analytical strategies. Due to their volatility and neutral character, precursor compounds are not well-suited for the common Liquid Chromatography/Mass Spectrometry (LC/MS) methods used for ionic PFAS. Instead, Gas Chromatography/Mass Spectrometry (GC/MS) is the more appropriate technique.

A key challenge, however, is effectively extracting and preconcentrating these volatile compounds from complex matrices where they are often present at trace levels prior to analysis. Solid Phase Microextraction (SPME), a solvent-free sample preparation technique developed by Pawliszyn in 1989, offers an ideal solution [4, 5, 8]. It integrates sampling, extraction, and preconcentration into a single, automated step, aligning with the principles of Green Analytical Chemistry.

This Application Note discusses a comparative study by Williams et al. (2025) that evaluates two SPME geometries - the traditional SPME Fiber and the more recent SPME Arrow - for the analysis of volatile PFAS. The study leverages the full automation capabilities of a PAL RTC System to ensure high precision and reproducibility.

Results and Discussion

The study by Williams et al. (2025) systematically investigated the impact of experimental parameters on the extraction efficiency of volatile PFAS. The experiments were fully automated using a PAL RTC System to ensure precise control and high reproducibility. The core of the investigation focused on three main variables: the SPME geometry (Fiber vs. Arrow) and the extraction mode (Headspace vs. Direct Immersion). The following sections detail the findings for each of these experiments.

Experiment 1: SPME Geometry

The core of the investigation was a direct comparison between the SPME Fiber and the SPME Arrow, both coated with a Divinylbenzene/Carbon Wide Range/Polydimethylsiloxane (DVB/C-WR/PDMS) phase. This phase was selected for its effectiveness in extracting a broad range of volatile PFAS precursors from both aqueous and gaseous samples [7].

The SPME Arrow demonstrated enhanced sensitivity (a 10-fold lower LOQ of 0.005 µg L-1) for several key volatile compounds, including 4:2 FTOH, Me_2FOSA, and EtFOSA. It also showed a lower LOQ for 8:2 FTOH (0.05 µg L-1) compared to the SPME Fiber (1 µg L-1).

However, this trend was not universal. For 6:2 FTOH, both geometries had the same LOQ (0.05 µg L-1). For the most hydrophobic, semi-volatile compound, MeFOSE, the SPME Fiber actually achieved a lower LOQ (0.25 µg L-1) than the SPME Arrow (0.5 µg L-1) [1].

The linear dynamic ranges also varied. While the SPME Arrow offered a slightly wider range for some analytes like EtFOSA, the SPME Fiber provided a significantly broader linear range for others, such as 6:2 FTOH and Me_2FOSA [1]. This illustrates that the larger sorbent volume of the Arrow does not uniformly benefit all analytes, especially in a competitive mixture [1, 6].

This highlights that the choice of geometry may be analyte-dependent, an important consideration in method development. This difference in performance is illustrated in Figure 2.

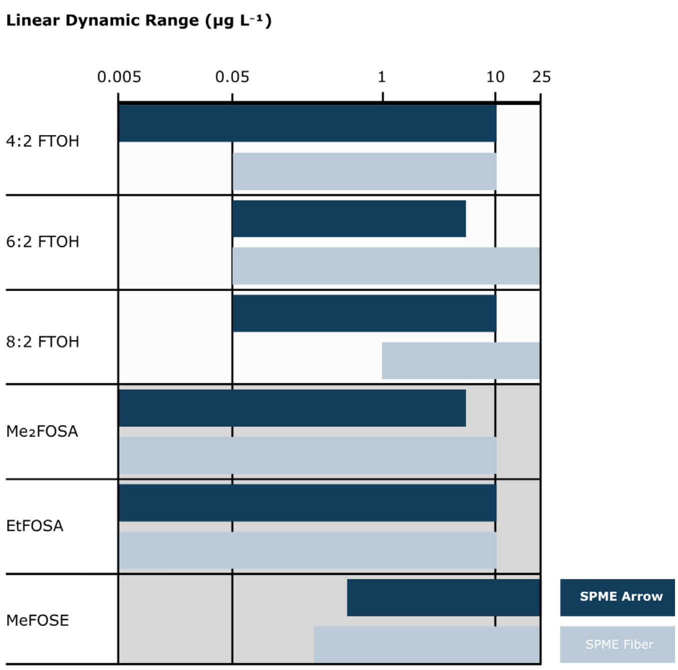

Figure 2: Conceptual chart comparing the linear range of SPME Arrow and SPME Fiber for a volatile FTOH and a semi-volatile FOSE, showing the Arrow's higher response for FTOHs and the Fiber's advantage for MeFOSE. Data extracted from Williams et al. (2025), Supplementary Information, Tables S2 and S3.

SPME Fiber vs. SPME Arrow

The evolution from SPME Fiber to SPME Arrow represents a noteworthy advancement in microextraction technology, addressing limitations of the original design.

	SPME Arrow	SPME Fiber
Durability	Mechanically stable	Prone to breakage
Sensitivity	Enhanced	Good
Surface Area	Larger	Limited
Core Design	Stainless steel	Fused Silica

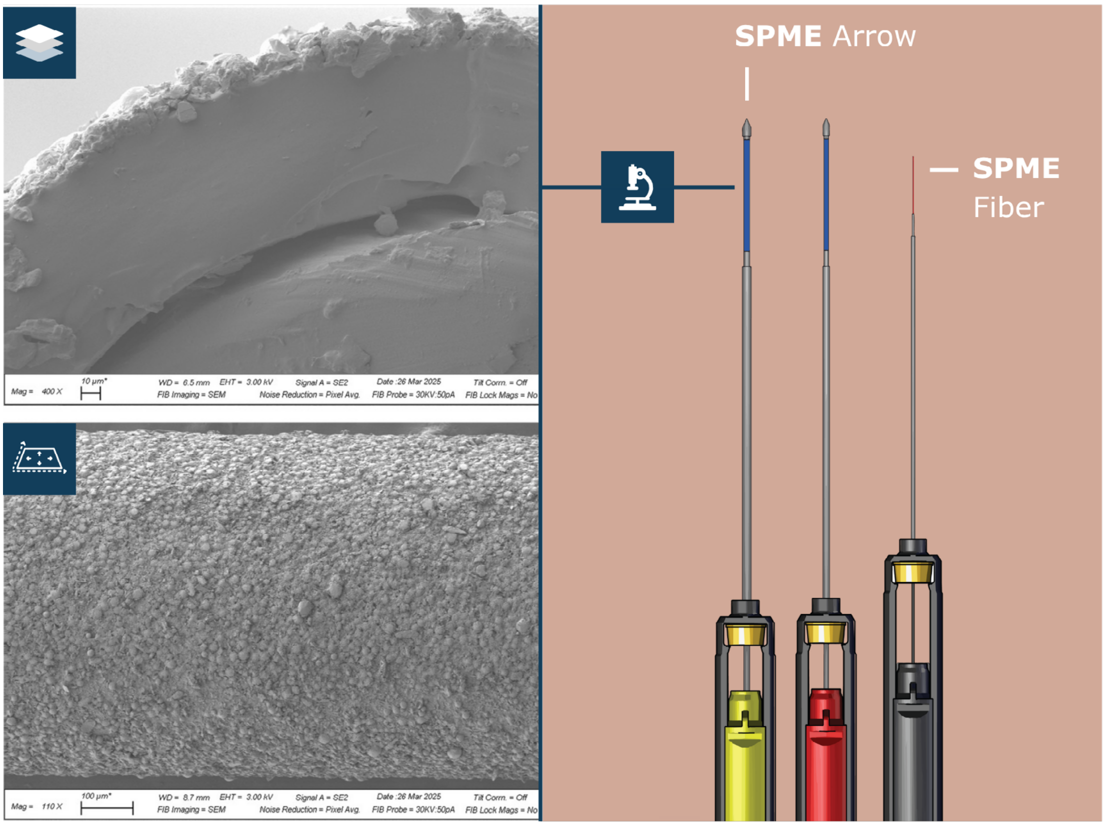

Figure 1: A comparison of SPME Fiber and SPME Arrow geometries and a scanning electron microscopy (SEM) image of the robust, porous DVB/C-WR/PDMS SPME Arrow coating (cross-section and surface). The larger sorbent volume and surface area of the SPME Arrow lead to higher extraction capacity and faster extraction kinetics, which can considerably improve sensitivity for trace analysis [6].

Experiment 2: Extraction Mode

The choice between headspace (HS) and direct immersion (DI) extraction depends heavily on the analyte's volatility, which is related to its Henry's Law constant. The PAL System's ability to precisely automate both HS and DI extractions allowed for a direct and reliable comparison, confirming that the extraction mode must be carefully selected based on the physicochemical properties of the target PFAS, as illustrated in Figure 3.

- Headspace (HS-SPME): As anticipated, HS mode was more effective for the more volatile analytes. For 4:2 FTOH, which readily partitions into the gas phase, HS extraction consistently yielded higher responses regardless of the SPME geometry used [1].

- Direct Immersion (DI-SPME): For semi-volatile and more hydrophobic compounds like Me_2FOSA, EtFOSA, and MeFOSE, DI extraction was noticeably more efficient. Direct contact between the sorbent and the liquid sample is necessary to extract these less volatile compounds effectively [1].

An interesting exception was noted for 8:2 FTOH, which exhibited an opposite trend. Extraction with the SPME Arrow favored DI, while extraction with the SPME Fiber showed greater efficiency in HS mode [1]. This demonstrates that interactions between analyte properties, SPME geometry, and extraction mode can be complex and are not always predictable based on general trends. Highlighting the importance of rigorous and systemic optimization of SPME parameters.

Competitive Adsorption and Extraction Time

An interesting phenomenon observed in the study was the effect of competitive adsorption when analyzing a mixture of PFAS, detailed in Figure 4.

When 4:2 FTOH was extracted from a multi-component mixture using an SPME Fiber, its signal decreased after reaching a peak at around 35 minutes. However, when extracted as a single component, its signal increased and then plateaued as expected.

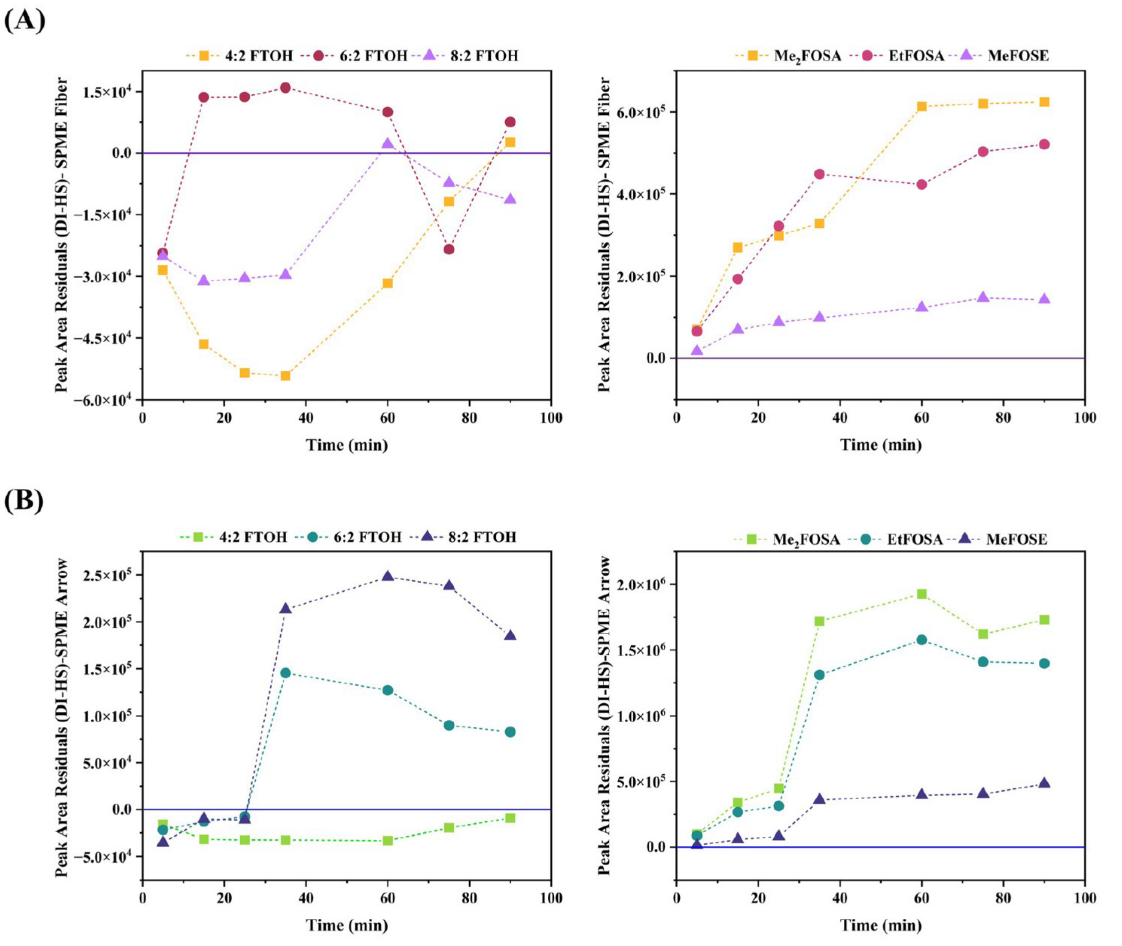

Figure 3: Residual plot analysis comparing the difference in analyte response over time between HS and DI for (A) fiber and (B) arrow. Differences between analyte responses at different time points using DI and HS are plotted. When the value is above 0, it is indicative that the DI response is higher than HS at those time points, while when the value is below 0, it indicates that the HS response is greater than DI. Adapted from Williams et al. (2025).

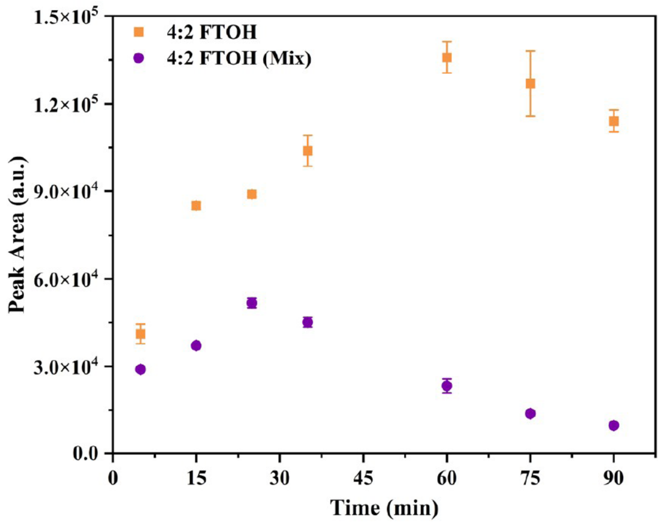

Figure 4: Extraction time profiles of 4:2 FTOH extracted as a single component (square) and as part of a PFAS mixture (circle), demonstrating competitive adsorption on the SPME Fiber after 35 minutes. Adapted from Williams et al. (2025).

This behavior suggests that at longer extraction times, the more hydrophobic and higher-affinity analytes (like MeFOSE or EtFOSA) begin to displace the less affine, more volatile 4:2 FTOH from the finite number of binding sites on the sorbent. This displacement results in a lower measured response for 4:2 FTOH in the mixture compared to when it is analyzed alone.

This finding demonstrates that for multi-analyte methods, longer extraction times are not always better. It is important to carefully optimize the extraction time to balance the recovery of all target compounds and avoid the negative effects of competitive adsorption on less strongly-bound analytes.

Additional Optimizations

Further research from the same laboratory by Martínez-Pérez-Cejuela et al. (2025) provides additional insights into optimizing SPME methods for volatile PFAS. Two parameters investigated were extraction temperature and the ionic strength of the sample.

- **Extraction Temperature**: For HS-SPME, increasing the temperature generally enhances the extraction efficiency of FTOHs. Higher temperatures increase the vapor pressure of the analytes, promoting their partitioning into the headspace where they can be captured by the SPME Fiber or SPME Arrow.

- **Ionic Strength (Salting-Out Effect)**: The addition of salt (e.g., NaCl) to the aqueous sample can have an impact on extraction. This "salting-out" effect can increase the activity of polar analytes, driving them out of the aqueous phase and improving extraction efficiency. However, for more hydrophobic PFAS, adding salt may actually decrease their extraction. This is because high salt concentrations can alter the properties of the sorbent phase and affect the partitioning equilibrium.

These findings highlight the importance of a multi-parameter optimization approach. The ideal temperature and salt concentration are analyte-specific and must be balanced to achieve the best overall performance for the target compound list.

Conclusion and Outlook

The comparative study by Williams et al. (2025) effectively demonstrates that SPME is a highly suitable technique for analyzing volatile and semi-volatile PFAS. The use of an automated platform was instrumental in systematically evaluating multiple parameters and achieving reproducible results. The findings lead to clear, scientifically backed recommendations for method development.

The research confirms that there is no single optimal configuration for all volatile PFAS. The choice of SPME geometry, extraction mode, and other parameters must be tailored to the specific physicochemical properties of the target analytes. For volatile compounds like FTOHs, the SPME Arrow in headspace mode offers enhanced sensitivity due to its larger sorbent volume. For more hydrophobic, semi-volatile compounds such as MeFOSE, the SPME Fiber in direct immersion mode provides lower detection limits. Furthermore, the study highlights the importance of extraction time, noting that phenomena like competitive adsorption can affect the analysis of complex mixtures.

Ultimately, this work showcases a data-driven approach to method development for challenging environmental contaminants. The insights gained enable laboratories to make informed decisions when developing their own SPME-GC/MS methods, resulting in more sensitive, accurate, and reliable data for monitoring volatile PFAS.

Materials and Methods

All experiments were performed on a PAL RTC System coupled to an Agilent 8890/5997C GC/MS. SPME Fibers and SPME Arrows (DVB/C-WR/PDMS) were provided by CTC Analytics. Samples were prepared in ultrapure water. All extractions were performed in triplicate using independent samples. For a detailed description of the experimental parameters, please refer to the primary publication by Williams et al. (2025) [1].

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