

# PFAS in Bottled Water: A Simple Approach Using HS-SPME GC/MS/MS for Volatile Contaminant Analysis

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## 1. Introduction

Concerns about per- and polyfluoroalkyl substances (PFAS) contamination in bottled water, linked to significant health risks, are growing. The Food and Drug Administration (FDA) has published plans surveying bottled water for PFAS in 2024-2025. While Liquid Chromatography/Mass Spectrometry (LC/MS) is the primary analytical method for PFAS, it struggles to analyze certain PFAS related compounds like fluorotelomer alcohols (FTOHs), perfluoroalkyl iodides (PFIs), and (n:2) fluorotelomer iodides (FTIs). Gas Chromatography/Mass Spectrometry (GC/MS) offers a complementary approach for volatile PFAS. This study utilizes Head-Space Solid Phase Microextraction Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS) to analyze PFAS in bottled water. This technique offers several advantages, including minimal sample preparation, making it a valuable tool for comprehensive PFAS analysis.

## 2. Methods

A volatile PFAS analysis method was developed on a Shimadzu GCMS-TQ8040 NX with an AOC-6000 Plus multifunctional autosampler equipped with a solid phase microextraction (SPME) module (**Figure 1**).

Thirteen PFAS target compounds were included in the Multiple Reaction Monitoring (MRM) method. The PFAS chemical classes were perfluoroalkyl iodides (PFIs), (n:2) fluorotelomer iodides (FTIs), (n:2) fluorotelomer acrylates (FTACs), (n:2) fluorotelomer methacrylates (FTMACs), (n:2) fluorotelomer alcohols (FTOHs) and perfluoroalkane sulfonamides (FASAs). Internal standards (IS) FTOHs, FASAs and FTAC mass-labelled compounds were added to each vial prior to extraction. Concentrations of the target compounds were calculated using isotope dilution.

An internal calibration curve was prepared in 10 mL of reagent water at concentrations of 2000, 1000, 500, 100, 50, 10, 2.5 and 1 ng/L. The IS were spiked at 100 ng/L to each calibrator. Sodium Chloride (NaCl) was added to each vial to achieve a final salinity concentration of 2% NaCl (w/v). These calibrators were vortex for 30 seconds and then placed on the AOC-6000 Plus autosampler rack for analysis.

The optimized parameters of the HS-SPME GC/MS method for the targeted PFAS are listed in **table 1**. Quantitative and reference ions for each PFAS target are listed in **table 2**. The associated internal standard used for each compound is also listed in **table 2**.

A laboratory control sample (LCS) was analyzed to determine the general performance of the method in a clean matrix. The bottled water samples were analyzed to determine the effect of matrix on method performance. The type of bottled water analyzed was purified water.



**Figure. 1** Shimadzu GCMS-TQ8040 NX configured with an AOC-6000 Plus

**Table. 1** GC/MS and HS-SPME operating conditions

Gas Chromatography	Nexis GC-2030
Injection mode	Splitless
Carrier gas	Helium
Injection port temperature (°C)	240
Column	SH-I-624Sil MS Capillary, 30 m x 0.25 mmID x 1.40 µm
Flow control mode (cm/sec)	Linear velocity, 45
Total flow (mL/min)	50
Oven temperature	40°C (7 min.), 5°C/min. to 190°C (0 min.), 40°C/min. to 300°C, (5 min.)
Mass Spectrometer	GCMS-TQ8040 NX
Interface temperature (°C)	280
Ion source temperature (°C)	200
Detector voltage (kV)	Relative to Tune 0.4
Threshold	0
Acquisition mode	MRM, Loop time: 03 sec
Tuning mode	Normal mode
SPME analysis	AOC-6000 Plus
SPME Fiber	50/30 µm DVB/CAR/PDMS
Incubation time (min)	5
Extraction time (min)	30
Desorption time (min)	7
Agitation speed (rpm)	300
Extraction temperature (°C)	50
Sample volume (mL)	10
Desorption temperature (°C)	240
Sampling salinity	2 % NaCl (w/v)

**Table. 2** Retention time, quantitative ion, reference ions, and internal standard group for each targeted PFAS compounds

Compound Type	Name	Ret. Time (min)	Quantifier (m/z)	Qualifier #1 (m/z)	Qualifier #2 (m/z)	Internal standard group
Targets	PFHxI	6.7	119.0>69.0	319.0>69.1	319.0>231.0	3
	PFOI	12.5	169.0>69.0	119.0>69.0	419.0>69.1	3
	4:2 FTI	15.0	373.9>227.0	373.9>163.1	373.9>113.1	3
	6:2 FTI	19.6	473.9>326.9	69.0>50.0	473.9>263.0	1
	8:2 FTOH	22.5	95.0>69.0	127.1>77.1	95.0>45.1	1
	6:2 FTAC	23.1	418.1>99.1	99.1>43.1	99.1>57.1	2
	8:2 FTI	23.5	574.0>426.9	169.0>69.0	574.0>65.1	2
	10:2 FTOH	25.7	95.0>69.0	127.1>77.1	95.0>45.1	3
	6:2 FTMAC	25.6	86.1>68.1	432.1>113.1	432.1>86.1	1
	8:2 FTAC	26.4	518.0>99.1	99.1>57.1	99.1>43.1	1
	8:2 FTMAC	28.7	86.0>68.1	86.0>41.1	532.00>113.1	2
	MeFOSA	33.6	131.1>69.1	169.0>69.0	94.00>91.8	4
	EiFOSA	34.2	108.1>80.0	448.0>69.1	108.10>44.1	4
Internal Standards	8:2 FTOH <sup>13</sup> C2	22.4	98.0>69.0	131.1>81.1	98.00>48.1	1
	6:2 FTAC d3	23.1	101.1>57.1	101.1>45.0	102.00>45.0	2
	10:2 FTOH <sup>13</sup> C2	25.6	98.0>69.0	131.1>81.1	98.00>48.1	3
	EiFOSA d5	34.1	113.1>81.0	81.0>64.0	450.10>69.0	4

Prior to sample analysis, the system background was evaluated by analyzing method blanks to confirm that the instrument and reagents were free of interferences. An initial calibration verification (ICV) was performed to verify the accuracy of the calibration curve. Continuing calibration verifications (CCV) were performed to ensure the accuracy of the calibration curve was maintained.

A demonstration of precision and accuracy was first performed on the LCS, followed by precision and accuracy tests on the spiked bottled water samples. All analytes were fortified into the QC samples, which were prepared using the same workflow applied during the development of the internal calibration curve

## 3. Results

The system was deemed free of contaminants and interferences. None of the target PFAS in the method blank were found in quantifiable concentration. In the study, the calibration curve included at least seven calibrators. Calibration curve results showed a good linear fit for all compounds with coefficient of determination ( $R^2$ )  $\geq$  0.994. The linear range and  $R^2$  of each PFAS target are shown in **Table 3**.

**Table. 3** Summary of PFAS calibration range and coefficient of determination.

Compound	Calibration range (ng/L)	R <sup>2</sup>
PFHxI	2.5-2000	0.995
PFOI	2.5-1000	0.994
4:2 FTI	2.5-2000	0.999
6:2 FTI	1.0-2000	0.998
8:2 FTOH	2.5-2000	0.999
6:2 FTAC	2.5-2000	0.998
8:2 FTI	2.5-2000	0.997
6:2 FTMAC	2.5-2000	0.994
10:2 FTOH	2.5-2000	>0.999
8:2 FTAC	2.5-2000	0.995
8:2 FTMAC	2.5-2000	0.997
MeFOSA	2.5-2000	>0.999
EiFOSA	1.0-2000	>0.999

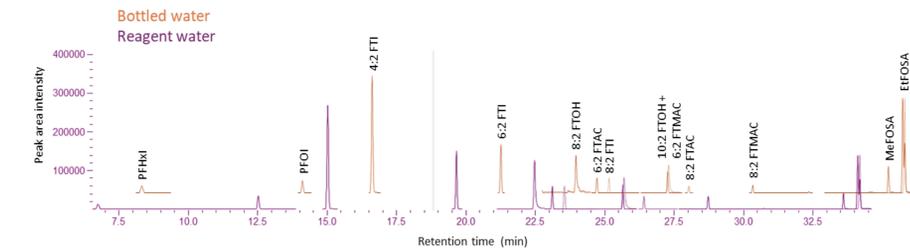
When compared to the initial calibration curve, the ICV accuracy for all compounds was within 70 - 130 %, established as the method criteria. A CCV standard was run after the ICV and at the end of the analytical batch to evaluate the stability of the calibration curve and its ability to quantify targeted compounds in the samples. In comparison to the initial calibration curve, the CCV accuracy for all compounds was within 70 - 130 %.

For the LCS, the concentration of each analyte in the replicate analyses (n=5) was calculated. The mean % recovery ranged from 76 to 128, while the % RSD for analytes in these replicates ranged from 1.1 to 8.9 (**Table 4**).

**Table. 4** Precision and Accuracy (n=5) of PFAS in LCS.

Compound	Reagent Water (LCS)	
	Mean % Recovery	% RSD
PFHxI	121	8.9
PFOI	128	3.3
4:2 FTI	100	5.2
6:2 FTI	97	1.4
8:2 FTOH	90	1.1
6:2 FTAC	82	2.6
8:2 FTI	82	4.5
6:2 FTMAC	104	2.5
10:2 FTOH	93	1.4
8:2 FTAC	104	4.9
8:2 FTMAC	76	5.2
MeFOSA	94	3.4
EiFOSA	91	1.5

The effect of bottled water matrix on the method performance was evaluated through a precision and accuracy experiment. Total ion current (TIC) chromatograms of all targeted PFAS compounds in water samples are shown in **figure 2**. No significant matrix effects on chromatography peak shape were observed in bottled water compared to reagent water.



**Figure. 2** TIC chromatogram of the 13 targeted PFAS compounds at 100 ng/L.

The concentration of each analyte in the replicate analyses (n=3) for each spike and unspiked samples was calculated using the ICAL. None of the targeted PFAS were found in the unspiked sample in quantifiable concentrations. The mean percent recovery for the targeted compounds in the bottled water ranged from 69 to 124, while the % RSD for these analytes ranged from 0.3 to 13.2 (**Table 5**). The mean % recovery was within 60-140 % and % RSD was less than 15 % for all compounds.

**Table. 5** Precision and Accuracy (n=3) of PFAS in bottled water.

Compound	Bottled Water	
	Mean % Recovery	% RSD
PFHxI	124	12.3
PFOI	121	13.2
4:2 FTI	104	12.5
6:2 FTI	84	5.5
8:2 FTOH	85	0.3
6:2 FTAC	72	0.6
8:2 FTI	77	6.2
6:2 FTMAC	83	0.5
10:2 FTOH	87	2.3
8:2 FTAC	77	3.1
8:2 FTMAC	69	6.4
MeFOSA	87	0.9
EiFOSA	88	0.8

## 4. Conclusion

The PFAS family includes thousands of compounds across diverse chemical classes, making comprehensive analysis challenging and often necessitating multiple analytical techniques. LC-MS is widely used and well-established for PFAS analysis but is less effective for detecting certain compounds - particularly volatile PFAS. In contrast, GC-MS excels at analyzing volatile PFAS and serves as a valuable complement to LC-MS, offering a more complete and balanced approach to PFAS detection. By extending the range of detectable compounds, GC-MS helps overcome PFAS analysis limitations previously imposed by instrumentation constraints. This study demonstrates the strong performance of an HS-SPME GC/MS/MS method for measuring volatile PFAS in bottled water. The application presents a simple, rapid, robust, precise, and accurate workflow that significantly improves the ability to detect a broader spectrum of PFAS compounds in bottled water.