Gas Chromatography Mass Spectrometry

Application News

Analysis of Volatile PFAS in Drinking Water Using Head-Space Solid Phase Microextraction - Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS)

User Benefits

◆ Rapid quantitation of volatile PFAS in drinking water with minimum sample preparation can be performed by HS-SPME GC/MS/MS.

◆ The simplified sample preparation procedure by automated SPME method using the AOC-6000 Plus reduces the operation error for PFAS analysis.

◆ Low limits of quantification for PFAS are achieved using a highly sensitive and selective triple quadrupole GC/MS, like the GCMS-TQ8040 NX, while minimizing false positives from matrix interferences.

■ Introduction

The targeted and the non-targeted analysis of per- and polyfluoroalkyl substances (PFAS) are pivotal in environmental analysis.[1] To date, there are several Environmental Protection Agency (EPA) standardized PFAS methods such as 533, 537.1, 8327, 1633, OTM-45, and OTM-50. Most of these methods are based on Liquid Chromatography/Mass Spectrometry (LC/MS) techniques. However, LC/MS is not suitable to analyze all PFAS compounds because of the diverse physico-chemical properties of chemicals within the PFAS family. For example, ionization suppression of fluorotelomer alcohols (FTOHs) from the buffered mobile phase and the ionization challenge of perfluoroalkyl iodides (PFIs) and fluorotelomer iodides (FTIs) in electrospray-ionization have been reported.[2]

Gas Chromatography/Mass Spectrometry GC/MS as a complementary technique can address volatile PFAS compounds that are challenging to analyze by LC/MS. Currently, the demand of using GC/MS to measure PFAS in water and other sample types is increasing. Therefore, it is crucial to develop GC/MS based methods workflows to provide a complete solution for PFAS analysis. This technique has advantages of analyzing volatile PFAS in water with minimum sample preparation procedure.

In this study, a Head-Space Solid Phase Microextraction-Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS) analytical method is used to analyze PFAS in drinking water. This application news demonstrates the capability of a Shimadzu GCMS-TQ8040 NX triple quadrupole GC/MS in Multiple Reaction Monitoring (MRM) mode configured in tandem with an AOC-6000 Plus multifunctional autosampler to precisely and accurately measure PFAS in reagent water and drinking water samples.

■ Experimental Approach

Instrumentation

The instrument system configuration for the application consisted of a Shimadzu GC/MS, model GMCS-TQ8040 NX, a multifunctional autosampler (AOC-6000 Plus) equipped with a SPME module and a split/spitless inlet (**Figure 1**).

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

Standards and Reagents

The thirteen PFAS target list consisted of PFIs, FTIs, FTACs, FTMACs, FTOHs and FASAs. Internal standards were FTOHs, FASAs, and FTAC mass-labelled compounds. A stock solution of each analyte was prepared at 1000 mg/L in methanol. This standard was further diluted to make an intermediate stock at 10 mg/L. These standards were stored at 4 °C. LC/MS grade water and methanol were purchased from Honeywell.

An internal calibration curve was prepared in 10 mL of water at the concentration of 2000, 1000, 500, 100, 50, 10, 2.5, and 1 ng/L. Details of the calibration curve range method development can be found in Shimadzu application news GCMS-2403.[3] The mass labelled internal standard compounds were spiked at 100 ng/L for each calibrator. Sodium Chloride (NaCl) was added to each vial to achieve a final salinity concentration of 2% NaCl (w/v). This sample was vortexed for 30 seconds and then placed on the AOC-6000 Plus autosampler rack for HS-SPME analysis.

HS-SPME GC/MS/MS Analysis

The SPME method in this study is based on a method publication by Bach et.al. (2016). Instead of using direct immersion SPME, a HS-SPME method was used to improve method performance when analyzing complex aqueous samples.[2]

The optimized parameters of the instrument method for the targeted PFAS are listed in **Table 1**. A quantifier and qualifiers for each PFAS target are listed in **Table 2**. Quantitation was performed by an internal standard method. The associated internal standards used for each compound are also listed in **Table 2**.

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

Gas Chromatography	Nexis GC-2030
Injection port 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 um
Flow control mode (cm/sec)	Linear velocity: 45
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	Acquisition mode: MRM, Loop time: 0.3 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, quantifier, qualifiers, and internal standard group information for each of the targeted PFAS compounds.

	Compound	Ret. Time (min)	Quantifier (m/z)	CE	Qualifier #1 (m/z)	CE	Qualifier #2 (m/z)	CE	Internal standard group
Targets	PFHxI	6.7	119.0>69.0	12	319.0>69.1	24	319.0>231.0	6	3
	PFOI	12.5	169.0>69.0	21	119.0>69.0	21	419.0>69.1	27	3
	4:2 FTI	15.0	373.9>227.0	9	373.9>163.1	21	373.9>113.1	27	3
	6:2 FTI	19.6	473.9>326.9	12	69.0>50.0	27	473.9>263.0	21	1
	8:2 FTOH	22.5	95.0>69.0	15	127.1>77.1	15	95.0>45.1	27	1
	6:2 FTAC	23.1	418.1>99.1	15	99.1>43.1	9	99.1>57.1	12	2
	8:2 FTI	23.5	574.0>426.9	15	169.0>69.0	9	574.0>65.1	24	2
	10:2 FTOH	25.7	95.0>69.0	15	127.1>77.1	15	95.0>45.1	27	3
	6:2 FTMAC	25.6	86.1>68.1	6	432.1>113.1	12	432.1>86.1	21	1
	8:2 FTAC	26.4	518.0>99.1	15	99.1>57.1	12	99.1>43.1	9	1
	8:2 FTMAC	28.7	86.0>68.1	6	86.0>41.1	15	532.00>113.1	21	2
	MeFOSA	33.6	131.1>69.1	24	169.0>69.0	12	94.00>91.8	57	4
	EtFOSA	34.2	108.1>80.0	6	448.0>69.1	27	108.10>44.1	3	4
Internal Standards	8:2 FTOH $^{13}C_2$	22.4	98.0>69.0	15	131.1>81.1	15	98.00>48.1	27	1
	6:2 FTAC d_3	23.1	101.1>57.1	12	101.1>45.0	9	102.00>45.0	9	2
	10:2 FTOH $^{13}C_2$	25.6	98.0>69.0	12	131.1>81.1	12	98.00>48.1	27	3
	EtFOSA d_5	34.1	113.1>81.0	6	81.0>64.0	24	450.10>69.0	27	4

Sample Collection

Reagent water and drinking water from two locations were analyzed in the study. LC/MS grade water was used as reagent water. This laboratory control sample (LCS) was analyzed to determine the general performance of the method in a clean matrix.

The drinking water samples were collected from two households; one sample was from a private well and the second household receives water from a utility with surface water as its source. These water samples were analyzed to determine the effect of the matrix on method performance. Approximately 400 mL of sample was collected in a clean glass bottle. The water sample was then poured into 40 mL amber volatile organic analyte (VOA) vials so that no head space remained at the top of the vial. These vials were then capped and delivered to the laboratory. The samples were stored at 4 °C. All drinking water samples were analyzed within 24 hours.

PFAS contamination can occur during sampling from various sources such as consumables. All consumables used during sample collection were analyzed and deemed free from PFAS. During sample collection from the faucet, the tap was opened, and the system was flushed for approximately five minutes. Samples were collected from the flowing faucet.

Sample Preparation

The reagent water and drinking water samples were prepared for instrument analysis using 10 mL of samples. Five replicate aliquots of LCS were analyzed. The drinking water samples from each of the two locations were analyzed in triplicated aliquots for both spiked and un-spiked samples. LCS and spiked drinking water samples were fortified with all analytes and mass labelled internal standard compounds at 100 ng/L, which represented the midrange concentration of the initial calibration (ICAL). Unspiked samples were only fortified with mass labelled internal standard compounds at 100 ng/L.

The ICAL verification (ICV) and continuing calibration verification (CCV) quality control (QC) samples were prepared for instrument analysis using 10 mL of reagent water. These QC samples were fortified with all analytes and mass labelled internal standard compounds at 100 ng/L. This concentration also represented the midrange concentration of the ICAL.

Sodium chloride (NaCl) was added to all water and QC samples to achieve a final salinity concentration of 2% NaCl (w/v). Each sample vial was vortexed for 30 seconds; and then placed on the AOC-6000 Plus rack for HS-SPME analysis.

Instrumental Analysis

A demonstration of proficiency study of the instrumentation method capability to conduct PFAS analysis on drinking water was performed. Prior to analysis of samples, the system background was evaluated by analyzing method blanks to confirm that the instrument and reagents were free of contaminants and interferences. Subsequently, an ICAL was analyzed. Prior to analyzing the samples, an ICV was performed to verify the accuracy of the calibration curve. In addition, a CCV was analyzed within the batch to ensure the accuracy of the calibration curve was maintained and no major drift was observed. Both ICV and CCV data are used to validate the integrity of the calibration curve, which is used to generate sample results. In this study, the ICV and CCV accuracy should be within 70-130 % for the calibration curve to be considered valid.

A demonstration of precision and accuracy was first performed on the LCS, followed by precision and accuracy tests on the spiked drinking water samples. Concentration of the target PFAS in the unspiked samples, if present, was taken into consideration for computing the precision and accuracy.

■ Results and Discussion

As a quality control measure, an initial demonstration of low system background was conducted before developing the calibration curve and analyzing samples. Method blanks were analyzed, and the system was deemed free of contaminants and inferences. None of the target PFAS in the method blank were found in quantifiable concentration. In the study, a calibration curve for all analytes was prepped from 1 to 2000 ng/L. Calibration curve results showed a good linear fit for all compounds with coefficient of determination (R^2) ≥ 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^2
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
EtFOSA	1.0-2000	>0.999

An ICV standard was run prior to sample analyses. When compared to the initial calibration curve, the ICV accuracy for all compounds was within 70-130 %. A CCV standard was ran 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 using the ICAL. The mean percent recovery (mean % recovery) and percent relative standard deviation (% RSD) were calculated for each analyte of interest. 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
EtFOSA	91	1.5

The effect of drinking water matrix effect 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 either the drinking water from the private well or surface water treatment plant compared to reagent water. 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 drinking water sourced from the surface water treatment plant ranged from 71 to 129, while the % RSD for these analytes ranged from 0.3 to 4.7 (**Table 5**). For the drinking water sourced from private well, the mean percent recovery for the targeted compounds ranged from 64 to 120, while the % RSD for these analytes ranged from 0.1 to 4.9 (**Table 5**). Overall, the mean % recovery was within 64-129 % and % RSD was ≤4.9 % for all compounds.
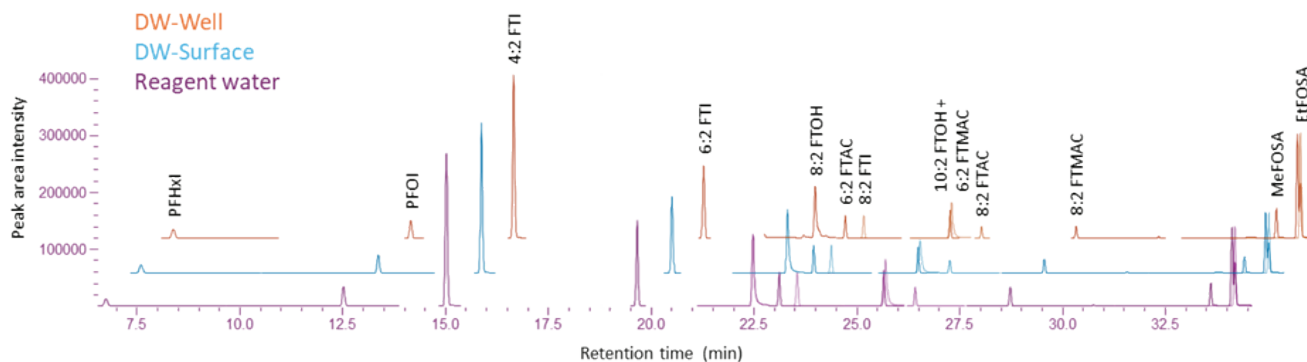
Figure 2: TIC chromatogram of the 13 targeted PFAS compounds at 100 ng/L. No significant matrix effects were observed on the analyte chromatography peak shape for drinking water from well (DW-Well) and from surface water treatment plant (DW-Surface) compared to reagent water.

Table 5: Precision and recovery (n=3) of PFAS in drinking water from a surface water source and private well.

Compound	(DW-Surface)		(DW-Well)	
	Mean % Recovery	% RSD	Mean % Recovery	% RSD
PFHxI	118	0.3	120	4.9
PFOI	129	2.3	118	3.0
4:2 FTI	104	1.6	108	3.7
6:2 FTI	102	3.1	90	1.1
8:2 FTOH	92	1.2	88	0.6
6:2 FTAC	77	2.7	74	2.4
8:2 FTI	87	4.7	64	3.1
6:2 FTMAC	104	2.7	90	2.6
10:2 FTOH	91	1.9	88	0.1
8:2 FTAC	95	3.4	81	1.1
8:2 FTMAC	71	3.4	65	3.9
MeFOSA	85	1.3	93	0.3
EtFOSA	87	0.6	90	0.3

■ Conclusion

This study demonstrated the satisfactory performance of a HS-SPME GC/MS/MS method to measure PFAS in drinking water. In the study a Shimadzu GCMS-TQ8040 NX triple quadrupole instrument configured with an AOC-6000 Plus solid phase microextraction unit was used to measure PFAS in reagent water and drinking water from a private well and a surface water treatment plant. Method blanks showed no quantifiable PFAS in the background. Calibration results showed good linearity for all compounds and coefficient of determination (R^2) ≥ 0.994 were obtained. ICV and CCV recoveries for all compounds were within 70-130 %.

For LCS precision and accuracy analysis, the mean % recovery PFAS in LCS was within 76-128 % and % RSD was ≤8.9 % for all compounds. For drinking water sample precision and accuracy analysis, the mean % recovery of PFAS in fortified drinking water from both a private well and surface water treatment plant was within 64-129 % and % RSD was less than 4.9 % for all compounds. These values are well within the accepted ranges for these QC parameters in LCS and samples.

This HS-SPME GCMS-TQ8040 NX method demonstrated quantitative capability in analyzing nanogram per liter PFAS compounds in not only the reagent water but also in water samples from various sources. This application demonstrates a simple, fast, robust, precise, and accurate workflow for measuring volatile PFAS in drinking water.

References

1. Mok, S., Lee, S., Choi, Y., Jeon, J., Kim, Y. H., & Moon, H. B. (2023). Target and non-target analyses of neutral per-and polyfluoroalkyl substances from fluorochemical industries using GC-MS/MS and GC-TOF: Insights on their environmental fate. *Environment International*, 182, 108311. https://doi.org/10.1016/j.envint.2023.108311

2. Bach, C., Boiteux, V., Hemard, J., Colin, A., Rosin, C., Munoz, J., & Dauchy, X. (2016). Simultaneous determination of perfluoroalkyl iodides, perfluoroalkane sulfonamides, fluorotelomer alcohols, fluorotelomer iodides and fluorotelomer acrylates and methacrylates in water and sediments using solid-phase microextraction-gas chromatography/mass spectrometry. *Journal of Chromatography* A, 1448, 98-106. https://doi.org/10.1016/j.chroma.2016.04.025

3. Shimadzu Application News. GCMS-2403. (2024, March). Volatile PFAS in water analysis using Head-Space Solid Phase Microextraction-Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS). GCMS-2403_PFAS_HS_SPME_GCMS.pdf (shimadzu.com)

Consumables

Item Name	Item Description	Part Number
Capillary column	GC, SH-I-624Sil MS Capillary, 30 m x 0.25 mm ID x 1.40 um	221-75962-30
SPME Inlet liner	SPME liner 0.75mm x 5.0 x 95 for Shimadzu GCs Deact., 5pk (Restek)	REST-22279
Head-Space sample vials	20ml magnetic screw-cap clear heads pace vial kit	220-97331-16
Liquid injection sample vials	1.5 ml Amber glass vial w/Cap & septa	220-97331-31
Methanol	Methanol, LCMS Honeywell Chromasolv(R); 99.9%	220-91545-11
Ultra-pure water	Water, LCMS Honeywell Chromasolv(R); 99. 9%	220-91545-12
SPME fiber	SPME fiber assembly (DVB/CAR/PDMS) (Millipore Sigma)	57298-U
Methylene Chloride	Methylene Chloride (GC Resolv ™) Fisher Chemical (Fisher Scientific)	D154-4

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