Application News

GCMS-QP2020 NX Gas Chromatograph Mass Spectrometer / AOC™-6000 Plus

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

User Benefits

- HS-SPME GC/MS can analyze selected PFAS in water samples with minimum sample preparation procedure.
- The simplified sample preparation procedure and automated SPME method using the AOC-6000 Plus reduces the operation error for PFAS analysis.
- This single quadrupole GC/MS application provides a cost-effective solution to analyze volatile PFAS in comparison to high resolution or even triple quadrupole GC/MS.

■ Introduction

Per- and Polyfluoroalkyl Substances (PFAS) are environmental pollutants with recognized health and environmental concerns due to their probable toxicity, persistence, and ubiquitousness throughout the environment, and consumer and industrial products. PFAS encompass a large family of chemicals with varying physicochemical properties. These properties affect their toxicity and environmental fate. Additionally, different analytical techniques are required for monitoring these different classes. The classes of PFAS evaluated in this study are PFIs, FTIs, FTACs, FTMACs, FTOHs and FASAs. (**Table 1**).

In this application, a Head-Space Solid Phase Microextraction-Gas Chromatography Mass Spectrometry (HS-SPME GC/MS) analytical method was developed to analyze volatile PFAS in water. Currently, there are several established PFAS standard methods, such as EPA methods 1633, 8327, 533, and 537.1. All these methods analyze these compounds by Liquid Chromatography/Mass Spectrometry (LC/MS). However, LC/MS is unable to analyze all PFAS compounds for various reasons. For example, ionization suppression of FTOHs from the buffered mobile phase and the ionization challenge of PFIs and FTIs in electrospray-ionization have been reported.[1] Therefore, it is crucial to develop complimentary analytical techniques to provide a complete solution for PFAS analysis.

HS-SPME GC/MS is pivotal as a complementary technique to LC/MS as it offers numerous advantages, such as its ability to analyze these compounds in complex matrices.

When compared to other analytical techniques, HS-SPME GC/MS analysis has less sample preparation (no need for solvent extraction), minimal sources of contamination and less potential for analytical error. This technique can be fully automated. Thus, being less laborious.

■ Experimental Approach

Instrumentation

The instrument system configuration for the application consisted of a Shimadzu GC/MS, model QP2020 NX, and a multifunctional autosampler (AOC-6000 Plus) equipped with a SPME module and a split/spitless inlet (**Figure 1**).

Figure 1: Shimadzu GCMS-QP2020 NX configured with an AOC-6000 Plus

Standards and reagents

The PFAS target list consists of PFIs, FTIs, FTACs, FTMACs, FTOHs and FASAs. Internal standards were FTOHs, FASAs, and FTAC mass-labelled compounds. The individual compounds from each chemical class are listed in **table 1**. 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, 800, 500, 250, 100, 50, 25, 10, 5 and 2.5 ng/L. The mass labelled internal standard compounds were spiked at 1000 ng/L to each calibrator.

Sodium Chloride (NaCl) was added to each vial to achieve a final salinity concentration of 2% NaCl (w/v). This sample was vortex for 30 seconds and then placed on the AOC-6000 Plus autosampler rack for HS-SPME analysis.

Table 1: Per- and Polyfluoroalkyl Substances (PFAS) analyzed in this study

Chemical Class (acronym)	**Compound**	**Acronym**	**CAS Number**	**Vendor**
Perfluoroalkyl iodides (PFIs)	Perfluorohexyl iodide	PFHxI	355-43-1	Millipore Sigma
	Perfluorooctyl iodide	PFOI	507-63-1	
(n:2) Fluorotelomer iodides (FTIs)	4:2 Fluorotelomer iodide	4:2 FTI	2043-55-2	TCI America
	6:2 Fluorotelomer iodide	6:2 FTI	2043-57-4	Millipore Sigma
	8:2 Fluorotelomer iodide	8:2 FTI	2043-53-0	
(n:2) Fluorotelomer acrylates (FTACs)	6:2 Fluorotelomer acrylate	6:2 FTAC	17527-29-6	Millipore Sigma
	8:2 Fluorotelomer acrylate	8:2 FTAC	27905-45-9	
	1H,1H,2H,2H-Perfluoro-n-octyl acrylate-d3	*6:2 FTAC* d_3	*7527-29-6*	*Sapphire North America*
(n:2) Fluorotelomer methacrylates (FTMACs)	6:2 Fluorotelomer methacrylate	6:2 FTMAC	2144-53-8	Millipore Sigma
	8:2 Fluorotelomer methacrylate	8:2 FTMAC	1996-88-9	
(n:2) Fluorotelomer alcohols (FTOHs)	8:2 Fluorotelomer alcohol	8:2 FTOH	678-39-7	AccuStandard
	10:2 Fluorotelomer alcohol	10:2 FTOH	865-86-1	
	2-perfluorooctyl-[1,1-2H2-1,2-13C2]-ethanol	*8:2 FTOH* $^{13}C_2$	*872398-73-7*	*Cambridge Isotope*
	2-perfluorodecyl-[1,1-2H2-1,2-13C2]-ethanol	*10:2 FTOH* $^{13}C_2$	*865-86-1*	
Perfluoroalkane sulfonamides (FASAs)	N-Methyl perfluorooctane sulfonamide	MeFOSA	31506-32-8	AccuStandard
	N-Ethyl perfluorooctane sulfonamide	EtFOSA	4151-50-2	
	n-ethyl-d5-perfluoro-1-octanesulfonamide	*EtFOSA* d_5	*936109-40-9*	*Cambridge Isotope*

Internal standards are highlighted in grey.

HS-SPME GC/MS Analysis

HS-SPME is a technique based on the movement of the targeted compounds in the sample to the sorption phase in the fiber via the partition coefficient. To increase the amount concentrated in the fiber the sorption phase must be selected to suit the analyte and the sample must be salted out, increasing the sorption phase partition coefficient.[2]

The SPME method in this study is based on a method by Bach et.al. (2016). Instead of using direct immersion SPME, a HS-SPME method was used to increase the method capability of addressing complex water matrices in the future. Unlike direct immersion SPME, which involves interaction between the SPME fiber and a water matrix, HS-SPME sampling has less interaction with this matrix.

The fiber, using HS-SPME, interacts solely with gaseous molecules, thus being less affected by polar compound interferences. First, a Selected Ion Monitoring (SIM) method was developed for analysis of the targeted PFAS compounds, using liquid injection.

The optimized parameters of the HS-SPME GC/MS method for the targeted PFAS are listed in **table 2**. Quantitative and reference ions for each PFAS target are listed in **table 3**. Quantitation was performed by an internal standard method. The associated internal standards used for each compound are listed in **table 3**.

Table 2: GC/MS and HS-SPME operating conditions

Gas Chromatography	**Nexis GC-2030**
Injection mode	Splitless
Carrier gas	Helium
Injection port temperature (°C)	240
High pressure injection	Auto, 250 kPa, 1 min
Column	SH-I-624Sil MS Capillary, 30 m x 0.25 mmID x 1.40 um
Flow control mode (cm/sec)	Linear velocity, 44.4
Total flow (mL/min)	50
Oven temperature	40 °C (7 min.), 5 °C/min. to 188 °C (0 min.), 40 °C/min. to 300 °C, (5 min.)
Mass Spectrometer	**QP2020 NX**
Interface temperature (°C)	280
Ion source temperature (°C)	200
Detector voltage (kV)	Relative to Tune 0.4
Threshold	0
Acquisition mode	Qualitative analysis: Full scan: *m/z* 50 to 600 Quantitative analysis: SIM, Event time 0.3 sec.
Tuning mode	High Sensitivity
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 3: Retention time, quantitative ion, reference ions, and internal standard group information for each of the targeted PFAS compounds

Compound Type	**Name**	**Ret. Time (min)**	**Quantitative ion (*m/z*)**	**Reference ion #1 (*m/z*)**	**Reference ion #2 (*m/z*)**	**Internal standard group**
Targets	PFHxI	6.3	319	69	231	3
	PFOI	12.5	169	419	119	3
	4:2 FTI	15.1	374	227	69	3
	6:2 FTI	19.7	474	141	327	1
	8:2 FTOH	22.6	127	131	119	1
	6:2 FTAC	23.2	418	327		2
	8:2 FTI	23.6	574	119	427	2
	10:2 FTOH	25.8	505	563		3
	6:2 FTMAC	25.7	432	113	367	1
	8:2 FTAC	26.5	518	169	456	4
	8:2 FTMAC	28.8	532	86	113	4
	MeFOSA	33.7	131	94	119	4
	EtFOSA	34.3	448	80	108	4
Internal Standards	8:2 FTOH $^{13}C_2$	22.5	450	400	417	1
	6:2 FTAC d_3	23.2	421	101	327	2
	10:2 FTOH $^{13}C_2$	25.7	510	169	500	3
	EtFOSA d_5	34.3	450	113	169	4

Laboratory Blanks and Carryover Effect

Laboratory blanks were analyzed in each batch, prior to calibration curve analysis, to detect any contamination from the laboratory environment and consumables. These blanks were prepared by using ultrapure water and 100 µL methanol, the same solvent used to prepare the stocks solution containing targets and IS.

The evaluation of carryover from the highest calibration standard was conducted by running a blank after this standard. A peak area of this blank was evaluated and compared to peak area of the previous calibrator (highest level of the quantitation range).

■ Results and Discussion

A chromatography method separating the 13 targeted PFAS compounds was developed. Total ion current (TIC) chromatogram of all targeted compounds using the scan method and liquid injection is shown in **Figure 2**. Most compounds were chromatographically separated except for 10:2 FTOH and 6:2 FTAC. These compounds were separated by unique mass to charge ratio in the SIM analysis.

Representative PFAS SIM chromatograms for all target compounds in 100 ng/L standard are included in **Figure 3**.

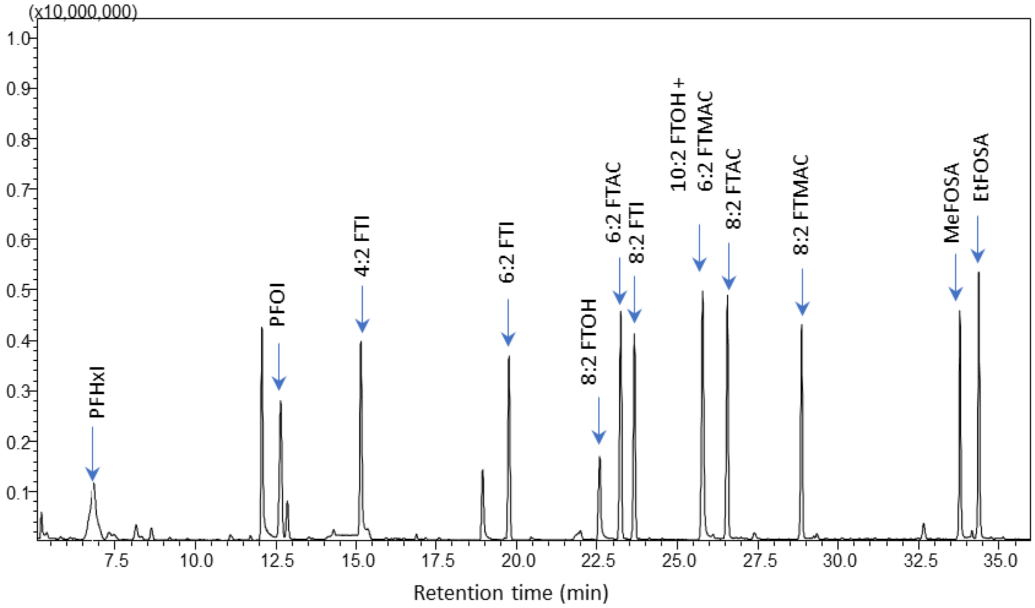


Figure 2: TIC chromatogram of the 13 targeted PFAS compounds at 5 mg/L

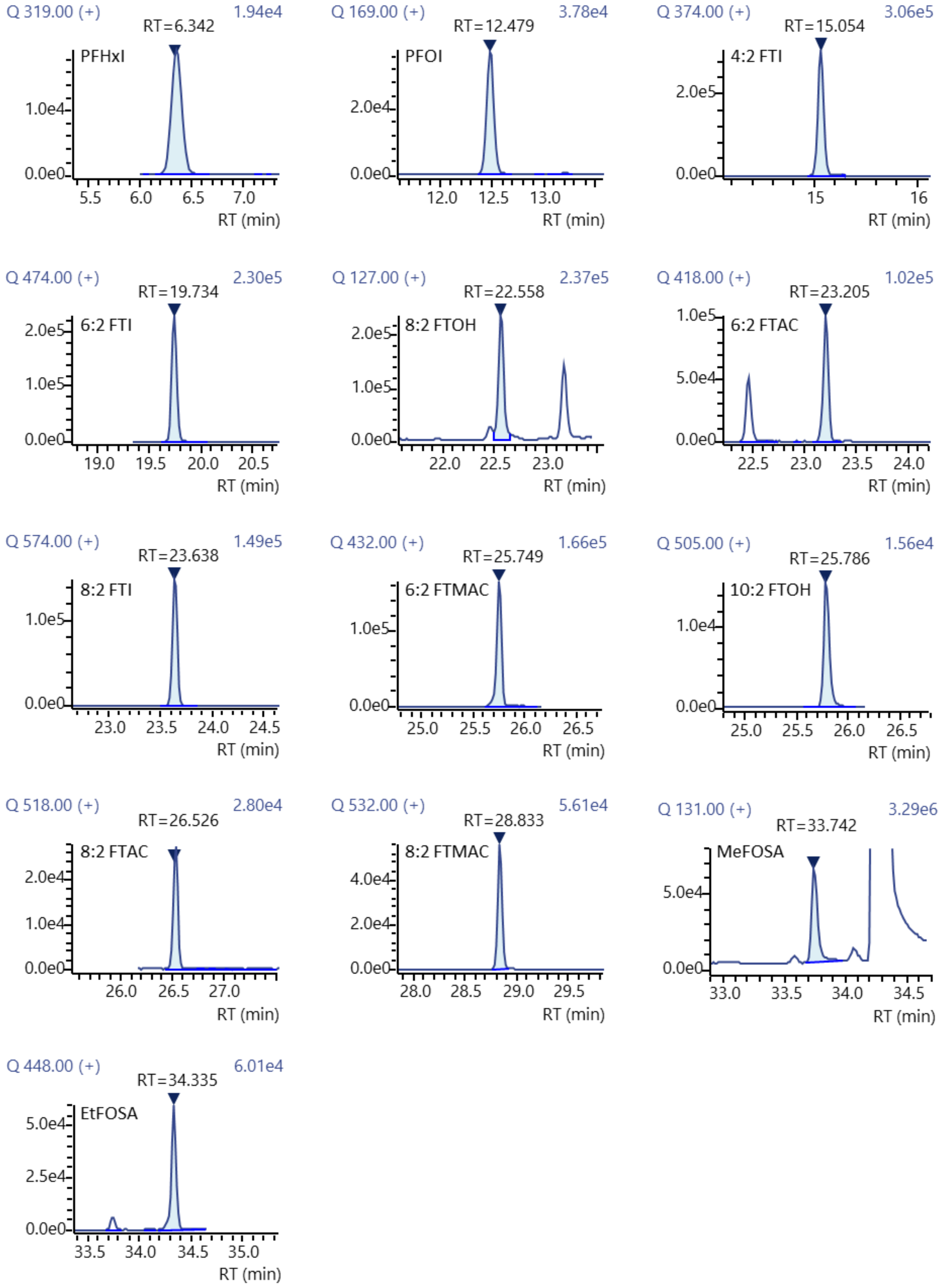


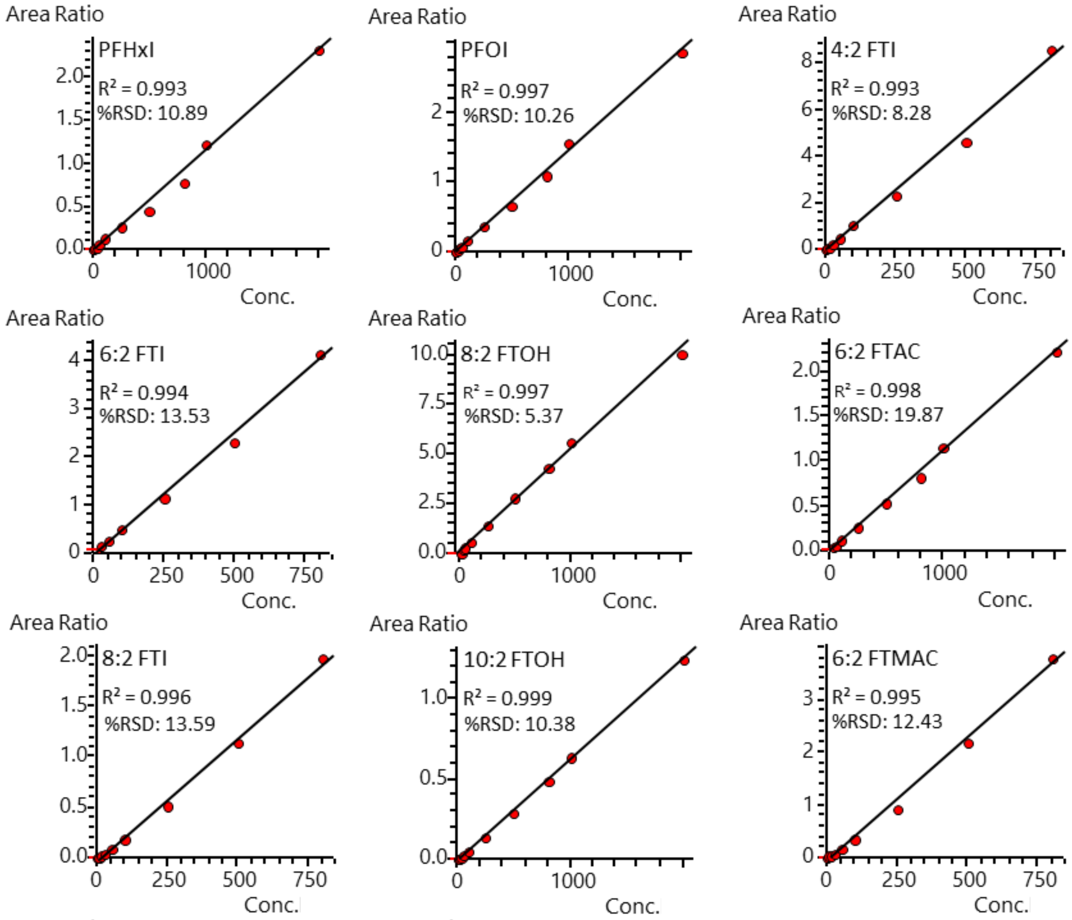
Figure 3: SIM chromatograms for the targeted PFAS compounds at 100 ng/L in ultrapure water

The linear range of each PFAS target is shown in **table 4** and includes at least seven calibrators. Other calibration information including coefficient of determination (R^2) and RF % RSD of the 13 PFAS compounds are also shown in **table 4**.

Calibration curve results showed a good linear fit for all compounds with $R^2 \geq 0.993$ and RF %RSD < 20. **Figure 4** illustrates calibration curves for all compounds.

Table 4: Summary of PFAS calibration range and linearity results

Compound	Calibration Range (ng/L)	R^2	RF (Response Factor) %RSD
PFHxI	2.5-2000	0.993	10.89
PFOI	2.5-2000	0.997	10.26
4:2 FTI	2.5-800	0.993	8.28
6:2 FTI	25-800	0.994	13.53
8:2 FTOH	25-2000	0.997	5.37
6:2 FTAC	25-2000	0.998	19.87
8:2 FTI	2.5-800	0.996	13.59
10:2 FTOH	2.5-2000	0.999	10.38
6:2 FTMAC	2.5-800	0.995	12.43
8:2 FTAC	5-250	0.995	14.81
8:2 FTMAC	2.5-250	0.998	19.51
MeFOSA	5-2000	>0.999	17.79
EtFOSA	10-2000	0.999	11.40



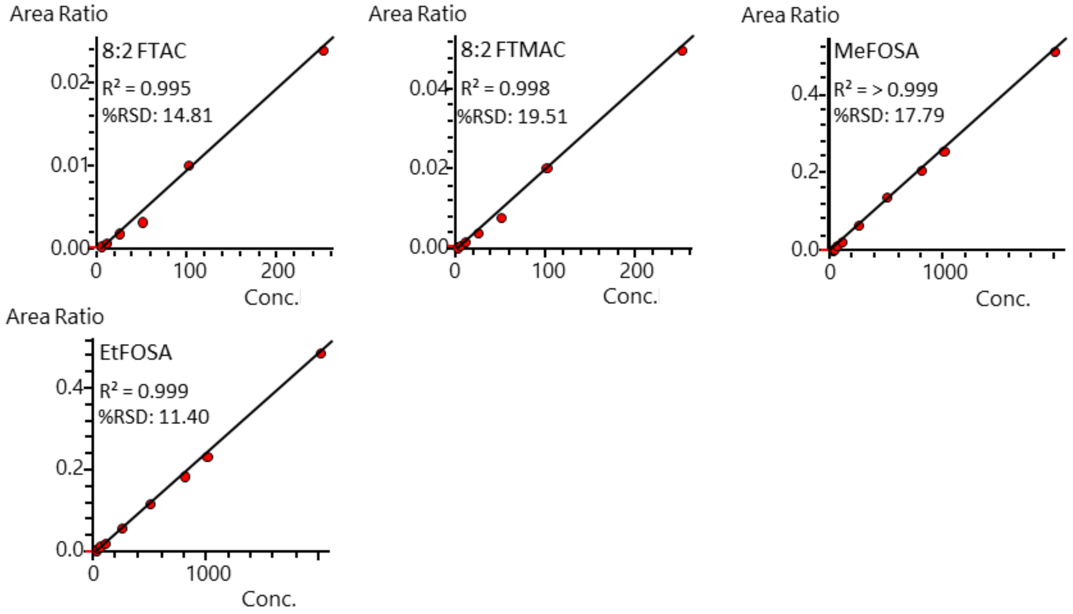


Figure 4: Calibration curves for the 13 targeted PFAS compounds

PFAS are ubiquitous and can exist within laboratory environments and consumables. Therefore, laboratory blank analysis is pivotal to determine possible PFAS contamination. In this study, none of the target PFAS in the laboratory blank samples showed quantifiable results.

The carryover effect of PFAS was evaluated by analyzing a blank sample immediately after the highest calibrator. The results showed < 0.2 % carryover effect. PFAS in the blank were below the quantitation range of this method.

The SIM GC/MS HS-SPME method developed was selective and provided high sensitivity to measure targeted PFAS compounds at nano gram per liter concentrations. The method in this application can measure PFAS at equivalent concentration in the sample at least to the lowest calibration level as listed in **table 4**.

This indicates that low parts per trillion concentrations are measured directly in the sample without additional sample concentration techniques and mathematical back calculations being applied, as typically conducted in liquid sample introduction in GC/MS analysis.

■ Conclusion

This study demonstrated the use of a Shimadzu GC/MS-QP2020 NX single quadrupole instrument configured with the AOC-6000 Plus multifunctional autosampler and an automated head space solid phase microextraction unit for measurement of PFAS compounds in water. The method used a HS-SPME technique and a GC/MS SIM method for PFAS identification and quantitation.

In this application, HS-SPME was used to increase the method capability of addressing complex water matrices in the future. Linear calibration curves were obtained for all compounds ($R^2 \geq 0.993$ and RF %RSD < 20 %). Laboratory blanks and a carryover effect study showed no quantifiable PFAS in the background, respectively, from the laboratory environment as well as instrument analysis.

The HS-SPME GC/MS-QP2020 NX method demonstrated qualitative and quantitative capability in analyzing PFAS compounds in water matrix. HS-SPME is a single-step sample preparation technique that minimizes the sources of PFAS contamination from laboratory consumables and other supplies. With the capability to generate an automated SPME method, the AOC-6000 Plus can further reduce operation error for volatile PFAS in water analysis.

■ References

1. 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
2. C146-E424A Smart SPME Fibers and Arrow Selection Guide (shimadzu.com)
https://www.shimadzu.com/an/sites/shimadzu.com.an/files/pim/pim_document_file/brochures/13985/c146e424.pdf

■ Consumables

Item Name	Item Description	Part Number
Capillary column	GC, SH-I-624Sil MS Capillary, 30 m x 0.25 mmID 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 headspace 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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