SHIMADZU

TP 093

Analysis of PFAS in water using Head-Space Solid Phase Microextraction-Gas Chromatography/Mass Spectrometry (HS-SPME GCMS)

Andy L. Sandy Ph.D.; Evelyn Wang Ph.D.; Ruth Marfil-Vega Ph.D.; Yoshiyuki Okamura
Shimadzu Scientific Instruments, Columbia, MD

1. 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 not only affect their toxicity and environmental fate, but also complicates chemical analysis.

In this work, a Head-Space Solid Phase Microextraction-Gas Chromatography/Mass Spectrometry (HS-SPME GCMS) analytical method was developed to analyze six classes of volatile PFAS in water. This HS-SPME method presents the advantage of simplifying sample extraction and handling for the analysis of volatile PFAS in water, hence, minimizing operational costs, potential errors, and risk of sample-cross contamination.

2. Methods

A volatile PFAS analysis method was developed on a Shimadzu GCMS QP2020 NX with the AOC-6000 multifunctional autosampler equipped with a SPME module (**Figure 1**).

Thirteen target compounds were included in the Selected Ion Monitoring (SIM) 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 water at concentrations of 2000, 1000, 800, 500, 250, 100, 50, 25, 10, 5 and 2.5 ng/L. The IS 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). These calibrators were vortex for 30 seconds and then placed on the AOC-6000 Plus autosampler rack.

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**.

Figure. 1 Shimadzu GCMS-QP2020 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
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. 2 Retention time, quantitative ion, reference ions, and internal standard group for each 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}C2	22.5	450	400	417	1
	6:2 FTAC d3	23.2	421	101	327	2
	10:2 FTOH ^{13}C2	25.7	510	169	500	3
	EtFOSA d5	34.3	450	113	169	4

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 stock 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).

3. Results

A chromatography method separating the 13 targeted PFAS compounds was developed. Total ion current (TIC) chromatogram of all targeted compounds using a scan method and liquid injection is shown in **figure 2.**

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

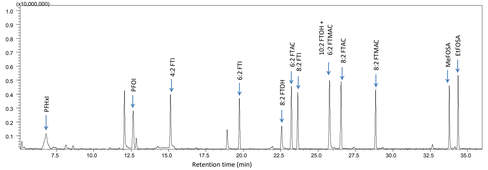

Figure. 2 TIC chromatogram of the 13 targeted PFAS compounds at 5 mg/L

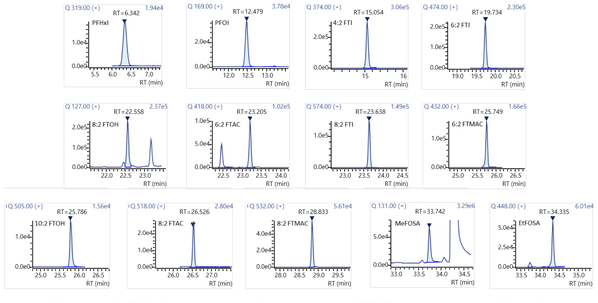

Figure. 3 SIM chromatograms for the targeted PFAS compounds at 100 ng/L in ultrapure water

The linear range of each PFAS target is shown in **table 3** 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 3.**

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. 3 Summary of PFAS calibration range and linearity results

Compound	Calibration Range (ng/L)	R2	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

In this study, none of the target PFAS in the laboratory blank samples showed quantifiable results. The area of these blanks were less than 1/5 of the lowest calibrator area.

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 (**Table 3**).

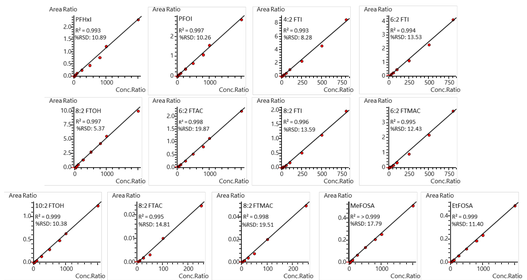

Figure. 4 Calibration curves for the 13 targeted PFAS compounds

4. 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 volatile PFAS compounds in water. Linear calibration curves were obtained for all compounds ($R^2 \geq 0.993$ and RF %RSD < 20 %). The HS-SPME GC/MS-QP2020 NX method demonstrated qualitative and quantitative capability of analyzing PFAS compounds.