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Advancing PFAS Detection in Drinking Water: GC-MS as a Complementary Technique to LC-MS for Closing PFAS Mass Balance

Andy Sandy; Ruth Marfil-Vega; Evelyn Wang; Alan Owens
Shimadzu Scientific Instruments, Columbia, MD

1. Introduction

Analysis of per- and polyfluoroalkyl substances (PFAS) in the environment is pivotal. There are several standardized PFAS methods, such as EPA 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.

Gas Chromatography/Mass Spectrometry (GC/MS) as a complementary technique can address volatile PFAS compounds that are challenging to analyze by LC/MS. In this study, a Head-Space Solid Phase Microextraction Triple Quadrupole Gas Chromatography/Mass Spectrometry analytical method is used to analyze PFAS in drinking water. This technique has advantages of analyzing volatile PFAS in water with minimum sample preparation procedure.

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**. Quantifier and qualifier 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. Drinking water analyzed in the study were from a private well and an utility with surface water as its source.

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

Table 1. GC/MS and HS-SPME Method 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 um
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
	EtFOSA	34.2	108.1>80.0	448.0>69.1	108.10>44.1	4
Internal Standards	8:2 FTOH $^{13}C2$	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 $^{13}C2$	25.6	98.0>69.0	131.1>81.1	98.00>48.1	3
	EtFOSA d5	34.1	113.1>81.0	81.0>64.0	450.10>69.0	4

Prior to samples 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 drinking 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 inferences. 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) ≥ 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

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 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. 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 matrix effect of drinking water samples 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 or area count were observed in either the drinking water from the private well or surface water treatment plant compared to reagent water.

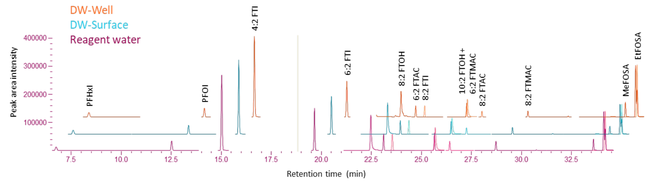

Figure. 2 TIC chromatogram of the 13 targeted PFAS compounds at 100 ng/L in drinking water from private well (orange), drinking water from surface water (blue), and reagent water (purple).

Analyte concentrations from triplicate analyses (n=3) were calculated using the ICAL. No targeted PFAS were detected in the unspiked water sample at quantifiable levels. In surface water–sourced drinking water, mean recoveries ranged from 71–129% with <4.7% RSD for all analytes. In private well water, recoveries ranged from 64–120% with RSD also <4.9%. Overall, mean recoveries were 64–129% with RSD ≤4.9% across all compounds (**Table 5**).

Table. 5 Precision and Accuracy (n=3) of PFAS in drinking water samples.

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

4. Conclusion

This study demonstrated the satisfactory performance of a HS-SPME GC/MS/MS method to measure PFAS in drinking water. The PFAS family is vast, comprising thousands of different compounds across various chemical classes. Due to this diversity, multiple analytical instruments are necessary to effectively analyze PFAS. While LC-MS is widely recognized for its ability to analyze many PFAS compounds, it is not always practical for measuring certain PFAS. This has led to a gap in the environmental mass balance, especially when it comes to measuring volatile PFAS compounds.

Fortunately, unlike LC-MS, GC-MS is well-suited for analyzing volatile PFAS compounds. GC-MS complements LC-MS-based PFAS methods, providing a more comprehensive analytical solution. By expanding the PFAS target list, GC-MS helps close gaps in the PFAS environmental mass balance. The method used in this study demonstrated quantitative capability in analyzing nanogram per liter PFAS compounds in an LCS and matrix influenced drinking water samples.

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