

## Application News

GCMS-TQ8040 NX Gas Chromatograph Mass Spectrometer / AOC™-6000 Plus

### Volatile PFAS in water analysis using Head-Space Solid Phase Microextraction - Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/MS)

#### User Benefits

- ◆ A Shimadzu HS-SPME GC/MS/MS system (AOC-6000 Plus and TQ8040 NX) can analyze volatile PFAS in water samples with a minimum sample preparation procedure.
- ◆ The simplified sample preparation procedure and automated SPME method using an AOC-6000 Plus reduces the operation error for PFAS analysis.
- ◆ The enhanced sensitivity and selectivity of triple quadrupole GC/MS used in this work often allows for achieving lower limits of quantification and minimizing false positives from matrix interferences than single quadrupole GC/MS.

#### ■ Introduction

The demand for detection and quantitation of per- and polyfluoroalkyl substances (PFAS) in environmental and food samples, and other consumer and industrial products (e.g., cosmetics, textiles, paints, ski waxes, etc.), has increased in recent years. These compounds present health and environmental concerns due to their probable toxicity, persistence, and ubiquitousness. To address this increasing demand, a Head-Space Solid Phase Microextraction-Triple Quadrupole Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS/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, 537.1 and OTM-45. All these methods analyze PFAS compounds by Liquid Chromatography/Mass Spectrometry (LC/MS). 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.<sup>1</sup> Therefore, it is crucial to develop GC/MS-based methods that are complementary to LC/MS workflows to provide a complete solution for PFAS analysis. GC/MS has the capability to analyze volatile PFAS compounds that are challenging to ionize in LC/MS. HS-SPME GC/MS offers numerous advantages, such as a simplified sample preparation procedure since it eliminates solvent extraction steps, minimal sources of contamination and less potential for analytical error through its full automation.

A previous PFAS study was conducted using a Shimadzu single quadrupole GC/MS (GCMS QP2020 NX) and the SPME technique to analyze these compounds in water.<sup>2</sup> This application news focuses on the use of the Shimadzu triple quadrupole GC/MS (GCMS TQ8040 NX) in MRM mode configured in tandem with a multifunctional autosampler (AOC-6000 Plus). Compared to single quadrupole GC/MS, the triple quadrupole GC/MS has better sensitivity and selectivity, resulting in lower limits of quantitation as well as less false positives from interferences in complex matrices.

#### ■ Experimental Approach

##### *Instrumentation*

The instrument system configuration for the application consisted of a Shimadzu GC/MS, model TQ8040 NX, an 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 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, 2.5, 1, and 0.5 ng/L. 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 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   | PFHxl                                       | 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         |                               |
|  | <i>1H,1H,2H,2H-Perfluoro-n-octyl acrylate-d3</i>                                    | <i>6:2 FTAC d<sub>3</sub></i>               | <i>7527-29-6</i>   | <i>Sapphire North America</i> |
| (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           | Cambridge Isotope             |
|  | <i>2-perfluorooctyl-[1,1-2H<sub>2</sub>-1,2-<sup>13</sup>C<sub>2</sub>]-ethanol</i> | <i>8:2 FTOH <sup>13</sup>C<sub>2</sub></i>  | <i>872398-73-7</i> |                               |
|  | <i>2-perfluorodecyl-[1,1-2H<sub>2</sub>-1,2-<sup>13</sup>C<sub>2</sub>]-ethanol</i> | <i>10:2 FTOH <sup>13</sup>C<sub>2</sub></i> | <i>865-86-1</i>    |                               |
| Perfluoroalkane sulfonamides (FASAs)       | N-Methyl perfluorooctane sulfonamide  | MeFOSA                                      | 31506-32-8         | AccuStandard                  |
|  | N-Ethyl perfluorooctane sulfonamide   | EtFOSA                                      | 4151-50-2          | Cambridge Isotope             |
|  | <i>n-ethyl-d<sub>5</sub>-perfluoro-1-octanesulfonamide</i>                          | <i>EtFOSA d<sub>5</sub></i>                 | <i>936109-40-9</i> |                               |

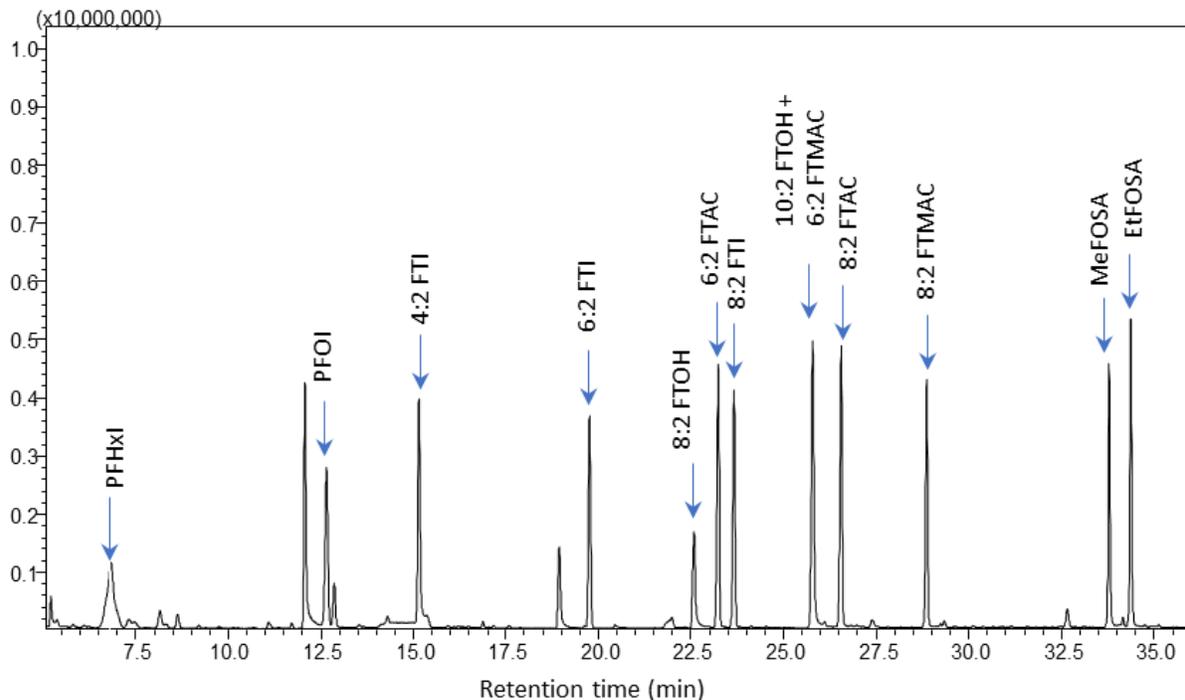
Internal standards are highlighted in grey.

### HS-SPME GC/MS/MS Analysis

HS-SPME is a technique based on the movement of the targeted compounds in the sample to a sorptive phase in the fiber via the partition coefficient. Increasing the sorption phase partition coefficient by salting out the sample and carefully selecting the appropriate sorptive phase results in increased sorption efficiency on the fiber.<sup>3</sup>

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. With HS-SPME, the fiber interacts solely with gaseous molecules, unlike direct immersion SPME, where fiber is immersed in the sample. Thus, interferences from polar compounds are eliminated.

For GC/MS method development, a scan analysis of the targeted PFAS compound is needed for identification first. Details of the scan method can be found in Shimadzu application news GCMS-2402.<sup>2</sup> The Total ion current (TIC) chromatogram of all targeted compounds using the scan method and liquid injection is shown in **figure 2**. After identification, a Multiple Reaction Monitoring (MRM) method using liquid injection was developed for analysis of the targeted PFAS compounds.



**Figure 2:** TIC chromatogram of the 13 targeted PFAS compounds at 5 mg/L.<sup>2</sup>

Subsequently, a HS-SPME GC/MS/MS method was developed for the volatile PFAS compounds. The optimized parameters of the instrument method for the targeted PFAS are listed in **table 2**. A quantifier and qualifiers 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 also listed in **table 3**.

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

| <b>Gas Chromatography</b>       | <b>Nexis GC-2030</b>   |
|---------------------------------|--|
| 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 µm                         |
| 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.) |
| <b>Mass Spectrometer</b>        | <b>TQ8040 NX</b>   |
| 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  |
| <b>SPME analysis</b>            | <b>AOC-6000 Plus</b>   |
| 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, quantifier, qualifiers, and internal standard group information for each of the targeted PFAS compounds.

|                    | <b>Compound</b>                        | <b>Ret. Time (min)</b> | <b>Quantifier (m/z)</b> | <b>CE</b>  | <b>Qualifier #1 (m/z)</b> | <b>CE</b>   | <b>Qualifier #2 (m/z)</b> | <b>CE</b> | <b>Internal standard group</b> |
|--------------------|--|------------------------|-------------------------|------------|---------------------------|-------------|---------------------------|-----------|--------------------------------|
| Targets            | PFHxl                                  | 6.8                    | 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                                | 15.1                   | 373.9>227.0             | 9          | 373.9>163.1               | 21          | 373.9>113.1               | 27        | 3                              |
|                    | 6:2 FTI                                | 19.7                   | 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                                | 23.6                   | 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                              | 25.7                   | 86.1>68.1               | 6          | 432.1>113.1               | 12          | 432.1>86.1                | 21        | 1                              |
|                    | 8:2 FTAC                               | 26.5                   | 518.0>99.1              | 15         | 99.1>57.1                 | 12          | 99.1>43.1                 | 9         | 2                              |
|                    | 8:2 FTMAC                              | 28.8                   | 86.0>68.1               | 6          | 86.0>41.1                 | 15          | 532.00>113.1              | 21        | 2                              |
|                    | MeFOSA                                 | 33.7                   | 131.1>69.1              | 24         | 169.0>69.0                | 12          | 94.00>91.8                | 57        | 4                              |
| EtFOSA             | 34.3                                   | 108.1>80.0             | 6                       | 448.0>69.1 | 27                        | 108.10>44.1 | 3                         | 4         |                                |
| Internal Standards | 8:2 FTOH <sup>13</sup> C <sub>2</sub>  | 22.4                   | 98.0>69.0               | 15         | 131.1>81.1                | 15          | 98.00>48.1                | 27        | 1                              |
|                    | 6:2 FTAC d <sub>3</sub>                | 23.1                   | 101.1>57.1              | 12         | 101.1>45.0                | 9           | 102.00>45.0               | 9         | 2                              |
|                    | 10:2 FTOH <sup>13</sup> C <sub>2</sub> | 25.6                   | 98.0>69.0               | 12         | 131.1>81.1                | 12          | 98.00>48.1                | 27        | 3                              |
|                    | EtFOSA d <sub>5</sub>                  | 34.2                   | 113.1>81.0              | 6          | 81.0>64.0                 | 24          | 450.10>69.0               | 27        | 4                              |

*Laboratory blanks and carryover effect*

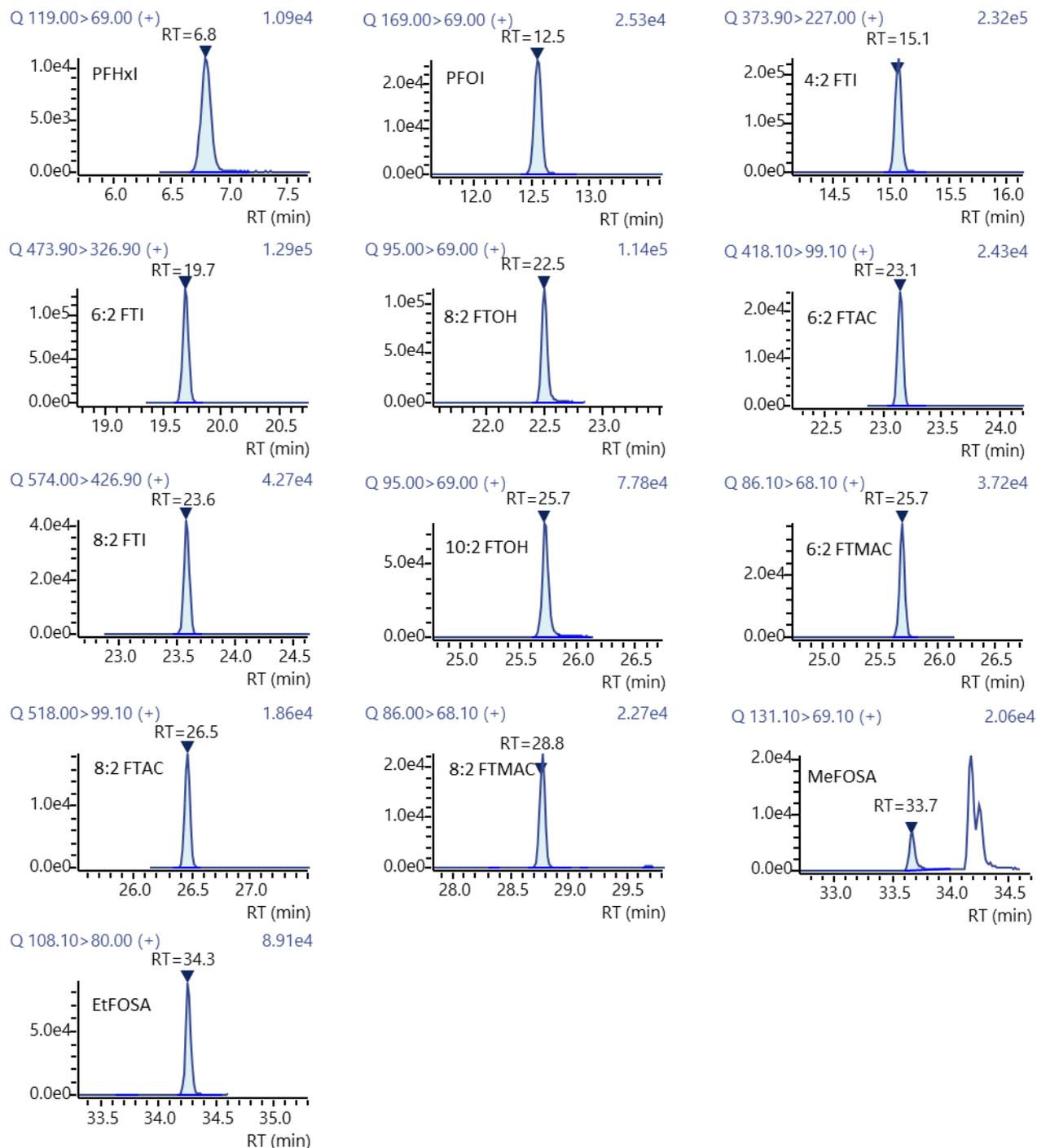
Laboratory blanks were analyzed in each batch, prior to calibration curve analysis, to detect any contamination from the laboratory environment and consumables. These blanks were prepared by using ultrapure water with 50 µL of IS and 50 µL of methanol, the same solvent used to prepare the stock solution containing targets and IS.

The evaluation of carryover from the highest calibration standard was conducted by running a solvent blank after this standard. This blank was prepared by using ultrapure water and 100 µL methanol, the same solvent used to prepare the stock solution containing targets and IS. A peak area of this blank was evaluated and compared to the peak area of the previous calibrator (highest level of the quantitation range).

### ■ Results and Discussion

MRM transitions for each targeted PFAS compound were optimized on a Shimadzu GC/MS triple quadrupole TQ8040 NX. Although most compounds were chromatographically separated, 10:2 FTOH and 6:2 FTAC could only be separated by unique MRM transitions.

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



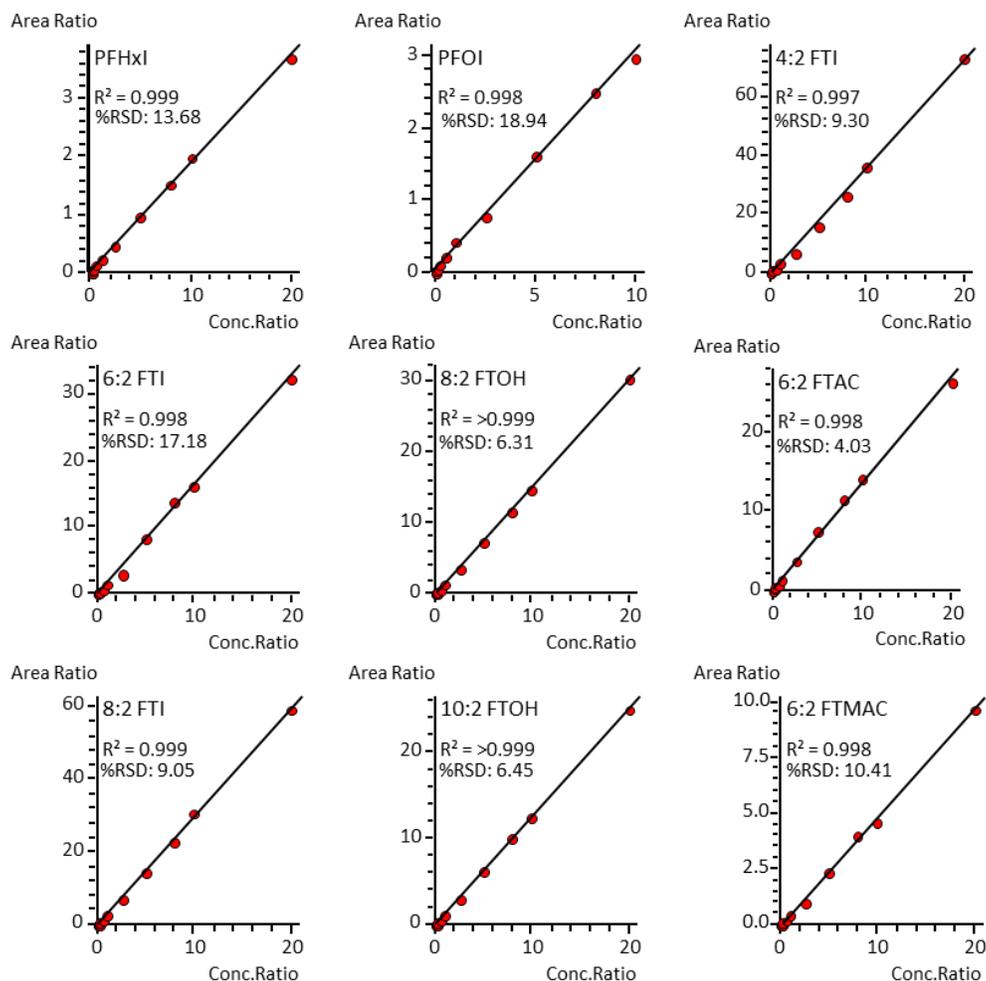
**Figure 3:** MRM chromatograms for the targeted PFAS compounds at 100 ng/L in ultrapure water.

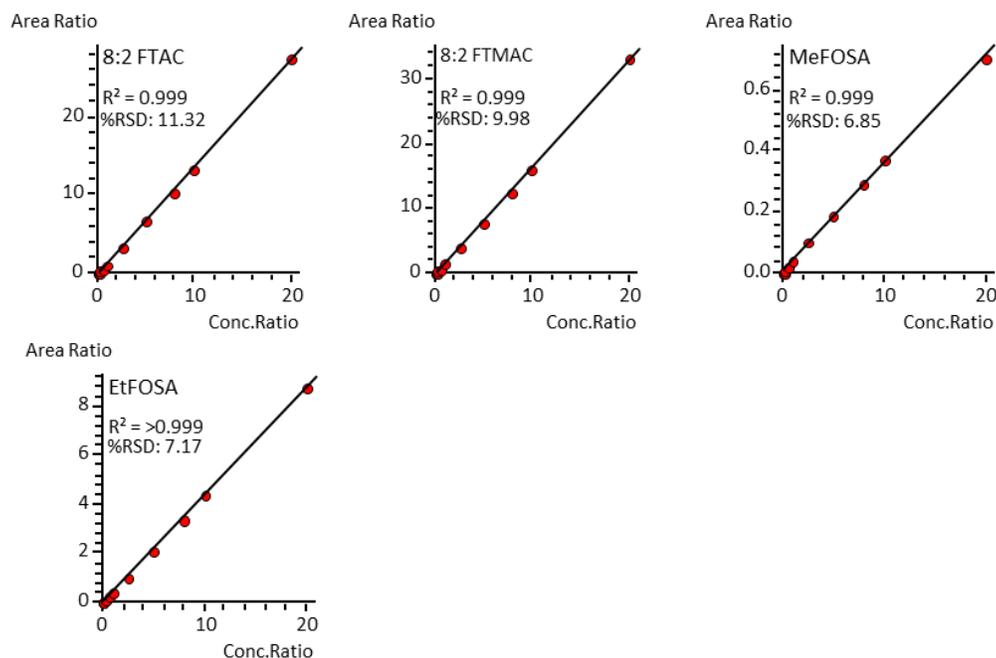
A selective and sensitive HS-SPME GC/MS/MS MRM method was developed to measure targeted volatile PFAS compounds at nanogram per liter concentrations. The linear range of each PFAS target is shown in **table 4** and includes at least seven calibrators.

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  $R^2 \geq 0.997$  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                 | 0.999  | 13.68                     |
| PFOI      | 2.5-1000                 | 0.998  | 18.94                     |
| 4:2 FTI   | 2.5-2000                 | 0.997  | 9.30                      |
| 6:2 FTI   | 1-2000                   | 0.998  | 17.18                     |
| 8:2 FTOH  | 2.5-2000                 | >0.999 | 6.31                      |
| 6:2 FTAC  | 2.5-2000                 | 0.998  | 4.03                      |
| 8:2 FTI   | 2.5-2000                 | 0.999  | 9.05                      |
| 10:2 FTOH | 2.5-2000                 | >0.999 | 6.45                      |
| 6:2 FTMAC | 2.5-2000                 | 0.998  | 10.41                     |
| 8:2 FTAC  | 2.5-2000                 | 0.999  | 11.32                     |
| 8:2 FTMAC | 2.5-2000                 | 0.999  | 9.98                      |
| MeFOSA    | 2.5-2000                 | 0.999  | 6.85                      |
| EtFOSA    | 1-2000                   | >0.999 | 7.17                      |





**Figure 4:** Calibration curves for the 13 targeted PFAS compounds.

This method demonstrates that low parts per trillion concentrations are measured directly in the sample without the need of additional sample preconcentration steps, like liquid-liquid extraction or SPE, as typically conducted in liquid sample introduction in GC-MS analysis.

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 were found in quantifiable concentrations.

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

## ■ Conclusion

This study demonstrated an effective solution to measure volatile PFAS in water using a Shimadzu GC/MS-TQ8040 NX triple quadrupole instrument in MRM mode configured with a multifunctional autosampler (AOC-6000 Plus) that has an automated headspace solid phase microextraction unit.

In this application, HS-SPME was used to increase the method capability for the analysis of complex water matrices. Linear calibration curves were obtained for all compounds ( $R^2 \geq 0.997$  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.

This HS-SPME GC/MS-TQ8040 NX method demonstrated quantitative capability in analyzing nanogram per liter 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, AOC-6000 Plus can further reduce operation error for the analysis of volatile PFAS in water.

## ■ 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. Shimadzu Application News. GCMS-2402. (2024, March). Analysis of volatile PFAS in water using Head-Space Solid Phase Microextraction-Gas Chromatography/Mass Spectrometry (HS-SPME GC/MS). [GCMS-2402 PFAS HS SPME GCMS.pdf \(shimadzu.com\)](#)
3. [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](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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