Abstract

This Application Note describes a method for the separation and detection of 28 per- and polyfluorinated alkyl substances (PFASs) in water samples. The method uses an Agilent 1290 Infinity II LC coupled to an Agilent 6470A triple quadrupole LC/MS system with Agilent MassHunter workstation software. All the PFASs included in the ASTM 7979 method are analyzed, and the same sample preparation protocol is used. Water samples of 5 mL are diluted with an equal volume of methanol and injected directly for a reporting limit of 10 parts per trillion (ppt, ng/L) or lower for most of the compounds.
Introduction

There are growing concerns about the use of PFASs due to their detection in all environmental media including air, water, and soil. Persistent chemicals have the potential to accumulate in the environment and impact the food chain, affecting fish, birds, livestock, and humans. Detection of PFASs at ppt (ng/L) levels is often required. This study evaluates a method for screening, identification, and quantification of 28 PFAS compounds at trace levels in water samples by ultrahigh-performance liquid chromatography with tandem mass spectrometry (UHPLC/MS/MS). The method was evaluated in water, and quantified with external standards, showing satisfactory results including specificity, linearity, reporting limits, accuracy, and precision. This method can be used for the simultaneous detection and quantification of PFAS residues in reagent, tap, surface, ground, and wastewater matrices. Table 1 lists the PFAS compounds analyzed in this study, including the surrogates.

Table 1. PFAS compounds and their abbreviations.

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<tr>
<th>Compound</th>
<th>Abbreviation</th>
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<tr>
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<td>9Cl-PF3ONS</td>
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Experimental

Equipment
All experiments in this study were performed using an Agilent 1290 Infinity II LC consisting of a G7167B multisampler, a G7120A binary pump, and a G7116B multicol... LC/MS system. Instrument control, data acquisition, qualitative and quantitative data analysis, and reporting was done using Agilent MassHunter workstation software.

Samples and standards
The study matrices were reagent water and water samples. PFAS native and surrogate mix standards were obtained from Wellington Laboratories (Guelph, Ontario, Canada). The samples and standards were stored refrigerated at 5 °C.

Method
Description
The method consisted of dispersing the water sample in methanol (1:1 v:v) followed by filtration (Captiva NY/GF 0.2 µm, p/n 5190-5132) and adjusting the pH to acidic with acetic acid. The analytical determination was performed by LC/MS using negative electrospray ionization mode. Table 2 gives the analyte-specific LC/MS conditions. The supporting method reference was ASTM 7979.

Chromatographic conditions

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Evaluation procedure
Method performance was evaluated by analyzing a representative reagent water sample (as a matrix blank) together with six replicates of QC spikes at 160 ng/L and three replicates at low spiking levels of 10 and 20 ng/L. The quantitation was performed using an external calibration curve with 1/x weight.

Evaluation criteria

System suitability
- The difference between the calculated and expected value of checking standard (CS) at 80 ng/L is within ±30 %
- The relative error (RE%) of RT of each CS to the average of standard peaks is less than 2 %

Specificity
- The RE% of RT of each analyte peak to the average of standard peaks is less than 2 %
- The ion ratio is within the tolerance of 30 %

Linearity and range
- Calibration curve has $R^2 > 0.99$
- The residual of each working standard is within ±30 %
- The calibration standards should bracket the analyte concentration level

Precision
RSDs from at least three replicates are ≤30 %.

Accuracy
Mean recovery for spiking at 160 ng/L is within 70 to 130 %, and mean recovery for spiking at 10 and 20 ng/L is within 50 to 150 %.

Results and discussion

System suitability
Suitability was determined to be acceptable if %RE of RT of all compounds including surrogates in CS did not exceed 2 %. The accuracy of all compounds in CS met the 70 to 130 % criterion, see Figure 1.

Specificity
Multiple reaction monitoring (MRM) was used for PFAS detection. Monitoring MS/MS transitions with evaluation of the ratio of their relative intensities and RT of analyte peaks enables the target analyte to be distinguished from potential interferences in quantitative analysis. Figure 2 shows an example of an extracted ion chromatogram of a 80 ng/L composite working standard (WS) containing all the analytes in 0.1 % acetic acid in 1:1 (v:v) ultrapure water:methanol. Figure 3 shows a reagent blank of 0.1 % acetic acid in 1:1 (v:v) ultrapure water:methanol.

Figure 1. Accuracy and %RE on RT of CS.
Figure 2. Extracted ion chromatogram of a composite working standard of all analytes at 80 ng/L in 0.1 % acetic acid in 1:1 (v:v) ultrapure water:methanol.

Figure 3. Extracted ion chromatogram of a reagent blank of 0.1 % acetic acid in 1:1 (v:v) ultrapure water:methanol.
Range and linearity
The method was evaluated over the range of 5 to 200 ng/L.
To evaluate the linearity of the method, WS solutions of each PFAS including the surrogates were made at 5, 10, 20, 40, 60, 80, 100, 150, and 200 ng/L. The calibration curve residuals were ≤ 30% for WS1 to WS9 except for one injection of WS1 of PFHpS. Figure 4 demonstrates the statistical data of the calibration curve residuals. The linearity was determined using a linear calibration with a 1/x weighting factor. The $R^2$ values were > 0.99 for all analytes.

Accuracy and precision
Accuracy was determined by fortifying samples before extraction with the analyte standard solution at levels of 10, 20, and 160 ng/L. The results were not normalized using internal standards. Eighteen isotopically labeled standards, representing different PFAS groups, were used as surrogates to monitor method and instrument performance, but were not used for response normalization as done in ASTM 7979. Internal standards were fortified at 160 ng/L for all samples. The precision was evaluated by analysis of fortification at levels of 160 ng/L in six replicates and 10 and 20 ng/L in three replicates.
The spike recovery for accuracy and % RSD of precision met the acceptance criteria for all 28 PFASs tested. Figure 5 shows the accuracy and precision results at 160 ng/L. Table 3 shows the detailed accuracy and precision results at 10 and 20 ng/L.
Method reporting limits
The method determined reporting limits (RLs) rather than limits of quantitation (LOQs). These were determined for each analyte as the spiking levels of 10 and 20 ng/L that met the evaluation criteria for recoveries and RSD of precision, see Table 3. The RL for each PFAS analyte was set at 10 ng/L, except PFDS and PFHpS, which were set at 20 ng/L. In practice, RLs of <10 ng/L for many of the compounds could be achieved and for ultimate sensitivity users can employ the Agilent 6495 Triple Quadrupole LC/MS.

Table 3. Accuracy (spike recovery) and precision (% RSD) at 10 and 20 ng/L (n = 3), surrogates spiked at 160 ng/L (continued next page).

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The evaluated method was applied to several unknown water samples. The sample results and the surrogate spike recoveries are shown in Table 4. The surrogate spike recoveries were within 70 to 130 %, and met the acceptance criteria for all PFASs tested.

Table 4. Sample results and surrogate spike recoveries for water samples (continued next page).
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**Note:** Empty cells for surrogate recovery indicate that no stable isotope standard was available or included for the native compound in this study.
Conclusions

A UHPLC/MS/MS method was presented for the quantitative analysis of 28 PFASs in water samples using a 1290 Infinity II LC coupled to a 6470A triple quadrupole LC/MS system with MassHunter workstation software. The evaluation demonstrated that the method can achieve adequate specificity, linearity, accuracy, and precision for analysis of the listed PFAS analytes in water. For additional sensitivity required beyond levels in ASTM 7979 or EPA draft method 8327, the Agilent 6495 triple quadrupole LC/MS can be employed.