Waters™

Application Note

Oasis WAX for Extraction of Per- and Polyfluorinated Alkyl Substances (PFAS) from Drinking Water in Accordance with EPA Method 533

Kari L. Organtini, Beatriz Renner, Mary E. Lame, Keil Brinster, Kenneth J. Rosnack

Waters Corporation

This is an Application Brief and does not contain a detailed

Experimental section.

Abstract

This application brief demonstrates the extraction of PFAS from drinking water samples using the Waters Oasis WAX for PFAS Analysis Cartridge as an equivalent SPE chemistry for the methodology described in EPA method 533.

Benefits

- Demonstration of Oasis WAX Cartridge to extract PFAS from drinking water according to EPA method 533

Introduction

Many water testing laboratories in the United States currently use the EPA 537.1 methodology for the analysis of per- and polyfluorinated alkyl substances (PFAS) in drinking water. In 2019, the EPA released a companion method, EPA 533, for drinking water analysis. This new method extends the list of targeted analytes in drinking water to 25, incorporating both short chain and emerging PFAS compounds. To efficiently and accurately recover this extended list of PFAS, EPA 533 has also updated the required solid phase extraction (SPE) chemistry and extraction protocol. The specified cartridge must contain 500 mg of a mixed-mode polymeric sorbent having a pKa >8 to ensure a positive charge during extraction.

The Oasis WAX Cartridge, containing a mixed-mode sorbent with a pKa of ~10 (p/n: 186009568 < https://www.waters.com/nextgen/global/shop/sample-preparation--filtration/186009568-oasis-wax-for-pfas-analysis-6-cc-vac-cartridge-500mg-sorbent-per.html>), is a direct equivalent to the chemistry mandated in EPA method 533, and meets the necessary analytical requirements mandated by the method.

Results and Discussion

Drinking water was evaluated for 25 PFAS, following the requirements of EPA method 533. Sample collection

and preservation procedures required in EPA method 533 were followed prior to sample extraction. Solid phase extraction was performed using 6-cc, 500-mg Oasis WAX SPE Cartridges. The suite of 25 PFAS designated in the method were analyzed using an ACQUITY UPLC I-Class PLUS System (configured with flow-through needle) modified with the PFAS Kit (p/n: 176004549 < http://www.waters.com/nextgen/global/shop/application-kits/176004549-pfas-solution-installation-kit--with-oasis-500mg-kit-2.html>) coupled to a Xevo TQ-S micro Tandem Quadrupole Mass Spectrometer. LC and MS method conditions, including multiple reaction monitoring transitions (MRM), can be found in previous work (Waters Corporation Application Note, 720006471EN < https://www.waters.com/nextgen/in/en/library/application-notes/2019/legacy-emerging-perfluorinated-alkyl-substances-pfas-environmental-water-samples-using-solid-phase-extraction-spe-and-lc-ms-ms.html>).

One of the quality control standards of EPA method 533 is the accuracy of replicate extractions must be demonstrated to have an average percent recovery within the range of 70–130%. Figure 1 demonstrates the average percent recoveries of all 25 PFAS at 2 and 12 ng/L. Using the Oasis WAX Cartridge with the sample preparation and extraction method described in EPA method 533, recoveries easily met the requirements.

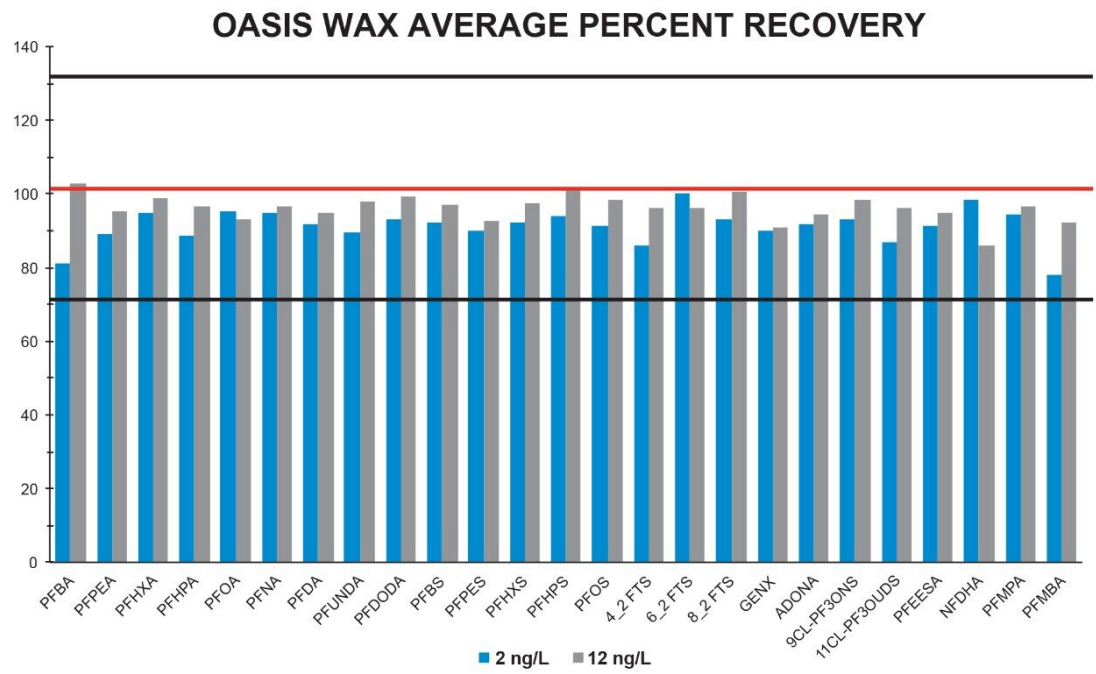

Figure 1. PFAS recovery in drinking water following sample extraction using Oasis WAX Cartridges and EPA 533 method. All compounds are well within the method recovery guidelines of 70–130%.

In addition to accuracy, precision of the drinking water extraction must be demonstrated. Precision is measured using percent relative standard deviation (%RSD) values for replicate sample extractions. EPA 533 requires all %RSDs to be less than 20%. Figure 2 highlights the %RSDs for each compound from four replicate extractions of drinking water spiked at 2 and 12 ng/L. Except for 6:2 FTS in the 12 ng/L replicates, all PFAS had %RSD values well below the 20% requirement. In fact, most RSDs were 5% or below, indicating a very robust method.The high %RSDs for 6:2 FTS are due to a well-known contamination of this compound in common laboratory equipment and supplies.

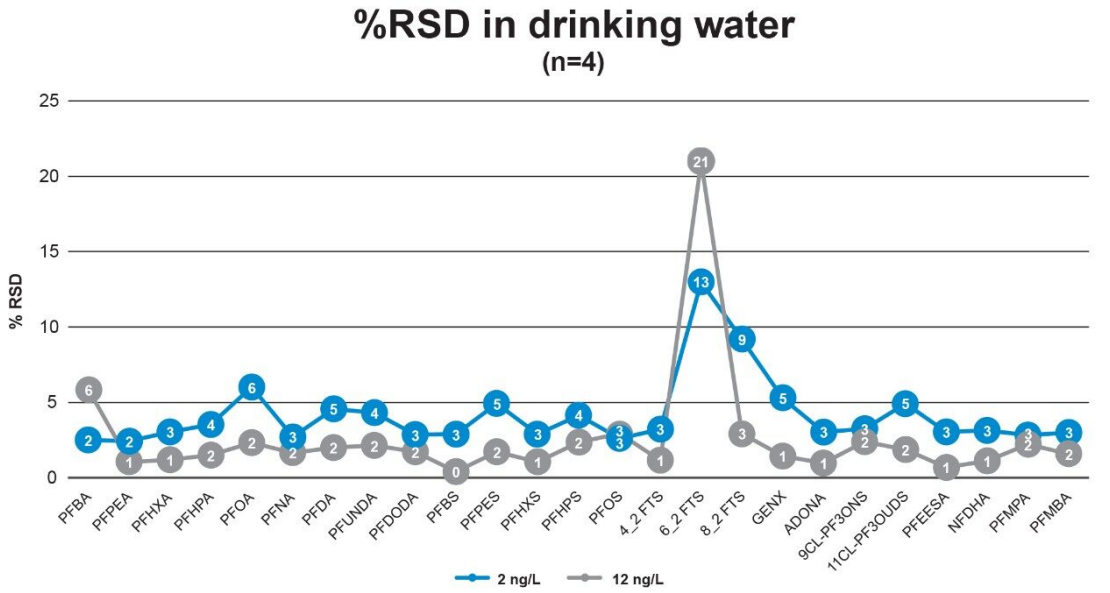

Figure 2. %RSD of recovery values for four replicates of PFAS spiked into drinking water at 2 and 12 ng/L following SPE extraction with Oasis WAX Cartridges.

Following quantitative performance assessment of this method using the Oasis WAX Cartridge, the full EPA 533 methodology was evaluated on a drinking water sample (performed in triplicate) to determine the levels of PFAS present. Of the 25 PFAS targeted from this method, nine were detected in the drinking water sample with mean concentrations ranging from 0.48 to 5.28 ng/L (Figure 3). PFHpA, PFHxS, PFOS, and PFMBA were all detected at concentrations less than 1 ng/L. PFBA, PFPeA, PFHxA, PFOA, and PFBS were detected at concentrations greater than 1 ng/L. The total concentration of the 25 targeted PFAS in the drinking water sample was 19.6 ng/L, which is below the current EPA advisory of 70 ng/L.

Compound	Drinking water (ng/L)
PFBA	**4.60**
PFPeA	**2.24**
PFHxA	**1.92**
PFHpA	**0.68**
PFOA	**5.28**
PFNA	ND
PFDA	ND
PFUnDA	ND
PFDoDA	ND
PFBS	**2.92**
PFPeS	ND
PFHxS	**0.60**
PFHpS	ND
PFOS	**0.92**
4:2 FTS	ND
6:2 FTS	ND
8:2 FTS	ND
GenX	ND
ADONA	ND
9ClPF3ONS	ND
11ClPF3OUdS	ND
PFEESA	ND
NFDHA	ND
PFMPA	ND
PFMBA	**0.48**

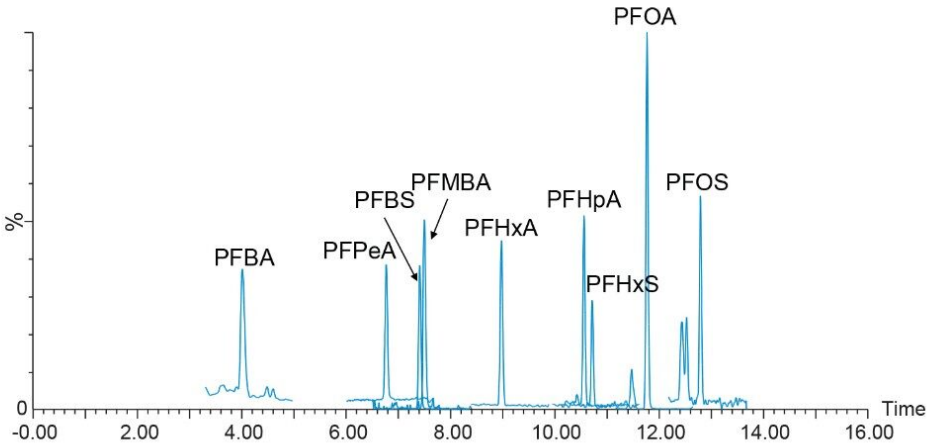

Figure 3. PFAS detected in drinking water. System: ACQUITY UPLC I-Class PLUS modified with PFAS Kit coupled to Xevo TQ-S micro. Column: ACQUITY BEH C_{18} Column 2.1 x 100 mm, 1.7 µm at 35 °C. Mobile phase A: 95:5 Water:Methanol with 2 mM ammonium acetate. Mobile phase B: Methanol with 2 mM ammonium acetate. Flow rate: 0.3 mL/min from 0–14 min, 0.4 mL/min from 14–17 min, 0.3 mL/min from 17–22 min. Gradient: Initial at 100% A, gradient to 80% A in 1 min, gradient to 55% in 5 min, gradient to 20% A in 7 min, gradient to 5% A in 1 min, hold for 3 min, return to 100% A in 1 min, hold 4 min (total run time of 22 min).

Conclusion

The Oasis WAX Cartridge is equivalent to the required phase for EPA 533, in both chemical composition and required performance. Accuracy, demonstrated by percent recovery, was determined to be within the required range. Recoveries for 2 ng/L samples were in between 80 to 100% and ranged from 90 to 103% for a 12 ng/L samples. Precision, measured by %RSD of replicate extracts, was also well within the range of requirements, with all RSDs below 10% except for a well-known laboratory contaminant (6:2 FTS). Using the Oasis WAX Cartridge for drinking water analysis, nine PFAS were detected in a sample at concentrations ranging from 0.5–5.3 ng/L. Overall, using an Oasis WAX Cartridge for sample preparation along with the ACQUITY UPLC I-Class PLUS System and the Xevo TQ-S micro MS provides a system solution that meets

and exceeds the regulatory analysis prescribed in EPA method 533.

Featured Products

ACQUITY UPLC I-Class PLUS System <https://www.waters.com/134613317>

Xevo TQ-S micro Triple Quadrupole Mass Spectrometry <https://www.waters.com/134798856>

720006808, Revised December 2020