Application of a New WAX SPE Cartridge for The Analysis of PFAS in Drinking Water

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Introduction

In December 2019, Environmental Protection Agency (EPA) detailed a new methodology for testing short chain per- and polyfluoroalkyl substances (PFAS) in drinking water, EPA 533. This method includes 14 of the 18 compounds from the original PFAS analysis method, EPA 537.1, in addition to 11 short chain (C4-C12) PFAS compounds. Included in the expanded list were two polar compounds, PFBA and PFPeA, which were purposely excluded from EPA 537.1 due to their inability to be extracted by a styrene divinylbenzene (SDVB) solid phase extraction (SPE) sorbent during sample preparation. EPA 533 can include these additional compounds, along with the short chain PFAS compounds, because the new method requires the use of a polymeric weak anion-exchange (WAX) sorbent in place of SDVB in the sample preparation step. Supelclean™ ENVI-WAX™ SPE cartridge is a direct equivalent to the chemistry mandated in EPA method 533 and meets the necessary analytical requirements mandated by the method.

Methods

SPE Method

A vacuum manifold (Supelco Cat. No. 57030-U) with a high-volume sampling kit prepared with silicone tubing was used to reduce potential contamination.

Supelclean™ ENVI-WAX™ cartridges (500 mg) were used for the extraction in accordance with method EPA 533 (section 6.8.1). Cartridges were cleaned and conditioned following EPA 533 (section 11.4.1). Each water sample (250 mL) was fortified with isotopically labeled analogues of the method analytes before being loaded onto the Supelclean™ ENVI-WAX™ cartridge. Cartridges were washed with ammonium acetate in water followed by methanol prior to elution with methanol containing 2% ammonium hydroxide (v/v). Extracted samples were dried down and reconstituted to a final volume of 1 mL in 96:4 Methanol: H_2O.

LC-MS Method

The analysis of the 25 PFAS compounds was performed as detailed in EPA 533 (section 17) using an Agilent 6546 LC/Q-TOF high resolution LC-MS.

Mobile Phase: (A) 20 mM Ammonium Acetate, (B) Methanol

Gradient:

Time (min)	% B
0	5
0.5	5
3	40
16	80
18	80
20	95
22	95
25	5
35	5

LC-MS Method (cont.)

Column: Ascentis® C18 HPLC Column, 3 µm, 15 cm x 2.1 mm (Cat. No. 581302-U)
Delay Column: Ascentis® C18 HPLC Column, 3 µm, 5 cm x 2.1 mm (Cat. No. 581300-U)
Injection Volume: 10 µL
Flow Rate: 0.25 mL/min
MS Detection: Electrospray Ionization Tandem Mass Spectrometry (ESI-MS/MS)

Results

Demonstration of Low Background

Due to the ubiquity of PFAS compounds, it is essential to determine if PFAS analytes of interest are being introduced from equipment, glassware, reagents, or extraction components. To examine if the cartridges contain any of the PFAS compounds, solid phase extraction (SPE) was performed in accordance with EPA 533 by analyzing 250 mL UHPLC-MS water.

Results were then compared with standard calibration curves corresponding to the 25 PFAS compounds from EPA 533. No significant background levels were observed as indicated in **Table 1**.

Table 1

Observed Background Levels of PFAS Analytes of Interest Using 500 mg Supelclean™ ENVI-WAX™ SPE Cartridge

Compound	Background (ng/L)
Perfluoroundecanoic acid	*
Perfluoropentanoic acid	*
Perfluoropentanesulfonic acid	*
Perfluorooctanoic acid	*
Perfluorononanoic acid	*
Perfluorohexanesulfonic acid	*
Perfluoroheptanoic acid	*
Perfluorobutanoic acid	*
Perfluoro-4-methoxybutanoic acid	*
Perfluoro-3,6-dioxaheptanoic acid	*
9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	*
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	*
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	*
Sodium dodecafluoro-3H-4,8-dioxanonanoate	*
Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	*
Perfluorooctanesulfonic acid	*
Perfluorohexanoic acid	3[1]
Perfluoroheptanesulfonic acid	*
Perfluorododecanoic acid	*
Perfluorodecanoic acid	*
Perfluorobutanesulfonic acid	*
Perfluoro(2-ethoxyethane) sulfonic acid	*
Perfluoro-3-methoxypropanoic acid	2[2]
Hexafluoropropylene oxide dimer acid	*
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	*

* Less than instrumental LOD
[1] LCMRL is 5.3 ng/L per EPA method 533
[2] LCMRL is 3.8 ng/L per EPA method 533

Results (cont.)

Accuracy and Precision

Replicates of fortified samples were prepared, extracted, evaporated, reconstituted, and analyzed in accordance with EPA method 533. The accuracy and precision results of the method in reagent water are presented in **Table 2**. Recoveries of all analytes were within 50-130%. The calculated RSDs were all less than 20%, suggesting good precision.

Table 2

Percent Recovery of PFAS Surrogates from Reagent Water Spiked at 40 ng/L or 160 ng/L as indicated in EPA 533

Compound	500 mg WAX cartridges
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-13C2]hexane sulfonate	80 ± 9
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy13C3-propanoic acid	59 ± 4
Perfluoro-n-[1,2,3,4,5,6,7- 13C7]undecanoic acid	75 ± 9
Perfluoro-n-[1,2- 13C2]dodecanoic acid	128 ± 20
Perfluoro-n-[1,2,3,4- 13C4]butanoic acid	63 ± 5
Sodium perfluoro-1-[2,3,4-13C3]butanesulfonate	94 ± 4
Perfluoro-n-[1,2,3,4- 13C4]heptanoic acid	79 ± 8
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2-13C2]-octane sulfonate	102 ± 6
Perfluoro-n-[13C9]nonanoic acid	68 ± 11
Perfluoro-n-[1,2,3,4,5- 13C5]pentanoic acid	53 ± 14
Perfluoro-n-[1,2,3,4,6- 13C5]hexanoic acid	59 ± 7
Sodium perfluoro-1-[1,2,3-13C3]hexanesulfonate	86 ± 8
Perfluoro-n-[13C8]octanoic acid	74 ± 13
Sodium perfluoro-[13C8]octanesulfonate	66 ± 6
Perfluoro-n-[1,2,3,4,5,6- 13C6]decanoic acid	51 ± 7

Summary

Examining the background of both WAX cartridges (200 mg and 500 mg) showed that the concentration of all PFAS compounds mentioned in the EPA533 is below the LOD or between 2-3 ppt. This indicates that the WAX cartridges are extremely clean and suitable for PFAS analysis.

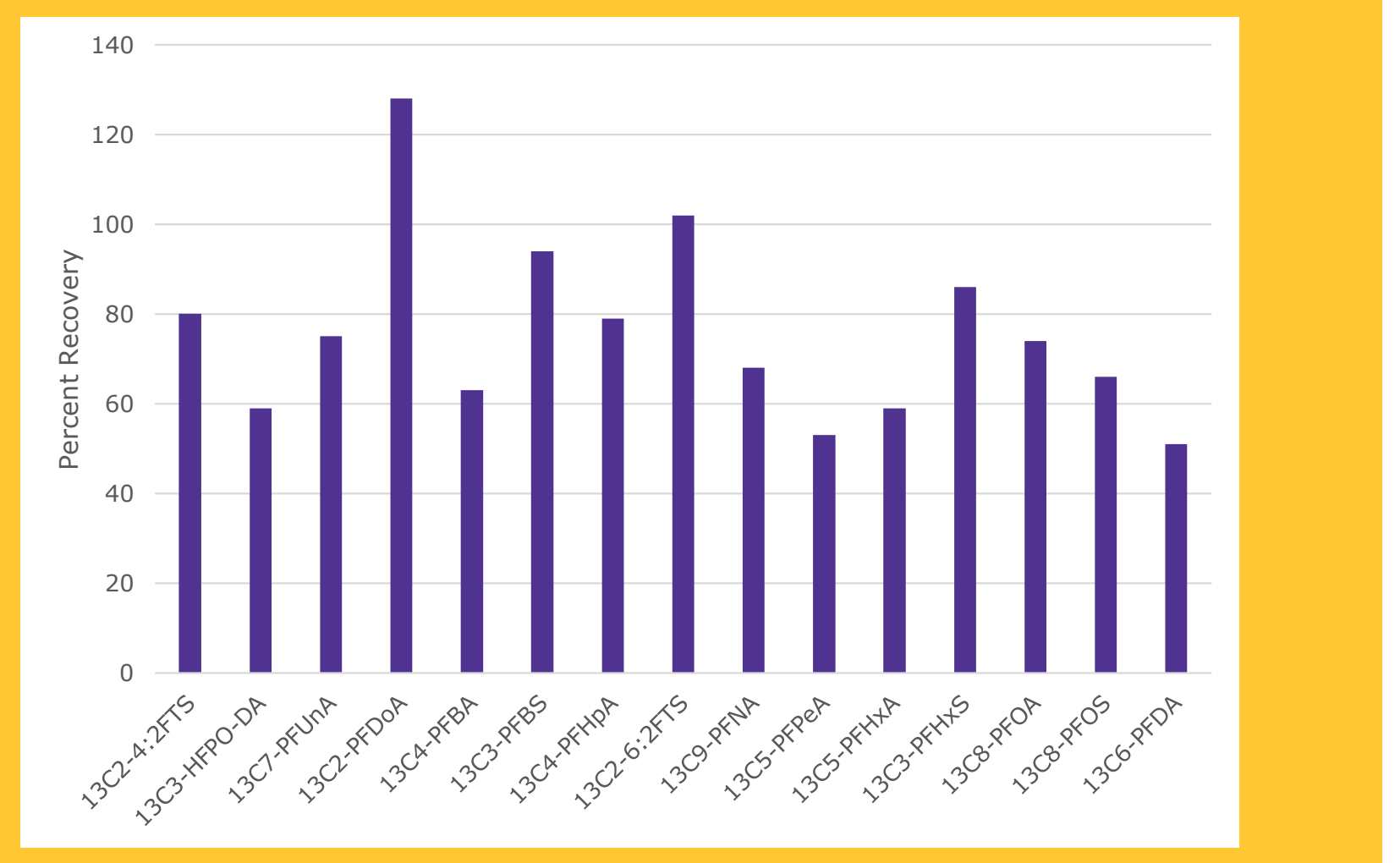
Studying the recovery of these WAX cartridges indicated that all 25 out of 25 PFAS compounds mentioned showed a good recovery between 50% - 150% being in accordance with the EPA533. The calculated RSDs were all less than 20%, suggesting good precision.

Discussion

Surrogate Recovery

Sample preparation for recovery determination was done at least two independent times and the average was calculated.

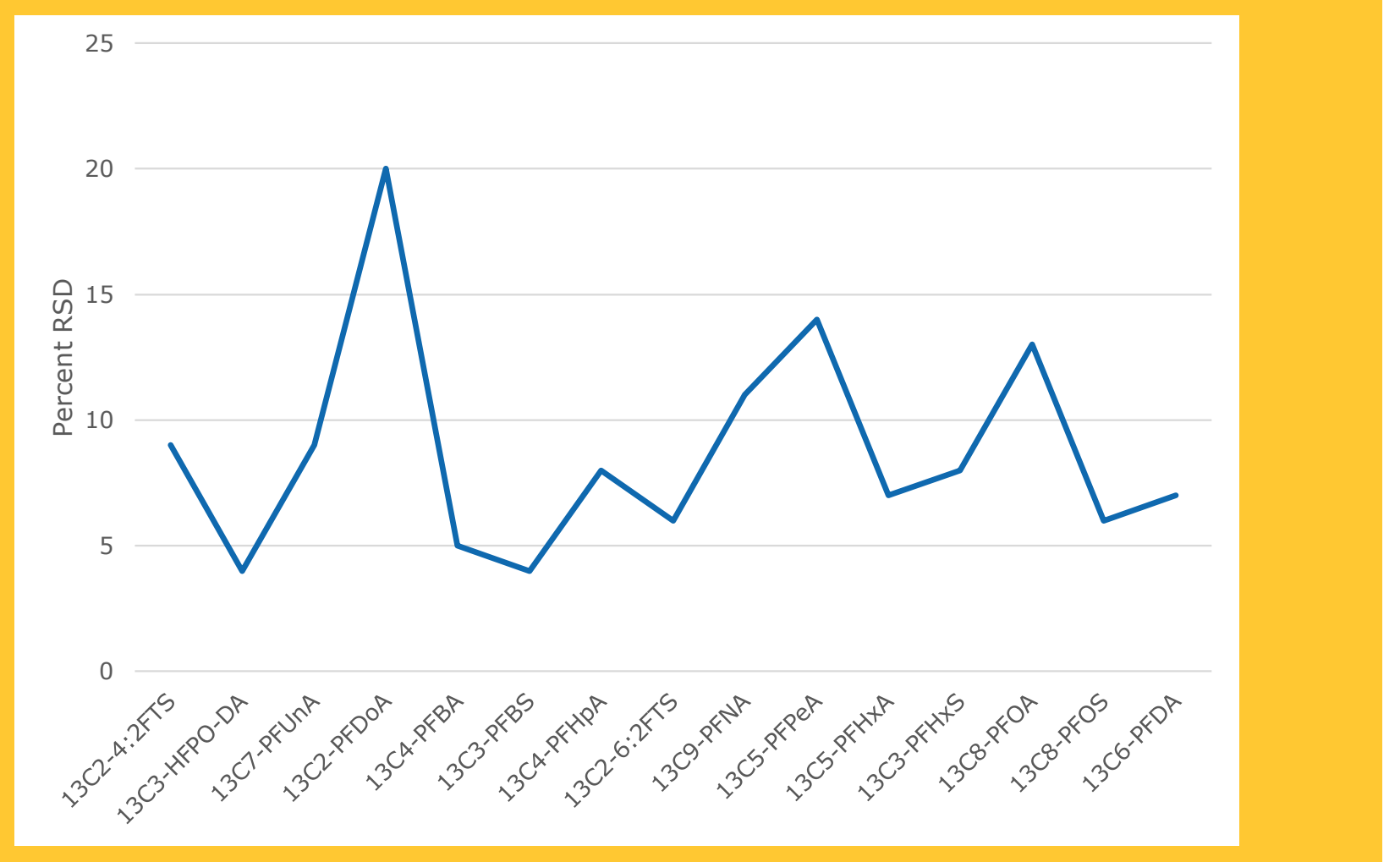
All PFAS Surrogate compounds show a good recovery according to EPA533 (between 50% - 150%)



Surrogate recovery for the 25 PFAS compounds examined in EPA 533

Method Precision

EPA 533 requires all %RSDs to be less than 20%. This chart highlights the %RSDs for each compound from replicate extractions of drinking water spiked according to EPA 533. All PFAS had %RSD values below the 20% requirement.



Percent RSD for the PFAS compounds of interest

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