Critical Review and Screening of Laboratory Supplies for PFAS Analysis in Water Samples

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Introduction

The ubiquitous nature of PFAS in the environment makes ensuring a contaminant-free workflow (Figure 1) essential. In this presentation, we demonstrate that Resprep S-DVB SPE cartridges and related sample preparation products are consistently free of background interferences. In addition, a PFAS delay column effectively removes any contamination that may be present in the instrument. Using the materials and procedure presented here, EPA Method 537.1 requirements for cleanliness, accuracy, and precision were reliably met.

Figure 1: Sample preparation following EPA Method 537.1

Conditioning

- Mount Resprep S-DVB SPE cartridges (6 mL, 500 mg) onto the vacuum manifold.
- Pass 15 mL MeOH through the cartridges.
- Pass 18 mL reagent water through the cartridges.
- Mount the sample reservoirs onto the SPE cartridges as show in the figure 2.

Extraction

- Load the samples into the reservoirs and establish a flow rate of 10-15 mL/min.
- After the samples pass through the cartridges, rinse the sample bottles – and then the sample reservoirs with 7.5 mL of reagent water.
- Rinse the sample bottles, and then the sample reservoirs with a second 7.5 mL aliquot of reagent water.
- Dry the SPE cartridges by drawing air through the manifold for 5 min at high vacuum (10-15 in. Hg).

Elution

- Place the collection tubes in the manifold and elute the analytes with two 4 mL aliquots of MeOH.
- Remove the collection tubes from the manifold and concentrate the extracts to dryness at 65°C under a gentle flow of nitrogen.
- Reconstitute with 1 mL 96:4 MeOH:water and add internal standard; then, vortex to mix.
- Transfer to polypropylene vials and cap with polyethylene caps.

Methods and Results

- Laboratory reagent blanks were prepared for three different lots of Resprep S-DVB SPE cartridges
- Entire workflow, including manifolds, sample vials, solvents, reservoirs and connectors were free of PFAS contaminants tested in EPA Method 537.1 (Figure 2) via LC-MS/MS on a Shimadzu 8045.
- The use of a PFAS delay column provided excellent chromatography, by retaining any PFAS contaminants in the LC
- Raptor C18 analytical LC column gives excellent selectivity for PFAS compounds (Figure 3).
- Recoveries and %RSDs meet all acceptance criteria for EPA Method 537.1 (Table I)

Figure 2: Reagent Blanks (LRB) from the Entire Extraction Workflow with Multiple Lots of S-DVB SPE

Description	Restek Cat. #
Resprep S-DVB SPE (6 mL, 500 mg)	28937
Resprep Vacuum Manifold (12 or 24 port)	28298-VM, 28299-VM
Reservoirs (Polypropylene)	26015
Connectors (Polypropylene)	26007
Vials (Polypropylene)	23245
Vial Caps (Polyethylene)	23247

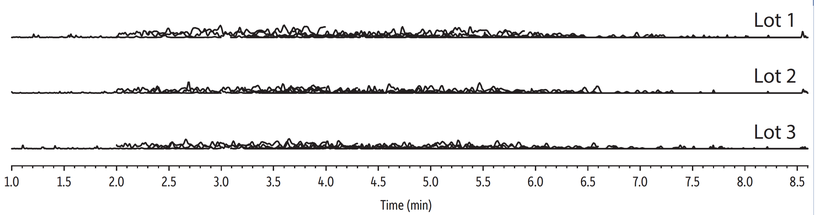
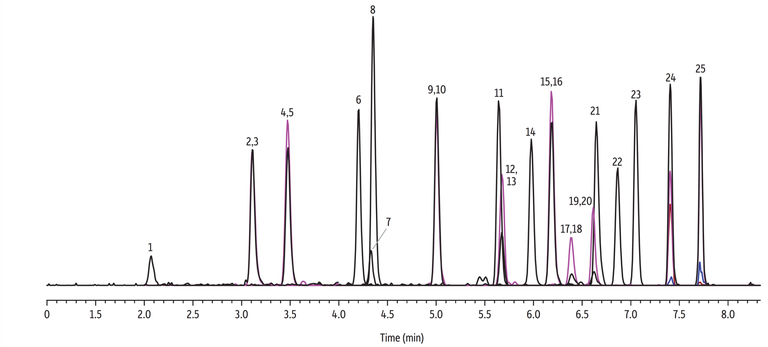


Table I: Precision and Accuracy Results for Method 537.1 PFAS Analysis (n = 4)

Analyte	%RSD*	Mean Recovery**
Perfluorobutanesulfonic acid (PFBS)	11.9%	91.1%
Perfluorohexanoic acid (PFHxA)	7.96%	99.4%
Hexafluoropropylene oxide dimer acid (HFPO-DA)	6.34%	94.4%
Perfluoroheptanoic acid (PFHpA)	4.19%	92.7%
Perfluorohexanesulfonic acid (PFHxS)	11.9%	89.4%
4,8-Dioxa-3H-perfluorononanoic acid (ADONA)	5.18%	96.6%
Perfluorooctanoic acid (PFOA)	5.21%	91.6%
Perfluorononanoic acid (PFNA)	6.79%	97.2%
Perfluorooctanesulfonic acid (PFOS)	6.78%	87.8%
9-Chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)	8.59%	85.1%
Perfluorodecanoic acid (PFDA)	6.96%	93.6%
N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	10.1%	82.8%
N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	16.5%	106%
Perfluoroundecanoic acid (PFUnA)	2.30%	97.5%
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	5.47%	87.6%
Perfluorododecanoic acid (PFDoA)	5.73%	99.0%
Perfluorotridecanoic acid (PFTrDA)	12.7%	89.1%
Perfluorotetradecanoic acid (PFTA)	8.90%	89.7%

Figure 3: Laboratory Fortified Blank (LFB) at Midrange (40ppt)



Peaks	tR (min)	Conc. (ng/L)	Precursor Ion	Product Ion
1. Perfluorobutanesulfonic acid (PFBS)	2.08	40	299.0	80.0
2. Perfluoro-*n*-[1,2-$^{13}C_2$]hexanoic acid ($^{13}C_2$-PFHxA)	3.11	20	315.1	270.1
3. Perfluorohexanoic acid (PFHxA)	3.11	40	313.2	269.0
4. Tetrafluoro-2-heptafluoropropoxy-$^{13}C_3$-propanoic acid ($^{13}C_3$-HFPO-DA)	3.47	20	332.1	287.3
5. Hexafluoropropylene oxide dimer acid (HFPO-DA)	3.47	40	328.9	284.9
6. Perfluoroheptanoic acid (PFHpA)	4.19	40	363.2	319.2
7. Perfluorohexanesulfonic acid (PFHxS)	4.33	40	399.2	79.9
8. 4,8-Dioxa-3H-perfluorononanoic acid (ADONA)	4.34	40	376.9	251.0
9. Perfluoro-[1,2-$^{13}C_2$]octanoic acid ($^{13}C_2$-PFOA)	5.00	20	414.9	370.0
10. Perfluorooctanoic acid (PFOA)	5.00	40	413.1	369.1
11. Perfluorononanoic acid (PFNA)	5.64	40	463.1	419.0
12. Perfluorooctanesulfonic acid (PFOS)	5.66	40	499.2	80.1
13. Perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonic acid ($^{13}C_4$-PFOS)	5.67	60	503.1	80.2
14. 9-Chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)	5.97	40	531.0	350.9
15. Perfluoro-*n*-[1,2-$^{13}C_2$]decanoic acid ($^{13}C_2$-PFDA)	6.18	20	515.2	470.1
16. Perfluorodecanoic acid (PFDA)	6.18	40	512.9	468.9
17. N-methyl perfluorooctanesulfonamidoacetic acid (N-MeFOSAA)	6.38	40	570.2	419.0
18. N-deuteriomethylperfluoro-1-octanesulfonamidoacetic acid (d3-N-MeFOSAA)	6.38	80	573.1	419.1
19. N-deuteriomethylperfluoro-1-octanesulfonamidoacetic acid (d5-N-EtFOSAA)	6.61	80	589.2	419.1
20. N-ethyl perfluorooctanesulfonamidoacetic acid (N-EtFOSAA)	6.62	40	583.8	418.9
21. Perfluoroundecanoic acid (PFUnA)	6.64	40	563.2	519.1
22. 11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)	6.86	40	630.8	451.1
23. Perfluorododecanoic acid (PFDoA)	7.05	40	613.1	569.1
24. Perfluorotridecanoic acid (PFTrDA)	7.40	40	663.0	619.2
25. Perfluorotetradecanoic acid (PFTA)	7.71	40	713.1	669.0

Column	Raptor C18 (cat.# 9304A52)
Dimensions:	50 mm x 2.1 mm ID
Particle Size:	2.7 µm
Pore Size:	90 Å
Temp.:	40 °C
Sample	
Diluent:	96:4 Methanol:water
Conc.:	5-20 ng/mL in the final solution after sample preparation (equivalent to 20-80 ppt in laboratory reagent water sample prior to extraction)
Inj. Vol.:	2 µL
Mobile Phase	
A:	Water, 5 mM ammonium acetate
B:	Methanol

Time (min)	Flow (mL/min)	%A	%B
0.00	0.4	70	30
8.00	0.4	10	90
8.01	0.4	70	30
10.0	0.4	70	30

Detector	MS/MS
Ion Mode:	ESI-
Mode:	MRM
Instrument	HPLC
Notes	A PFAS delay column (cat.# 27854) was installed before the injector. The sample was prepared using Resprep S-DVB SPE cartridges (cat.# 28937) mounted on a Resprep vacuum manifold (cat.# 29298-VM) following the procedure in U.S. EPA Method 537.1. While internal standard concentrations varied, all target analytes were fortified at 40 ppt.

Conclusions

- Eliminating PFAS contaminants from workflows is difficult.
- The above conditions and products provide an entire sample preparation workflow and HPLC method that is free of PFAS contaminants.
- The entire workflow meets the criteria for drinking water analysis as set forth by the EPA 537.1 Method.

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