Utilizing Solid Phase Extraction to Overcome Contamination and Recovery Challenges when Extracting Perfluorinated Compounds from Drinking Water and Wastewater

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Perfluorinated Compounds

Monitoring and measuring

- U.S. EPA Method 537.1:
  - Method for extracting and quantifying polyfluoroalkyl substances (PFAS) compounds in drinking water
  - ***The*** method for PFAS in water – specific to drinking water
  - Analyte list is specific up to 18 compounds
  - Uses LC/MS/MS for quantification
- Challenges:
  - Method is prescriptive for 18 PFAS in drinking water
    - What if you're quantifying compounds that aren't included in the method?
    - What if you're quantifying compounds in a different matrix such as groundwater or wastewater?

Perfluorinated Compounds

Method 537.1 “Modified”

- Overview
  - Addresses the challenges and limitations of Method 537
  - Modifications to QC requirements for quantifying an expanded list of PFC compounds in an expanded set of sample matrices (wastewater, groundwater, soil, food, etc)
  - Each laboratory must establish their own set of modifications and QC requirements, based on which PFC compounds they are quantifying and in which matrices
- Cautions:
  - Modifications to an existing method – not a new method
  - No “EPA validated” set of modifications
  - Modifications and QC requirements may differ significantly from laboratory to laboratory

EPA Method 537
Challenges

Method Validation

- Biggest challenges are in relation to Initial Demonstration of Capability (IDC) – demonstration of low system background
- Accurately measure blanks to demonstrate no measureable interferences or carryover effects
  - Extractor Platforms: Manual and Automated
    - External and internal components
    - All consumables
    - Reagents
- Results must indicate no more than 1/3 MRL measureable PFAS concentrations

Method Interferences: EPA 537

- Method interferences can be caused by contaminants in transfer lines, solvents (methanol), reagents (including reagent water), sample bottles, caps, rinsing components, solvent stones/frits and even SPE cartridges
- New lots must be routinely demonstrated to be free from interferences (less than 1/3 the MRL for each method analyte)
- How can you minimize PFAS contamination
  - Where would you start?

Minimizing PFAS Contamination

Tips for minimizing PFAS contamination

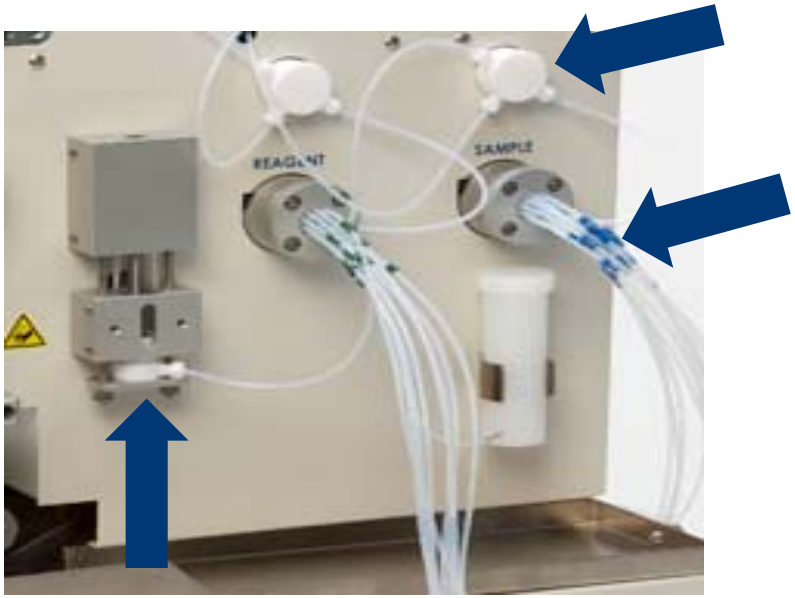
- Try to eliminate PTFE (polytetrafluoroethylene) products as much as possible
- Replace sample and solvent lines with polypropylene and or Peek tubing if possible
  - LRBs will need to be rotated among the ports (PTFE)
- Replace solvent and reagent filtering stones with stainless steel
- Ensure all solvent and reagents are purged clear to eliminate any leaching

Possible Contamination Routes

Vacuum Extraction Manifold

Platform Cleaning

- Clean system tubing
- Clean sample line
- Clean Plunger



PTFE Contamination (IDC)

Results with PTFE solvent transfer lines in positions 1-5

IDC Sample	% Recovery of PFOS
Blank	ND
LFB1	138%
LFB2	146%
LFB3	145%
LFB4	109%

Solvent transfer lines that run/rinsed with methanol have the least amount of PFOS contamination.

Example Contamination

Sample Delivery and Solvent Rinsing

Demonstration of Low Background

No SPE Cartridge

Analyte	Measured Analyte Concentration in 12 Sample Lines (ng/L)					
	Sample Lines 1 and 7	Sample Lanes 2 and 8	Sample Lines 3 and 9	Sample Lines 4 and 10	Sample Lines 5 and 11	Sample Lines 6 and 12
IS-13C2-PFOA	53.2	52.4	53.6	52.6	53.8	52.5
IS-13C4-PFOS	106	105	107	106	108	105
IS-d3-NMeFOSAA	208	203	209	205	207	203
SS-13C2-PFHxA	0.07	0.06	0.06	0.06	0.06	0.06
SS-13C2-PFDA	0.17	0.13	0.13	0.12	0.13	0.13
SS-d5-NEtFOSAA	0.37	0.23	0.20	0.26	0.16	0.17
PFBS	0.02	0.03	0.03	0.02	0.02	0.03
PFHxA	0.05	0.05	0.05	0.06	0.06	0.04
PFHpA	0.04	0.04	0.05	0.05	0.04	0.04
PFHxS	0.02	0.02	0.02	0.02	0.02	0.02
PFOA	0.25	0.18	0.18	0.17	0.21	0.18
PFNA	0.05	0.05	0.09	0.04	0.08	0.02
PFOS	0.10	0.10	0.10	0.10	0.09	0.10
PFDA	0.06	0.04	0.05	0.06	0.04	0.06
NMeFOSAA	0.23	0.08	0.06	0.07	0.05	0.05
NEtFOSAA	0.30	0.13	0.10	0.11	0.11	0.11
PFUnA	0.17	0.12	0.10	0.13	0.12	0.06
PFDoA	0.12	0.04	0.00	0.02	0.03	0.04
PFTrDA	0.15	0.06	0.08	0.08	0.12	0.05
PFTA	0.17	0.02	0.00	0.02	0.02	0.03

Demonstration of Low Background

Full Extraction System, Including SPE Cartridge

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» All reagent/solvent lines, valves, plunger and cartridges were tested

Analyte	Target Conc in LRB (ng/L)	Measured Conc per Sample Line Number (ng/L)					
		1, 7	2, 8	3, 9	4, 10	5, 11	6, 12
IS-13C2-PFOA	50	50.8	52.3	50.5	52.1	51.7	50.9
IS-13C4-PFOS	100	100	103	100	102	103	101
IS-d3-NMeFOSAA	200	187	193	185	194	193	188
SS-13C2-PFHxA	50	49.4	46.9	48.4	48.9	49.5	48.1
SS-13C2-PFDA	100	96.1	89.2	92.3	94.2	96.1	92.8
SS-d5-NEtFOSAA	200	177	171	174	171	185	175
PFBS	N/A	0.01	0.03	0.01	0.01	0.00	0.00
PFHxA	N/A	0.85	0.08	0.09	0.52	0.07	0.08
PFHpA	N/A	0.08	0.02	0.02	0.10	0.02	0.02
PFHxS	N/A	0.00	0.00	0.00	0.00	0.00	0.00

Analyte	Target Conc in LRB (ng/L)	Measured Conc per Sample Line Number (ng/L)					
		1, 7	2, 8	3, 9	4, 10	5, 11	6, 12
PFOA	N/A	0.32	0.13	0.14	0.41	0.14	0.12
PFNA	N/A	0.06	0.01	0.07	0.21	0.05	0.03
PFOS	N/A	0.03	0.03	0.03	0.03	0.03	0.03
PFDA	N/A	0.06	0.02	0.05	0.08	0.04	0.04
NMeFOSAA	N/A	0.12	0.30	0.07	0.38	0.06	0.07
NEtFOSAA	N/A	0.14	0.28	0.07	0.17	0.09	0.08
PFUnA	N/A	0.11	0.03	0.13	0.09	0.07	0.03
PFDoA	N/A	0.05	0.01	0.03	0.04	0.03	0.03
PFTrDA	N/A	0.09	0.03	0.07	0.05	0.05	0.02
PFTA	N/A	0.06	0.03	0.00	0.00	0.00	0.00

PFAS- High Level Aqueous Samples

- Waste Water

- Surface Water

- Landfills
- Groundwater

Sample Filtering: In-line Option

- Must measure for interferences before use
- Avoid PTFE syringe filters
  - Polypropylene
- Must be able to pass rinse solvent through the filter

Demonstration of Low Background

3.0 µm In-line filter -Polypropylene

Analyte (LRB)	Conc (µg/L)	Recovery (%)	Analyte (LRB)	Conc (µg/L)	Recovery (%)
Perfluoro-n-[1,2-13C2]decanoic acid (13C2-PFDA) (SUR)	18.60	93.0	Perfluorodecanesulfonate (PFDS)	ND	
Perfluoro-n-[1,2-13C2]hexanoic acid (13C2-PFHxA) (SUR)	20.39	102.0	Perfluoroheptanoic acid (PFHpA)	ND	
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid (d5-ETFOSAA) (SUR)	15.33	76.7	Perfluoroheptanesulfonate (PFHpS)	ND	
Fluorotelomer sulfonate 4:2 (4:2 FTS)	ND		Perfluorohexanoic acid (PFHxA)	0.27	
Fluorotelomer sulfonate 6:2 (6:2 FTS)	ND		Perfluorohexanesulfonate (PFHxS)	ND	
Fluorotelomer sulfonate 8:2 (8:2 FTS)	ND		Perfluorononanoic acid (PFNA)	ND	
N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA)	ND		Perfluorononanesulfonate (PFNS)	ND	
Perfluorooctanesulfonamide (PFOSA)	0.16		Perfluorooctanoic acid (PFOA)	ND	
N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA)	ND		Perfluorooctanesulfonate (PFOS)	ND	
Perfluorobutyric acid (PFBA)	ND		Perfluoropentanoic acid (PFPeA)	ND	
Perfluorobutanesulfonate (PFBS)	ND		Perfluoropentanesulfonate (PFPeS)	ND	
Perfluorodecanoic acid (PFDA)	ND		Perfluorotetradecanoic acid (PFTeDA)	ND	
Perfluorododecanoic acid (PFDoA)	0.24		Perfluorotridecanoic acid (PFTrDA)	ND	
Perfluorododecanoic acid (PFDoA)	0.24		Perfluoroundecanoic acid (PFUdA)	ND	

Spike and Carryover Determination

250µg/L – (10X Dilution)

Analyte	Spiked at 250 LFSM		LRB Run After The LFSM	
	Concentration (µg/L)	Recovery (%)	Concentration (µg/L)	Recovery (%)
Perfluoro-n-[1,2-13C2]decanoic acid (13C2-PFDA) (SUR)	1.84	92.0	18.87	94.4
Perfluoro-n-[1,2-13C2]hexanoic acid (13C2-PFHxA) (SUR)	1.97	98.5	19.23	96.2
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid (d5-ETFOSAA) (SUR)	1.77	88.5	15.89	79.5
Fluorotelomer sulfonate 4:2 (4:2 FTS)		0.00	ND	
Fluorotelomer sulfonate 6:2 (6:2 FTS)		0.00	ND	
Fluorotelomer sulfonate 8:2 (8:2 FTS)		0.00	ND	
N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA)		0.00	ND	
Perfluorooctanesulfonamide (PFOSA)		0.00	ND	
N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA)		0.00	ND	
Perfluorobutyric acid (PFBA)		0.00	ND	
Perfluorobutanesulfonate (PFBS)	28.70	115	ND	
Perfluorodecanoic acid (PFDA)		0.00	ND	
Perfluorododecanoic acid (PFDoA)	0.21	0.84	0.22	

Spike and Carryover Determination

250µg/L – (10X Dilution)

Analyte	Spiked at 250 LFSM		LRB Run After The LFSM
	Concentration (µg/L)	Recovery (%)	Concentration (µg/L)
Perfluorodecanesulfonate (PFDS)		0.00	ND
Perfluoroheptanoic acid (PFHpA)	26.01	104	ND
Perfluoroheptanesulfonate (PFHpS)		0.00	ND
Perfluorohexanoic acid (PFHxA)		0.00	ND
Perfluorohexanesulfonate (PFHxS)	28.37	113	ND
Perfluorononanoic acid (PFNA)	24.78	99.1	ND
Perfluorononanesulfonate (PFNS)		0.00	ND
Perfluorooctanoic acid (PFOA)	26.20	105	ND
Perfluorooctanesulfonate (PFOS)	27.21	109	ND
Perfluoropentanoic acid (PFPeA)		0.00	0.23
Perfluoropentanesulfonate (PFPeS)		0.00	ND
Perfluorotetradecanoic acid (PFTeDA)		0.00	ND
Perfluorotridecanoic acid (PFTrDA)		0.00	ND
Perfluoroundecanoic acid (PFUdA)		0.00	ND

Spike and Carryover Determination

2500µg/L – (100X Dilution)

Analyte	Spiked at 2500 LFSM		LRB Run After The LFSM	
	Concentration (µg/L)	Recovery (%)	Concentration (µg/L)	Recovery (%)
Perfluoro-n-[1,2-13C2]decanoic acid (13C2-PFDA) (SUR)	NA		19.89	99.5
Perfluoro-n-[1,2-13C2]hexanoic acid (13C2-PFHxA) (SUR)	NA		19.66	98.3
N-deuterioethylperfluoro-1-octanesulfonamidoacetic acid (d5-ETFOSAA) (SUR)	NA		16.22	81.1
Fluorotelomer sulfonate 4:2 (4:2 FTS)			ND	
Fluorotelomer sulfonate 6:2 (6:2 FTS)			ND	
Fluorotelomer sulfonate 8:2 (8:2 FTS)			ND	
N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA)			ND	
Perfluorooctanesulfonamide (PFOSA)			ND	
N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA)			ND	
Perfluorobutyric acid (PFBA)			ND	
Perfluorobutanesulfonate (PFBS)	26.87	107	ND	
Perfluorodecanoic acid (PFDA)			ND	
Perfluorododecanoic acid (PFDoA)	0.23	0.92	0.22	

Spike and Carryover Determination

2500µg/L – (100X Dilution)

Analyte	Spiked at 2500 LFSM		LRB Run After The LFSM
	Concentration (µg/L)	Recovery (%)	Concentration (µg/L)
Perfluorodecanesulfonate (PFDS)			ND
Perfluoroheptanoic acid (PFHpA)	25.74	103	ND
Perfluoroheptanesulfonate (PFHpS)			ND
Perfluorohexanoic acid (PFHxA)			ND
Perfluorohexanesulfonate (PFHxS)	25.30	101	ND
Perfluorononanoic acid (PFNA)	25.69	103	0.50
Perfluorononanesulfonate (PFNS)			ND
Perfluorooctanoic acid (PFOA)	25.80	103	0.24
Perfluorooctanesulfonate (PFOS)	25.71	103	0.77
Perfluoropentanoic acid (PFPeA)			ND
Perfluoropentanesulfonate (PFPeS)			ND
Perfluorotetradecanoic acid (PFTeDA)			ND
Perfluorotridecanoic acid (PFTrDA)			ND
Perfluoroundecanoic acid (PFUdA)			ND

Conclusion

- Ensure all components are tested for known analytes
  - It is not possible to remove all PFAS background contamination, but every bit helps to minimize the background levels.

- Cross contamination
  - Ensure all components of the extraction platforms sample flow path can be rinsed with methanol (manual or automated)
  - Clear out solvent/sample transfer lines (methanol) before long periods of idle time