Tips & Tricks for Extracting Perfluorinated Compounds from Drinking Water Using Solid Phase Extraction

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Introduction

Perfluorinated compounds (PFCs) are a group of compounds that have been used in a wide array of industrial and household applications, including fabric protectors, non-stick coatings for cookware, coatings for food packaging and in some fire-fighting foams. Due to the strength of the carbon-fluorine bonds within the molecule, PFCs are highly resistant to degradation even when metabolized or exposed to harsh environmental conditions. Their persistence in the environment allows them to accumulate in water sources, particularly those used for consumption.

Exposure to perfluorinated compounds has been found to negatively impact the health of the consumer, which motivated the U.S. EPA to add these compounds to the list of chemicals that are monitored in drinking water. The EPA has outlined a method for extracting and quantifying those analytes from drinking water in Method 537. One of the biggest challenges when tackling this application is in minimizing interferences and opportunities for contamination during sample preparation and analysis. As PFCs are highly stable and non-reactive, they have become commonly used materials for equipment parts and laboratory supplies.

This work will demonstrate the use of a cartridge-based extraction system to extract and quantify up to 24 PFC compounds in drinking water to highlight the challenges associated with this application. The work will emphasize a number of potential pitfalls that analysts face – including blank interferences, system interferences and carryover effects – along with tips for troubleshooting those interferences and avoiding them during future analyses.

EPA Method 537.1 (Updated Nov 2018)

Overview:

- Method for extracting and quantifying perfluorinated compounds in drinking water
- ***The*** method for PFCs in water – specific to drinking water
- Analyte list is specific to 18 compounds – not a reference method
- Uses LC/MS/MS for quantification

Challenges:

- Method is prescriptive for 18 PFCs in drinking water
- What if you're quantifying a PFC that isn't included in Method 537?
- What if you're measuring groundwater/soil/wastewater samples etc?

Modified Approach

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

Challenges:

- How do you confirm that the additional PFCs are being accurately extracted?
- How do you set performance expectations?

Method 537.1 Compounds

The compounds included in the "modified" version of EPA Method 537.1 are listed in Table 1 below. The list includes the 6 PFC compounds on the UCMR 3 list and the 18 compounds listed in EPA Method 537.1.

Compound	Compound
Perfluorooctanesulfonate (PFOS)	Perfluorohexanesulfonate (PFHxS)
Perfluoroundecanoic acid (PFUnA)	Perfluorobutyric acid (PFBA)
N-methyl perfluorooctanesulfonamidoacetic acid (NMeFOSAA)	Perfluorobutanesulfonate (PFBS)
Perfluoropentanoic acid (PFPeA)	Perfluoroheptanoic acid (PFHpA)
Perfluoropentanesulfonate (PFPeS)	Perfluoroheptanesulfonate (PFHpS)
Fluorotelomer sulfonate 6:2 (6:2 FTS)	Perfluorononanoic acid (PFNA)
N-ethyl perfluorooctanesulfonamidoacetic acid (NEtFOSAA)	Perfluorotetradecanoic acid (PFTA)
Perfluorohexanoic acid (PFHxA)	Fluorotelomer sulfonate 8:2 (8:2 FTS)
Perfluorododecanoic acid (PFDoA)	Perfluorononanesulfonate (PFNS)
Perfluorooctanoic acid (PFOA)	Perfluorotridecanoic acid (PFTrDA)
Perfluorodecanoic acid (PFDA)	Perfluorooctanesulfonamide (PFOSA)
Perfluorodecanesulfonate (PFDS)	Fluorotelomer sulfonate 4:2 (4:2 FTS)

Table 1. Perfluorinated compounds listed in EPA Method 537.1

Challenges When Quantifying PFCs

Contamination

Perfluorinated compounds are highly stable and non-reactive, so they have become commonly used materials in laboratory equipment which can contribute to contamination during preparation and analysis.

Common sources include:

- Solvents (including reagent water)
- Solvent storage and transfer lines
- Sample collection and storage containers
- PTFE components in the extraction system (valves, bearings, transfer lines, stopcocks, etc)
- PTFE components in the analytical system (injection valve, solvent lines, solvent bottles, sample vials)
- Solid phase extraction (SPE) cartridges

There are additional challenges when quantifying PFC compounds due to their varying chemical properties: high volatility, instability in certain solvents, prone to thermal degradation and poor interactions with certain SPE media types.

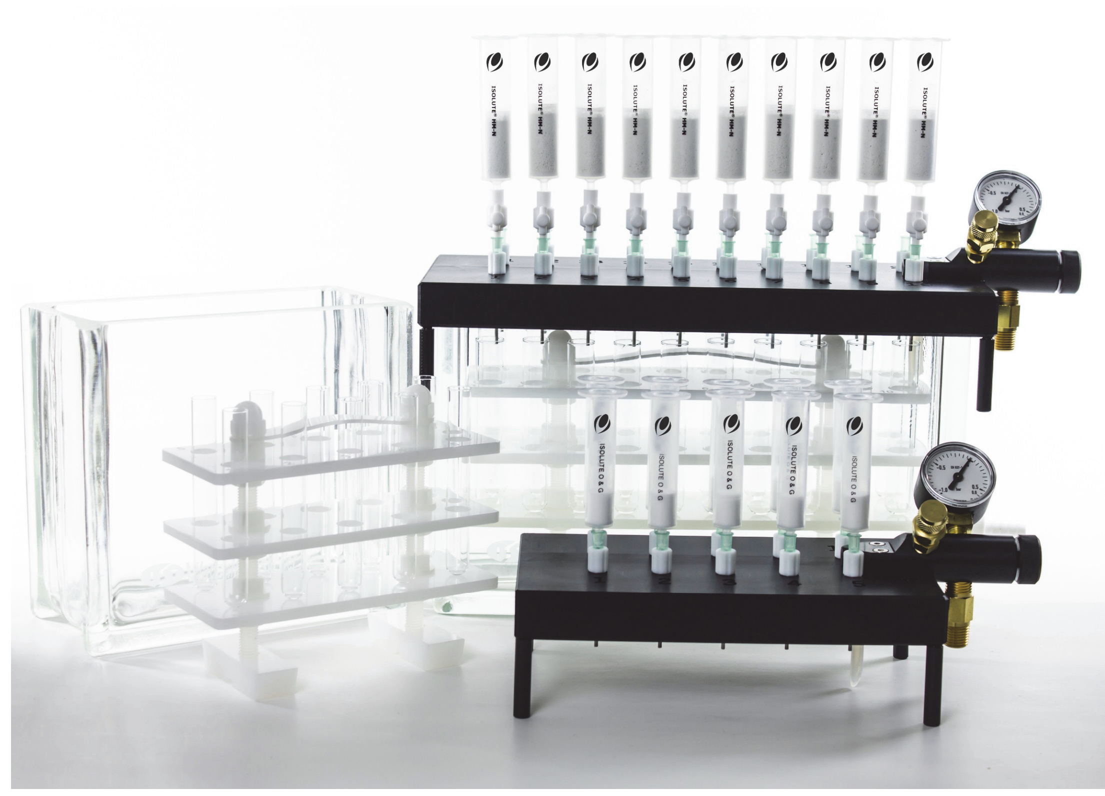
Method Validation

Initial Demonstration of Capability (IDC) – blank measurements

- Blank solutions must pass through all possible solvent lines and solvent pathways, then measured to ensure no significant PFC contributions are coming from the method or the systems
- Surrogates must be recovered between 70-130% of their known concentrations to support the validity of the blank measurement

System Contamination Examples

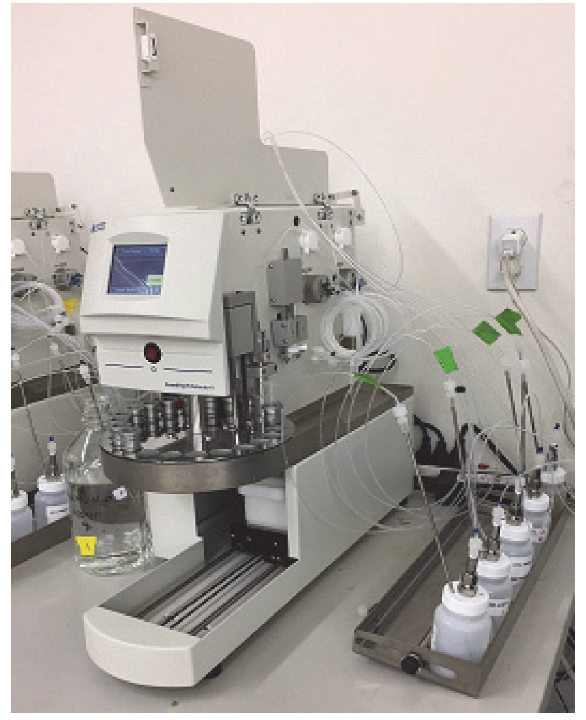
Vacuum Extraction Manifold

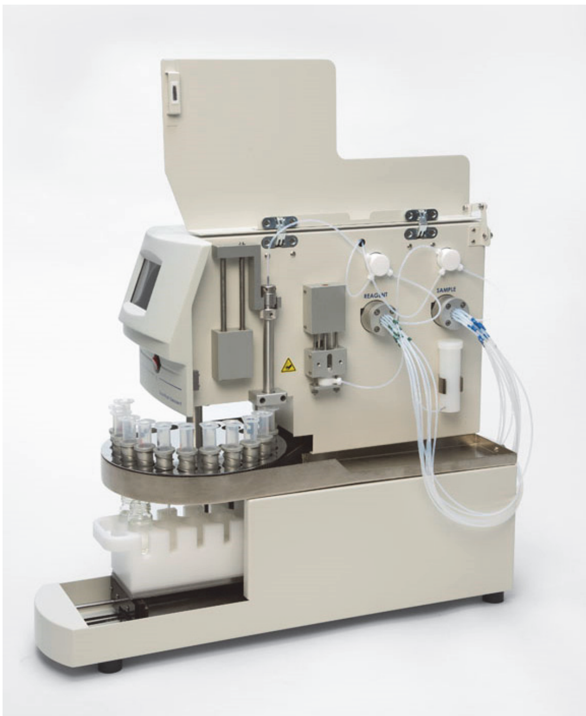


Sources of contamination could include:

- Stopcocks
- Transfer tubing from samples (if using vacuum to automatically pull solution out of large sample bottles)

Automated Extraction Manifold





Sources of contamination could include:

- Valves, bearings, pumps, syringe
- Transfer tubing from samples (if your extraction setup automatically draws solution out of large sample bottles)
- Sample delivery and solvent rinse lines
- Solvent storage bottles

Spike Recoveries and Carryover Measurements

Example Results – Vacuum Extraction

Compound	Fortified Blank Results		Laboratory Reagent Blank	
	Conc (ng/L)	Recovery (%)	Conc (ng/L)	Recovery (%)
Perfluorononanoic acid (PFNA)	24.8	123.9	ND	---
Perfluorooctanoic acid (PFOA)	23.9	119.5	0.28	---
Perfluorotetradecanoic acid (PFTA)	20.6	103.0	ND	---
Perfluorotridecanoic acid (PFTrDA)	23.2	116.0	ND	---
Perfluorooctanesulfonate (PFOS)	23.0	115.0	ND	---
N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA)	23.8	119.1	ND	---
Perfluoroheptanoic acid (PFHpA)	24.3	121.5	0.3	---
Perfluorobutanesulfonate (PFBS)	24.2	120.7	ND	---
Perfluorodecanoic acid (PFDA)	22.8	114.2	0.25	---
Perfluorododecanoic acid (PFDoA)	20.8	103.9	ND	---
Perfluorohexanesulfonate (PFHxS)	20.8	104.0	ND	---

Table 2. Results for spiked blank containing surrogates and analytes at 20 ng/L, followed by a laboratory reagent blank measurement. Results are listed as "ND" if the analyte concentration was below that of the lowest calibration standard.

Example Results – Automated Extraction

Compound	Fortified Blank Results		Laboratory Reagent Blank	
	Conc (ng/L)	Recovery (%)	Conc (ng/L)	Recovery (%)
Fluorotelomer sulfonate 4:2 (4:2 FTS)	19.74	98.7	ND	---
Fluorotelomer sulfonate 6:2 (6:2 FTS)	18.92	94.6	ND	---
Fluorotelomer sulfonate 8:2 (8:2 FTS)	22.01	110.1	ND	---
N-ethylperfluoro-1-octanesulfonamidoacetic acid (N-EtFOSAA)	17.55	87.7	ND	---
Perfluorooctanesulfonamide (PFOSA)	5.65	28.2	0.45	---
N-methylperfluoro-1-octanesulfonamidoacetic acid (N-MeFOSAA)	17.50	87.5	ND	---
Perfluorobutyric acid (PFBA)	19.59	97.9	ND	---
Perfluorobutanesulfonate (PFBS)	19.37	96.8	ND	---
Perfluorodecanoic acid (PFDA)	17.86	89.3	ND	---
Perfluorododecanoic acid (PFDoA)	17.27	86.3	0.25	---
Perfluorodecanesulfonate (PFDS)	16.18	80.9	ND	---

Table 3. Results for spiked blank containing surrogates and analytes at 20 ng/L, followed by a laboratory reagent blank measurement. Results are listed as "ND" if the analyte concentration was below that of the lowest calibration standard.

Conclusions

- It is not possible to remove all PFC background contamination but good laboratory practices with proper cleaning and storage procedures will help to minimize contamination issues
- Awareness of the most common contamination sources will make troubleshooting quicker and make contamination easier to mitigate
- Compounds such as PFOSA, NEtFOSA, NEtFOSE and NMeFOSE tend to suffer from low recoveries due to high volatility.
- Compounds such as PFBA and PFPA tend to suffer from low recoveries due to poor retention on SDVB media.

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