

Extraction of Per/Polyfluoroalkyl Substances in Water Using Agilent Offline Solid Phase Extraction

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Abstract

This Application Note describes a modified extraction for per- and polyfluorinated alkyl substances (PFASs) used in EPA Method 537 to extract 30 PFASs (including all 14 in EPA 537) in drinking water using an Agilent weak anion exchange (WAX) cartridge and analysis using an Agilent 1260/6470 LC/MS/MS system.

Introduction

PFASs have surfactant properties, with many specialty applications such as nonstick cookware, flame retardants, stain repellent clothing, and carpeting, as they are resistant to degradation or fire. This property also makes it difficult for organisms to metabolize them, repelling both lipids and water, leading to persistence in the environment. This wide assortment of anthropogenic chemicals generally bioaccumulates in proportion to the chain length, and may bind to blood proteins or accumulate in the liver, resulting in a variety of metabolic consequences.

Due to the persistence of these compounds in the environment, and subsequent bioaccumulation, the US EPA has established health advisory levels for the combined concentrations of two such compounds in drinking water of 70 parts per trillion, and has issued Method 537¹, which describes the quantification of 14 of these compounds in drinking water by LC/MS/MS. This Application Note describes an offline solid phase extraction (SPE) method comparable to EPA Method 537 that can extract and analyze 30 per/polyfluorinated alkyl substances from larger-volume water samples, specifically detailing the use of Agilent WAX cartridges.

Materials and conditions

LC Instrument

- Agilent 1260 series Infinity binary pump
 - **Delay column:** Agilent ZORBAX SB-C18 4.6 × 50 mm, 3.5 μm (p/n 835975-902)
- Agilent Infinity autosampler (G1367)
- Agilent Infinity thermostated column compartment (G1316) (50 °C) fitted with:
 - **Analytical column:** Agilent ZORBAX Eclipse Plus C18, 3.0 × 50 mm, 1.8 μm (p/n 959757-302)

Instruments were modified with PEEK fittings; polytetrafluoroethylene-free vials, caps, and septa were used to reduce PFAS background². Mobile phases (in LC grade solvents) were: A) 5 mM ammonium acetate in water, and B) 95/5 methanol/water + 5 mM ammonium acetate pumped at 0.4 mL/min in a 10–95 % gradient for 17 minutes. Details of the analytical method are provided in another application note (5991-7951EN)³.

LC/MS Instrument

An Agilent 1260 Infinity II LC coupled to a 6470 triple quadrupole MS/MS detector equipped with an Agilent Jet Stream ESI source was used³. Data were processed with Agilent MassHunter Quantitative software (B.07.01). Dynamic multiple reaction monitoring was run in electrospray negative mode, as detailed in Agilent Technologies Application Note, publication number 5991-7951EN³.

Chemicals and materials

Sample preparation solutions and mixtures PFAC-MXB and FTA-MXA were obtained from Wellington Laboratories (Guelph, Ontario, Canada) and mixed for use as previously described³. Tables 1 and 2 list the acronyms and structures for those used in this study including if they are present in the analyte list for EPA Method 537. Compounds additionally extracted and analyzed are shown in green in Table 1. A 250-mL sample of LC grade water or municipal tap water (Cochrane, Alberta, Canada) was quenched with 5 g/L Trizma, then spiked to 4 ng/L with a mixed solution of the included PFAS (the three FTA-e's were spiked at 80 ng/L). Four replicates of each water type and their water blanks were extracted with 6-mL WAX cartridges containing 150 mg sorbent (p/n 5982-3667), per the protocol detailed in Figure 1.

Table 1. PFASs analyzed in this study.

Acronym	Class	Fluorinated alkyl Chain	EPA 537 or Extended list
PFBA	Acid	C-04	Extended
PFPeA	Acid	C-05	Extended
PFHxA	Acid	C-06	537
PFHpA	Acid	C-07	537
PFOA	Acid	C-08	537
PFNA	Acid	C-09	537
PFDA	Acid	C-10	537
PFUdA	Acid	C-11	537
PFDoA	Acid	C-12	537
PFTrDA	Acid	C-13	537
PFTeDA	Acid	C-14	537
FOSA	FOSA	C-08	Extended
N-EtFOSAA	FOSAA	C-08	537
N-MeFOSAA	FOSAA	C-08	537
FHEA	FTA-e	C-06	Extended
FOEA	FTA-e	C-08	Extended
FDEA	FTA-e	C-10	Extended
PFHpPA	FTA-p	C-07	Extended
4-2 FTS	FTS	C-04	Extended
6-2 FTS	FTS	C-06	Extended
8-2 FTS	FTS	C-08	Extended
6-2 FTUA	FTUA	C-06	Extended
8-2 FTUA	FTUA	C-08	Extended
PFBS	Sulfonate	C-04	537
PFPeS	Sulfonate	C-05	Extended
PFHxS	Sulfonate	C-06	537
PFHpS	Sulfonate	C-07	Extended
PFOS	Sulfonate	C-08	537
PFNS	Sulfonate	C-09	Extended
PFDS	Sulfonate	C-10	Extended

Table 2. Structures of different classes of PFAS measured in this study.

Molecular type	PFAS class	General structure		
Perfluoroalkyl-carboxylic acids	Acids	R-CO ₂ H	R = CF ₃ (CF ₂) _n n = 0-20	
Fluorooctane sulfonamide	FOSA	R-CSO ₂ NH ₂	R = CF ₃ (CF ₂) _n n = 7	
Fluorooctane sulfonamide acetic acid	FOSAA	R-CSO ₂ NHR'R''	R = CF ₃ (CF ₂) _n n = 7	R' = CH ₂ CO ₂ H R'' = H or Me or Et
Fluorotelomer alcohol-ethanoic acid	FTA-e	R-CH ₂ CO ₂ H	R = CF ₃ (CF ₂) _n n = 0-15	
Fluorotelomer alcohol-propanoic acid	FTA-p	R-CH ₂ CH ₂ CO ₂ H	R = CF ₃ (CF ₂) _n n = 0-15	
Fluorotelomer sulfonate	FTS	R-CH ₂ CH ₂ SO ₃ ⁻	R = CF ₃ (CF ₂) _n n = 0-15	
Fluorotelomer unsaturated acid	FTUA	R-CO ₂ H	R = CF ₃ (CF ₂) _n CF=CH n = 0-15	
Perfluoroalkyl sulfonate	Sulfonates	R-CSO ₃ ⁻	R = CF ₃ (CF ₂) _n n = 0-20	

Solid phase extraction procedure

A manual vacuum SPE manifold with polypropylene reservoirs to hold the sample was used. The manifold was checked and refitted with parts not containing PTFE and fluoropolymers. The WAX cartridges were initially conditioned with 5 mL of 60/40 acetonitrile/methanol (ACN/MeOH) with 5 % ammonium hydroxide (NH₄OH) followed by 5 mL of ultrapure water, then 5 mL of 1 % acetic acid in ultrapure water. The conditioned cartridges were then loaded with 1 mL of 1 % acetic acid. The 250-mL water sample was adjusted to a pH of ~2 with the addition of 2.5 mL of glacial acetic acid. The water samples were then loaded onto the SPE cartridges at a flow rate of ~10 mL/min. The sample containers were rinsed with 7.5 mL of ultrapure water twice, and passed through the cartridge. The cartridge was then dried by vacuum at 10–15 mm Hg for five minutes. The sample reservoirs and sample bottles were rinsed twice with 4 mL of 5 % NH₄OH in a 60/40 ACN/MeOH mix. The rinse solution was added to the cartridge and left for five minutes, then passed through the cartridge to elute into 15-mL polypropylene vials. The eluate was evaporated under a gentle nitrogen stream at 55 °C to ~500 µL. Evaporating to dryness resulted in lower recovery of some of the additional PFAs added to this method. The final extract was adjusted to 1 mL in 96 % MeOH, ready for LC/MS analysis.

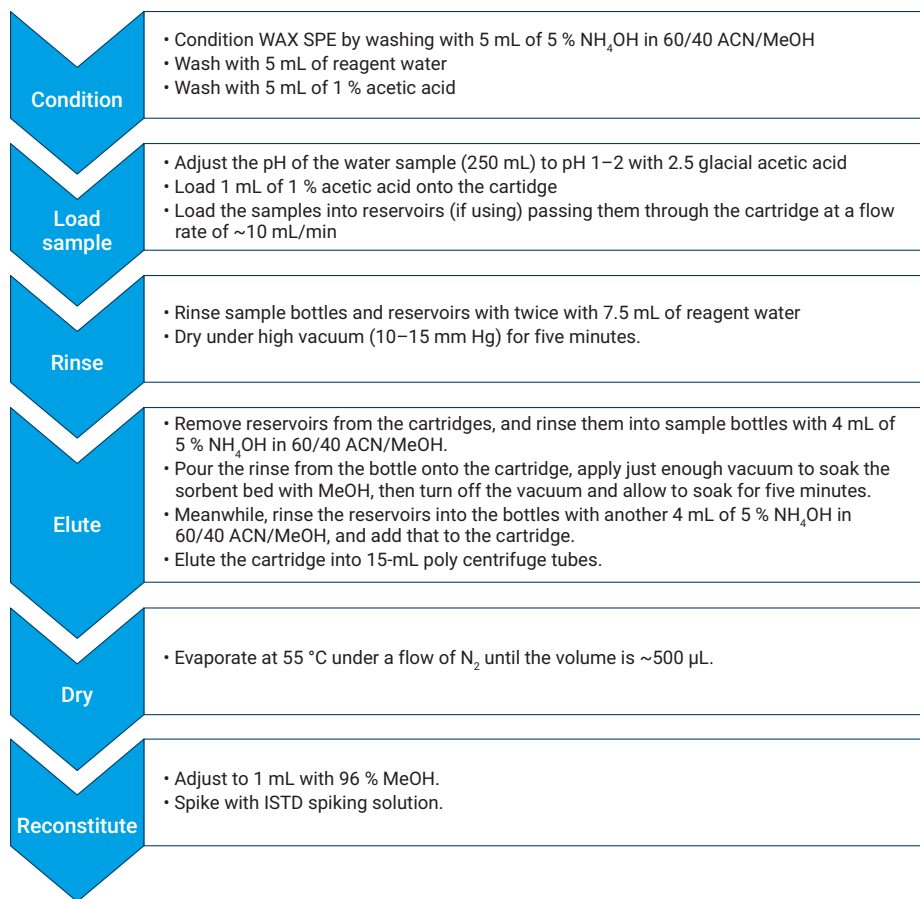


Figure 1. Protocol for extraction of PFAS using WAX cartridge.

Blank contamination

While every precaution was taken to avoid any sources of background contamination, the SPE manifold and procedure did introduce trace levels of contamination for a few PFASs. PFBA particularly, was present in the SPE blanks at high concentration. The instrument blanks had no detections of PFAS contamination (<0.1 ng/L), which indicates that the contamination was introduced from the SPE manifold or materials used in the SPE process.

PFAS spike recovery with WAX SPE

Table 3 lists the recoveries of 30 PFASs from solid phase WAX offline extractions for the two sources of water (LC reagent water and tap water). The list includes all 14 analytes described in EPA Method 537 in addition to 16 additional PFAS compounds of interest. Concentrations shown for the four replicates of each water type were calculated using labeled internal standards (compound-specific where possible) on a calibration curve (7–9 points), ignoring the origin, and using $1/x^2$ weighting.

All 14 compounds in the EPA 537 had recoveries between 70 and 130 % with RSD(%) <15 % for both water qualities tested.

Of the 16 additional compounds, four compounds had recoveries lower than 70 %, which is considered acceptable by the USEPA. Three of these compounds are the FTA-e's, but recoveries were still above 40 %.

For most of these 30 compounds, there were not differences in solid phase extraction recovery from either water source. This observation discounts the possibility that dissolved ions in tap water compared to purified water biased the recoveries.

The EPA instrumentation had a measurement range for this method of 2.9–14 ng/L, with the specification that recovery must be in the range of 50–150 %. The results from this study indicate that recoveries of the

14 compounds in the EPA method are acceptable using the Agilent WAX SPE cartridge. In addition, 16 other PFAS, including ones on the ASTM list, have good recoveries for the most part, and can be analyzed with this method.

Table 3. Recovery of all PFAS in two different water matrices.

Name	LC Grade water average recovery	LC Water %RSD	Tap water average recovery	Tap water %RSD
PFBA*	112	7 %	106	6 %
PFPeA	113	5 %	117	2 %
PFHxA	104	8 %	107	2 %
PFHpA	105	10 %	101	3 %
PFOA	102	10 %	106	2 %
PFNA	100	5 %	104	3 %
PFDA	101	5 %	95	6 %
PFUdA	100	6 %	102	3 %
PFDoA	86	3 %	88	2 %
PFTrDA	91	3 %	103	15 %
PFTeDA	96	10 %	86	8 %
FOSA	57	14 %	67	20 %
N-MeFOSAA	84	11 %	79	10 %
N-EtFOSAA	84	9 %	89	3 %
FHEA	107	6 %	90	8 %
FOEA	61	13 %	52	14 %
FDEA	56	21 %	58	15 %
PFHpPA	47	27 %	46	14 %
4-2 FTS	91	10 %	91	13 %
6-2 FTS	87	16 %	100	6 %
8-2 FTS	104	10 %	101	10 %
6-2 FTUA	118	8 %	106	3 %
8-2 FTUA	96	11 %	78	13 %
PFBS	85	14 %	99	1 %
PFPeS	97	15 %	104	2 %
PFHxS	97	15 %	102	1 %
PFHpS	83	11 %	83	3 %
PFOS	92	13 %	94	3 %
PFNS	93	12 %	91	8 %
PFDS	85	4 %	81	6 %

* The PFBA recoveries shown here (112 and 106 %) are background subtracted values.

Conclusions

This Application Note describes a method to extract and analyze 30 per-polyfluoroalkyl substances in water using a WAX SPE cartridge and a 1260/6470 LC/MS/MS system.

References

1. J. Shoemaker; *et al.* Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). *US EPA Document #*: EPA/600/R-08/092.
2. T. Anumol; *et al.* Recommended Plumbing Configurations for Reduction in Per/Polyfluoroalkyl Substance Background with Agilent 1260/1290 Infinity (II) LC Systems. *Agilent Technologies Application Note*, publication number 5991-7863EN.
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4. J. Stevens. Agilent's New Weak Anion Exchange (WAX) Solid Phase Extraction Cartridges: SampliQ WAX. *Agilent Technologies Technical Note*, publication number 5990-5394EN.

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Printed in the USA, September 17, 2018
5994-0250EN