

Analysis of PFAS Extractables in Millex® Syringe Filters using LC/MS/MS

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Introduction

Perfluoroalkyl substances (PFAS), a class of >4,000 perfluorinated compounds also known as “forever chemicals”, represents a class of chemicals utilized in a variety of industries from firefighting foams to non-stick cooking surfaces. Unfortunately, their excellent properties and broad use has led to their persistent accumulation in environmental and biological matrices.

The mounting evidence of potential negative health impacts of PFAS compounds combined with the regulatory landscape evolving at an unprecedented pace has posed a significant analytical challenge.

Rapidly evolving regulations and new matrices

Agencies in the US, Europe, and across the globe have taken action in the last several years, leading to an uptick in published analytical testing methods. Early LC/MS/MS methods such as EPA 537.1 and EPA 533 were focused on detecting PFAS compounds in drinking water matrices and involved limited sample preparation.

As methods began to consider more complex, particulate-laden matrices such as wastewater, biosolids, leachates, and environmental solids, filtration has become an important consideration to sample preparation. Filtering out particulates not only protects sample integrity and analysis, but also instrument and column lifetime. Some selected methods are listed in **Table 1**.

The concern about consumables

The PFAS methods require highly sensitive instruments with low limits of detection, and PFAS ubiquity in the environment increases concern that consumables such as collection bottles, tubing components, syringe filters, and others could be a contamination source for samples¹⁻².

Method(s)	Matrix/ Matrices	Sample Preparation	Analytical Method
EPA 537.1 & EPA 533	Drinking water	SPE	LC-MS/MS
SW-846 Method 8327	Non-potable groundwater, surface water, wastewater	SPE, filtration	LC-MS/MS
ASTM D7968-17a	Environmental solids	Solvent extraction, filtration	LC-MS/MS
ASTM D7979-19	Water matrix (no drinking water)	Solvent extraction, filtration	LC-MS/MS
ISO 21675	Drinking, natural and wastewater	SPE, filtration as needed	LC-MS/MS
OTM-45	Air Emissions	Sampling train: filtration, impingers	LC-MS/MS
EPA Draft 1633	Aqueous, soil, biosolids, sediment, tissue	SPE, filtration	LC-MS/MS

Table 1: A selection of PFAS analytical methods.

The **goal** of this study was to determine if there were detectable PFAS extractables in nonsterile Millex® syringe filters used for sample preparation in LC/MS/MS-based PFAS testing methods.

Experimental

A summary of the methods used for this study is shown in **Figure 1**. EPA 537.1, a test for drinking water, was used to test for PFAS contamination of filtration media in collaboration with SGS North America (Orlando, FL location).

A 250 mL water sample was spiked with surrogates. The internal spike of 0.08 ppb was used for QC blanks. To determine if sample filtration media contributes to PFAS contamination, the entire sample was passed through the filter and into a styrene divinylbenzene (SDVB) SPE cartridge. The sample bottles and tubes were rinsed with basic methanol, passed through the filter and into the cartridge. The entire sample was then subjected to SPE and concentrated to 1 mL in 96:4% (v/v) methanol:water prior to LC/MS/MS analysis using a C18 column. Analysis was performed using C13-labeled internal standards. The nylon and polyethersulfone (PES) syringe filters tested are listed in **Table 2**.

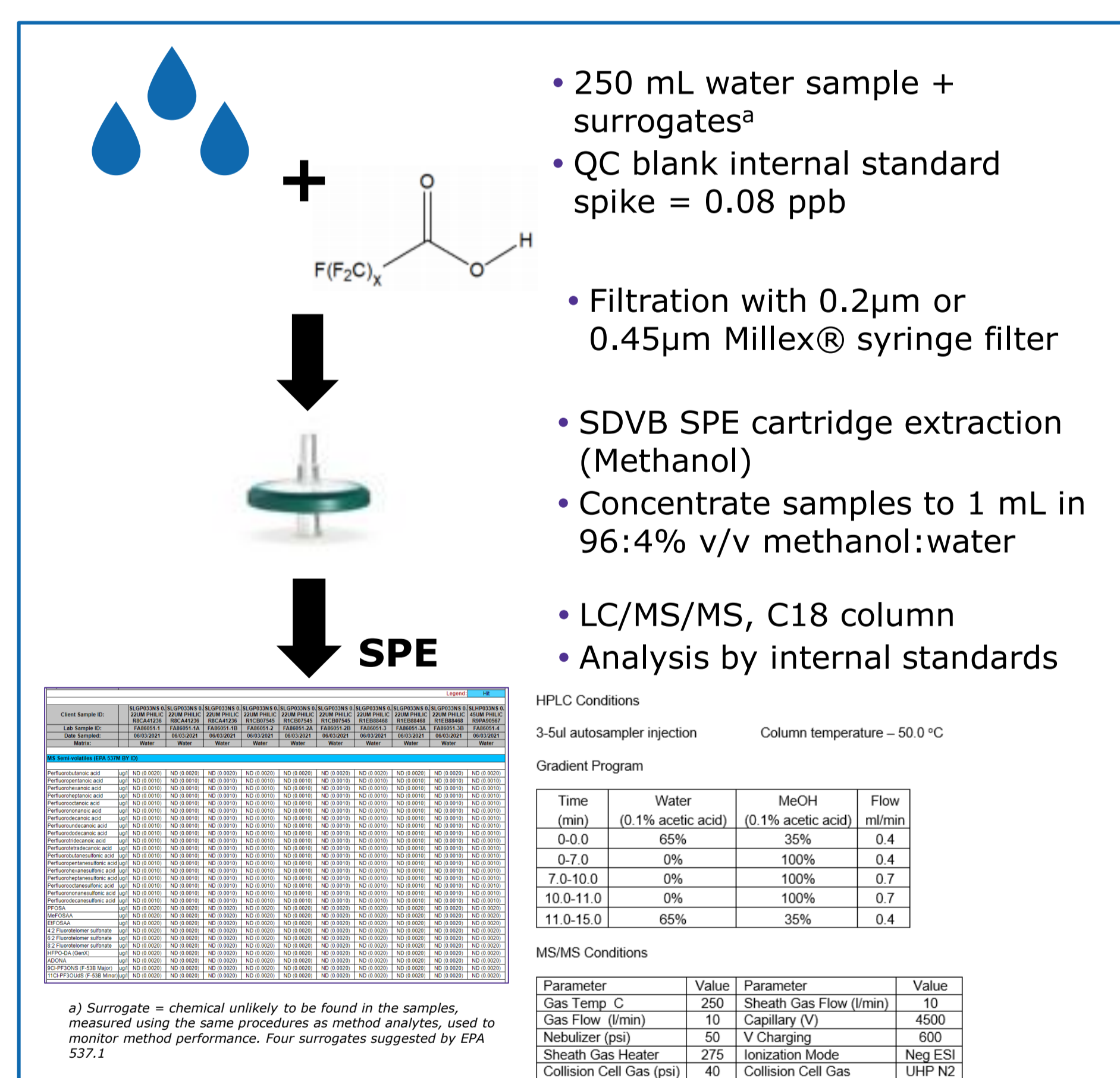


Figure 1: Workflow for testing PFAS extractables.

Cat. No.	Material	Pore (µm)	Diameter (mm)	No. Lots Tested
SLHP033NS	PES	0.45	33	3
SLGP033NS	PES	0.2	33	3
SLGN033NS	Nylon	0.2	33	3
SLGNM025NS	Nylon + glass fiber pre-filter	0.2	25	2

Table 2: Millex® syringe filter devices tested.

Results

Table 3: List of PFAS and extractables results.

Compound	Abbrev.	RL	MDL	Unit	PES 0.2µm			PES 0.45µm			Nylon 0.2µm			Nylon-HPF 0.2µm	
					Lot1	Lot2	Lot3	Lot1	Lot2	Lot3	Lot1	Lot2	Lot3	Lot1	Lot2
Perfluoroalkylcarboxylic acids															
Perfluorobutanoic acid	PFBA	0.0040	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluoropentanoic acid	PFPeA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorohexanoic acid	PFHxA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluoroheptanoic acid	PFHpA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorooctanoic acid	PFOA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorononanoic acid	PFNA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorodecanoic acid	PFDA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluoroundecanoic acid	PFUnDA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorododecanoic acid	PFDoDA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorotridecanoic acid	PFTTrDA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorotetradecanoic acid	PFTeDA	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluoroalkylsulfonic acids, perfluorooctanesulfonamides & perfluorooctanesulfonamidoacetic acids															
Perfluorobutanesulfonic acid	PFBS	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluoropentanesulfonic acid	PFPeS	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorohexanesulfonic acid	PFHxS	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluoroheptanesulfonic acid	PFHpS	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorooctanesulfonic acid	PFOS	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorononanesulfonic acid	PFNS	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Perfluorodecanesulfonic acid	PFDS	0.0020	0.0010	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
PFOSA	PFOSA	0.0040	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
N-MeFOSAA	MeFOSAA	0.0040	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
N-EtFOSAA	EtFOSAA	0.0040	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
Fluorotelomer sulfonates & next generation PFAS analytes															
4:2 Fluorotelomer sulfonate	8:2 FTS	0.0080	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
6:2 Fluorotelomer sulfonate	6:2 FTS	0.0080	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
8:2 Fluorotelomer sulfonate	8:2 FTS	0.0080	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
HFPO-DA	GenX	0.0040	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
ADONA	ADONA	0.0080	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
9C1-PF3ONS (F-53B Major)	--	0.0080	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				
11C1-PF3OUdS (F-53B Minor)	--	0.0080	0.0020	ppb	ND – not detected in filtrate						ND – not detected in filtrate				

Teal color = required compound by EPA 537.1

There were no PFAS extractables detected in any filtrate for the membranes tested below the instrument’s reporting and minimum detection limits (**Table 3**).

Summary & Conclusion

The filtrate collected after filtering with nonsterile Millex® syringe filters made of PES or nylon was tested for PFAS extractables using LC/MS/MS in EPA Method 537.1 in collaboration with SGS North America. None of the 28 PFAS or PFAS-related compounds were detected in the filtrate at the reporting or minimum detection limits of the instrumentation. Therefore, when the filtration of samples is required for those emerging methods involving higher-particulate matrices, nonsterile Millex® filters with PES, nylon, or nylon with a glass fiber prefilter are all suitable options.

References

- Lath S, Knight ER, Navarro DA, Kookana RS, McLaughlin MJ. 2019. Sorption of PFOA onto different laboratory materials: Filter membranes and centrifuge tubes. *Chemosphere*. 222671-678. <http://dx.doi.org/10.1016/j.chemosphere.2019.01.096>
- Labadie P, Chevrel M. 2011. Biogeochemical dynamics of perfluorinated alkyl acids and sulfonates in the River Seine (Paris, France) under contrasting hydrological conditions. *Environmental Pollution*. 159(12):3634-3639. <http://dx.doi.org/10.1016/j.envpol.2011.07.028>

Choosing the right membrane

For most analytical methods involving high particulate matrices, the analyst can choose which type of filter they prefer. **Primary considerations for this choice include:**

- Pore size & Retention
- Chemical Compatibility
- Material and Analyte Binding
- Sample Volume and Membrane Disc Size
- Prefiltration
- Housing Material

Cat. No.	Material	Lots Tested	Average retention of 0.5µm PS Beads
SLHN033NS	Nylon	3	100.0±0.05
SLHP033NS	PES	3	99.50±0.79

Cat. No.	Material	Lots Tested	Average retention of 0.24µm PS Beads
SLGN033NS	Nylon	4	100.0±0.1
SLGNM25NS	Nylon/HPF	2	54.2±27.3
SLGP033NS	PES	3	69.4±28.1

Retention of PES & Nylon Membranes. Pore size is important to consider in comparison to your column size. Many UPLC columns require a 0.2µm filter while for HPLC columns, 0.45µm filters are sufficient.

Abbreviations

MDL = minimum detection limits; RL = reporting limit; LOQ = limit of quantitation; SPE = solid phase extraction; PFAS = perfluoroalkyl substances; LC-MS/MS = liquid chromatography tandem mass spectrometry; PES = polyethersulfone; HPF = high particulate filter; ND = not detected