Polyfluoroalkyl substances (PFAS) in the environment

An investigation of contamination and recovery of PFAS in analytical methods that require filter membranes

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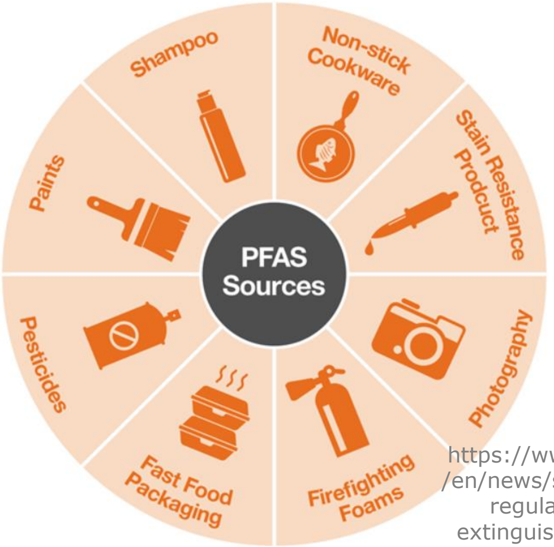
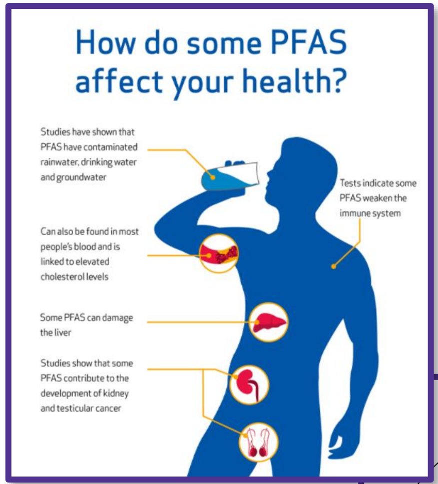
MilliporeSigma is the U.S. and Canada Life Science business of Merck KGaA, Darmstadt, Germany.

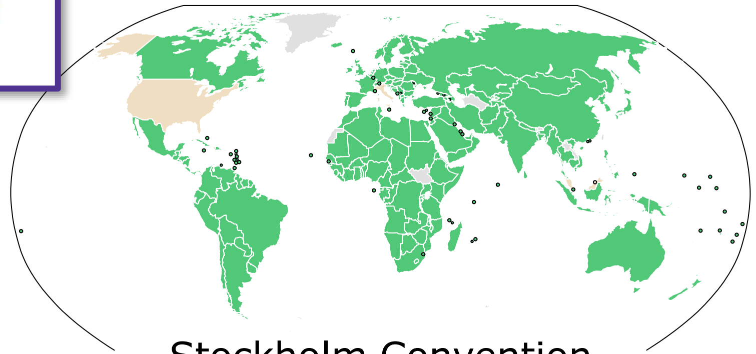
PFAS (Per- and Polyfluoroalkyl Substances)
Perspective on Forever Chemicals

- PFAS is a group of **>4,000** very stable synthetic chemicals [1]
- **Impact on human health** includes cancer, liver damage, weakened immune system, high cholesterol [2]
- Report of **PFAS** found **in the blood of 97% Americans** [1]
- **Stockholm Convention regulations** for **PFOS**, **PFOA** (subset of PFAS compounds). Effective in **2020** [3]
  - **Exemptions**: medical devices, active negotiations for other applications
- EPA's drinking water health advisory level is **70 parts per trillion** for PFAS
- **EPA** recommends testing wastewater for PFAS (**2020**)
- **EPA PFAS Strategic Roadmap (2021)** outlines actions for 2021-2024
- **US EPA proposed levels of PFOA and PFOS to 4.0 ppt (2022)**



https://www.saval.nl/en/news/stricter-eu-regulations-pfas-extinguishing-foam/





Stockholm Convention Signatory Countries

[1] https://www.niehs.nih.gov/health/materials/perfluoroalkyl_and_polyfluoroalkyl_substances_508.pdf
[2] EU/REACH webinar: https://echa.europa.eu/-/restriction-of-per-and-polyfluoroalkyl-substances-pfas-under-reach]
[3] Stockholm convention regulations: http://chm.pops.int/Countries/StatusofRatifications/Amendmentstoannexes/tabid/3486/Default.aspx

Analytical Methods for PFAS Developed at a Rapid Pace
Regulatory Landscape

Method(s)	Update/ Revision	Matrix/Matrices	Sample Prep	Analytical Method
EPA 537.1	Jun. 2020	Drinking water	SPE	LC-MS/MS
EPA 533	Dec. 2019	Drinking water	SPE	LC-MS/MS
SW-846 Method 8327*	Jul. 2021	Non-potable groundwater, surface water, wastewater	SPE, **filtration**	LC-MS/MS
ASTM D7968-17a	Sep. 2017	Environmental solids	Solvent extraction, **filtration**	LC-MS/MS
ASTM D7979-19	Sep. 2021	Water matrix (no drinking water)	Solvent extraction, **filtration**	LC-MS/MS
ISO 25101	Mar. 2019	Drinking water, non-potable water	SPE, solvent elution	LC-MS/MS
ISO 21675	Oct. 2019	Drinking, natural and wastewater	SPE, **filtration** as needed	LC-MS/MS
FDA C-010.02	Dec. 2021	Foods	QuEChERS, SPE, **filtration**	LC-MS/MS
OTM-45	Jan. 2021	Air Emissions (stationary sources)	Sampling train: **filtration**, impingers	LC-MS/MS
EPA Draft 1633	Feb. 2022	Aqueous, soil, biosolids, sediment, tissue	SPE, **filtration**	LC-MS/MS
EPA Draft 1621*	Apr. 2022	Aqueous matrices	TSS, GAC column cleanup	CIC

**screening method only*
Abbreviations: SPE = solid phase extraction; TSS = total suspended solids determination; GAC = granular activated carbon; CIC = combustion ion chromatography
Selected methods; does not include all drinking water and international methods

- Almost exclusively LC-MS/MS based methods
- SPE & filtration are common sample preparation
- Increased focus on high-particulate matrices

Analytical Methods for PFAS Developed at a Rapid Pace

Regulatory Landscape – Filtration only

Method(s)	Sample Prep	Matrix/Matrices	Filter(s) Required by Method
SW-846 Method 8327*	SPE, **filtration**	Non-potable groundwater, surface water, wastewater	0.2µm polypropylene syringe filter (hydrophilic)
ASTM D7968-17a	Solvent extraction, **filtration**	Environmental solids	0.2µm polypropylene syringe filter (hydrophilic)
ASTM D7979-19	Solvent extraction, **filtration**	Water matrix (no drinking water)	0.2µm polypropylene syringe filter (hydrophilic)
ISO 21675	SPE, **filtration** as needed	Drinking, natural and wastewater	1µm GFF syringe filter (rapid) 1-10µm nylon or GFF (if >2g/L suspended matter)
FDA C-010.02	QuEChERS, SPE, **filtration**	Foods	0.2µm nylon syringe filter
OTM-45	Sampling train: **filtration**, impingers	Air Emissions (stationary sources)	GFF or QFF (no pore size listed) membrane filter
EPA Draft 1633	SPE, **filtration**	Aqueous, soil, biosolids, sediment, tissue	0.2µm nylon syringe filter

- Polypropylene, nylon and glass fiber (GFF) are the most common materials
- Filters should not have detectable levels of PFAS compounds above reporting limit (RL) of method

**screening method only*

Abbreviations: SPE = solid phase extraction; TSS = total suspended solids determination; GAC = granular activated carbon; CIC = combustion ion chromatography; philic = hydrophilic; GFF = glass fiber filter; QFF = quartz fiber filter

Selected methods; does not include all drinking water and international methods

Developing Analytical Methods for PFAS
Major concerns about consumables in sample prep

1: Contamination

- Filter may be manufactured in a place with PFAS
  - *Trace amounts observed in nylon, for example* [1,2]
- Filter is fluorinated / contains fluorinated compounds
  - *Generally, want to avoid PVDF, PTFE, but they are common*
- Solvents and/or containers may be contaminated

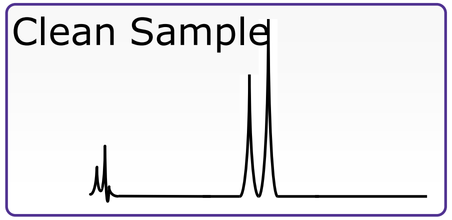
2: Adsorption

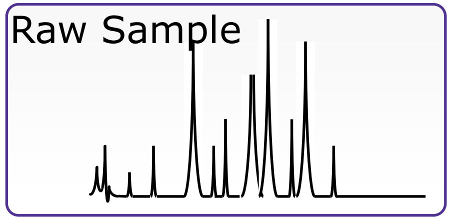
- Filters have different levels of non-specific binding and polarity
  - In nylon, flushing filters can help desorb PFAS analytes [3]
- Tubes, filters, containers all demonstrate time-dependent sorption of various PFAS compounds, leading to recovery losses [3]
  - *Glass fiber & quartz fiber sorption debated* [4]

[1] So, M.K., *et al. Archives of Environmental Contamination and toxicology*, **2006**, *50*, 240-8.
[2] Yamashita, N., *et al. Marine Pollution Bulletin*, **2005**, *51(8-12)*, 658-68.
[3] Lath, S., *et al. Chemosphere*, **2019**, *222*, 671-8.
[4] Zhou, J. et al. *Environmental Science: Processes Impacts*, **2021**, *23*, 580-7.

So, if filters can be "sticky", then why filter?
Importance of Sample Preparation

- Without sample preparation, data quality can be less than optimal





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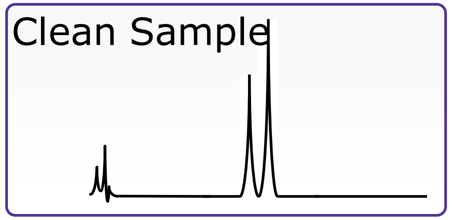
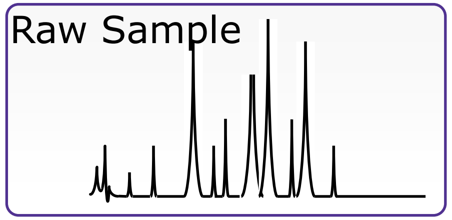
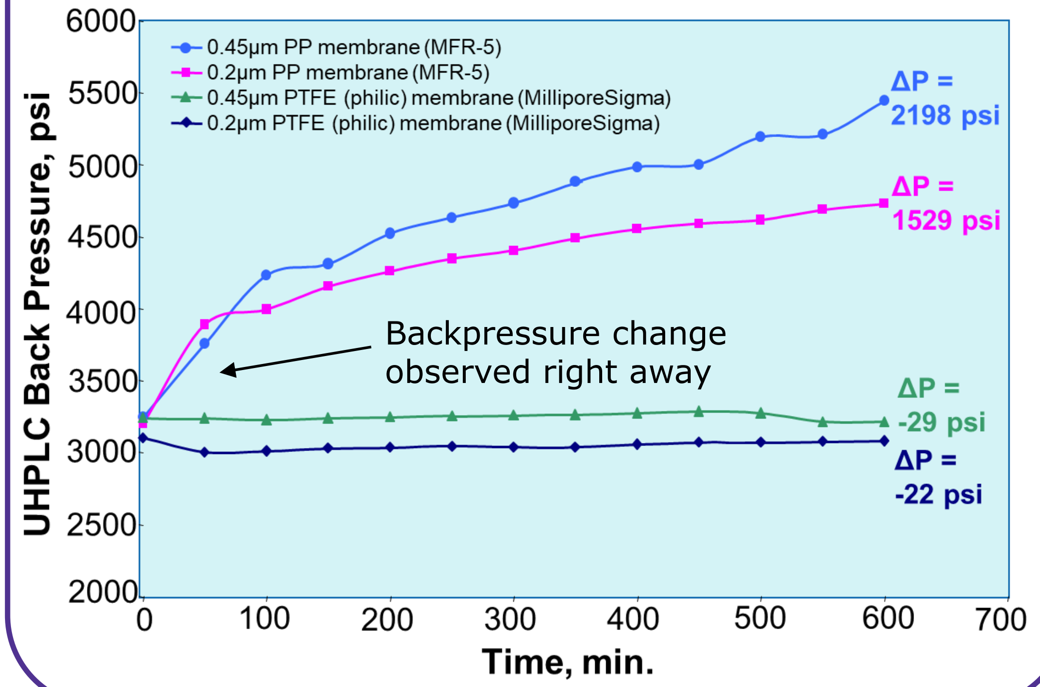




- Undissolved particles **mobile phase** can clog and reduce the life of the chromatography column



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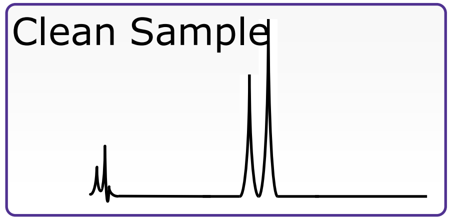

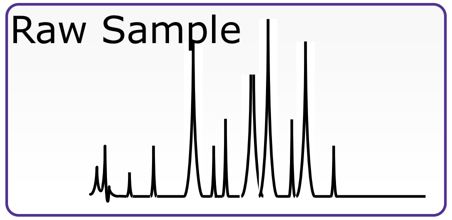

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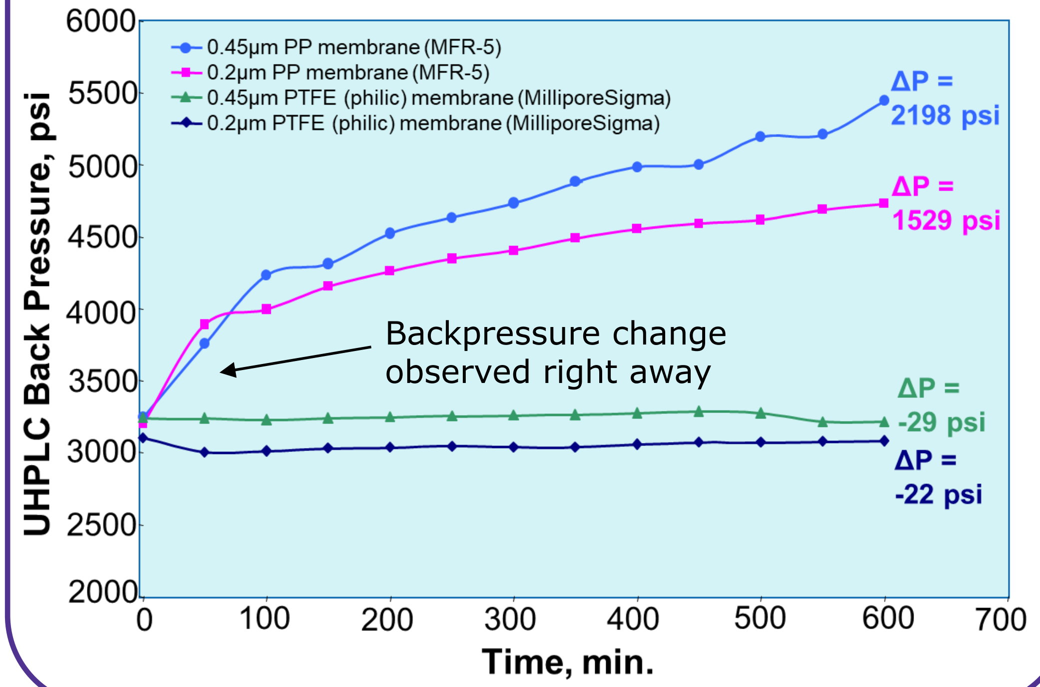
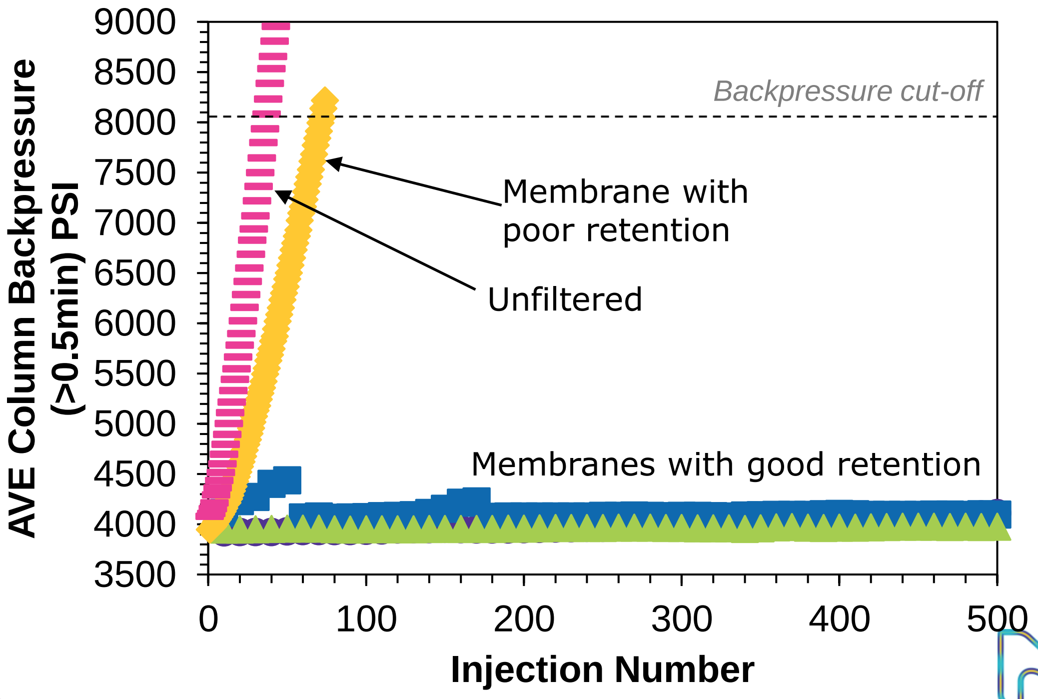
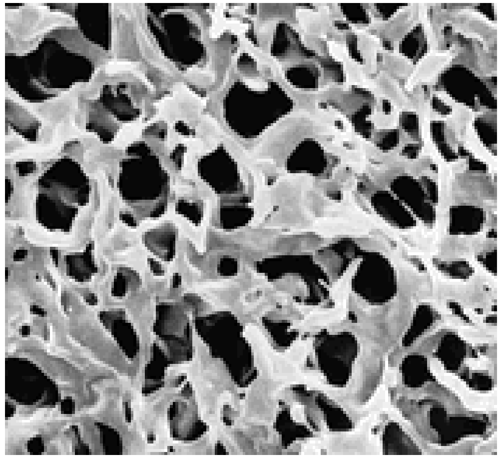


- Undissolved particles in a **sample** can do the same

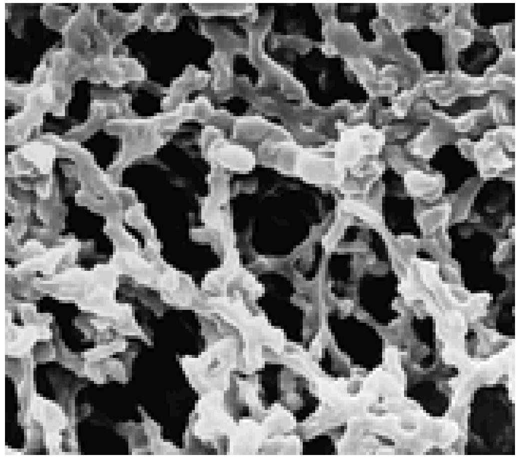


Which Membrane, and Why?

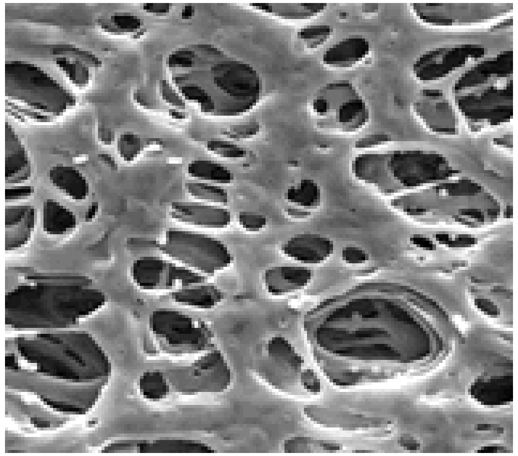
Membrane Morphology & Applications

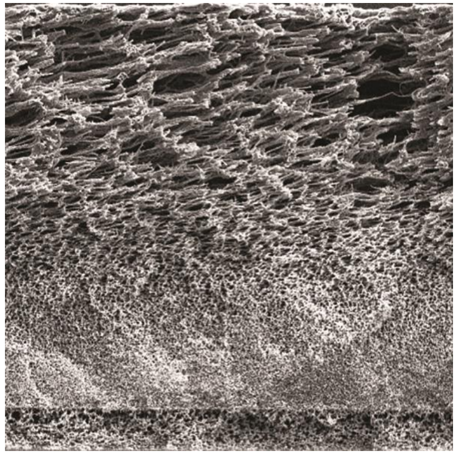


Polyvinylidine Fluoride (PVDF): *Low binding and fast flow for protein sample prep*



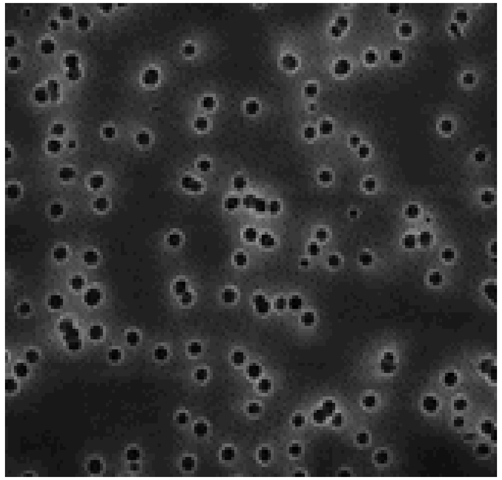
Mixed Cellulose Esters (MCE): *Biologically inert, versatile, smooth and uniform*



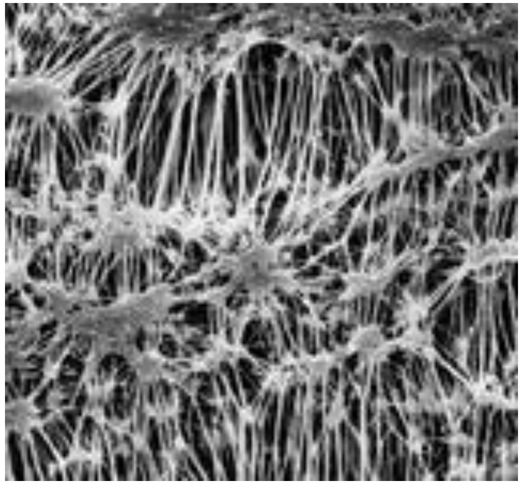


PES Cross-section

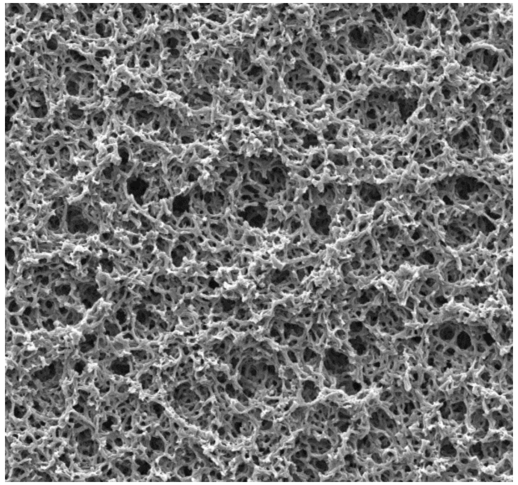
Polyethersulfone (PES): *Quick flow and high capacity, asymmetric for high-particulate water samples*



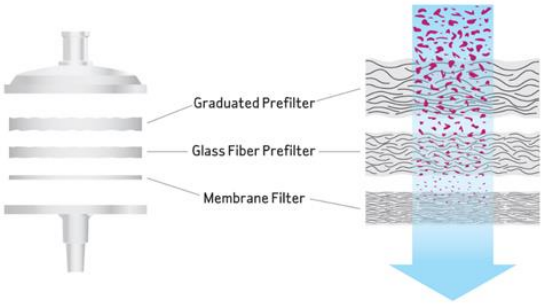
Polycarbonate (PC): *preferred for microscopy and cell-based applications*



Polytetrafluoroethylene (PTFE): *Low extractables and high chemical compatibility*



Nylon: *Broad compatibility and commonly used for HPLC*



Nylon with a Glass Fiber Prefilter (HPF): *One-step cleanup of large and small particulates without clogging*

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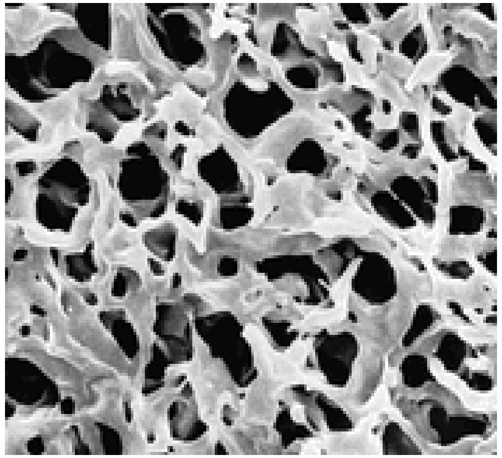

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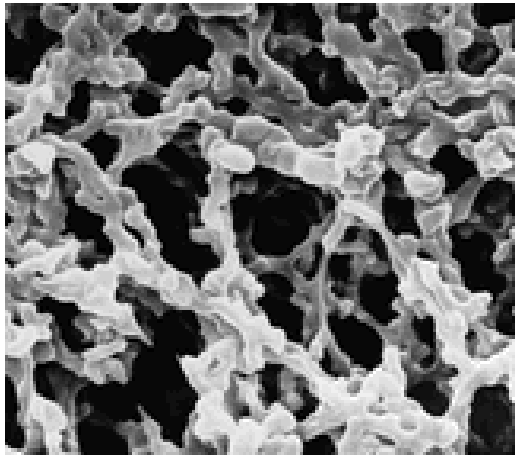

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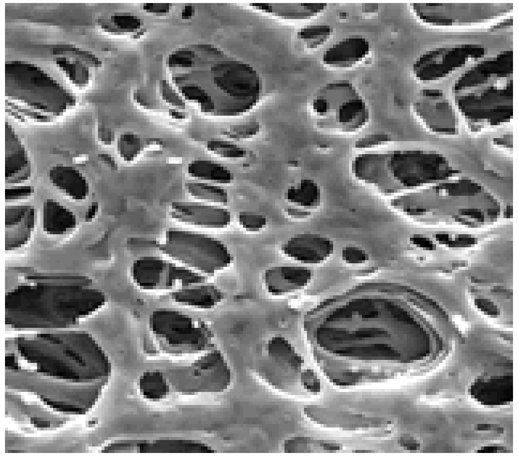

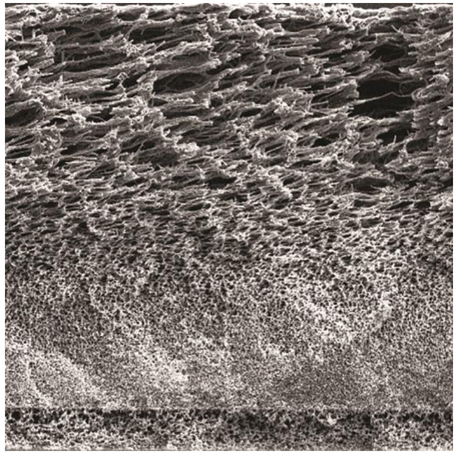

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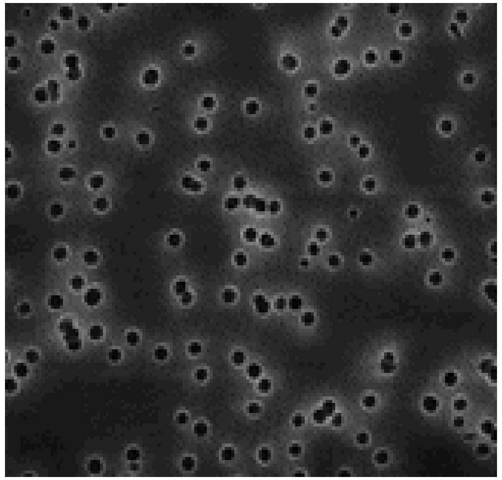

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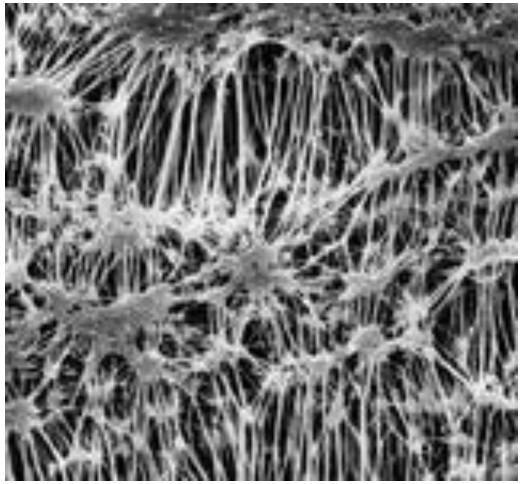

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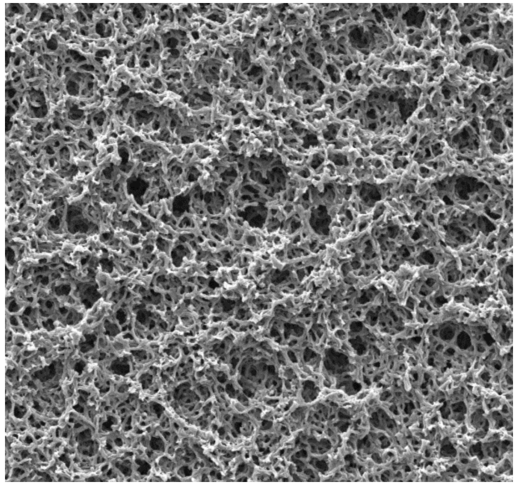
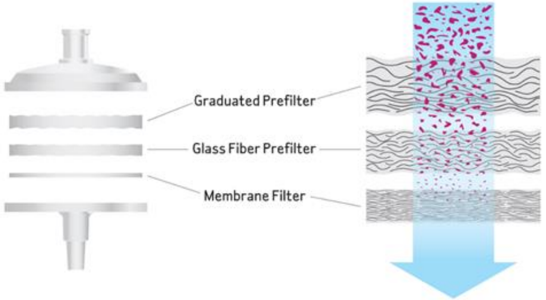


Nylon: *Broad compatibility and commonly used for HPLC*

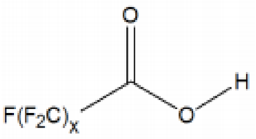


Nylon with a Glass Fiber Prefilter (HPF): *One-step cleanup of large and small particulates without clogging*

Are Membranes Contaminated with PFAS out-of-box?
Testing Syringe Filters using EPA 537.1

28 PFAS analyzed

Overview of Modified EPA 537.1



- 250 mL water sample + surrogates
  - QC blank internal standard spike = 0.08 ppb

- Filtration Millex® syringe filter:
  - 0.22µm PES (3 lots)
  - 0.45µm PES (3 lots)
  - 0.20µm Nylon (3 lots)
  - 0.20µm Nylon-HPF (2 lots)

SPE

- SDVB SPE cartridge extraction (Methanol)

Concentration

- Concentrate samples to 1 mL in 96:4% v/v Methanol:Water

LC-MS/MS

- LC-MS/MS, C18 column
- Analysis by internal standards

LC-MS/MS Conditions

Column:	C18, 100 x 2.1mm ID, 2.7 µm superficially porous particles
Mobile phase:	[A] DI Water, 0.1% (v/v) acetic acid; [B] Methanol (MeOH), 0.1% (v/v) acetic acid
Gradient:	See table below
Flow rate:	See gradient table
Detection:	MS/MS, ESI(-), details of MS/MS conditions can be requested from the author
Column temp:	50.0 °C
Injection volume:	3-5 µL autosampler injection
Sample :	SPE eluate concentrated to 1 mL methanol: water, 96:4% (v/v)

Gradient:

Time (min)	A %	B %	Flow (mL/min)
0-0.0	65%	35%	0.4
0-7.0	0%	100%	0.4
7.0-10.0	0%	100%	0.7
10.0-11.0	0%	100%	0.7
11.0-15.0	65%	35%	0.4

Data collected in collaboration with: SGS *(Orlando, FL)*

Testing Syringe Filters using EPA 537.1

Millex® syringe filters do not have detectable levels of PFAS contaminants

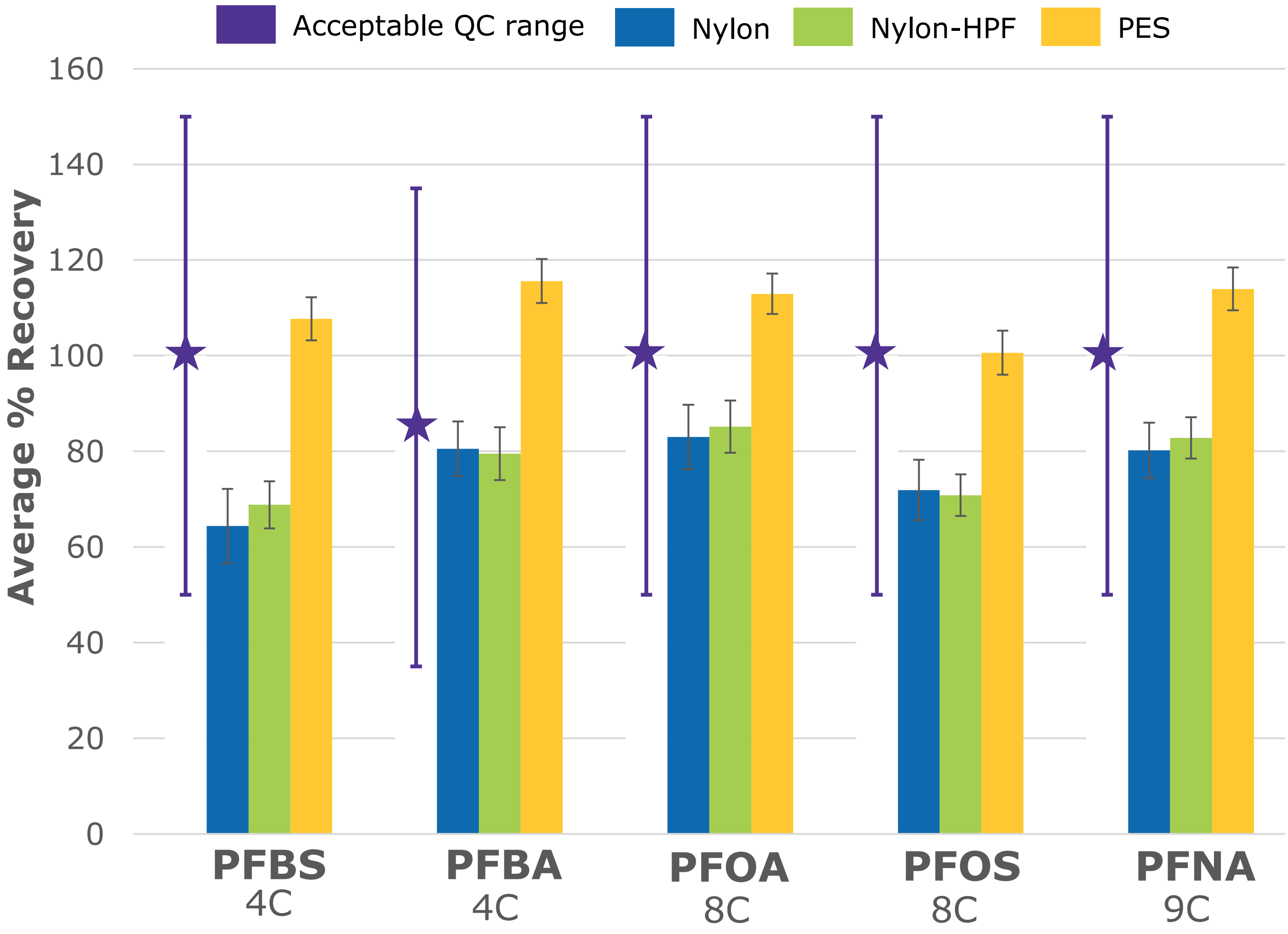
28 PFAS analyzed

Compound(s)	RL (ppb)	MDL (ppb)	Millex® Syringe Filter 0.22µm PES[a]	0.45µm PES[a]	0.20µm nylon[a]	0.20µm nylon-HPF[b]
Perfluoroalkyl carboxylic acids – PFBA	0.0040	0.0020	**ND** – not detected			
Perfluoroalkyl carboxylic acids – PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA	0.0020	0.0010	**ND** – not detected			
Perfluoroalkyl sulfonic acids – PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS	0.0020	0.0010	**ND** – not detected			
Fluorotelomer sulfonic acids – 4:2 FTS, 6:2 FTS, 8:2 FTS	0.0080	0.0020	**ND** – not detected			
Perfluorooctane sulfonamides – PFOSA	0.0040	0.0020	**ND** – not detected			
Perfluorooctane sulfonamidoacetic acids – N-MeFOSAA, NEt-FOSAA	0.0040	0.0020	**ND** – not detected			
Per and Polyfluoroether sulfonic acids – 9Cl-PF3ONS, 11Cl-PF3OUdS	0.0080	0.0020	**ND** – not detected			
Per and Polyfluoroether carboxylic acids – GenX	0.0040	0.0020	**ND** – not detected			
Per and Polyfluoroether carboxylic acids – ADONA	0.0080	0.0020	**ND** – not detected			

A] Values represent average of 3 lots tested, n=3 devices per lot; B] Values represent average of 2 lots tested, n=3 devices per lot.
ABBREVIATIONS: RL = reporting limit, ppb; MDL = minimum detection limit, ppb; PES = polyethersulfone

Testing Syringe Filters using EPA 537.1
There are variations in recovery of C-13 labeled standards

28 PFAS analyzed



- Filtered solvent: **water**
- Nylon demonstrates lower recoveries than PES
- Presence of glass fiber did not make a difference

- **Similar trends reported** previously for PES vs. nylon in aqueous solutions [1]

[1] Lath, S., *et al*. *Chemosphere*, **2019**, *222*, 671-8.

Analytical Methods for PFAS Developed at a Rapid Pace

Regulatory Landscape – EPA Draft 1633

Method(s)	Sample Prep	Matrix/Matrices	Filter(s) Required by Method
SW-846 Method 8327*	SPE, **filtration**	Non-potable groundwater, surface water, wastewater	0.2µm polypropylene syringe filter (hydrophilic)
ASTM D7968-17a	Solvent extraction, **filtration**	Environmental solids	0.2µm polypropylene syringe filter (hydrophilic)
ASTM D7979-19	Solvent extraction, **filtration**	Water matrix (no drinking water)	0.2µm polypropylene syringe filter (hydrophilic)
ISO 21675	SPE, **filtration** as needed	Drinking, natural and wastewater	1µm GFF syringe filter (rapid) 1-10µm nylon or GFF (if >2g/L suspended matter)
FDA C-010.02	QuEChERS, SPE, **filtration**	Foods	0.2µm nylon syringe filter
OTM-45	Sampling train: **filtration**, impingers	Air Emissions (stationary sources)	GFF or QFF (no pore size listed) membrane filter
EPA Draft 1633	SPE, **filtration**	Aqueous, soil, biosolids, sediment, tissue	0.2µm nylon syringe filter

- Polypropylene, nylon and glass fiber (GFF) are the most common materials
- Filters should not have detectable levels of PFAS compounds above reporting limit (RL) of method

**screening method only*

Abbreviations: SPE = solid phase extraction; TSS = total suspended solids determination; GAC = granular activated carbon; CIC = combustion ion chromatography; philic = hydrophilic; GFF = glass fiber filter; QFF = quartz fiber filter
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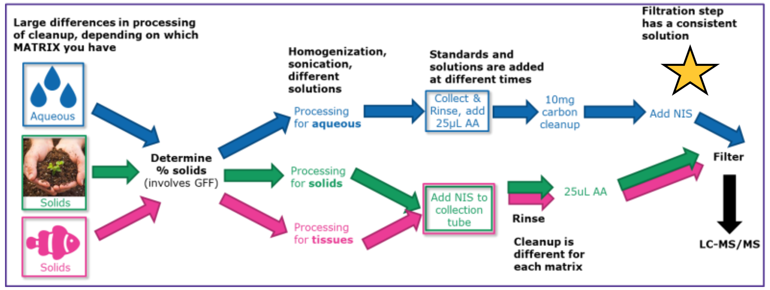
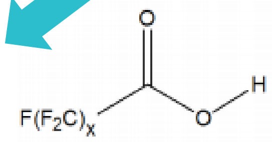
Are Membranes Contaminated with PFAS out-of-box?
Testing Syringe Filters using EPA 537.1

Overview of Modified EPA Draft 1633



- Isolate filtration portion of EPA Draft 1633 for Aqueous samples



- 5 mL methanol sample + extracted & non-extracted internal standards mixes (EIS/NIS)

- Filtration with Millex® syringe filter

LC-MS/MS

- LC-MS/MS, C18 column
- Analysis by internal standards

LC-MS/MS Conditions

Column:	C18, 2.7µm, 100x2.1mm ID, superficially porous column
Mobile phase:	[A] Acetonitrile [B] 2 mM ammonium acetate in 95:5 water: acetonitrile
Gradient:	see table below
Flow rate:	See gradient table
Detection:	MS/MS ESI(-), details of MS/MS conditions can be found at sigmaaldrich.com/pfassamplefiltration
Column temp:	50.0°C
Injection volume:	6-10µL autosampler injection
Sample:	5mL methanol sample + EIS/NIS mixes

Gradient:

Time (min)	A %	B%	Flow (mL/min)
0.20	10.0%	90.0%	0.350
4.00	30.0%	70.0%	0.350
7.00	55.0%	45.0%	0.350
9.00	75.0%	25.0%	0.350
10.00	95.0%	5.0%	0.400
10.30	95.0%	5.0%	0.400
10.40	2.0%	98.0%	0.400
11.80	2.0%	98.0%	0.400
13.00	2.0%	98.0%	0.400

Data collected in collaboration with: SGS *(Orlando, FL)*

Testing Syringe Filters using EPA Draft 1633

Millex® syringe filters do not have levels of PFAS above RL

40 PFAS analyzed

Compound(s)	RL* (ppb)	Syringe Filter Device: Millipore® 0.22µm PES[P]	Millipore® 0.20µm Nylon[P]	MFR-5 0.2µm Nylon[P]	Millipore® 0.20µm nylon-HPF: Lot1	Millipore® 0.20µm nylon-HPF: Lot2[Q]
Perfluoroalkyl carboxylic acids						
PFBA	0.8[A]	ND	ND	ND	ND	ND
PFPeA	0.4[B]	ND	ND	ND	ND	ND
PFHxA, PFHpA, PFOA, PFNA, PFUnDA, PFDoDA, PFTrDA, PFTeDA	0.2[C]	ND	ND	ND	ND[R]	ND
Perfluoroalkyl sulfonic acids						
PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS	0.2[D]	ND	ND	ND	ND	ND
Fluorotelomer sulfonic acids						
4:2 FTS, 6:2 FTS, 8:2 FTS	0.8[E]	ND	ND	ND	ND	ND
Fluorotelomer carboxylic acids						
3:3 FTCA	1[F]	ND	ND	ND	ND	ND
5:3 FTCA, 7:3 FTCA	5[G]	ND	ND	ND	ND	ND
Perfluorooctane sulfonamides, Perfluorooctane sulfonamidoacetic acids & Perfluorooctane sulfonoamido ethanols						
FOSA, N-MeFOSA, N-EtFOSA,	0.2[H]	ND	ND	ND	ND	ND
N-MeFOSAA, N-EtFOSAA	0.2[I]	ND	ND	ND	ND	ND
N-MeFOSE, N-EtFOSE	2[J]	ND	ND	ND	ND	ND
Per and Polyfluoroether carboxylic acids & Per and Polyfluoroether sulfonic acids						
GenX, ADONA	0.8[K]	ND	ND	ND	ND	ND
PFMPA, PFMBA, NFDHA	0.4[L]	ND	ND	ND	ND	ND
9Cl-PF3ONS, 11Cl-PF3OUdS	0.8[M]	ND	ND	ND	ND	ND
PFEESA	0.4[N]	ND	ND	ND	ND	ND

*Minimum detection limits, MDL (ppb), ranged depending on analyte of interest:

A] 0.4
B] 0.1
C] 0.05-0.081
D] 0.1-0.11
E] 0.4-0.41
F] 0.5
G] 1
H] 0.1
I] 0.1-0.13
J] 1
K] 0.2
L] 0.1-0.12
M] 0.2
N] 0.1

P] Average of 2 lots, n=3 devices per lot; Q] Fourth device tested after hits reported in first replicate device and result was ND; R] Out of n=3 devices, 1 demonstrated hits above MDL but below RL

ABBREVIATIONS: RL = reporting limit, ppb; MDL = minimum detection limit, ppb; PES = polyethersulfone; HPF = High particulate filter

Testing Syringe Filters using EPA Draft 1633

Millex® syringe filters do not have levels of PFAS above RL

40 PFAS analyzed

Compound(s)	RL* (ppb)	Syringe Filter Device				
		Millipore® 0.22µm PES[P]	Millipore® 0.20µm Nylon[P]	MFR-5 0.2µm Nylon[P]	Millipore® 0.20 nylon-HPF	
					Lot1	Lot
Perfluoroalkyl carboxylic acids						
PFBA	0.8[A]	ND	ND	ND	ND	NI
PFPeA	0.4[B]	ND	ND	ND	ND	NI
PFHxA, PFHpA, PFOA, PFNA, PFUnDA, PFDoDA, PFTrDA, PFTeDA	0.2[C]	ND	ND	ND	ND[R]	NI
Perfluoroalkyl sulfonic acids						
PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS	0.2[D]	ND	ND	ND	ND	NI
Fluorotelomer sulfonic acids						
4:2 FTS, 6:2 FTS, 8:2 FTS	0.8[E]	ND	ND	ND	ND	ND
Fluorotelomer carboxylic acids						
3:3 FTCA	1[F]	ND	ND	ND	ND	ND
5:3 FTCA, 7:3 FTCA	5[G]	ND	ND	ND	ND	ND
Perfluorooctane sulfonamides, Perfluorooctane sulfonamidoacetic acids & Perfluorooctane sulfonoamido ethanols						
FOSA, N-MeFOSA, N-EtFOSA,	0.2[H]	ND	ND	ND	ND	ND
N-MeFOSAA, N-EtFOSAA	0.2[I]	ND	ND	ND	ND	ND
N-MeFOSE, N-EtFOSE	2[J]	ND	ND	ND	ND	ND
Per and Polyfluoroether carboxylic acids & Per and Polyfluoroether sulfonic acids						
GenX, ADONA	0.8[K]	ND	ND	ND	ND	ND
PFMPA, PFMBA, NFDHA	0.4[L]	ND	ND	ND	ND	ND
9Cl-PF3ONS, 11Cl-PF3OUdS	0.8[M]	ND	ND	ND	ND	ND
PFEESA	0.4[N]	ND	ND	ND	ND	ND

Compound	Device1	Device2	Device3
PFHxA	ND	ND	**0.0835**
PFHpA	ND	ND	**0.0688**
PFOA	ND	ND	**0.0992**
PFNA	ND	ND	**0.0827**
PFDA	ND	ND	**0.115**
PFUnDA	ND	ND	**0.107**
PFDoDA	ND	ND	**0.113**
PFTrDA	ND	ND	**0.116**
PFTeDA	ND	ND	**0.149**

*Minimum detection limits, MDL (ppb), ranged depending on analyte of interest:

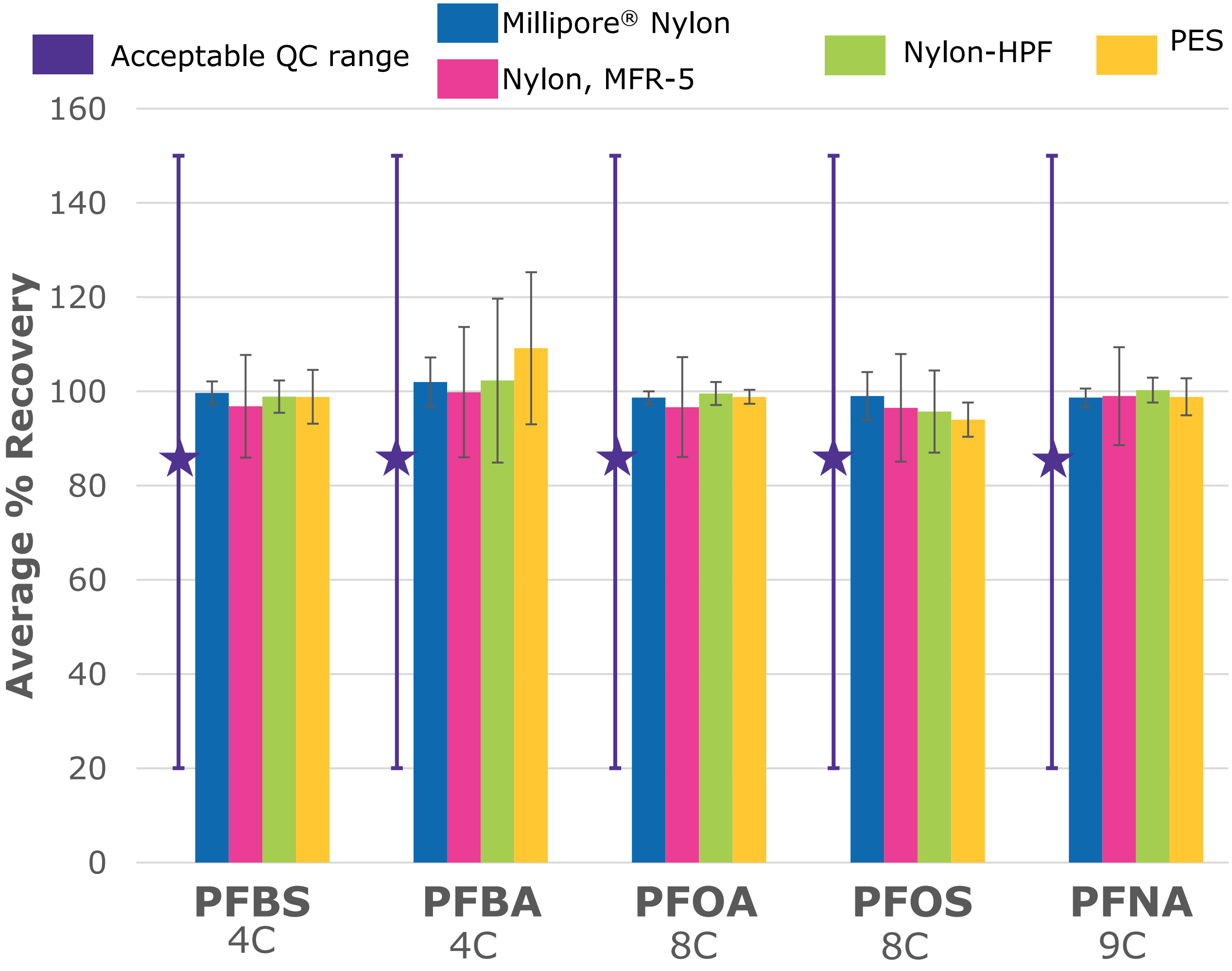
A] 0.4
B] 0.1
C] 0.05-0.081
D] 0.1-0.11
E] 0.4-0.41
F] 0.5
G] 1
H] 0.1
I] 0.1-0.13
J] 1
K] 0.2
L] 0.1-0.12
M] 0.2
N] 0.1

P] Average of 2 lots, n=3 devices per lot; Q] Fourth device tested after hits reported in first replicate device and result was ND; R] Out of n=3 devices, 1 demonstrated hits above MDL but below RL

ABBREVIATIONS: RL = reporting limit, ppb; MDL = minimum detection limit, ppb; PES = polyethersulfone; HPF = High particulate filter

Testing Syringe Filters using EPA Draft 1633
Methanol solvent improves PFAS analyte recoveries

40 PFAS analyzed



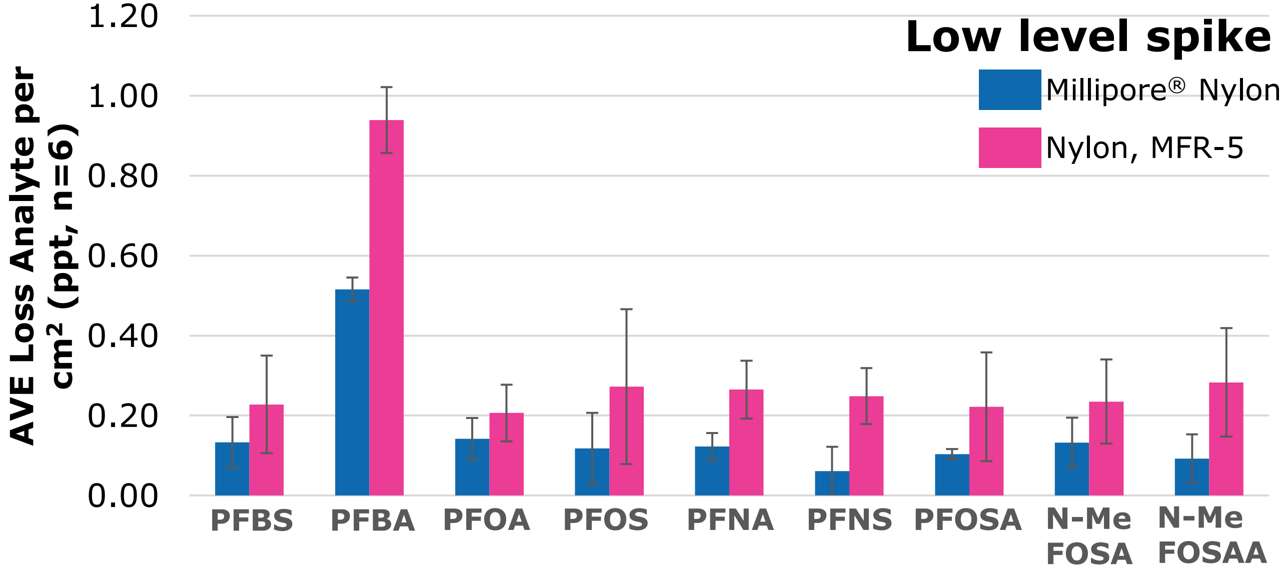
- Filtered solvent: **methanol**
- All filters show similar recoveries
- Presence of glass fiber did not make a difference
- Much improved recovery for Nylon and similar for PES (vs. **water**)

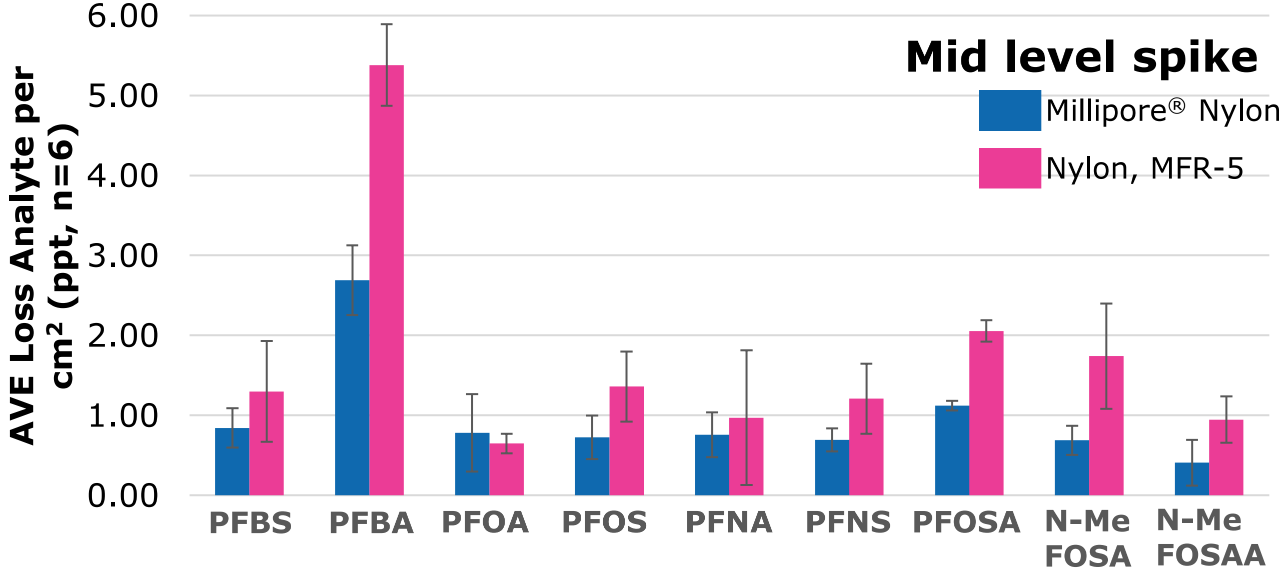
- **Consistent with literature:** a wash with methanol caused PFOS, PFOA and other PFAS to desorb significantly from nylon filter media [1]

[1] So, M.K., *et al. Archives of Environmental Contamination and toxicology*, **2006**, *50*, 240-8.

Testing Syringe Filters using EPA Draft 1633 in the ppt range
Millex® syringe filters do not have levels of PFAS above RL

40 PFAS analyzed





- **Full workflow of EPA Draft 1633 tested, using aqueous matrix**
  - **Spike**: Low- and Mid-level
  - **Solvent filtered**: **Methanol**
- **Syringe Filters Tested:**
  - Millipore® 0.20µm Nylon (33mm diameter)
  - MFR-5 0.20µm Nylon (25mm diameter)

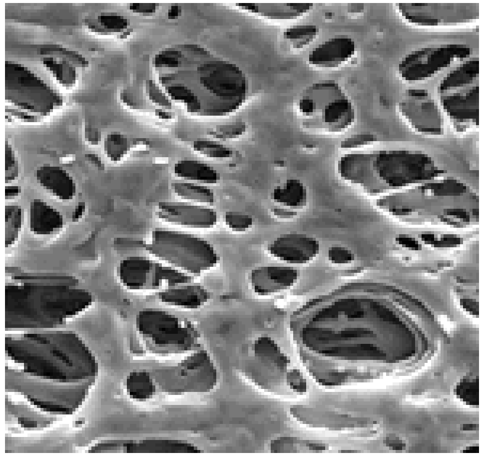
- No PFAS compounds detected in any device above RL **= no contamination**
- The loss of analyte was similar per cm^2 of filter area for each syringe filter type **= larger filtration areas do not lead to more analyte loss**

Data collected in collaboration with:

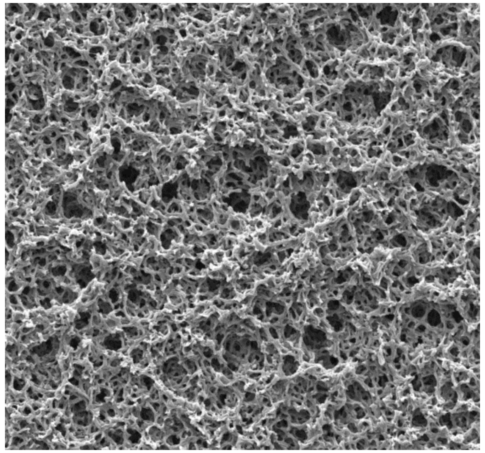
ALPHA ANALYTICAL World Class Chemistry

(Mansfield, MA)

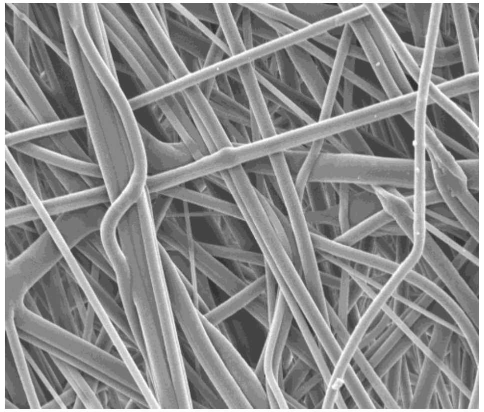
Which Membrane, and Why?
Membrane Morphology & Applications



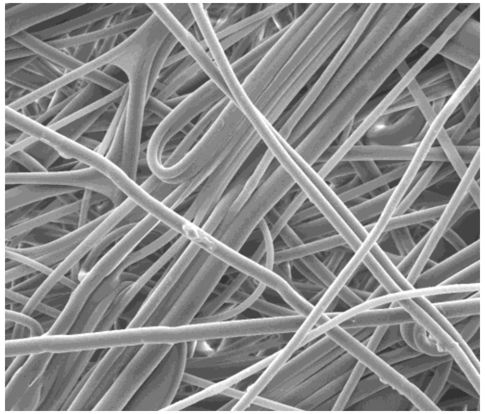
Polyethersulfone (PES)



Nylon



Hydrophilic polypropylene



Hydrophobic polypropylene

Syringe Filter Devices: Millex®

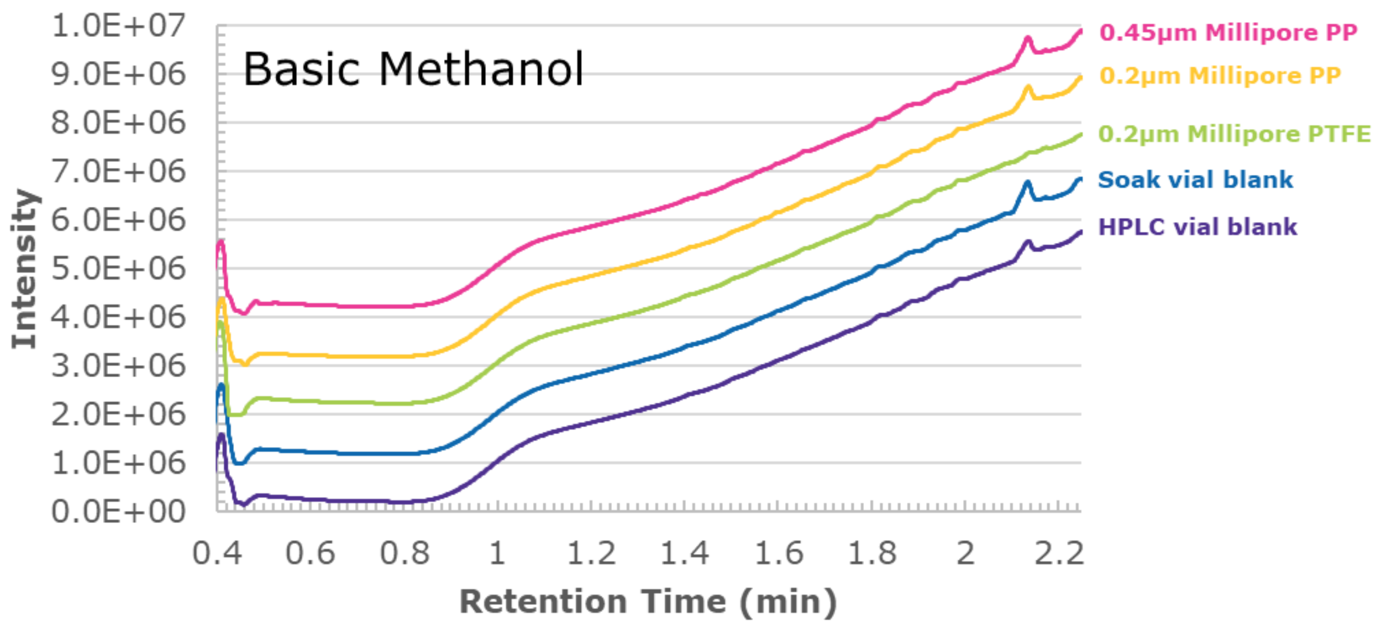
Millipore® cut disc membrane filters

A good option for mobile phase & sample prep because:

- Great chemical compatibility (comparable to hydrophilic PTFE) and low extractables
- Suitable retention of particles in both air and liquid
- High stability to heating
- Hydrophilic & hydrophobic options (most are hydrophobic)
- Suggested in some PFAS methods

Which Membrane, and Why?
Membrane Morphology & Applications

Low Extractables in PFAS relevant solvents



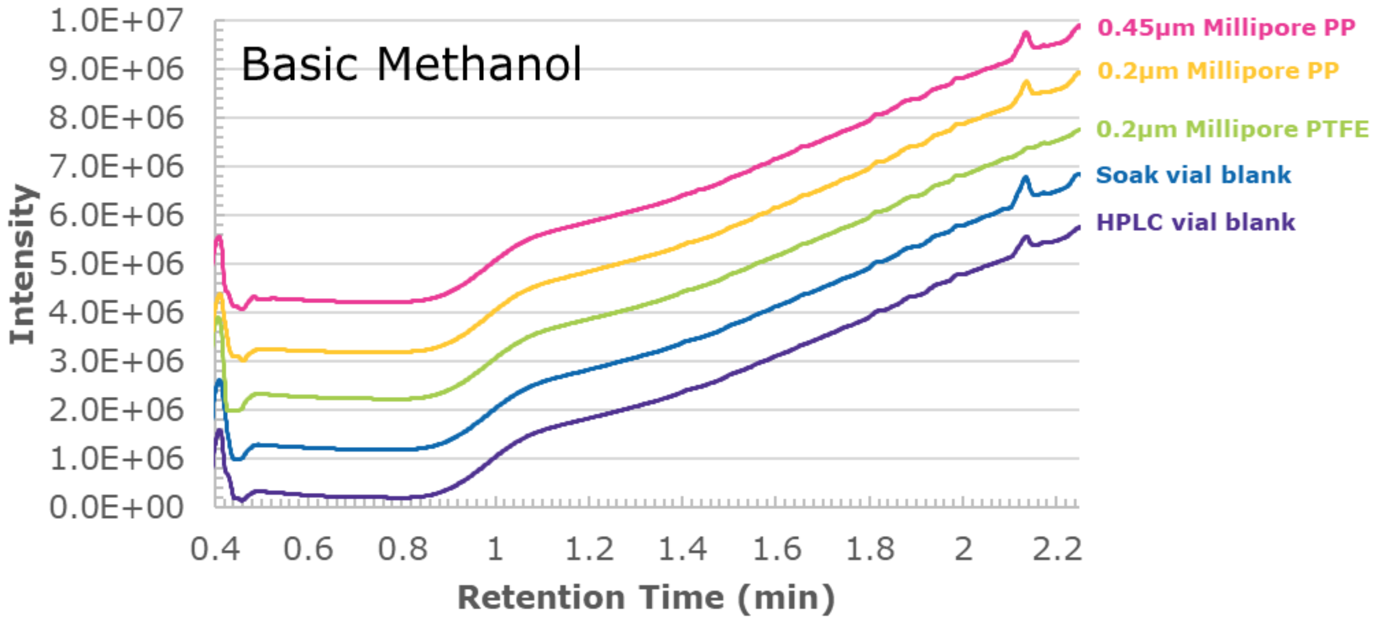
PTFE = polytetrafluoroethylene; PP = polypropylene (hydrophilic)

A good option for mobile phase & sample prep because:

- **Great chemical compatibility (comparable to hydrophilic PTFE) and low extractables**
- Suitable retention of particles in both air and liquid
- High stability to heating
- Hydrophilic & hydrophobic options (most are hydrophobic)
- Suggested in some PFAS methods

Which Membrane, and Why?
Membrane Morphology & Applications

Low Extractables in PFAS relevant solvents



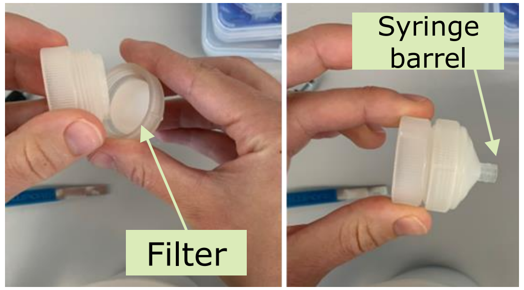
PTFE = polytetrafluoroethylene; PP = polypropylene (hydrophilic)

A good option for mobile phase & sample prep because:

- **Great chemical compatibility (comparable to hydrophilic PTFE) and low extractables**
- Suitable retention of particles in both air and liquid
- High stability to heating
- Hydrophilic & hydrophobic options (most are hydrophobic)
- Suggested in some PFAS methods

Use Swinnex® to test polypropylene according to EPA 537.1 (water)

Use Swinnex® to test polypropylene according to EPA Draft 1633 (methanol)



Swinnex®

28 PFAS analyzed

Testing Polypropylene Membranes using EPA 537.1

Polypropylene membrane filters (and Swinnex®) do not have detectable levels of PFAS contaminants

Compound(s)	RL (ppb)	MDL (ppb)	Millipore® Polypropylene Membranes in Swinnex®			
			Hydrophobic[a]		Hydrophilic[a]	
			0.20µm	0.45µm	0.2µm	0.45µm
Perfluoroalkyl carboxylic acids – PFBA	0.0040	0.0020	ND	ND	ND	ND
Perfluoroalkyl carboxylic acids – PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA	0.0020	0.0010	ND	ND	ND	ND
Perfluoroalkyl carboxylic acids – PFDoDA, PFTrDA, PFTeDA	0.0020	0.0010	ND[b]	ND[b]	ND	ND
Perfluoroalkyl sulfonic acids – PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS	0.0020	0.0010	ND	ND	ND	ND
Fluorotelomer sulfonic acids – 4:2 FTS, 6:2 FTS, 8:2 FTS	0.0080	0.0020	ND	ND	ND	ND
Perfluorooctane sulfonamides – PFOSA	0.0040	0.0020	ND	ND	ND	ND
Perfluorooctane sulfonamidoacetic acids – N-MeFOSAA	0.0040	0.0020	ND	ND	ND	ND
Perfluorooctane sulfonamidoacetic acids –NEt-FOSAA	0.0040	0.0020	ND[b]	ND[b]	ND	ND
Per and Polyfluoroether sulfonic acids – 9Cl-PF3ONS, 11Cl-PF3OUdS	0.0080	0.0020	ND	ND	ND	ND
Per and Polyfluoroether carboxylic acids – GenX	0.0040	0.0020	ND	ND	ND	ND
Per and Polyfluoroether carboxylic acids – ADONA	0.0080	0.0020	ND	ND	ND	ND

A] Values represent average of 3 devices tested over 1 lot; B] Associated internal standard outside of control limits for all three devices tested: 13C2-PFDoDA, 13C2-PFTeDA, d5-EtFOSAA.
ABBREVIATIONS: RL = reporting limit, ppb; MDL = minimum detection limit, ppb; PP = polypropylene; philic = hydrophilic; phobic = hydrophobic

Testing Hydrophilic Polypropylene Membranes using EPA Draft 1633

Hydrophilic polypropylene membrane filters (and Swinnex®) do not have detectable levels of PFAS contaminants

40 PFAS analyzed

Compound(s)	RL (ppb)	MDL Range* (ppb)	Millipore® Hydrophilic Polypropylene Membranes in Swinnex®, 0.2µm		
			Lot1	Lot2	Lot3
Perfluoroalkyl carboxylic acids					
PFBA	0.8	0.4	ND	ND	ND
PFPeA	0.4	0.1	ND	ND	ND
PFHxA, PFHpA, PFOA, PFNA, PFUnDA, PFDoDA, PFTrDA, PFTeDA	0.2	0.05-0.081	ND	ND	ND
Perfluoroalkyl sulfonic acids					
PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFDoS	0.2	0.1-0.11	ND	ND	ND
Fluorotelomer sulfonic acids					
4:2 FTS, 6:2 FTS, 8:2 FTS	0.8	0.4-0.41	ND	ND	ND
Fluorotelomer carboxylic acids					
3:3 FTCA	1	0.5	ND	ND	ND
5:3 FTCA, 7:3 FTCA	5	1	ND	ND	ND
Perfluorooctane sulfonamides, Perfluorooctane sulfonamidoacetic acids & Perfluorooctane sulfonoamido ethanols					
FOSA, N-MeFOSA, N-EtFOSA	0.2	0.1	ND	ND	ND
N-MeFOSAA, N-EtFOSAA	0.2	0.1-0.13	ND	ND	ND
N-MeFOSE, N-EtFOSE	2	1	ND	ND	ND
Per and Polyfluoroether carboxylic acids & Per and Polyfluoroether sulfonic acids					
GenX, ADONA	0.8	0.2	ND	ND	ND
PFMPA, PFMBA, NFDHA	0.4	0.1-0.12	ND	ND	ND
9Cl-PF3ONS, 11Cl-PF3OUdS	0.8	0.2	ND	ND	ND
PFEESA	0.4	0.1	ND	ND	ND

- 0.2µm hydrophilic polypropylene tested only

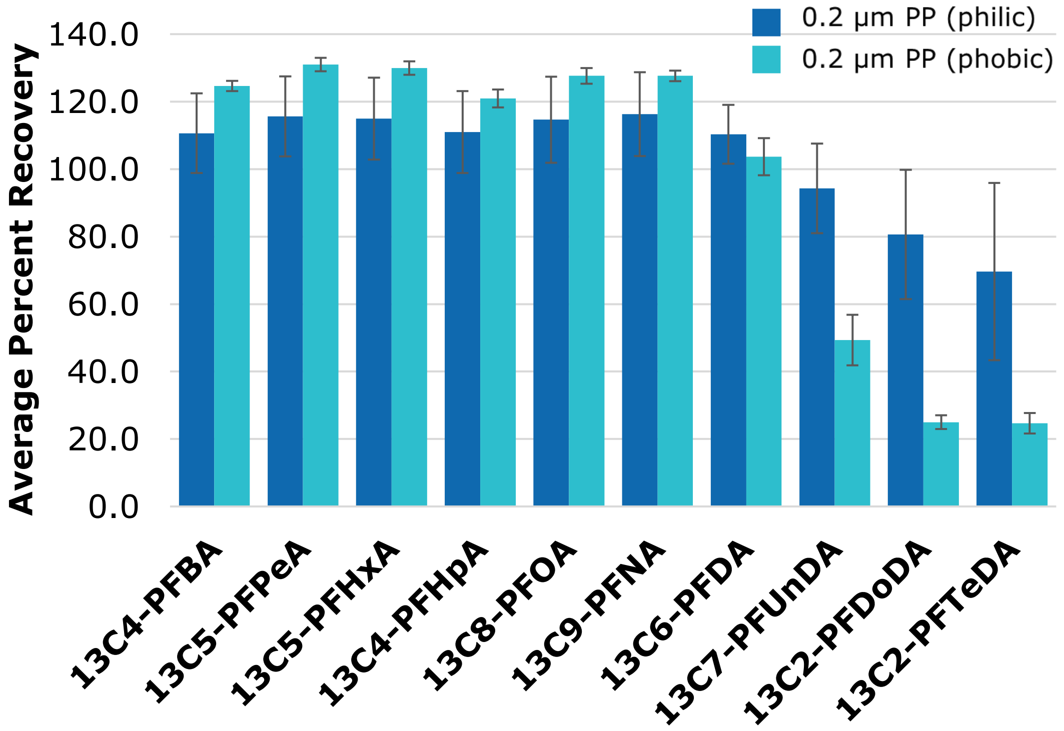
*Minimum detection limits, MDL (ppb), ranged depending on analyte of interest. Refer to sigmaaldrich.com/pfassamplfiltration for details.

a] Extracted internal standards (EIS): 13C4-PFBA, 13C5-PFPeA, 13C5-PFHxA, 13C4-PFHpA, 13C8-PFOA; b] Values represent the average of n=3 devices for each lot. No PFAS compound detected in any device above RL or MDL.

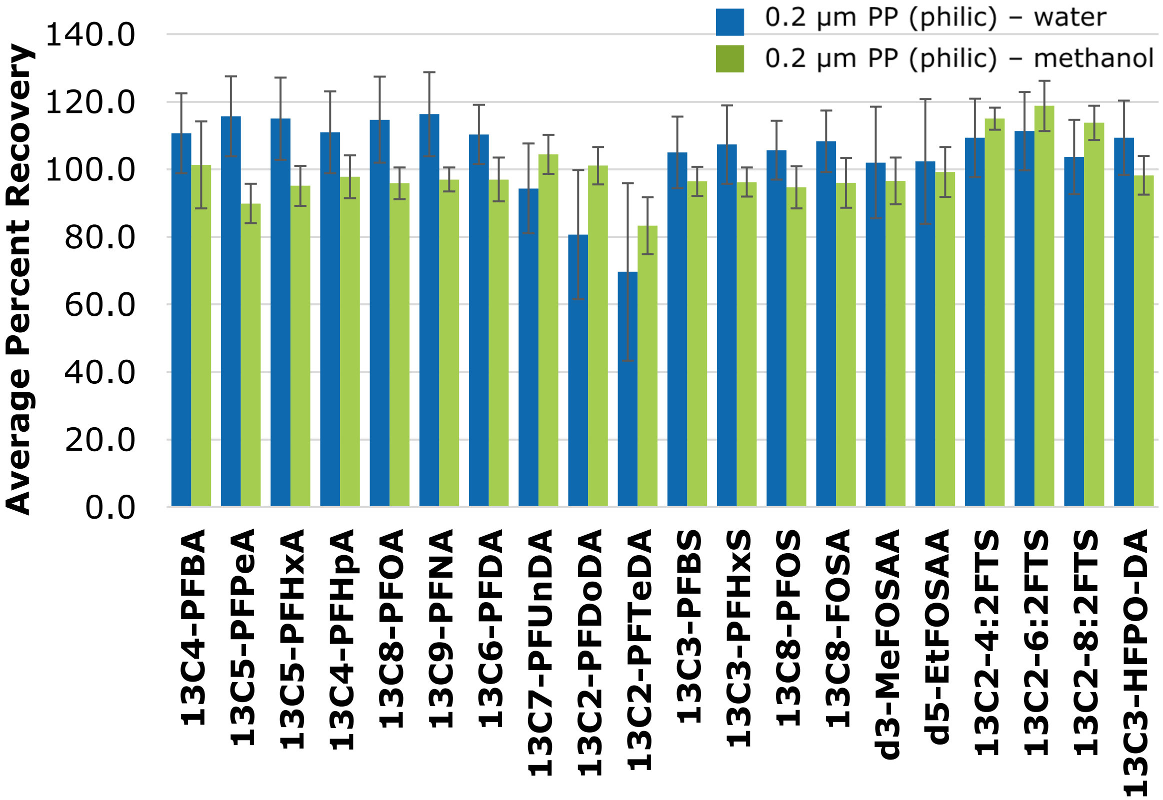
ABBREVIATIONS: RL = reporting limit, ppb; MDL = minimum detection limit, ppb; PP = polypropylene; philic = hydrophilic; phobic = hydrophobic

Testing Polypropylene Membranes with EPA 537.1 and EPA Draft 1633
Recoveries vary widely from philic to phobic, water to methanol

Average Recovery of C13 labeled standards in Water → lower for hydrophobic polypropylene



Average Recovery of C13 labeled standards in water and methanol for hydrophilic polypropylene → similar overall



Analytical Methods for PFAS Developed at a Rapid Pace

Regulatory Landscape – Air Testing & OTM-45

Method(s)	Sample Prep	Matrix/Matrices	Filter(s) Required by Method
SW-846 Method 8327*	SPE, **filtration**	Non-potable groundwater, surface water, wastewater	0.2µm polypropylene syringe filter (hydrophilic)
ASTM D7968-17a	Solvent extraction, **filtration**	Environmental solids	0.2µm polypropylene syringe filter (hydrophilic)
ASTM D7979-19	Solvent extraction, **filtration**	Water matrix (no drinking water)	0.2µm polypropylene syringe filter (hydrophilic)
ISO 21675	SPE, **filtration** as needed	Drinking, natural and wastewater	1µm GFF syringe filter (rapid) 1-10µm nylon or GFF (if >2g/L suspended matter)
FDA C-010.02	QuEChERS, SPE, **filtration**	Foods	0.2µm nylon syringe filter
OTM-45	Sampling train: **filtration**, impingers	Air Emissions (stationary sources)	GFF or QFF (no pore size listed) membrane filter
EPA Draft 1633	SPE, **filtration**	Aqueous, soil, biosolids, sediment, tissue	0.2µm nylon syringe filter

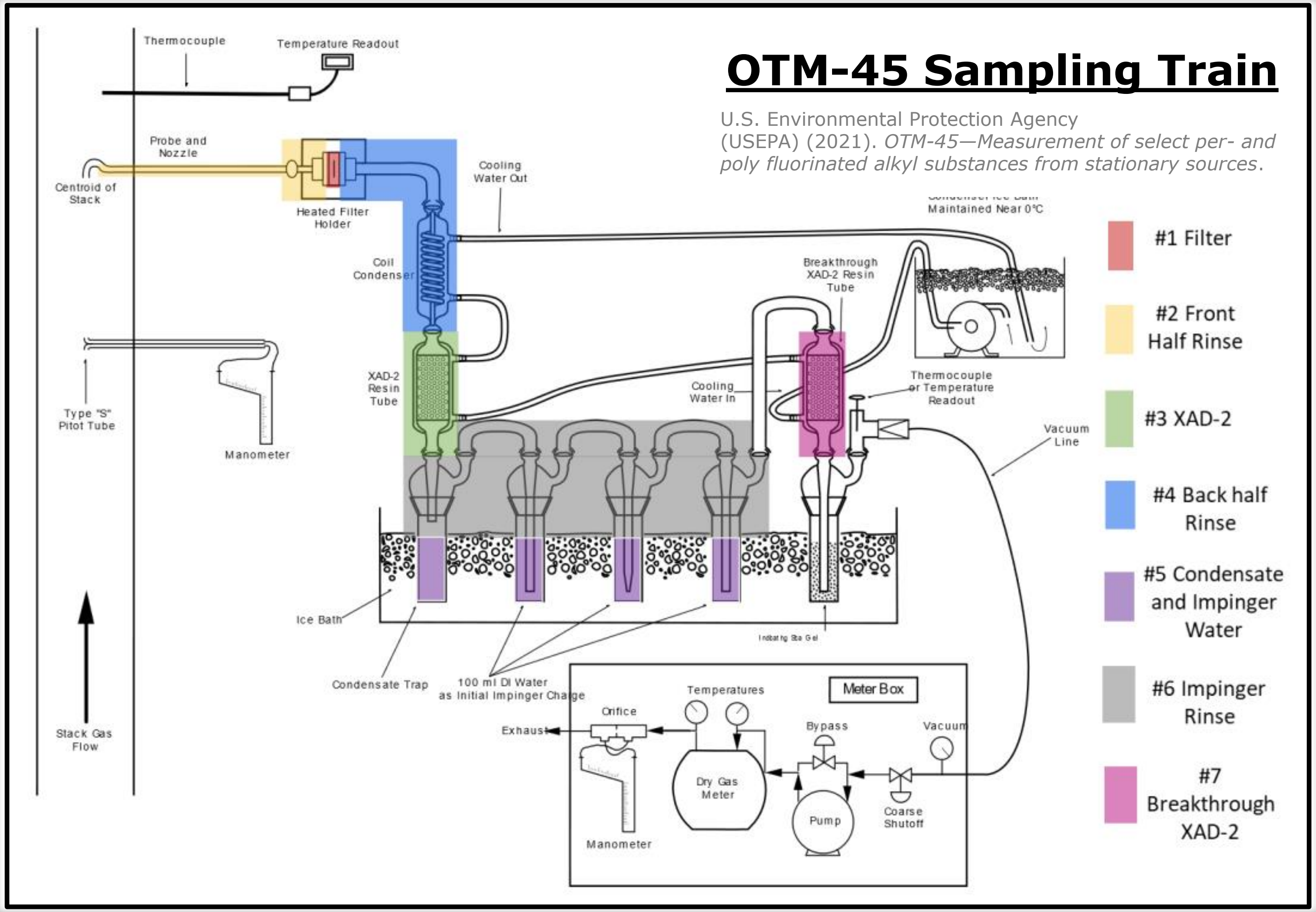
- Polypropylene, nylon and glass fiber (GFF) are the most common materials
- Filters should not have detectable levels of PFAS compounds above reporting limit (RL) of method

**screening method only*

Abbreviations: SPE = solid phase extraction; TSS = total suspended solids determination; GAC = granular activated carbon; CIC = combustion ion chromatography; philic = hydrophilic; GFF = glass fiber filter; QFF = quartz fiber filter; OTM = other test method

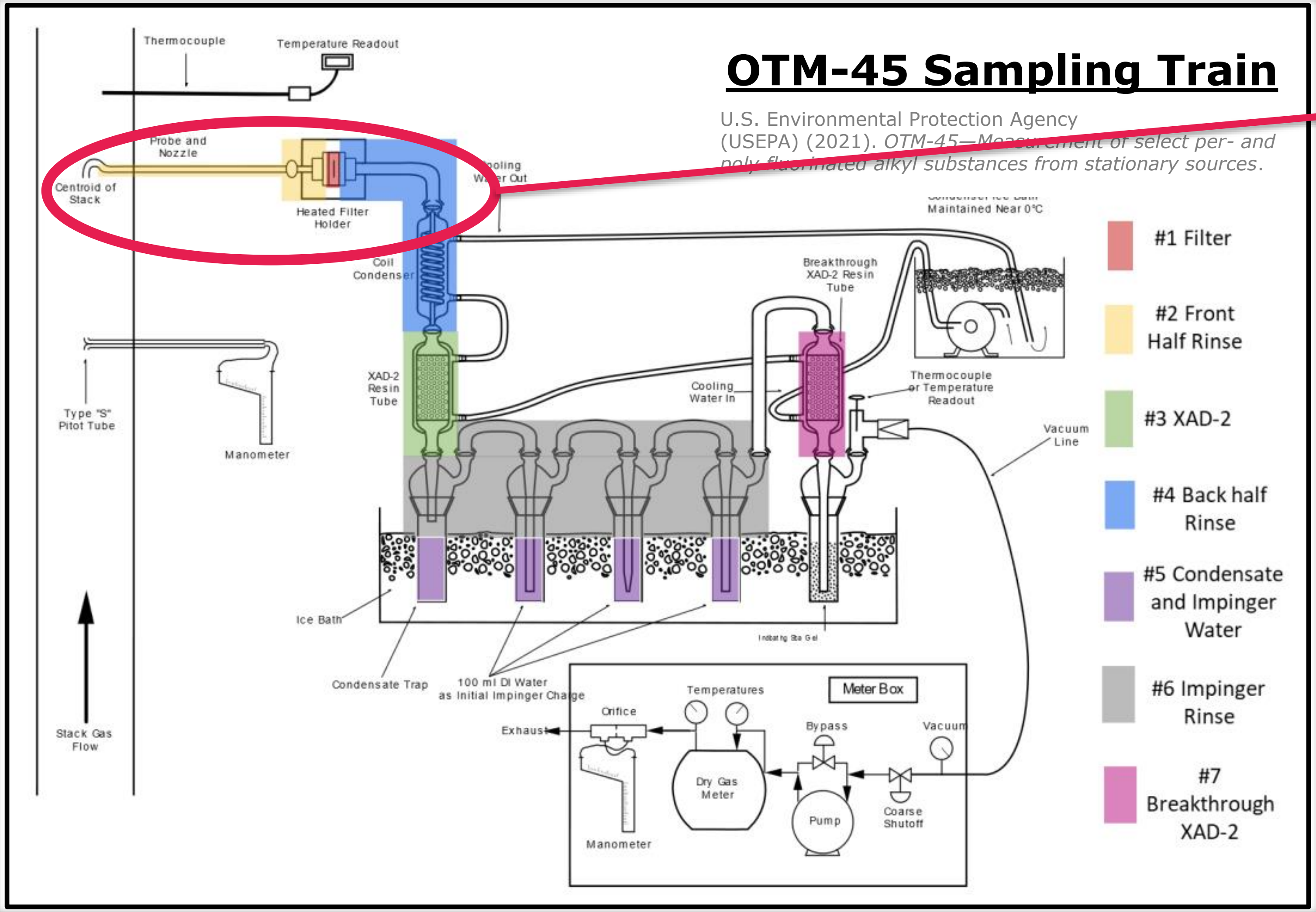
Selected methods; does not include all drinking water and international methods

The First PFAS Method in Air, Focused on Stack Emissions
Other Test Method (OTM)-45



U.S. Environmental Protection Agency (USEPA) (2021). *OTM-45—Measurement of select per- and poly fluorinated alkyl substances from stationary sources.*

The First PFAS Method in Air, Focused on Stack Emissions
Other Test Method (OTM)-45

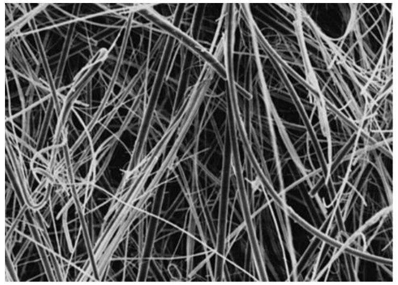


Filter for collecting particulate phase:

- 82, 82.6, 90 mm cut disc membrane filter
- Glass fiber without binder
- At least 99.95% efficiency on 0.3-µm dioctyl phthalate smoke particles

AP 40 Glass fiber (0.7µm)

- TSS
- TCLP
- Hot gases

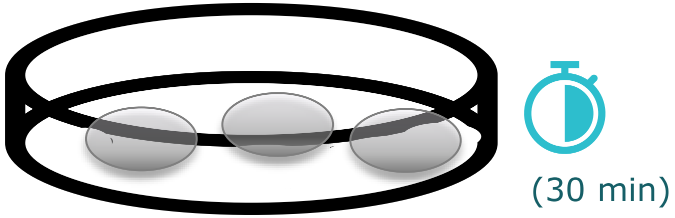


Are Membranes Contaminated with PFAS out-of-box?

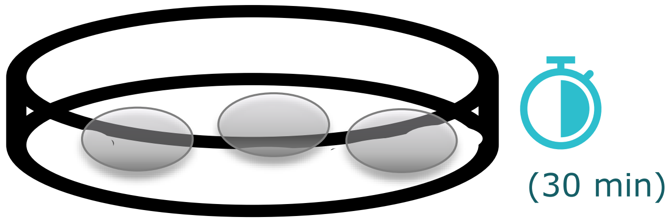
Testing Glass Fiber Membrane Filter Suitability for OTM-45

49 PFAS analyzed

Cleaning
(prior to sample collection)

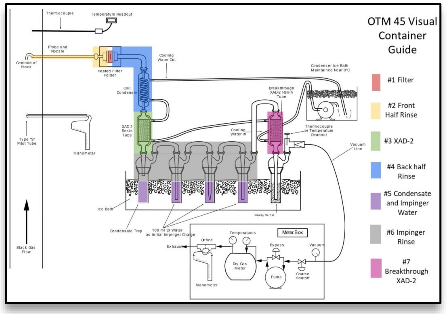


- Soak filters in 5% (v/v) NH_4OH in methanol

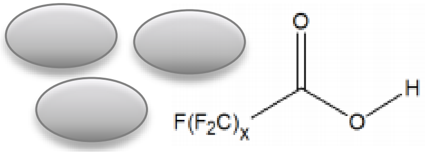


- Soak filters in methylene chloride

Sampling on Sample Train
(skipped in this study to examine filters alone)



Front-half Extraction



- Addition of isotope dilution internal standards to filters

- Extraction of filters in methanol, 18 hours

Concentration & Evaporation

- Hot-block concentration and blow-down step
  - *Add non-extracted internal standards*
  - *Final volume: 10mL (80% v/v methanol in water)*

LC-MS/MS

- Analyze by internal standards

Data collected in collaboration with: eurofins *(Knoxville, TN)*

Testing Glass Fiber Membrane Filter Suitability for OTM-45

Glass fiber membrane filters demonstrate similar levels of PFAS after cleaning and front-half extraction

49 PFAS analyzed

Compound(s)	RL (ng/ sample)	MDL** Range (ng/ sample	Millipore® Glass fiber without Binder		MFR-1, Glass Fiber without Binder
			Lot 1,[a] pooled	**Lot 2**,[a] pooled	**Lot 1**,[a] pooled
Perfluoroalkyl carboxylic acids					
PFHpA	1.00	0.620	**2.04**	**1.82**	**1.91**
PFBA	2.00	1.30	ND	ND	ND
PFHxA	1.00	0.210	**0.258[J]**	**0.270[J,I]**	ND
PFPeA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, PFODA	1.00	0.0850-0.650	ND	ND	ND
Perfluoroalkyl sulfonic acids					
PFBS, PFPeS, PFHxS, PFHpS, PFNS, PFDS, PFDoS	1.00	0.0950-0.890	ND	ND	ND
PFOS	1.00	0.450	**0.592[J]**	**0.565[J,I]**	**0.566[J,I]**
Perfluorooctane sulfonamides, Perfluorooctane Sulfonamidoacetic acids, Perfluorooctane sulfonamido ethanols					
PFOSA, N-EtFOSA, N-MeFOSA, N-MeFOSAA, N-EtFOSAA, N-EtFOSE	1.00	0.0880-0.160	ND	ND	ND
N-MeFOSE	5.00	4.90	ND	ND	ND
Fluorotelomer sulfonic acids					
4:2 FTS, 8:2 FTS, 10:2 FTS	1.00	0.0910-0.320	ND	ND	ND
6:2 FTS	5.00	4.70	ND	ND	ND
Per and Polyfluoroether carboxylic acids, Per and Polyfluoroether sulfonic acids, Fluorotelomer carboxylic acids, Next-Generation PFAS analytes					
GenX	5.00	4.70	ND	ND	ND
ADONA, 9Cl-PF3ONS, 11Cl-PF3OUdS, 6:2 FTUCA, **7:3 FTCA*,** 10:2 FTCA, 8:2 FTCA, PFEESA, 8:2 FTUCA, PFMPA, PFMBA, **5:3 FTCA*,** 6:2 FTCA, 3:3 FTCA, PFECHS, NFDHA	1.00	0.0980-480	ND	ND	ND

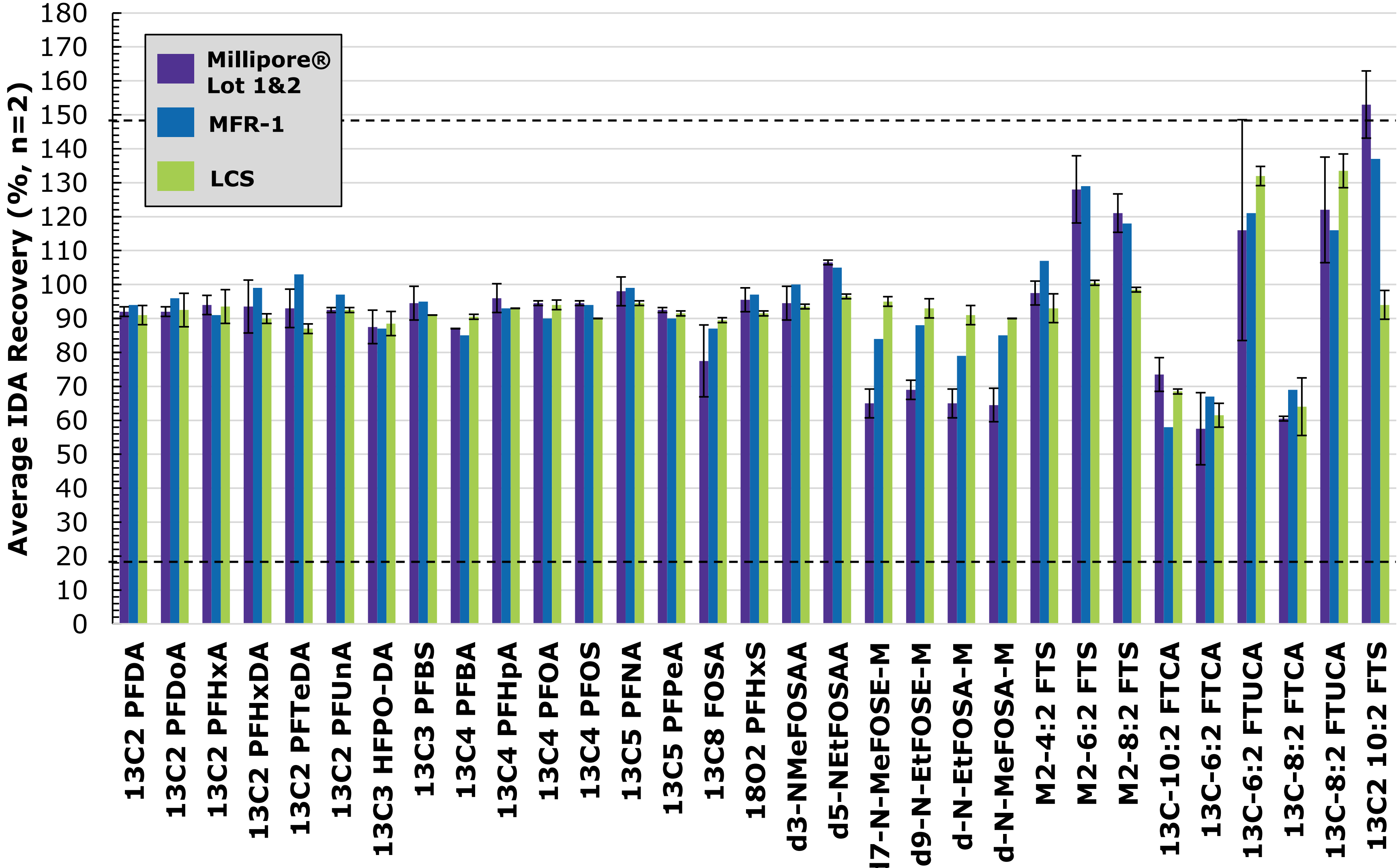
a] n=3 membranes per lot tested and results pooled together. J] less than RL but greater than MDL and concentration is estimated. I] Value is the estimated maximum possible concentration. * LCS and/or LSCD is outside acceptance limits. **MDL ranged depending on the analyte of interest.

ABBREVIATIONS: RL = reporting limit; MDL = minimum detection limit; ND = not detected; LCS = laboratory control sample; LSCD = laboratory control sample duplicate

Testing Glass Fiber Membrane Filter Suitability for OTM-45

Average recovery of standards fall within acceptable QC range

49 PFAS analyzed

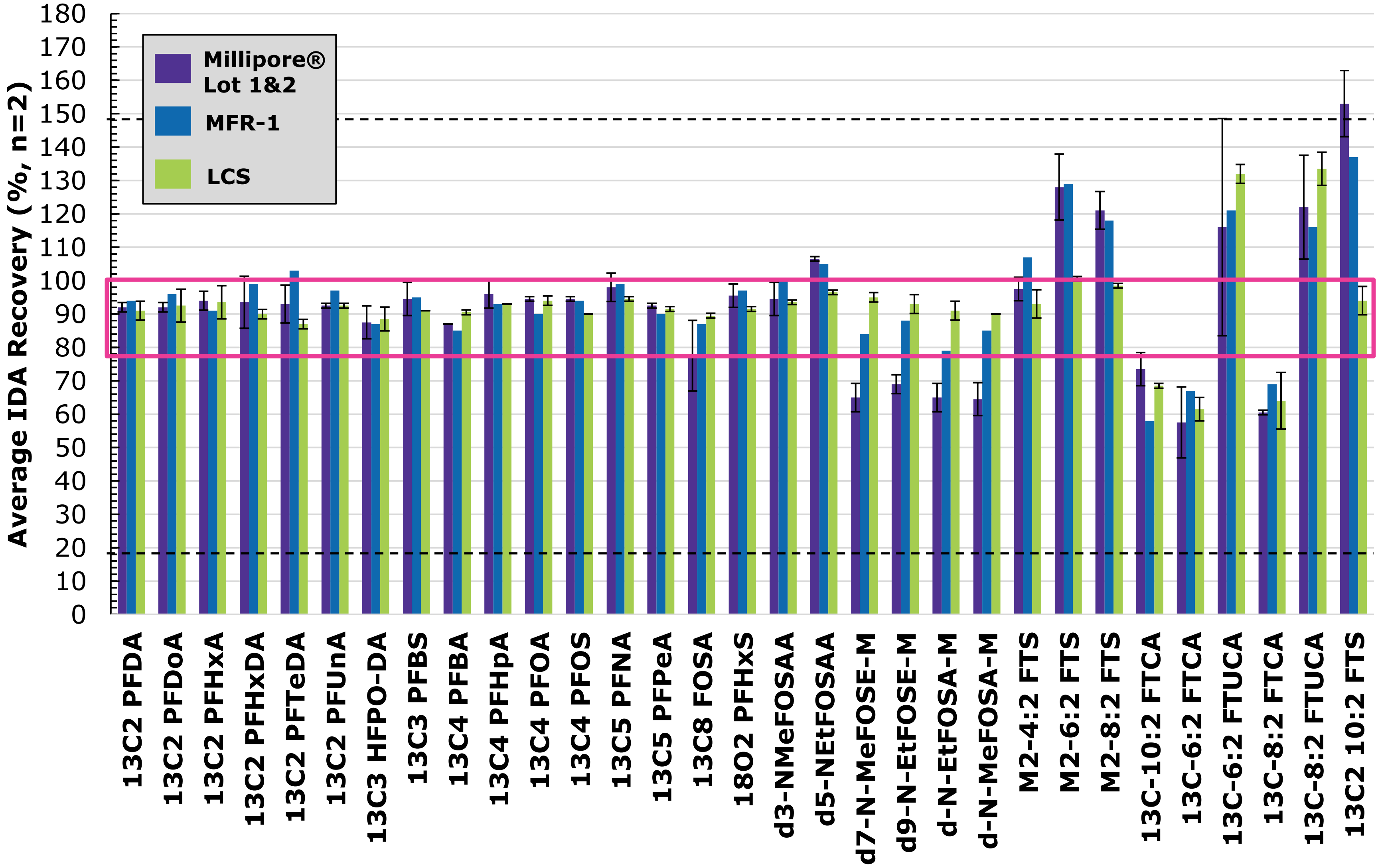


Most recoveries stay from 80-100%

Testing Glass Fiber Membrane Filter Suitability for OTM-45

Average recovery of standards fall within acceptable QC range

49 PFAS analyzed



Most recoveries stay from 80-100%

Investigation of Contamination and Recovery of PFAS in Filter Membranes
Summary & Conclusions

- Filtration is important for high data quality, however, **consumables must not interfere** with sensitive PFAS analysis

- <u>We tested different syringe filters and membrane filters in several PFAS methods</u>
  - Nylon, nylon with a glass fiber prefilter, polyethersulfone (PES), hydrophilic polypropylene, hydrophobic polypropylene, glass fiber without binder
  - **Analyzed extractables** to determine baseline contamination
  - **Analyzed** internal standard and analyte **recoveries** to determine adsorption

- The syringe filters and membrane filters tested were found to be **suitable for sample filtration/preparation** in:
  - Water (via EPA 537.1)
  - Methanol (via EPA Draft 1633)
  - Cleanup/Front-half extraction for stack sampling (via OTM-45)

Some key takeaways:

- PES and philic polypropylene show similar recoveries in water & methanol, while nylon does not
- Rinsing nylon with methanol desorbs certain PFAS
- Larger filtration areas do not lead to loss of analyte (33mm vs. 25mm)
- Polypropylene is a suitable alternative to PTFE for sample prep in many cases

For more details, see: sigmaaldrich.com/pfassamplefiltration

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