Analysis of Per and Polyfluorinated Alkyl Substances in non-Potable Water by co-solvation with methanol followed by tandem liquid chromatography mass spectrometry

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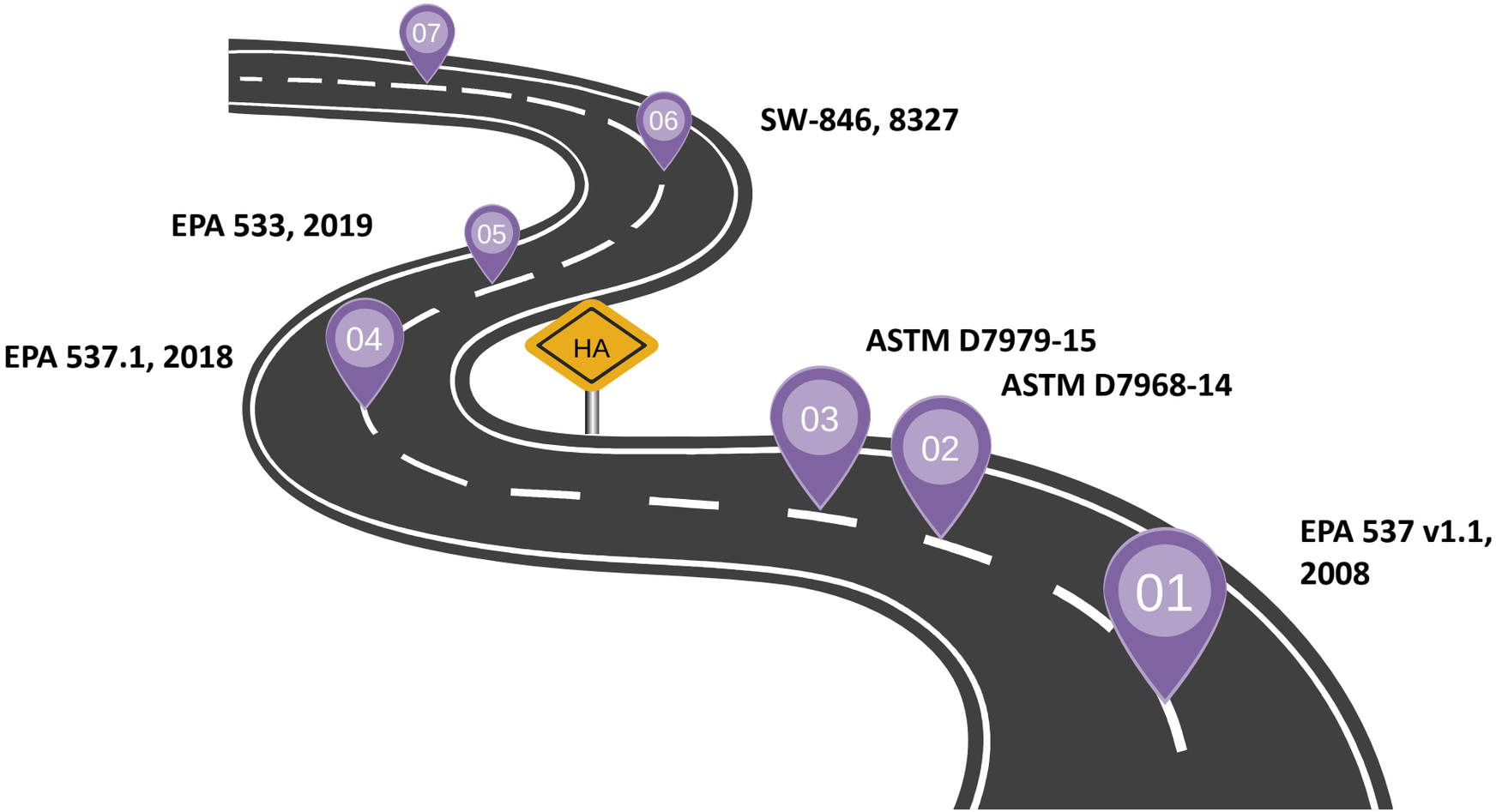
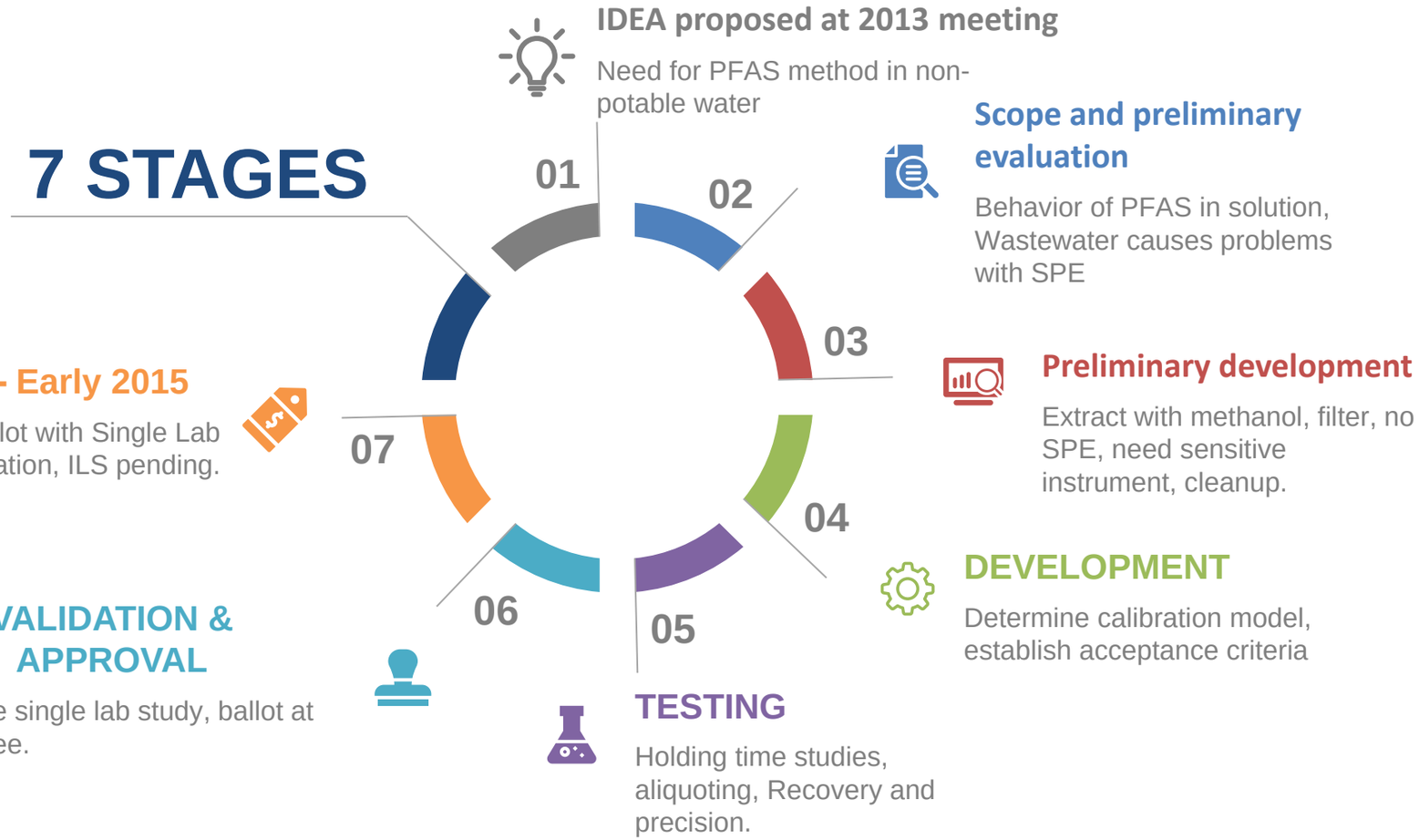
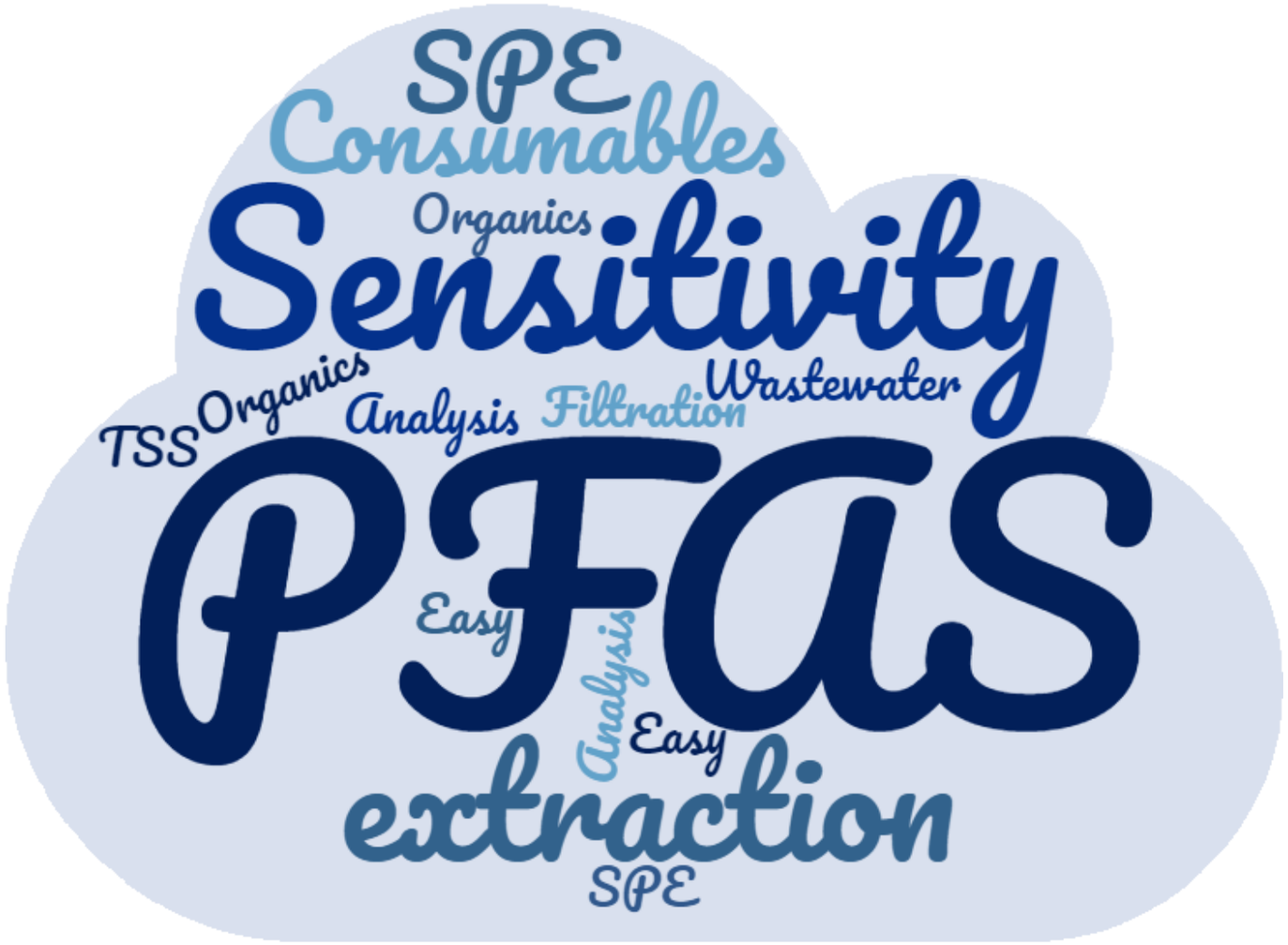
A long winding road of PFAS methods, each for different purposes



ASTM D7979 first published in 2015 for analysis of non-potable water, including wastewater



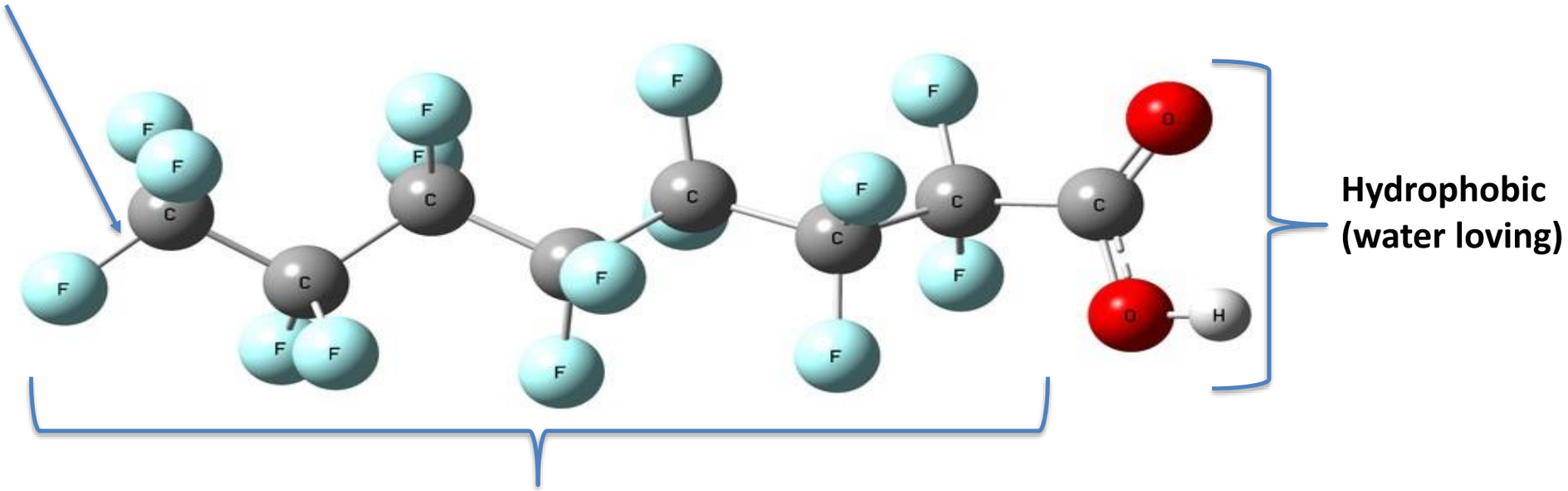
Multiple different facets are considered near simultaneously during method development



PowerPoint makes it linear

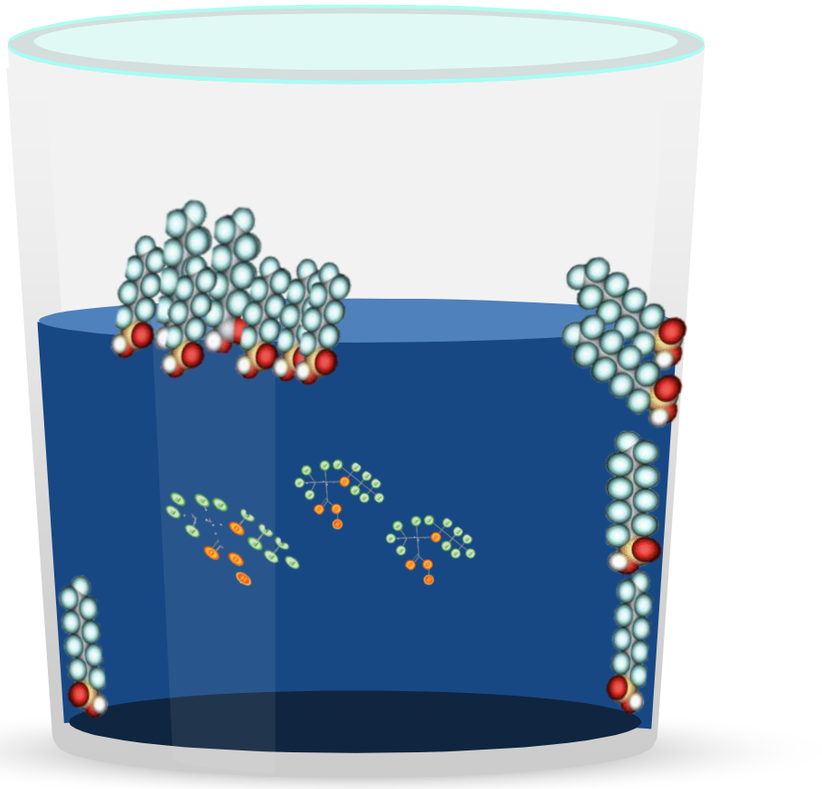
PFAS have unique chemical properties that must be considered

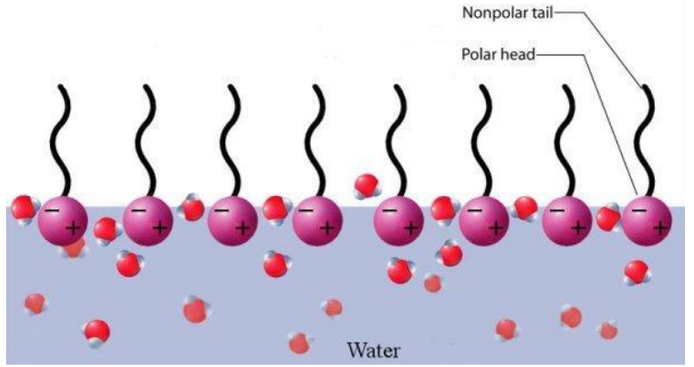
Strongest bond in organic chemistry



Hydrophobic (water repelling) , oleophobic (oil repelling), lipophobic (fat repelling)

PFAS compounds concentrate at interfaces



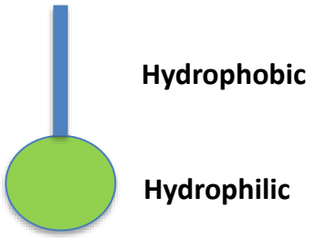


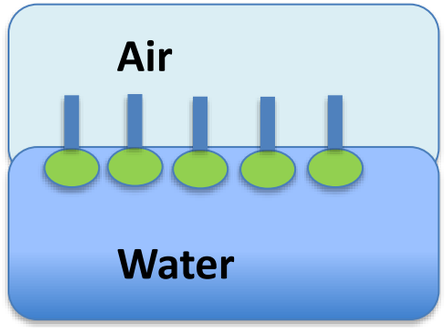
Bigger chains rise to the top faster

Smaller chains with more polar groups stay in solution longer

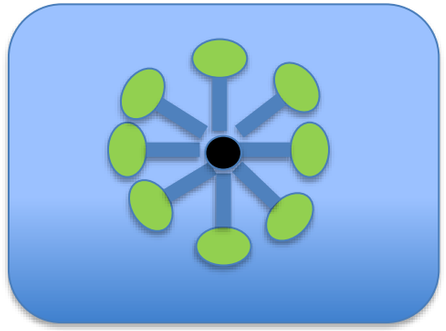
Polar heads – attach to surface

PFAS behaves like surfactants in solution

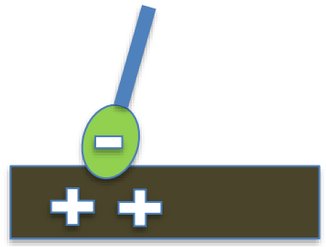




The C-F bond = weak Van der Waals and Hydrogen bonding

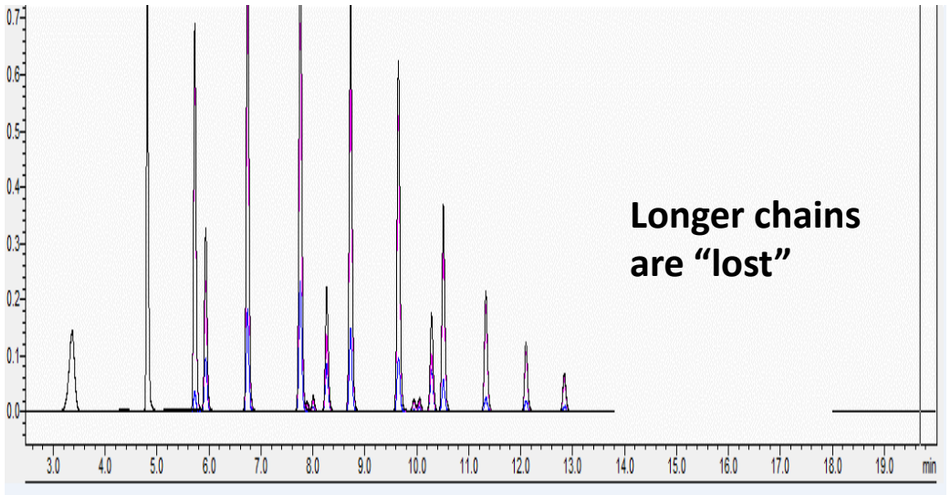


Critical Micelle Concentration(CMC) lowered by interaction with particles, organics, and soil.

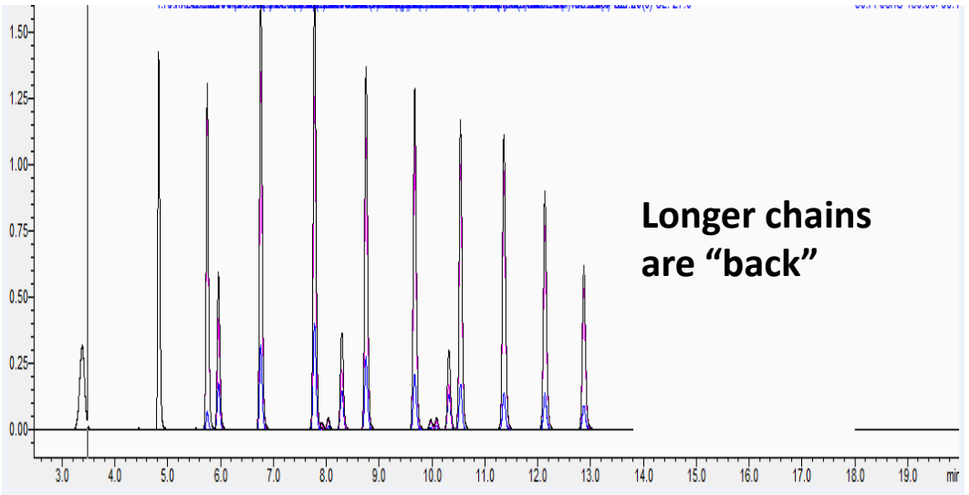


The negative charged head can interact with positive ions

The loss of PFAS upon standing in a vial



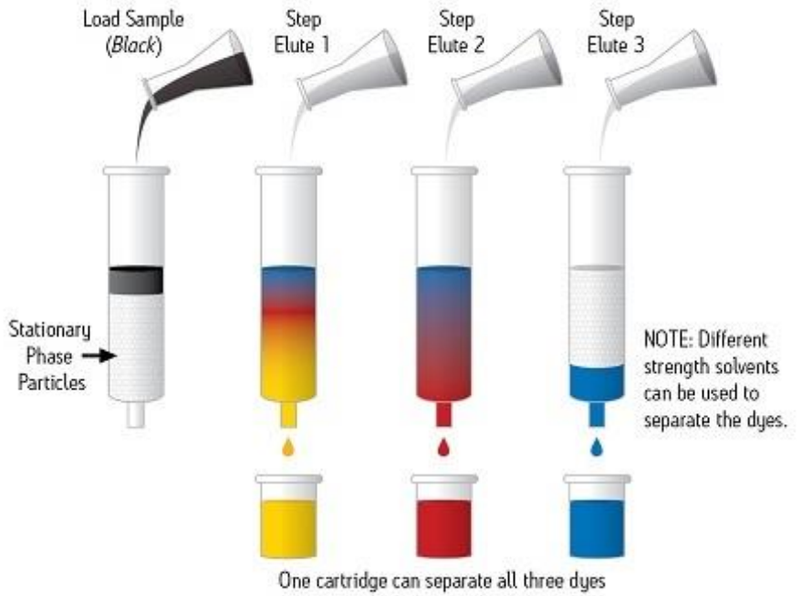
Standard allowed to sit in vial



Same standard after mixing

PFAS standards are “lost” upon sitting, but recovered by mixing, they “float”.
Potential for loss in subsampling

Existing Method 537 v1.1 used SPE - evaluation of Solid Phase Extraction

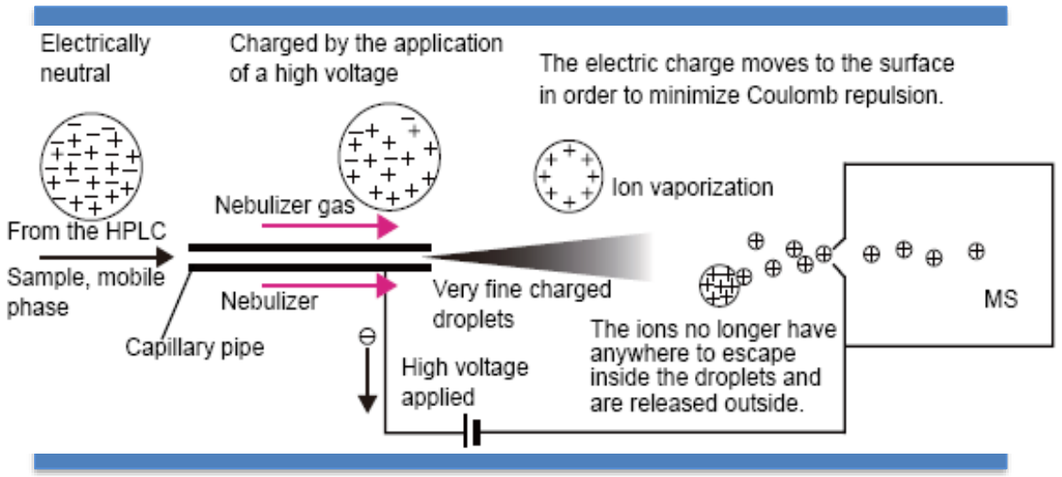


Benefits of SPE

1. ✗ **Compound Purification – removal of complex matrix**
2. ? **Reduce ion suppression or enhancement – MS**
3. ✗ **Fractionate compounds by class**
4. ✗ **Transfer sample from aqueous to organic phase (GC methods)**
5. ? **Enrichment of analyte concentration**

https://www.waters.com/waters/en_US/Solid-Phase-Extraction-SPE-Guide/nav.htm?cid=134721476&locale=en_US

Suppression or enhancement at the interface, investigation of cause and potential remedies



Matrix effects → coeluting compounds alter ionization energy at the interface

Improved separation best technique to overcome

Interferences usually elute early – divertor valve
Lower flow rates

Enhancement = increase in signal
Suppression = decrease in signal

Phospholipids main cause

Higher % solvent, lowers surface tension and boiling point resulting in more efficient de-solvation.

Weakly acidic (ammonium acetate) volatile solvent. Acetonitrile better then methanol

With correct mobile phase, column and gradient, interferences are minimized for most wastewater samples

Evaluation of Solid Phase Extraction for wastewater and highly polluted samples

SW-846 3535 Solid Phase Extraction – Not appropriate for samples with TSS > 1%

1. **Particulates may clog SPE media**
2. **For PFAS must wash out entire container**
3. **Preliminary filtration= two extractions per sample**

Filtration prior to extraction = analyte loss

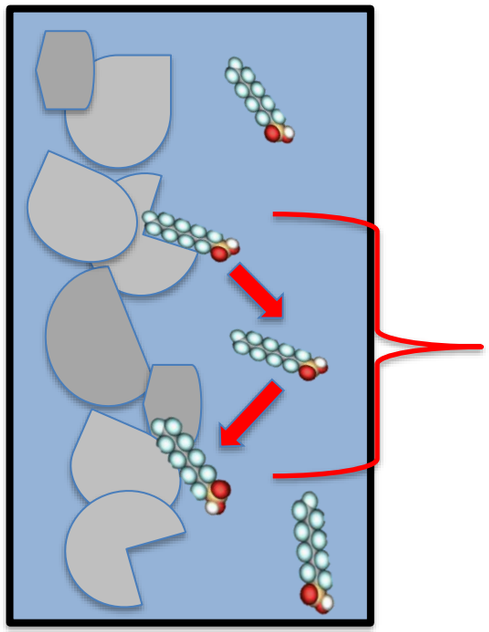
You want retention of targets and not interferences, but:

1. **Interferences may also be retained and eluted with analytes**
2. **Depending on media, some analyte may not be retained**
3. **Depending on media, some analytes may not be recovered**

Goal is to have one method for WW capable of extraction and analysis in a single, not two or more extractions.

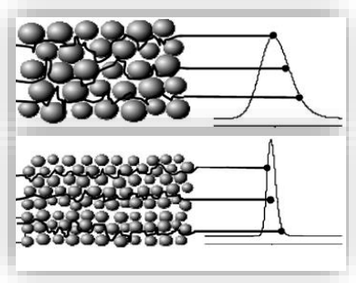
Preliminary filtration not an option, and SPE requires more than one media to quantitatively recover all target PFAS (C4 – C14)

A LC Column can be used as, and is essentially, SPE



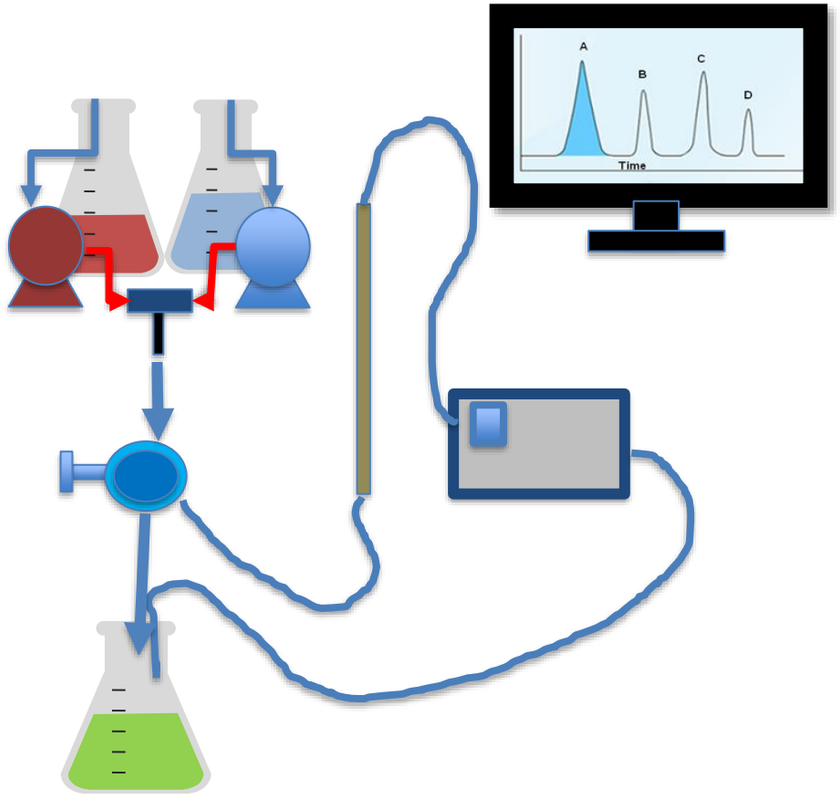
One Theoretical Plate

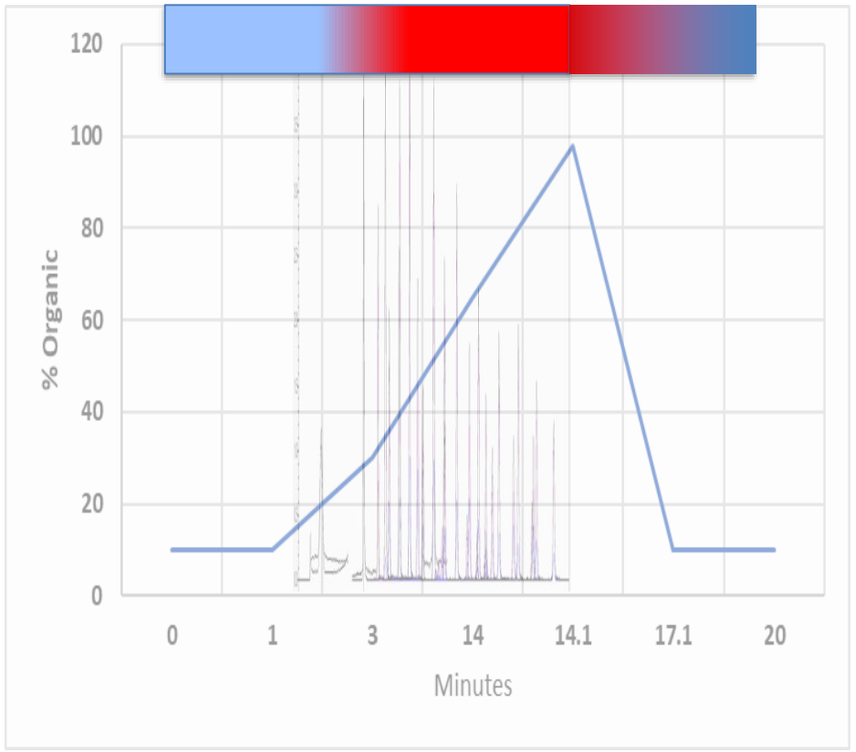
5 – 12 theoretical plates



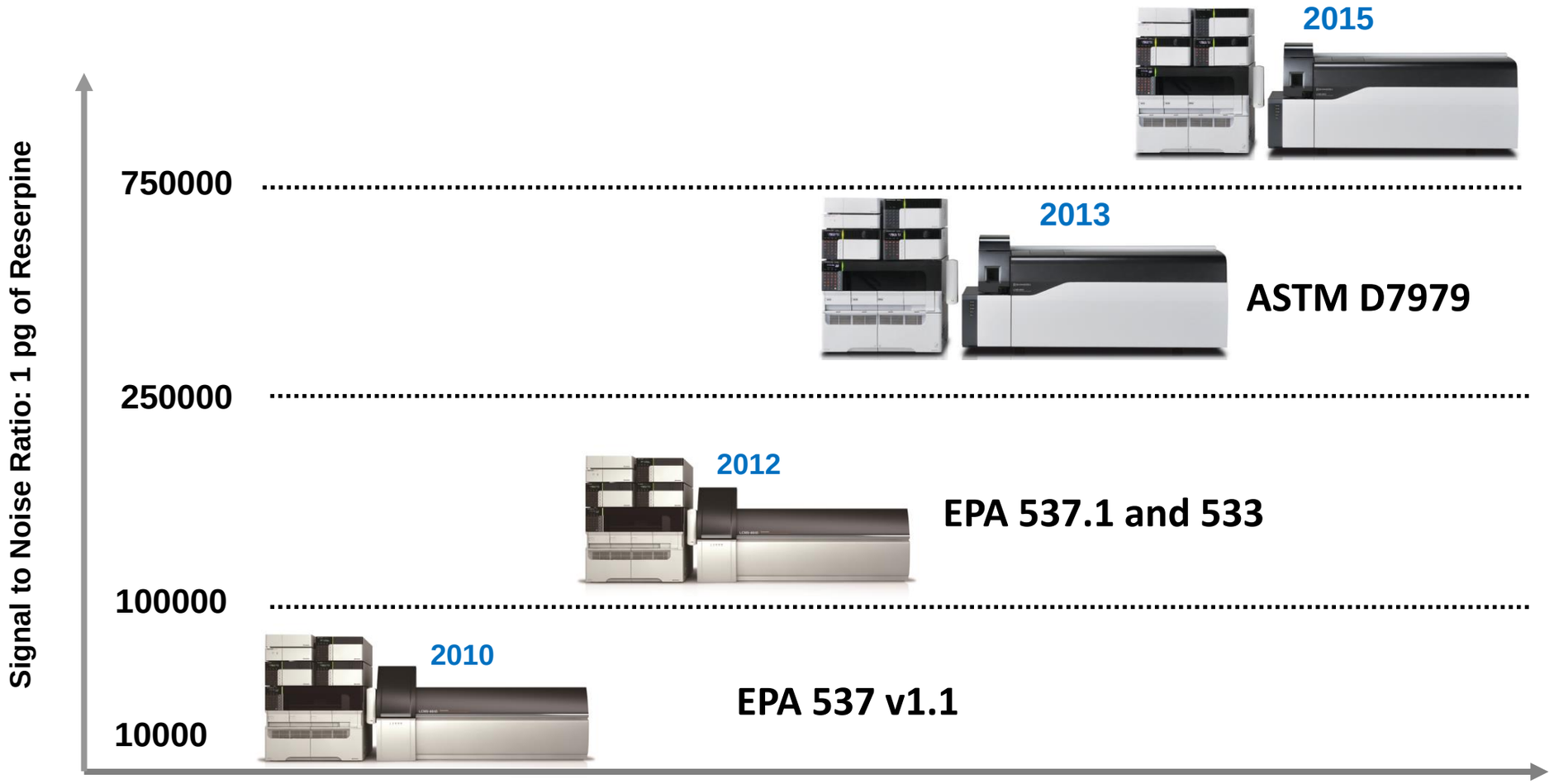
10,000- 20,000 theoretical plates

Correctly applied, the HPLC column serves as SPE

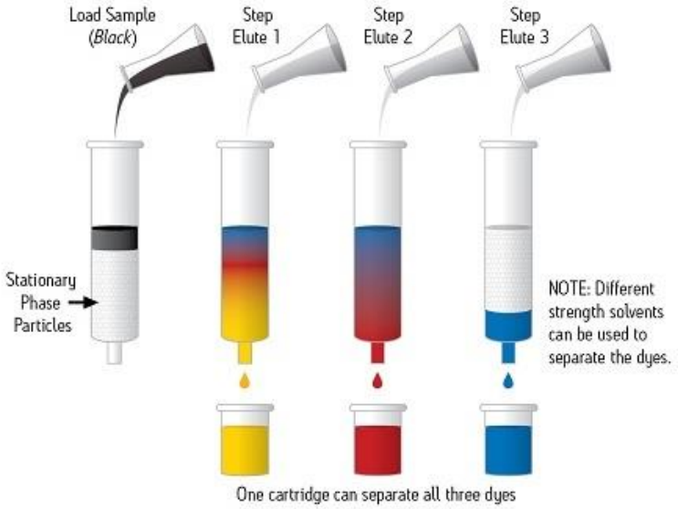




Enough sensitivity for 10 - 30 microliter injections, no preconcentration needed



Evaluation of Solid Phase Extraction, revisited



https://www.waters.com/waters/en_US/Solid-Phase-Extraction-SPE-Guide/nav.htm?cid=134721476&locale=en_US

Benefits of SPE

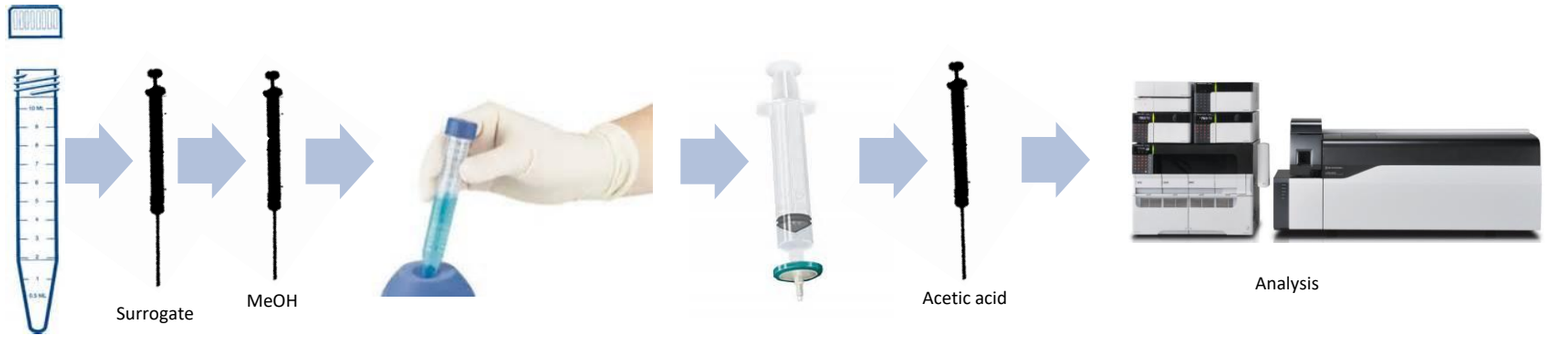
1. ~~Compound Purification – removal of complex matrix~~
2. Reduce ion suppression or enhancement – MS
3. ~~Fractionate compounds by class~~
4. ~~Transfer sample from aqueous to organic phase (GC methods)~~
5. Enrichment of analyte concentration

Potential interferences and need for analyte enrichment can be handled using modern instrumentation

Devise an extraction, verify if it works, if not change it

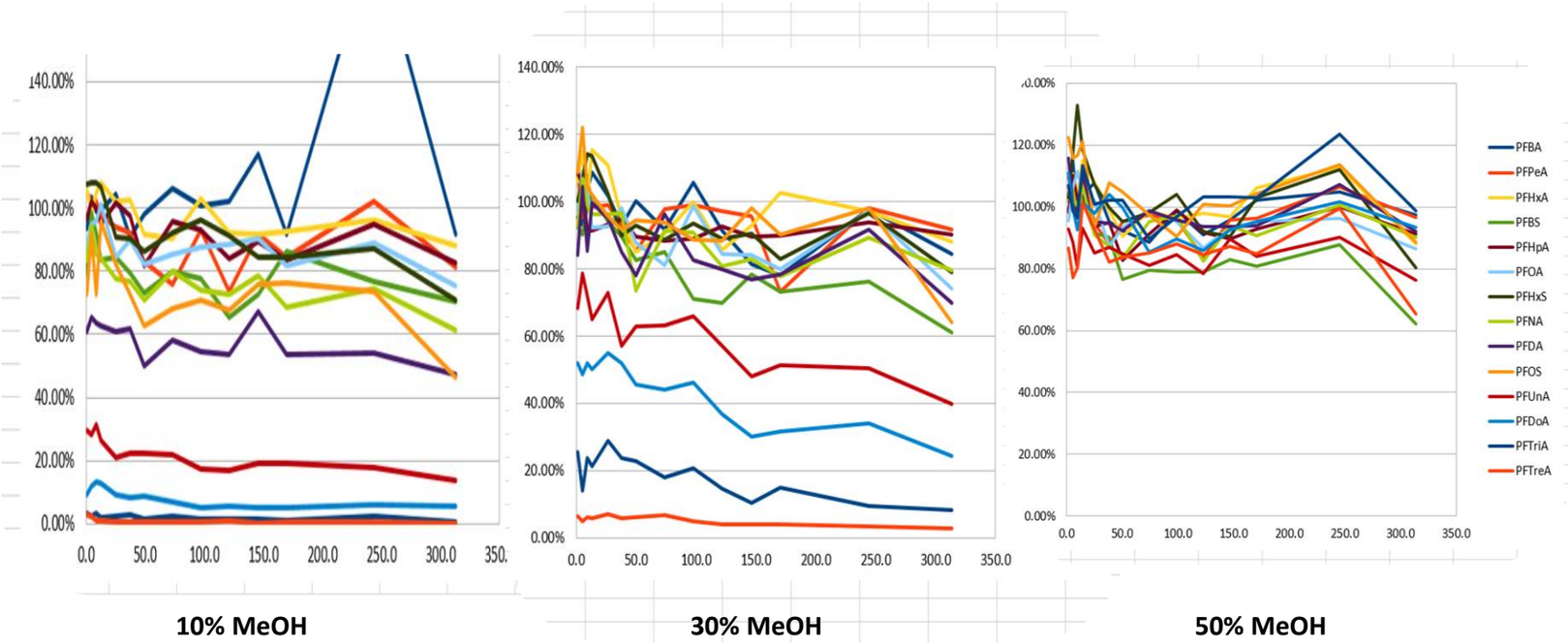
Method 537.1

Alternative



Consistent with ASTM sustainability and technology innovation goals
Extraction is “like” making standards

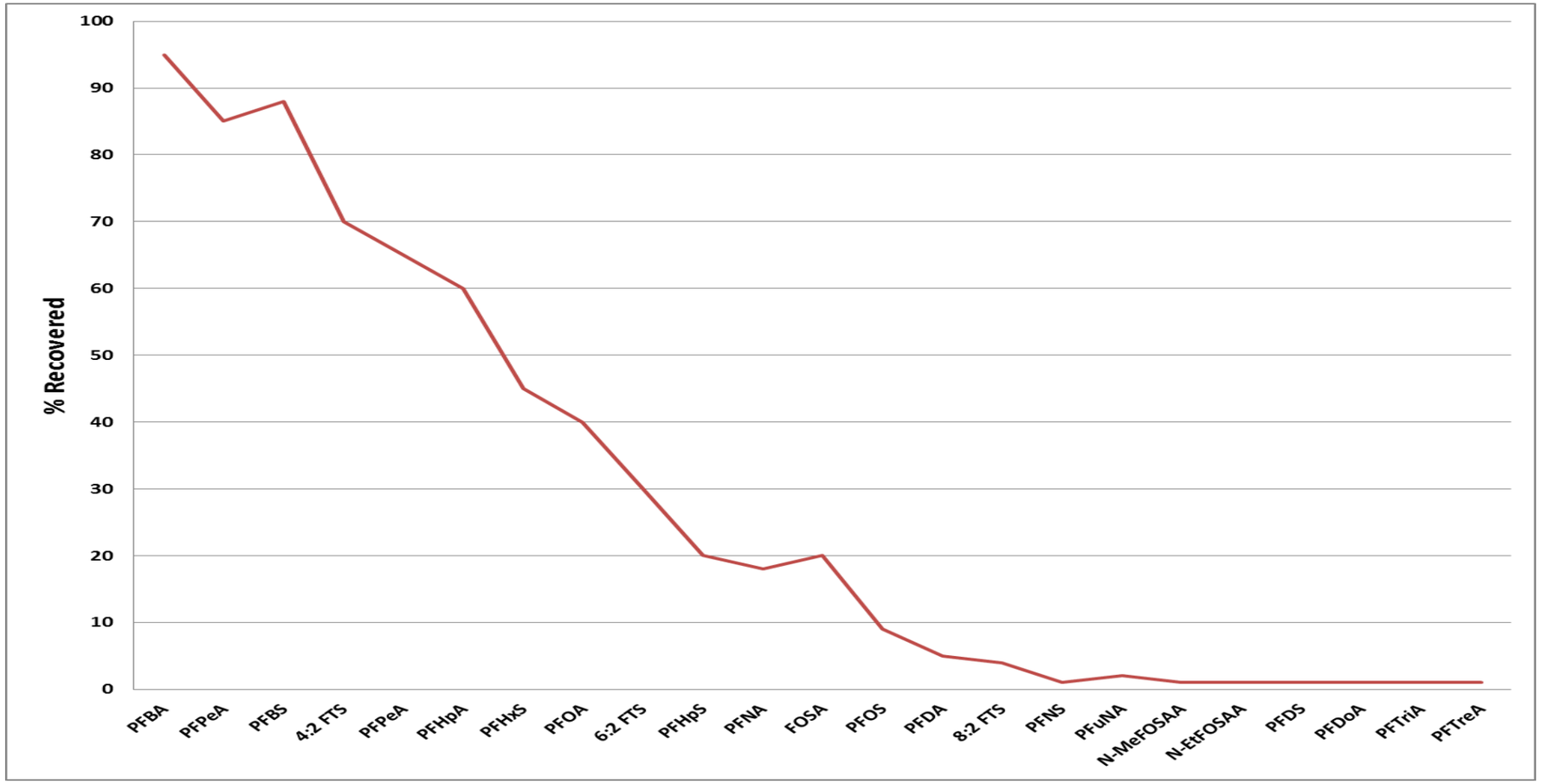
Solubility and stability of analytes in methanol



10% MeOH 30% MeOH 50% MeOH

Study demonstrates sample should be 50:50 Methanol and water for maximum solubility and minimum dilution. All standards and samples prepared in same way.

Activated carbon significantly removed analyte, so no clean-up step in the method.



Guidelines for determination of the appropriate calibration model, based on the single lab study

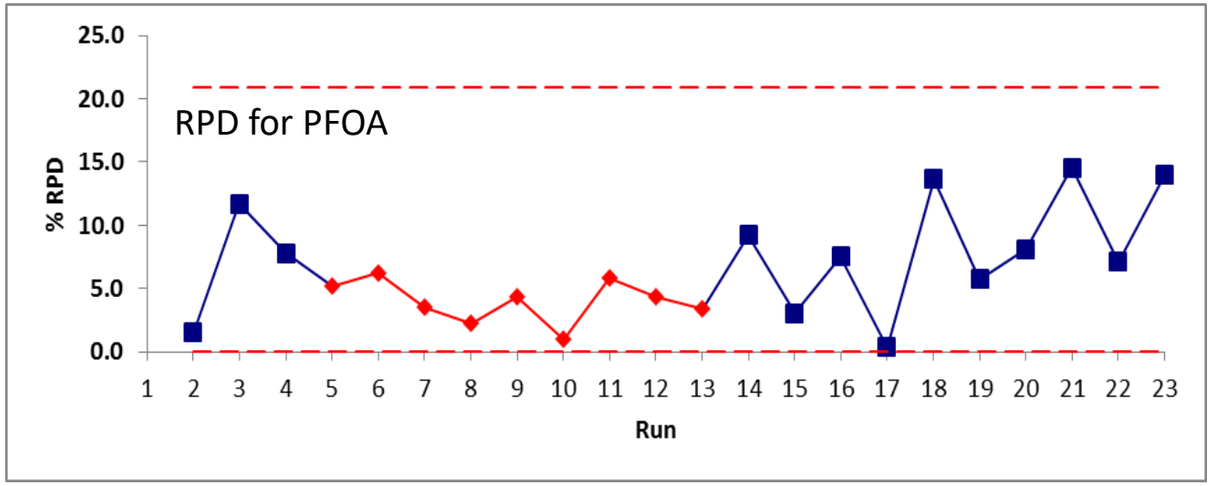
Recovery of mid range Spikes (all evaluated matrices)	RSD	Calibration Model
70 – 130 %	≤ 20%	External Standard
< 70 %	≤ 20%	External Standard [1]
> 130 %		Reject the analyte or modify the extraction
70 – 130 %	> 20%	Use internal standard calibration, or isotope dilution (if isotopes are available)

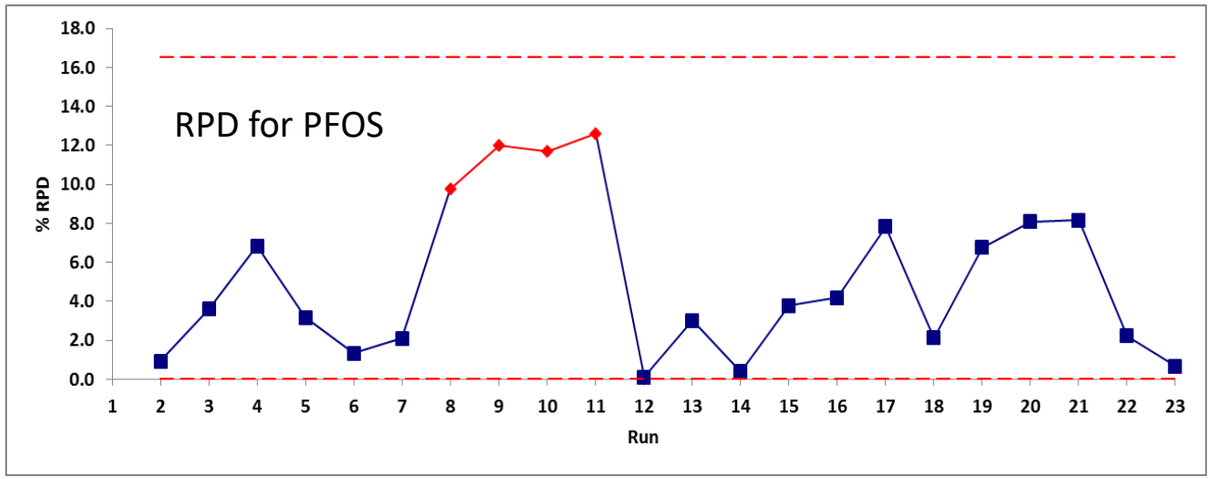
[1] External Standard Calibration is appropriate, however, consider rejecting the analyte or modifying the extraction

6 matrices met condition 1, therefore, external standard calibration was accepted

		Reagent Water		River water II		Sewage Plant IV Effluent		Sewage Plant IV Influent		Lake Water		Ground Water		Average across Matrices	
Unlabled Native Analyte	Concentration (ng/L)	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
PFTreA	160	91.9	8.6	100	4.04	82.7	4.75	81.7	2.44	99.1	1.98	93.6	2.31	91.5	4.02
PFTriA	160	91.7	4.4	104	2.57	88.5	3.79	88.9	2.9	99.6	2.32	98	3.16	95.1	3.19
PFDoA	160	92.2	4	100	1.94	90.3	3.36	91.1	2.48	98.8	1.93	97.3	2.12	95.0	2.64
PFUnA	160	92.9	2.5	97.1	2.16	89.8	2.84	91.3	4.54	94.4	2.41	93.8	2.35	93.2	2.80
PFDA	160	93.7	1.5	96.8	2.81	89.4	4	95.8	3.39	96.6	2.61	93.3	3.1	94.3	2.90
PFNA	160	94.4	2.2	97.6	3.17	90.7	3.46	94.3	4.05	96.8	1.73	96.6	1.25	95.1	2.64
PFOA	160	91.1	2.3	90.6	3.52	92.2	3.02	101	3.72	92.5	3.25	90.8	2.62	93.0	3.07
PFHpA	160	65.2	7.4	95.5	2.16	85.8	3.89	89.8	4.35	91.8	2.43	92.5	1.69	86.8	3.65
PFHxA	160	58	1.9	92.9	2.49	87	2.31	96.5	4.5	91.5	4.15	96.5	2.24	87.1	2.93
PFPeA	800	88.1	1.4	95.2	1.09	82.6	3.28	81	3.45	84.1	7.45	94.4	3.27	87.6	3.32
PFBA	800	70.4	1.7	68.3	4.82	47.3	10.6	47.3	8.46	60.3	17.3	65.8	5.83	59.9	8.12
PFBS	160	99	17.9	93.4	2.74	84.7	3.67	90.5	5.05	87.3	4.15	98.9	1.65	92.3	5.86
PFHxS	160	92.1	3.1	103	1.97	88.8	3.33	92.1	3.3	100	2.21	100	1.42	96.0	2.56
PFOS	160	94.3	3.8	102	2.79	91.7	2.56	95.1	4.03	103	3.22	102	1.74	98.0	3.02
PFDS	160	101.4	4.24	109	1.3	92.7	2.42	90.3	2.48	107	1.66	103	3.1	101	2.53
PFNS	160	99.8	3.21	106	2.33	90.8	2.22	91.8	2.47	106	1.55	103	1.22	99.6	2.17
PFHpS	160	98.8	4.55	104	1.43	90.8	2.42	90.8	2.78	103	2.66	102	2.49	98.2	2.72
PFPeS	160	93.5	2.89	101	1.15	87.5	2.72	89.4	3.35	97	3.19	96.6	2.7	94.2	2.67
FOSA	160	98.3	2.54	93.6	1.42	92.7	2.3	80.4	1.63	94.9	1.52	92.3	1.43	92.0	1.81
4:2 FTS	160	99.5	4.32	97.2	1.83	86.8	3.44	96.4	4.42	95.7	3.04	95	2.42	95.1	3.25
6:2 FTS	160	105.1	13.1	102	4.4	89.8	2.76	91.5	4.01	102	3.56	97.3	3.9	98.0	5.29
8:2 FTS	160	111.7	6.44	108	1.02	97.2	4.17	98.4	4.08	108	4	104	2.95	105	3.78
N-EtFOSAA	160	103.4	4.83	106	3.83	95.8	3.1	96.2	3.71	108	4	104	2.91	102	3.73
N-MeFOSAA	160	101.3	3.65	98.6	1.66	84	3.28	98	2.28	99.1	2.98	97.4	2.85	96.4	2.78
		Reagent Water		River water		Sewage Plant IV Effluent		Sewage Plant IV Influent		Lake Water		Ground Water		Average across Matrices	
Labeled Surrogate		% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
MPFBA	160	91.1	2.3	72.9	3.93	50.6	7.25	45.7	7.22	62.8	15.6	70.1	4.24	65.5	6.76
MPFHxA	160	98.2	1.4	95.8	1.56	90.4	2.17	94	4.38	93.8	4.13	95.7	1.82	94.7	2.58
MPFHxS	160	97.5	2.8	103	1.91	93.3	2.25	94.3	3.67	102	3.1	102	2.33	98.7	2.68
MPFOA	160	100.2	1.8	97.3	1.7	92	2.44	94.1	4.01	96.6	2.41	96.1	1.75	96.1	2.35
MPFNA	160	98.9	2.3	96.9	2.14	90.6	3.26	93.7	2.88	96.9	2.78	96.1	2.06	95.5	2.57
MPFOS	160	97.2	1.1	108	1.96	90.9	2.94	91.2	3.19	107	2.89	106	2.33	100	2.40
MPFDA	160	98.1	1.6	98.2	2.11	90.9	2.94	95.6	2.67	97.7	3.48	97	2	96.3	2.47
MPFUnA	160	97.8	0.9	99	1.5	91	2.52	92.1	3.76	97.9	2.82	97.5	1.9	95.9	2.23
MPFDoA	160	96.2	1.3	99.7	1.38	91.2	2.64	91.8	2.27	99.5	2.05	97.4	1.69	96.0	1.89
M 4:2 FTS	160	101.7	4.92	99.8	2.62	84.6	2.64	91.6	5.59	97.8	3.71	98.7	1.28	95.7	3.46
M 6:2 FTS	160	108.2	8.32	99.4	4.22	91.8	3.56	93.5	3.95	101	2.95	98.8	2.41	98.8	4.24
M 8:2 FTS	160	107.3	11.6	108	3.65	96.1	5.23	96.5	4.55	108	3.51	106	4.59	104	5.52
M NEtFOSAA	160	111	5.5	107	2.04	97.6	3.29	97.7	3.94	111	4.12	109	2.8	106	3.62
M NMeFOSAA	160	103.9	3.18	103	1.83	94.1	2.78	98.7	2.92	104	2.42	102	2.92	101	2.68

Evaluation of 5 ml samples size, precision in collocated samples, over one month



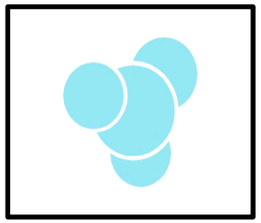


RPD of 5 ml samples of all matrices.

Holding time, vial material, and “aliquoting studies

Vial Material

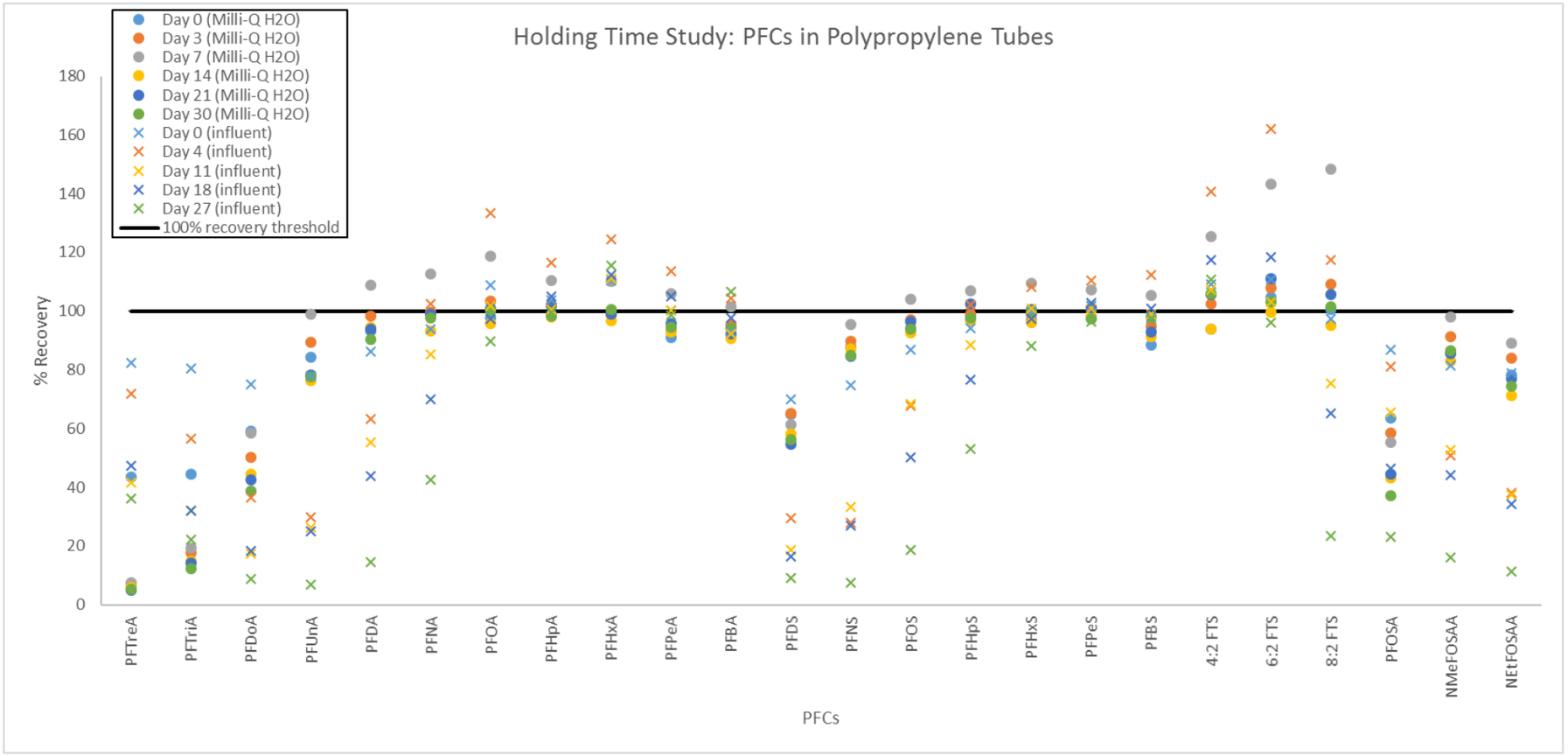
Aliquoting



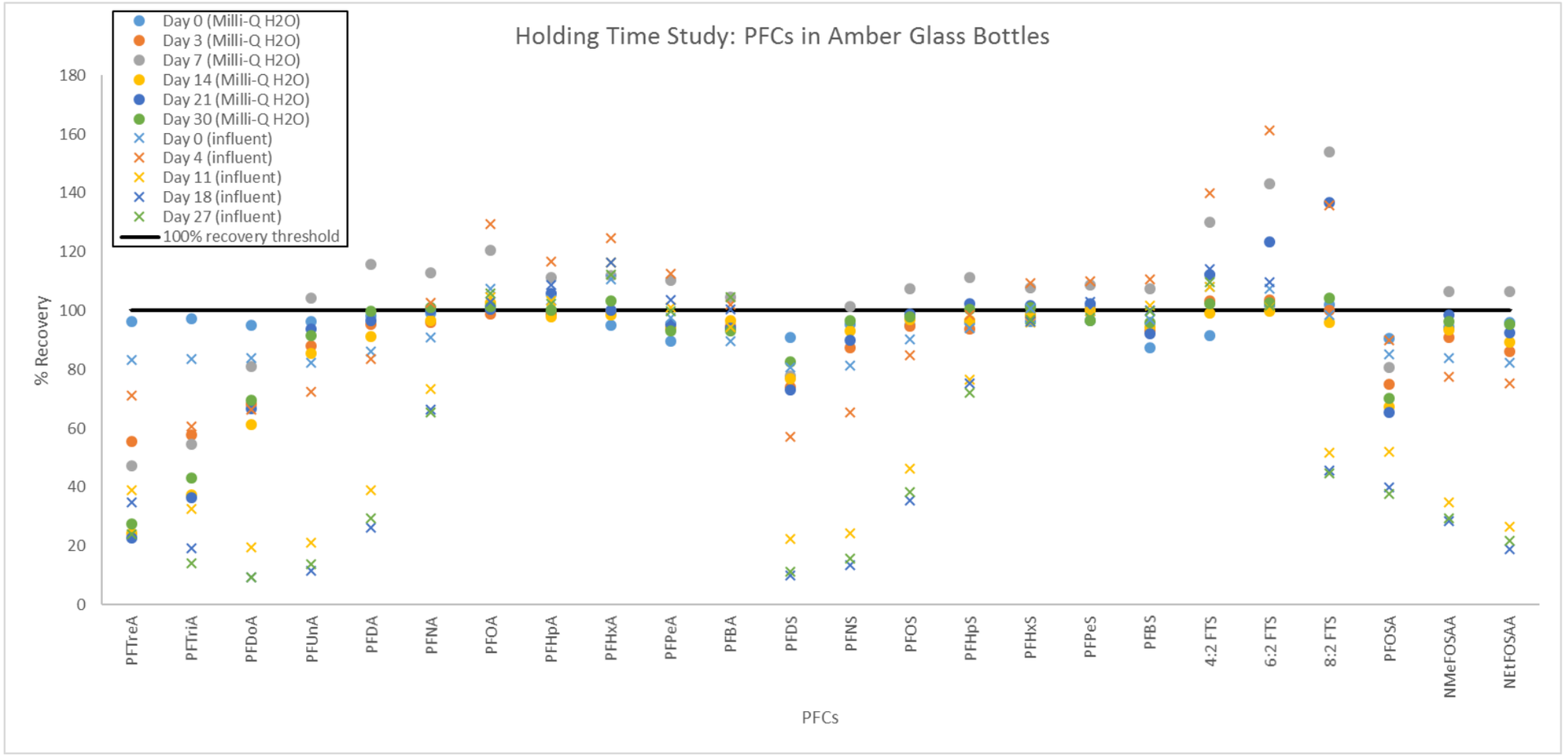
Different matrices

Number of Days

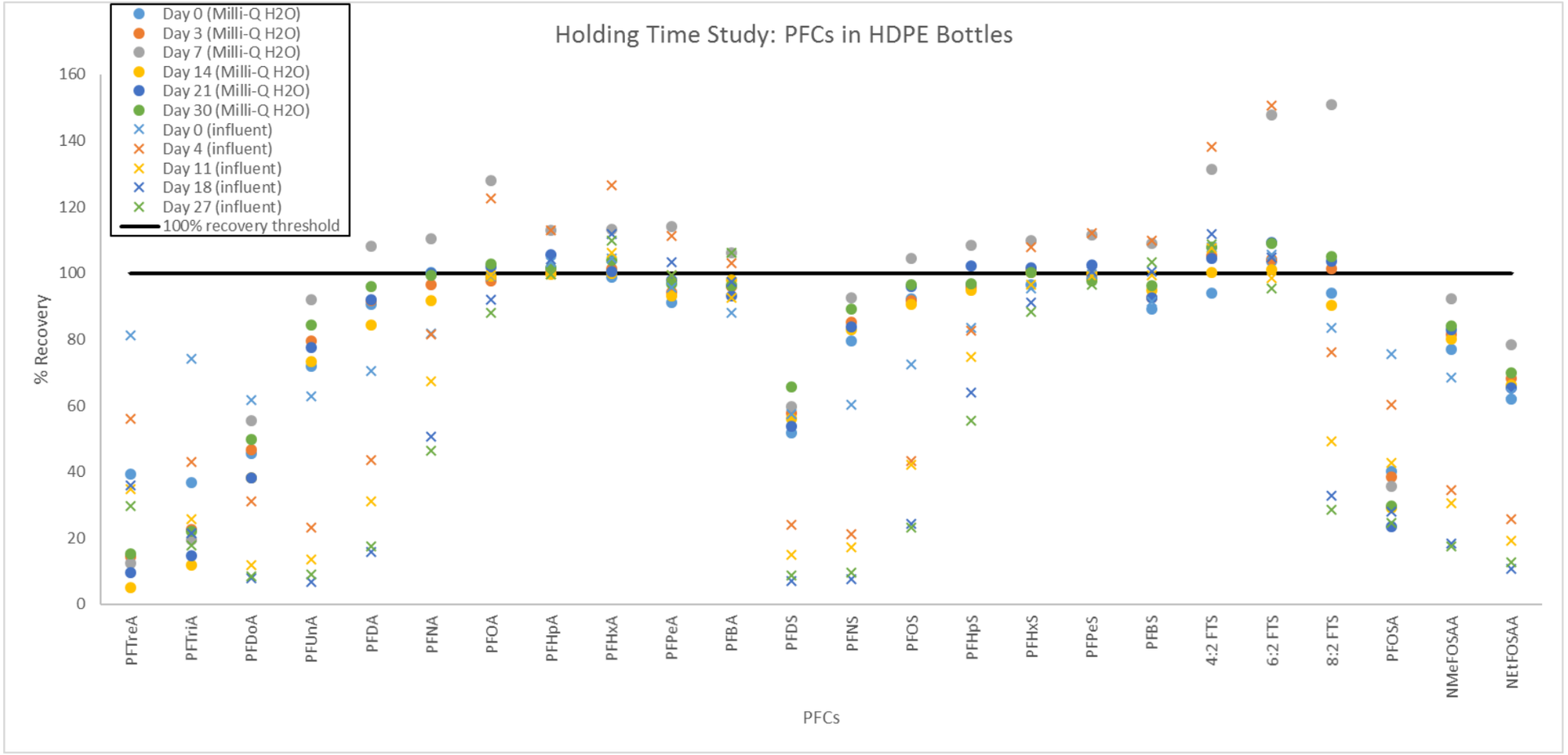
Aliquoting in Polypropylene tubes



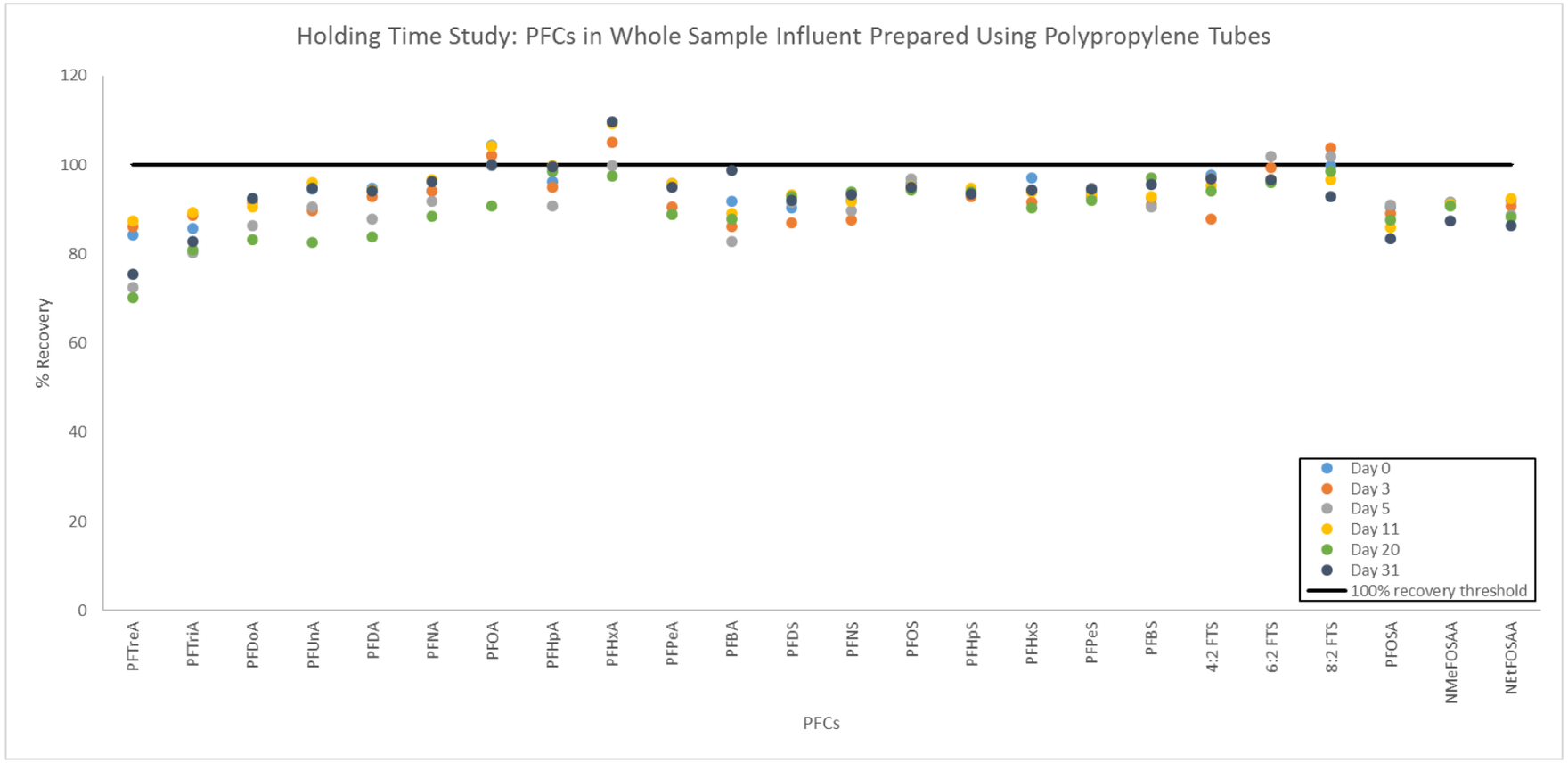
Aliquoting in amber glass bottles



Aliquoting in HDPE bottles

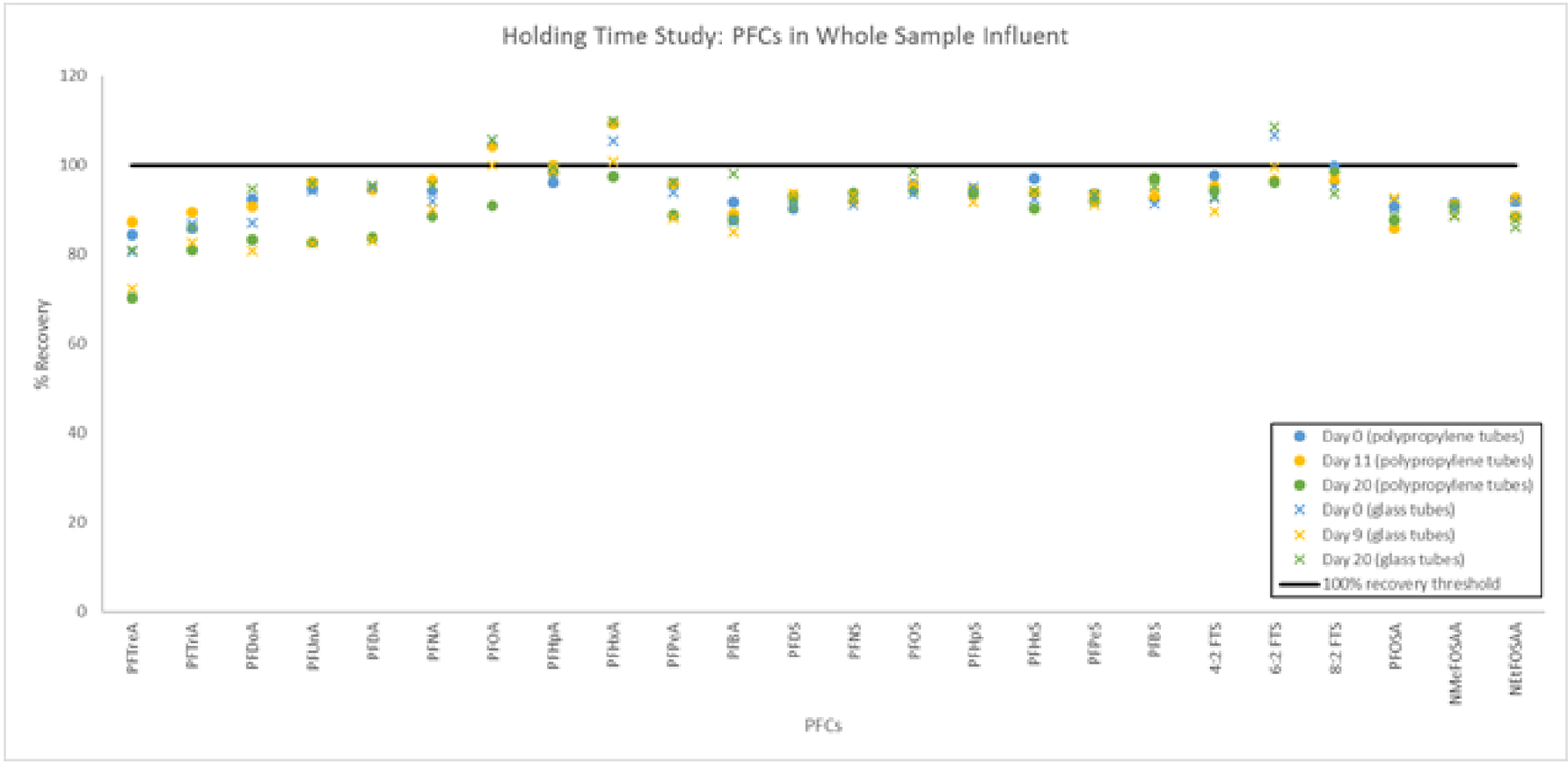


Whole sample “extracted” and analyzed from one Polypropylene (PP) tube, wastewater influent



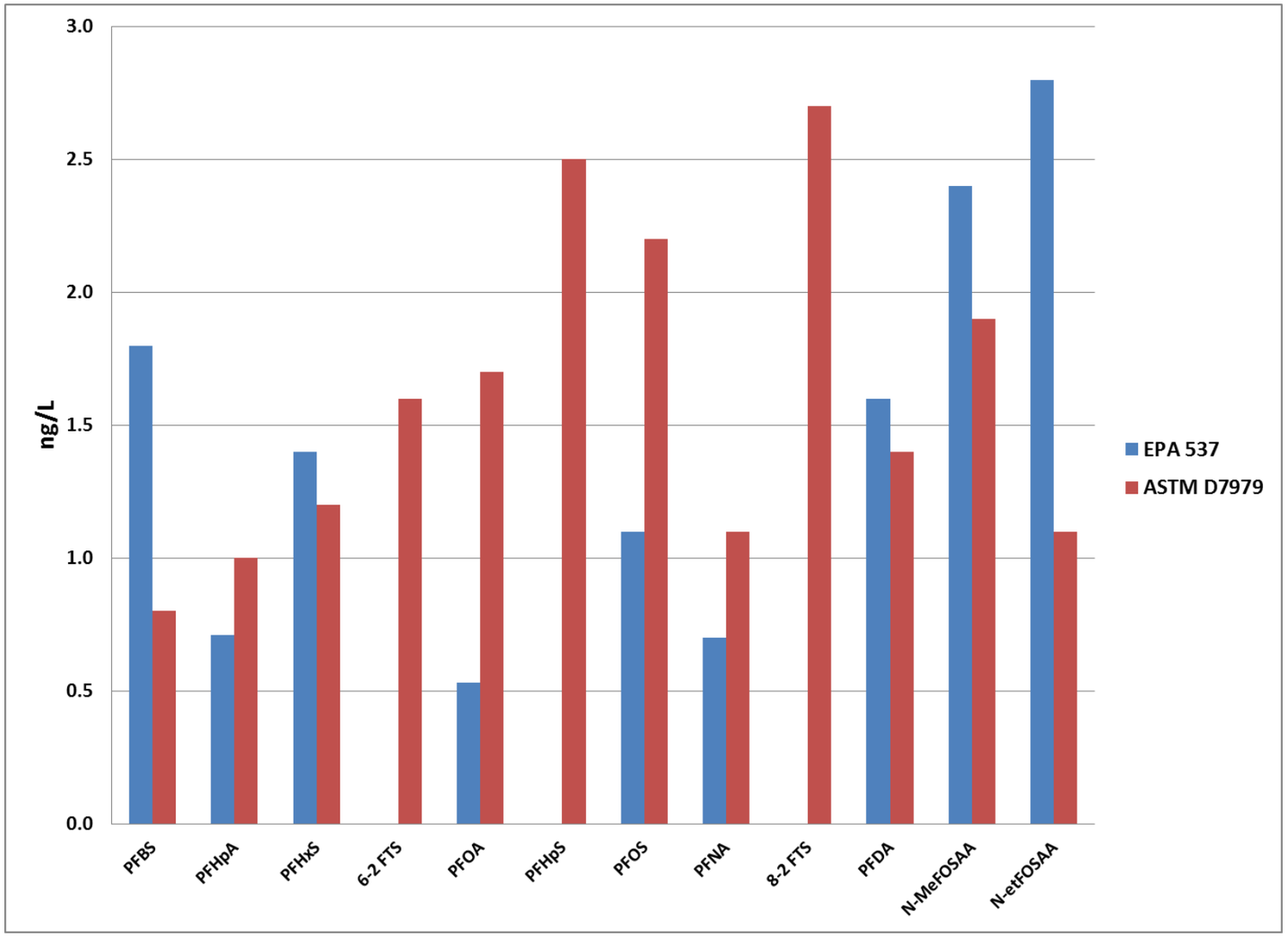
Acceptable recovery for all over 31 days

Whole sample “extracted” and analyzed from one glass tube, wastewater influent

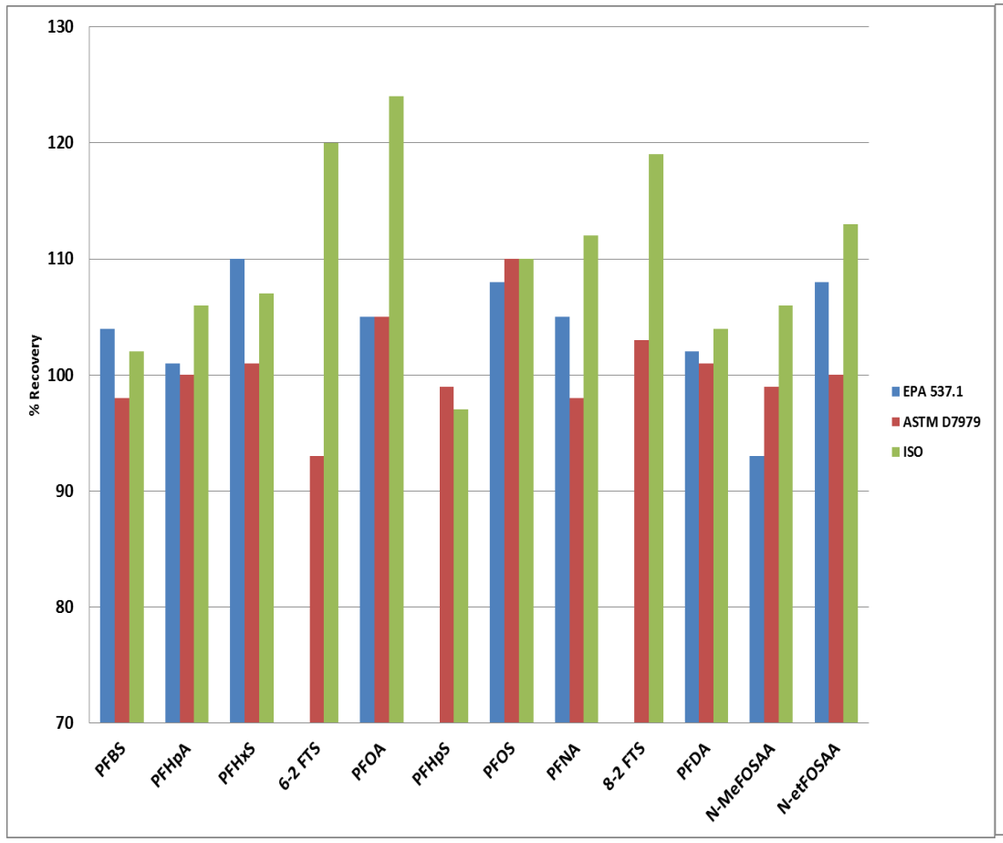


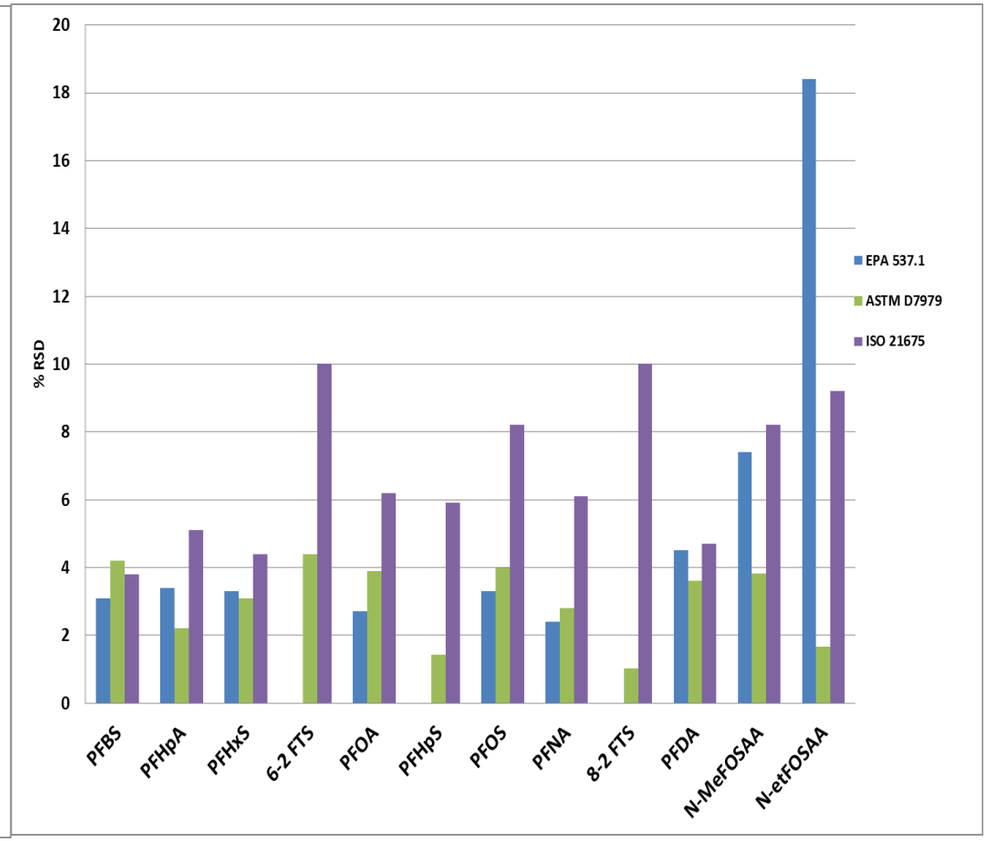
Acceptable recovery for all over 31 days, for safety D7979 uses PP

Comparison of D7979 detection limits with Method 537



Comparison of ASTM D7979 recovery and precision with EPA and ISO methods





Conclusion = D7979 validated for wastewater with comparable results to other PFAS methods

01 Validated in WW, with easy, “green” extraction

02 No SPE needed, filter after methanol added so high TSS not a factor

03 Detection limits, recovery, and precision comparable to other methods

Any Questions?

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