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Trusted Answers

The Evaluation of Novel Weak Anion Exchange and Graphitic Carbon Sorbent Blends for PFAS Extraction and Matrix Reduction in Environmental Extracts

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Brandon Mihelich, Michigan Department of Environment, Great Lakes, and Energy (EGLE) Environmental Laboratory, Lansing, MI, U.S.

Overview

- Benefits of blended solid phase extraction (SPE) sorbents versus layered
- Equivalency of blended and layered weak anion exchange (WAX) and graphitic carbon SPE for EPA Method 1633
- Approaches to reducing matrix interferences in challenging samples
  - Use of blended sorbents with smaller sample size and large volume injection
  - Post extraction matrix removal

Layered and Blended WAX/Carbon S SPE

Specifically designed, developed and manufactured for PFAS applications

- Combined polymeric weak anion exchange (PFAS WAX) and carbon (Carbon S) solid phase extraction (SPE)
- Tested for cleanliness (low PFAS residue)
- Tested for PFAS recovery
- Compliant with EPA Method 1633
- Performance equivalent to other commercial cartridges
- Compatible with automation using standard 6 mL SPE cartridge formats
- Aligns with Agilent's PFAS workflow solutions

New!

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Layered and Blended WAX/Carbon S SPE

Bond Elut PFAS WAX/Carbon S

Property	Specification
Sorbents	Dual-phase PFAS WAX and Carbon S
Formats	Blended and layered sorbents in 6 mL SPE cartridges

Description	Sample Types/Application	Part Number
Layered 200 mg PFAS WAX (top)/ 50 mg Carbon S (bottom)	Aqueous matrices/EPA 1633	5610-2237 (30/pk) 5610-2238 (250/pk)
Layered 500 mg PFAS WAX (top)/ 50 mg Carbon S (bottom)	Aqueous matrices/EPA537Mod	5610-2239 (30/pk) 5610-2240 (250/pk)
Layered 50 mg Carbon S (top)/ 200 mg PFAS WAX (bottom)	Solid matrices/EPA 1633	5610-2241 (30/pk) 5610-2242 (250/pk)
Blended 200 mg PFAS WAX/ 10 mg Carbon S	Aqueous, solids/EPA 1633	5610-2243 (30/pk) 5610-2244 (250/pk)
Blended 200 mg PFAS WAX/ 50 mg Carbon S	Aqueous, solids/EPA 1633	5610-2245 (30/pk) 5610-2246 (250/pk)

New!

Layered and Blended WAX/Carbon S SPE

Bond Elut PFAS WAX/Carbon S

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New!

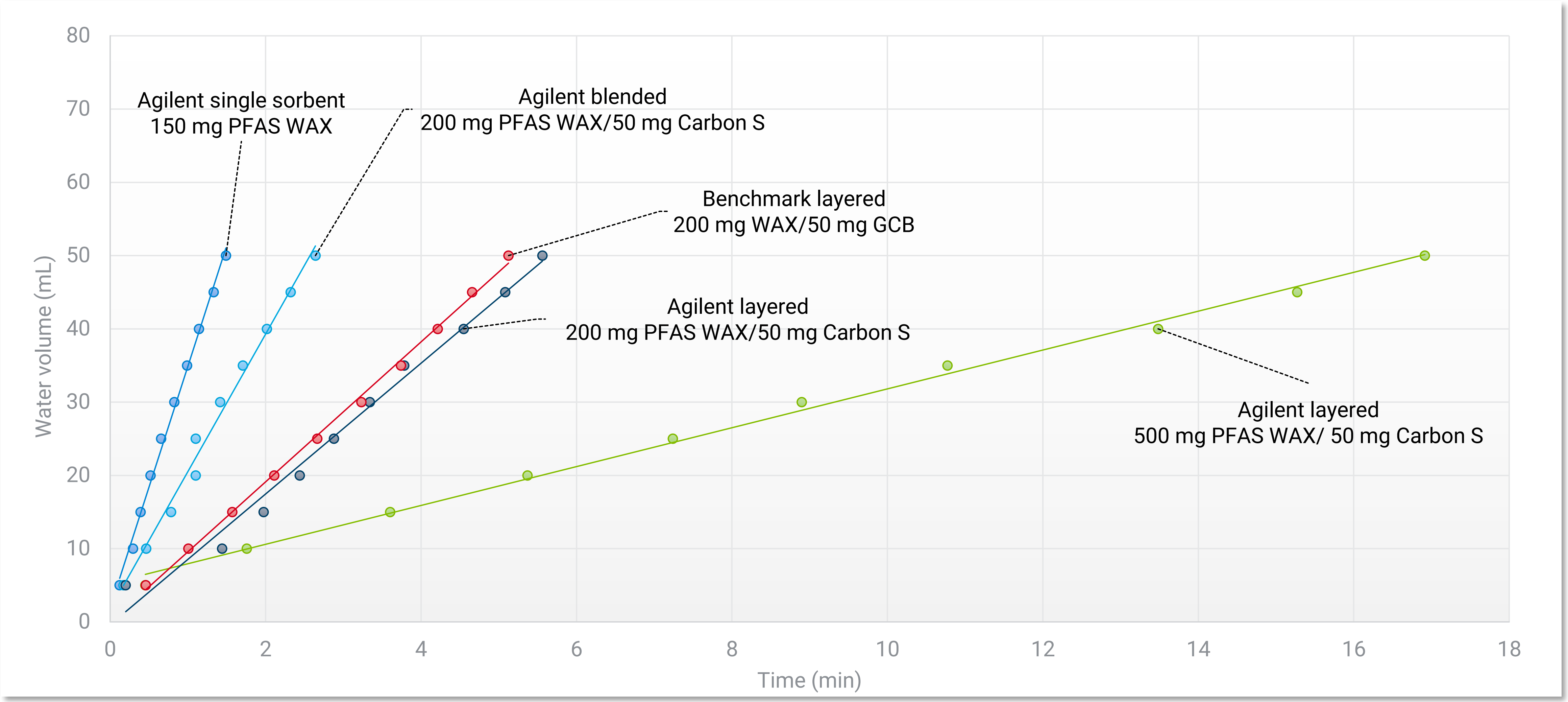
Blended Versus Layered SPE

Benefits of blended sorbents

- Greater permeability
- Wider range of sorbent masses available
- Greater number of sorbent mixtures possible
- Ease of manufacturing
- Lower cost of manufacturing
- Independent of SPE cartridge format
- Less complex, less prone to failure

Benefits of Blended SPE - Permeability

- Flow rate measured for water at 23 °C with 8 inHg vacuum in 5 mL increments



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Benefits of Blended SPE – Effective Pore Diameter

- Estimated permeability and pore diameter

Step 1

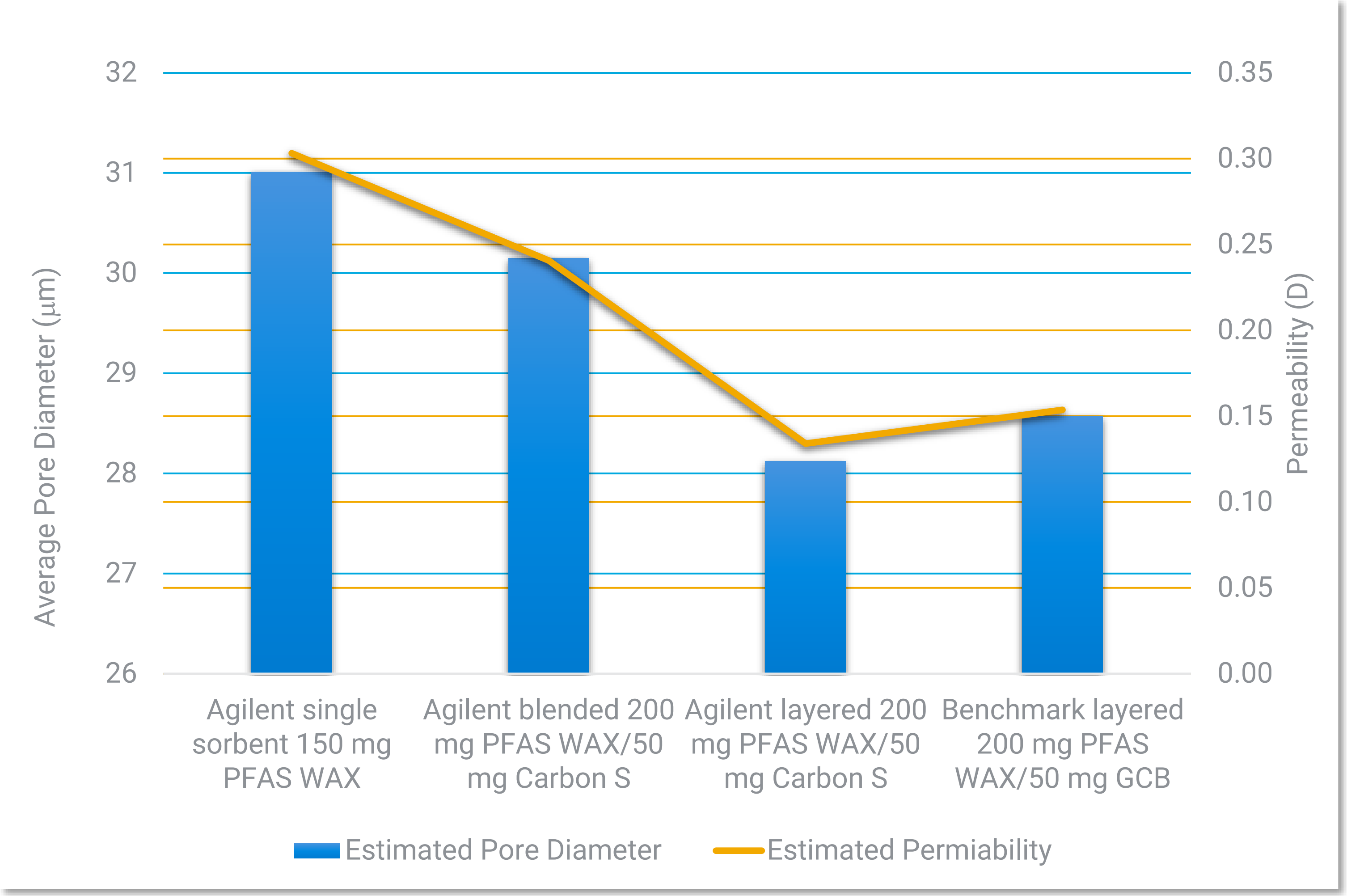
- Estimate permeability from Darcy's Law

$$k = \frac{Q\mu L}{A\Delta P}$$

Step 2

- Estimate pore diameter for Kozeny-Carman equation

$$d_p = \sqrt{\frac{180k(1-\varepsilon)^2}{\varepsilon^3}}$$



Blended Cartridges for EPA Method 1633 - Aqueous method validation

Anthony Novello, Element Materials Technology Group, Ltd., Fort Wayne, IN, U.S.
Brandon Mihelich, Michigan Department of Environment, Great Lakes, and Energy (EGLE) Environmental Laboratory, Lansing, MI, U.S.

Blended SPE Performance Evaluation - EPA Method 1633

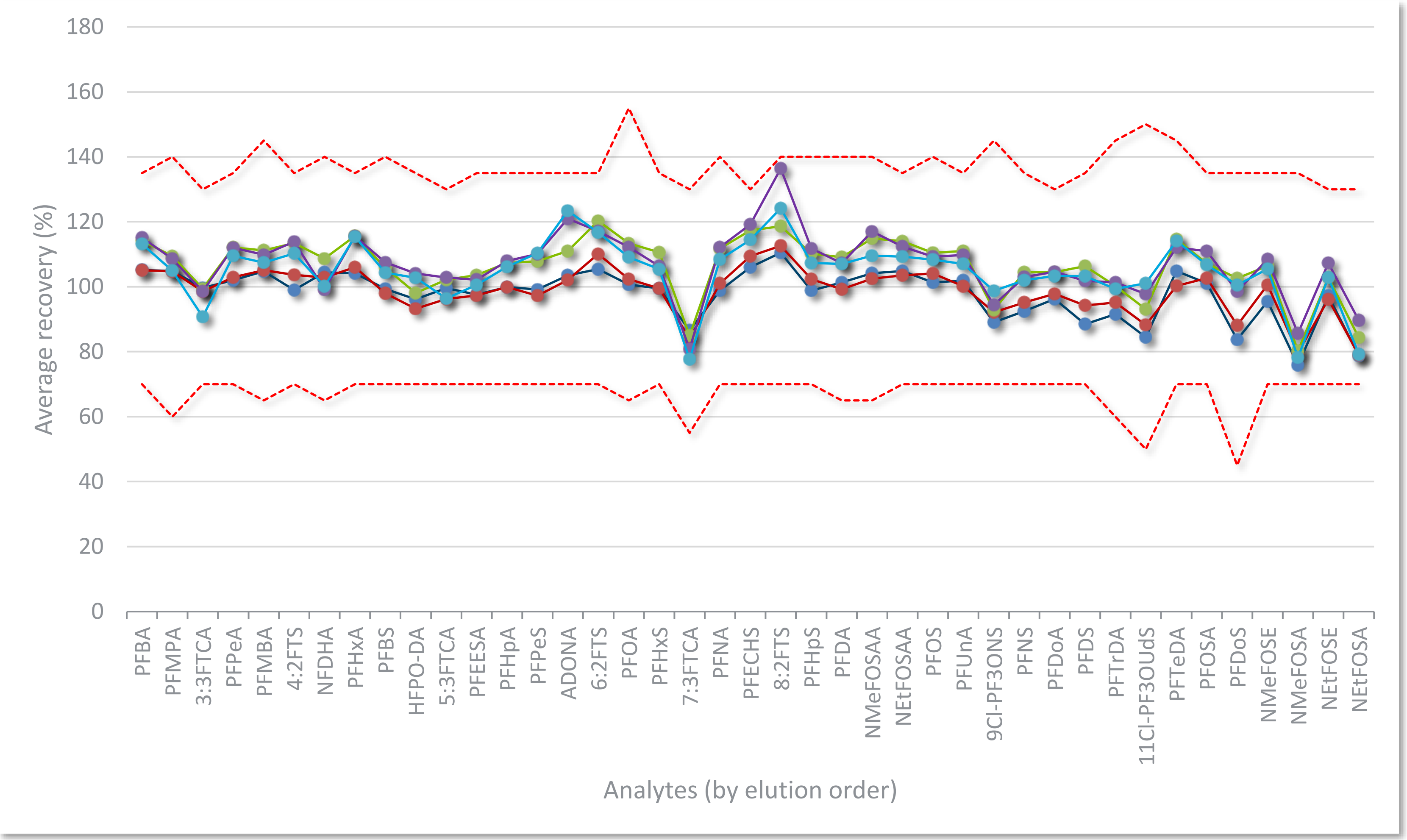
Method comparison – single-step versus two-step versus blended versus layer

Experiment

- Aqueous matrix spikes at 41 targets at 40 ng/L with seven replicates
- Followed EPA Method 1633 aqueous procedure (PromoChrom SPE-03)

Compared protocols

- 200 mg PFAS WAX and 10 mg loose ENVI-Carb™ (two-step)
- 200 mg PFAS WAX and 10 mg loose Carbon S (two-step)
- Blended 200/10 mg PFAS WAX/Carbon S (one-step)
- Blended 200/50 mg PFAS WAX/Carbon S (one-step)
- Layered 200/50 mg PFAS WAX/Carbon S (one-step)



Results

- One-step and two-step processes provided equivalent results
- All recoveries were within EPA Method 1633 acceptance limits

Blended SPE Performance Evaluation - EPA Method 1633

Method comparison – single-step versus two-step versus blended versus layer

Experiment

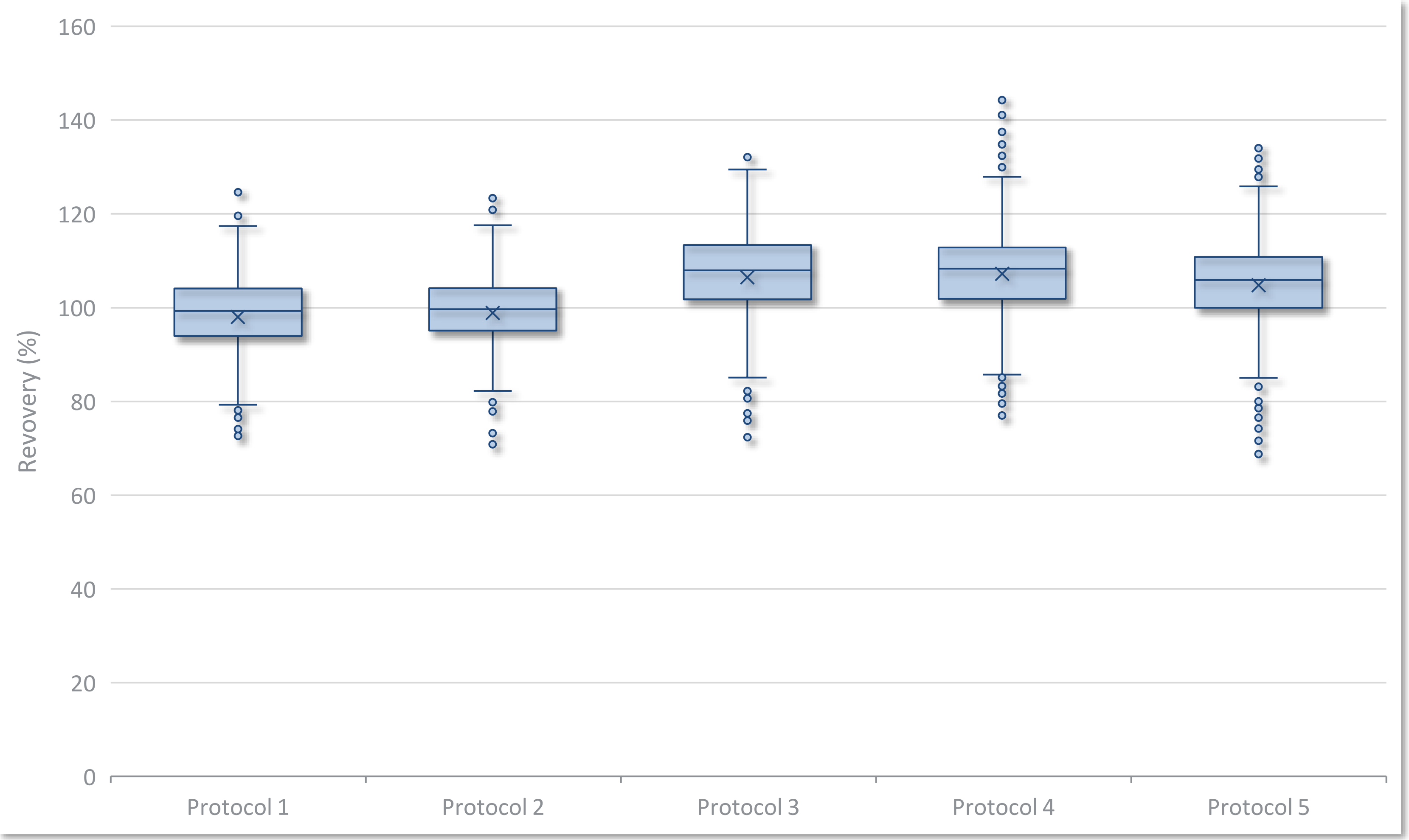
- Aqueous matrix spikes – 7 reps x 41 targets = 287 data points per protocol
- Followed EPA Method 1633 aqueous procedure (PromoChrom SPE-03)

Compared protocols

1. 200 mg PFAS WAX and 10 mg loose ENVI-carb (two-step)
2. 200 mg PFAS WAX and 10 mg loose Carbon S (two-step)
3. Blended 200/10 mg PFAS WAX/Carbon S (one-step)
4. Blended 200/50 mg PFAS WAX/Carbon S (one-step)
5. Layered 200/50 mg PFAS WAX/Carbon S (one-step)

Results

- Protocol 3 - high recovery, fewest outliers and uses the same mass of carbon as written in EPA 1633
- Selected for full method validation



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Blended SPE Performance Evaluation - EPA Method 1633

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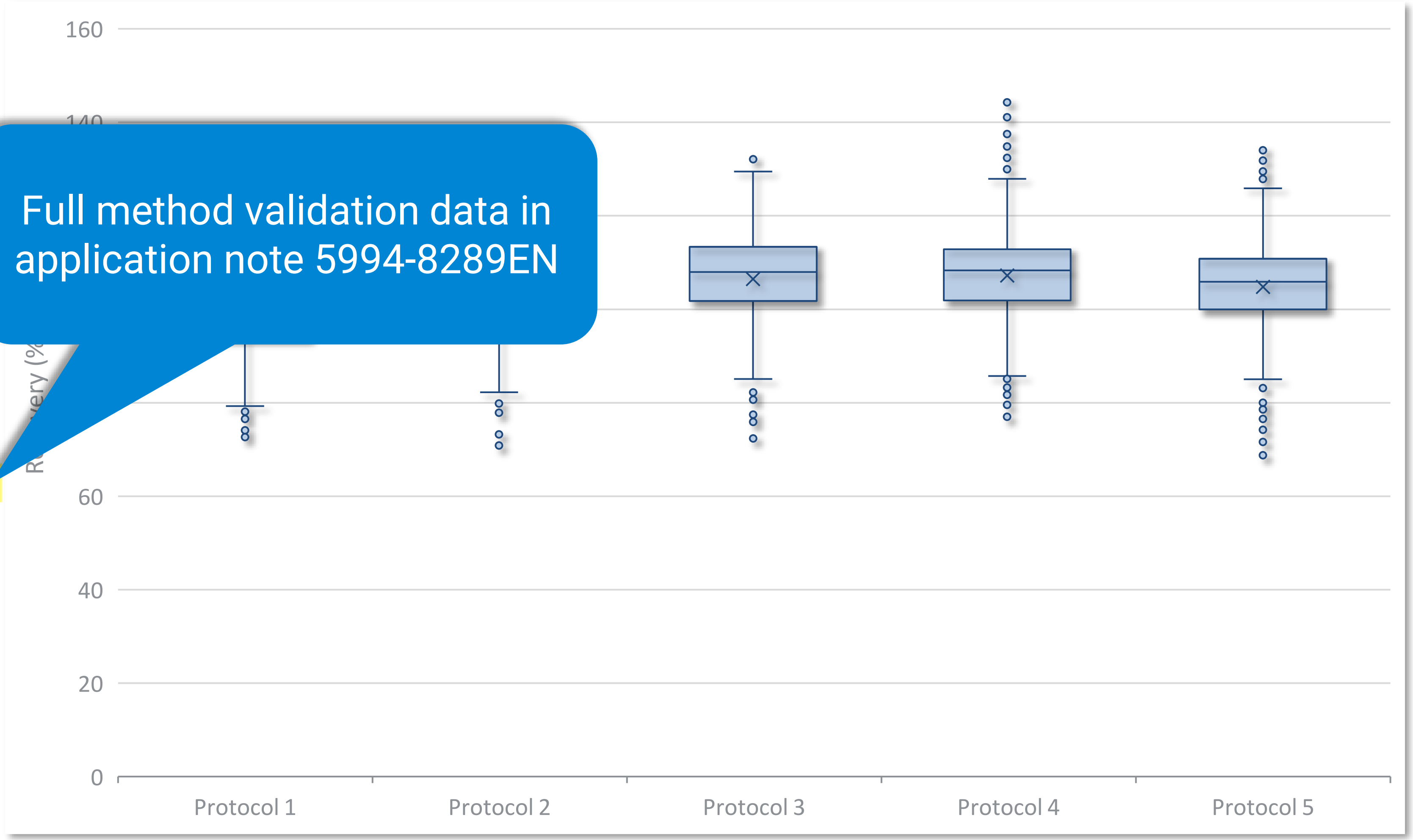

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Blended SPE Performance Evaluation - Sample Results

Production sample analysis

Experiment

- Analysis of customer samples

Protocol

- Two groundwater samples, private residential wells in different locations
- Wastewater storage lagoon
- Landfill monitoring well

Results

- Several positive PFAS targets quantified shown in table
- All other targets below LOQ

Compound	Groundwater Sample 1 (ng/L)	Groundwater Sample 2 (ng/L)	Wastewater Storage Lagoon (ng/L)	Landfill Monitoring Well (ng/L)
PFBA	3.88	2.41	4.13	35.66
3:3FTCA	< LOQ	< LOQ	< LOQ	< LOQ
PFPeA	< LOQ	< LOQ	4.01	8.28
PFHxA	2.09	< LOQ	7.20	8.55
PFBS	4.95	< LOQ	2.42	3.41
PFOA	2.78	< LOQ	3.07	2.67
PFHxS	3.17	2.45	< LOQ	< LOQ
PFDA	< LOQ	< LOQ	< LOQ	< LOQ
PFOS	< LOQ	< LOQ	2.61	< LOQ
PFUnA	< LOQ	< LOQ	< LOQ	< LOQ

Blended SPE Performance Evaluation - Sample Results

Production sample analysis – matrix spikes

Experiment

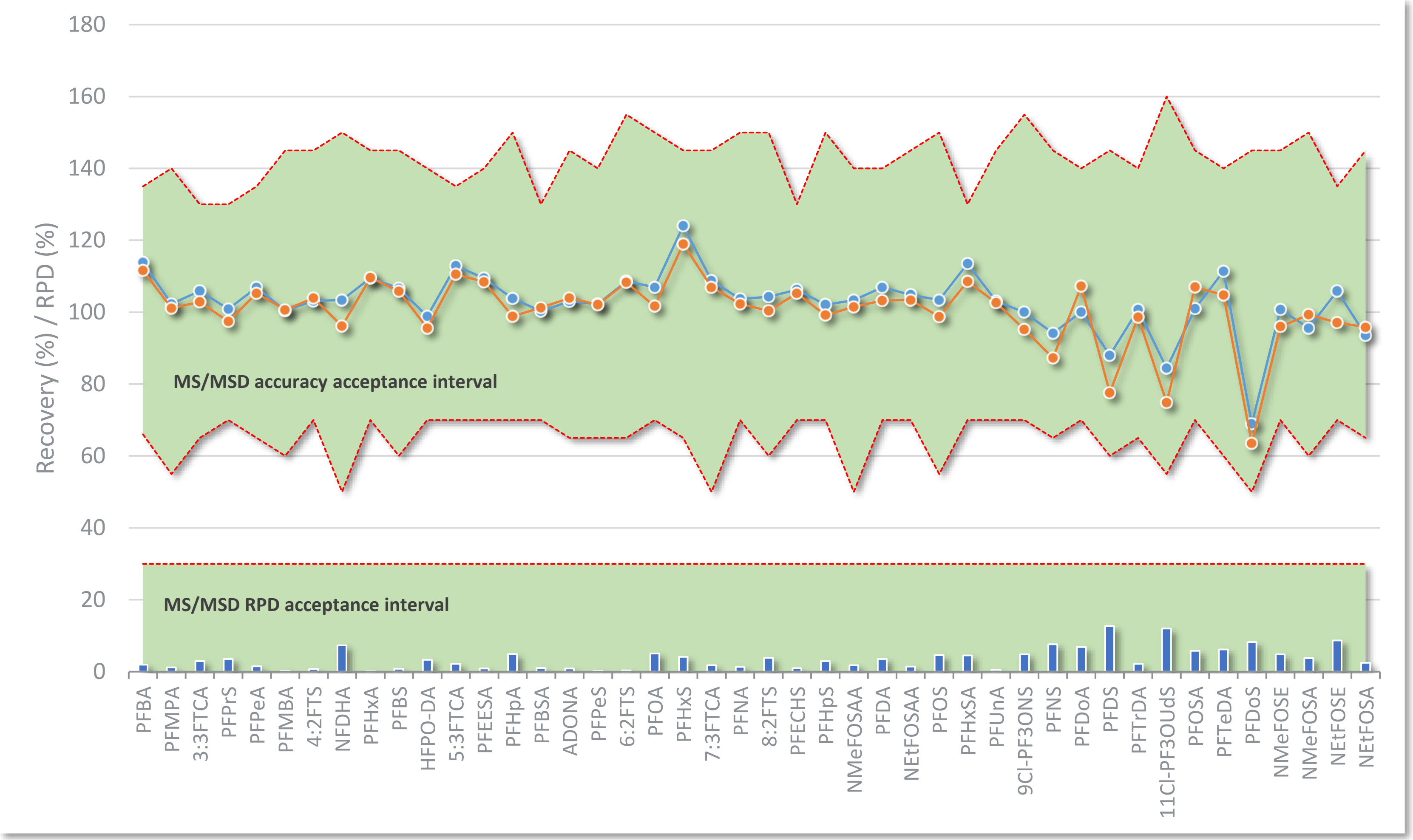
- Mid-level matrix spike (MS) and matrix spike duplicate (MSD) analysis of residential water sample

Protocol

- Analysis of one MS/MSD sample per batch required by Department of Defense and Department of Energy Quality Systems Manual for Environmental Laboratories
- Relative percent deviation (RPD) for targets must be within 30%
- All other EPA Method 1633 requirements must be met

Results

- All recoveries within accuracy and precision limits



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Sample Results

Production sample analysis – EIS and NIS recoveries

Experiment

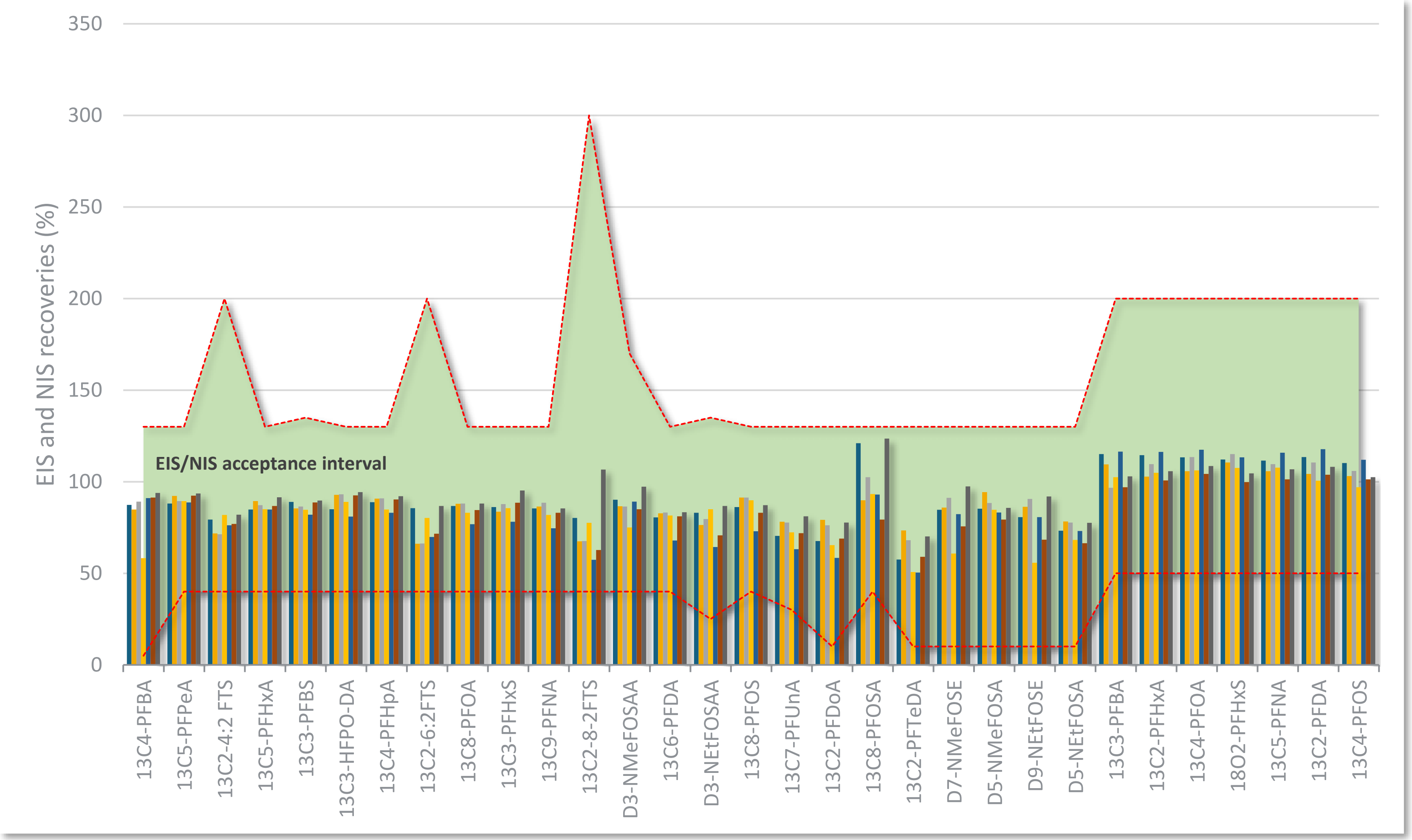
- Production samples EIS and NIS spikes

Protocol

- Groundwater sample 1
- Groundwater sample 2
- Landfill monitoring well
- Wastewater lagoon
- Groundwater field blank
- Groundwater trip blank
- Wastewater trip blank

Results

- All recoveries within accuracy and precision limits



Blended Cartridges for EPA Method 1633 - Solids method development

Approaches for Difficult Matrices for SPE and EPA Method 1633

Difficult matrices – particulates, precipitates and chemical interferants

Common Approaches

- Packing SPE tubes with glass wool
- Packing SPE tubes with plastic turnings
- Adding extra frits/filters to the SPE tube
- Extra filtration and centrifugation
- Using larger sorbent particle size
- Matrix removal with carbon (one or two steps) using GCB, activated carbon, Carbon S, etc.

Approaches for Difficult Matrices for SPE and EPA Method 1633

Difficult matrices – particulates, precipitates and chemical interferants

Approach investigated in this study

- Blended SPE cartridges
- Reduce sample size (10x)
- Increase injection volume (10x)
- For very difficult matrices, use post SPE cleanup (Carbon S, EMR PFAS)

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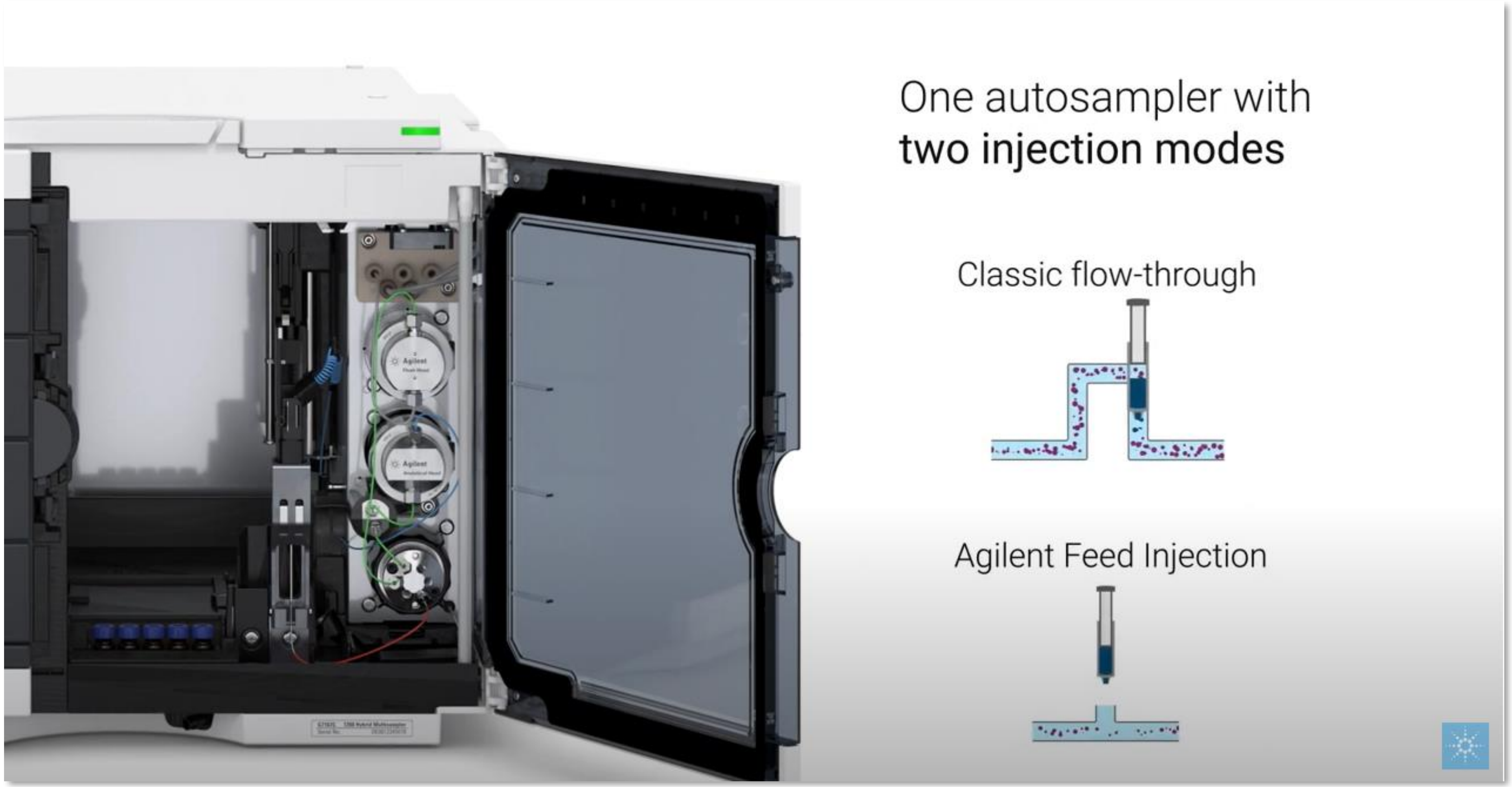
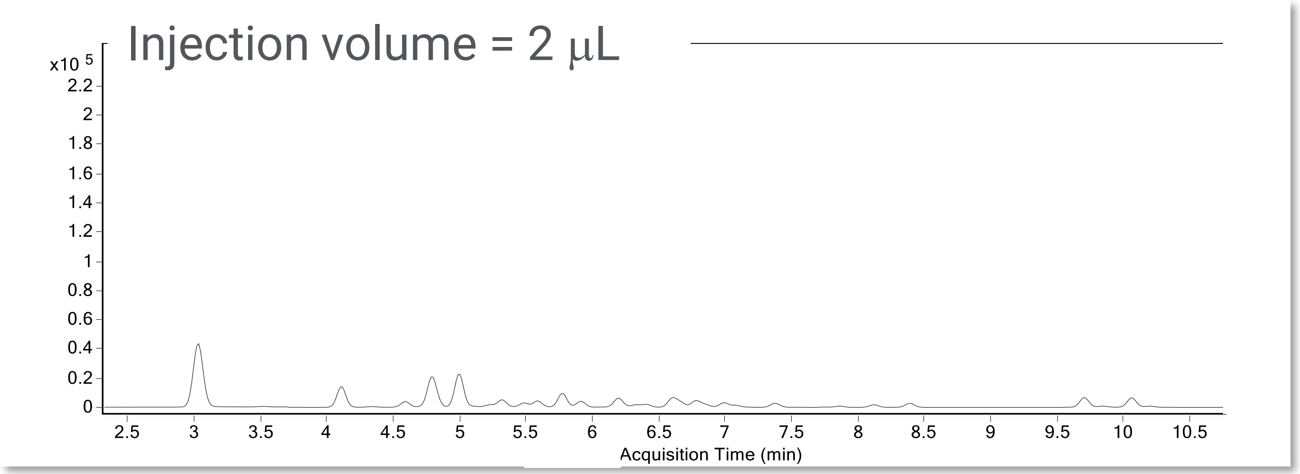
Reducing Sample Size and Increasing Injection Volume

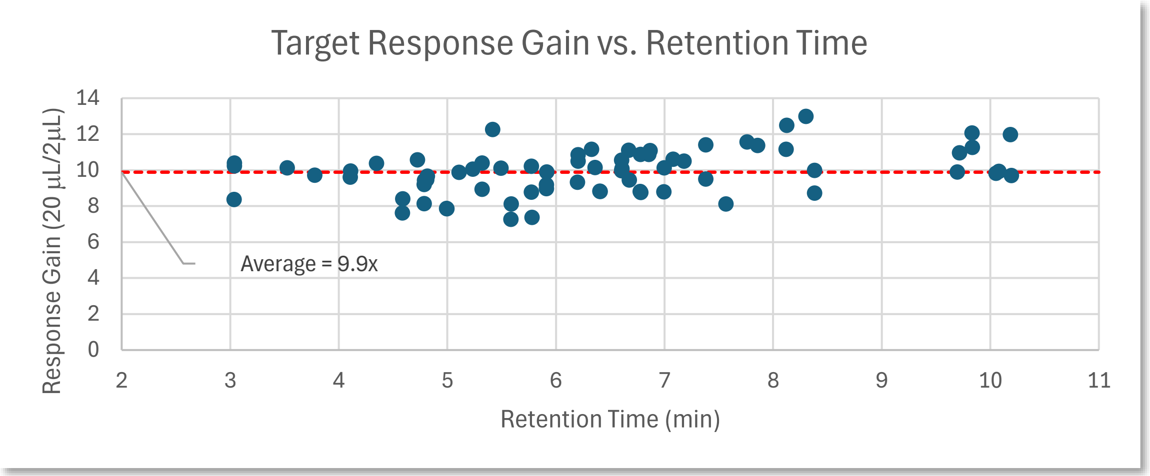
Agilent 1260 Infinity II Hybrid Multisampler

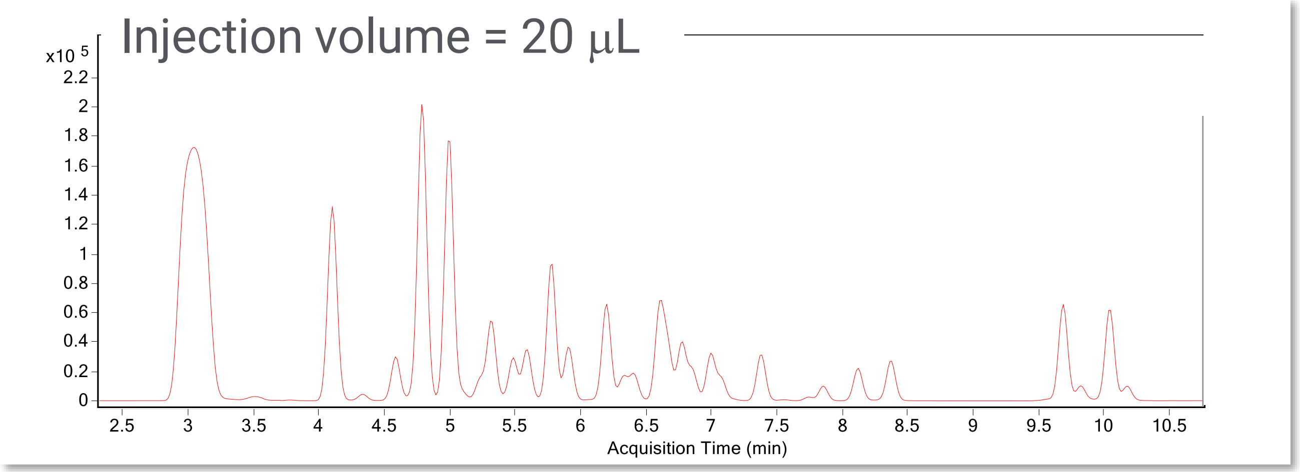


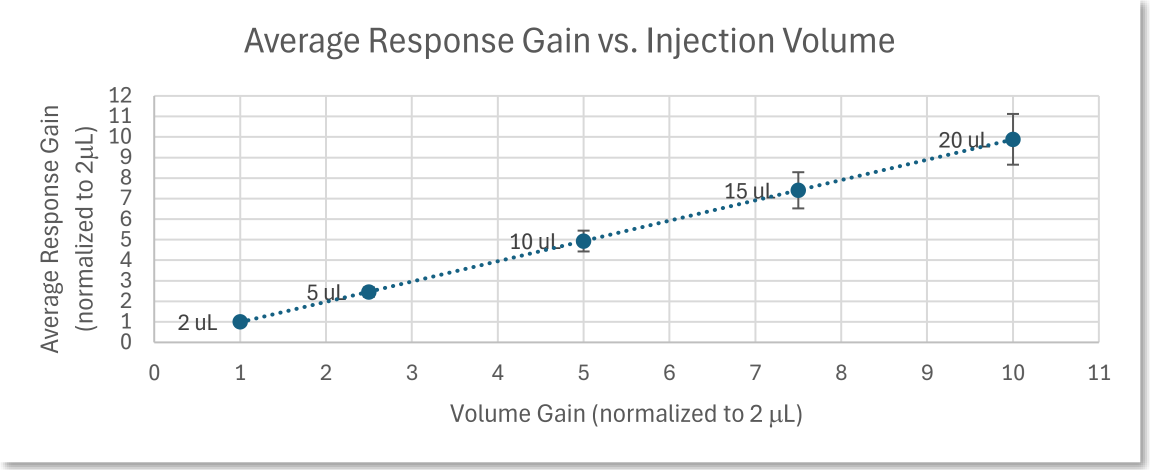
Reducing Sample Size and Increasing Injection Volume

Agilent 1260 Infinity II Hybrid Multisampler – Feed Injection









Instrument Method

LC Method

Parameter	Value		
Column temperature	50 ± 5 °C		
Injection volume	20 µL		
Flow rate	0.400 mL/min		
Mobile phases	A: 5 mM ammonium acetate in 95:5 water:acetonitile B: Acetonitrile		
Gradient	Time (min)	% A	% B
	0.00	98.00	2.00
	0.20	98.00	2.00
	11.00	0.00	100.00
	13.00	0.00	100.00
	13.10	98.00	2.00
Delay column	InfinityLab PFC Delay Column 4.6 x 30 mm (5062-8100)		
Guard column	ZORBAX RRHD Eclipse Plus C18 Column, 2.1 x 50 mm, 1.8 µm (959757-902)		
Analytical column	ZORBAX RRHD Eclipse Plus C18 Column, 2.1 x 100 mm, 1.8 µm (959758-902)		

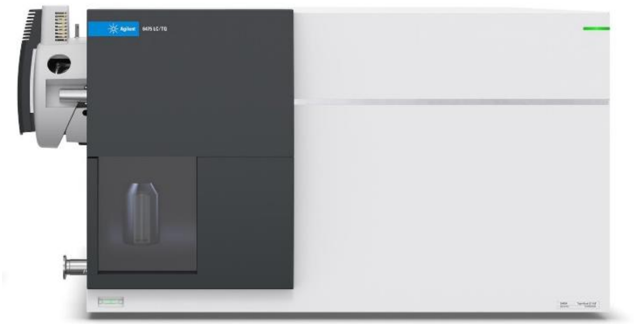
MS Source Conditions

Parameter	Setting
Polarity	Negative
Gas temperature	230 °C
Gas flow	15 L/min
Sheath gas flow	10.0 L/min
Nebulizer pressure	15 psi
Sheath gas temperature	355 °C
Capillary voltage	2500 V
Nozzle voltage	0

Hybrid Feed Injection

Parameter	Setting
Feed speed	40 µL/min
Flush out	4.00 µL
Outer wash	10s IPA:ACN 1:1 (S1) 5s MPB (S3)
Inner wash and seat wash	150 µL IPA:ACN 1:1 (S1) 150 µL Mobile Phase B (S3)
Reconditioning	Mobile Phase A (S2)

Agilent 1290 Infinity II (PFC-Free Kit)



Agilent 6475 LC/TQ

Sample Prep Method Development – Based on EPA Method 1633

0.5 g dry weight solid sample (spike with EIS)

Extract in 0.3% NH_4OH in MeOH

- Vortex 10 min
- Centrifuge 10 min
- Repeat 3x for 10, 15 and 5 mL for total of 30 mL

30 mL of extract in 0.3% NH_4OH in MeOH

- Evaporate down to 7.5 -10 mL
- Bring up to 50 mL with water

Agilent Blended Bond Elut 200 mg PFAS WAX/50 mg Carbon S

- Wash 5 mL of 1% NH_4OH in MeOH
- Condition with 5 mL 0.3M formic acid in water
- Load sample 5 mL/min
- Rinse 1:1 MeOH:0.1M formic acid in water
- Elute 5 mL of 1% NH_4OH in MeOH

Agilent PP vials

- Acidify extract

Agilent 1290 Infinity II
Agilent 6475 LC/TQ

Sample Prep Method Development

Topsoil (easy matrix)

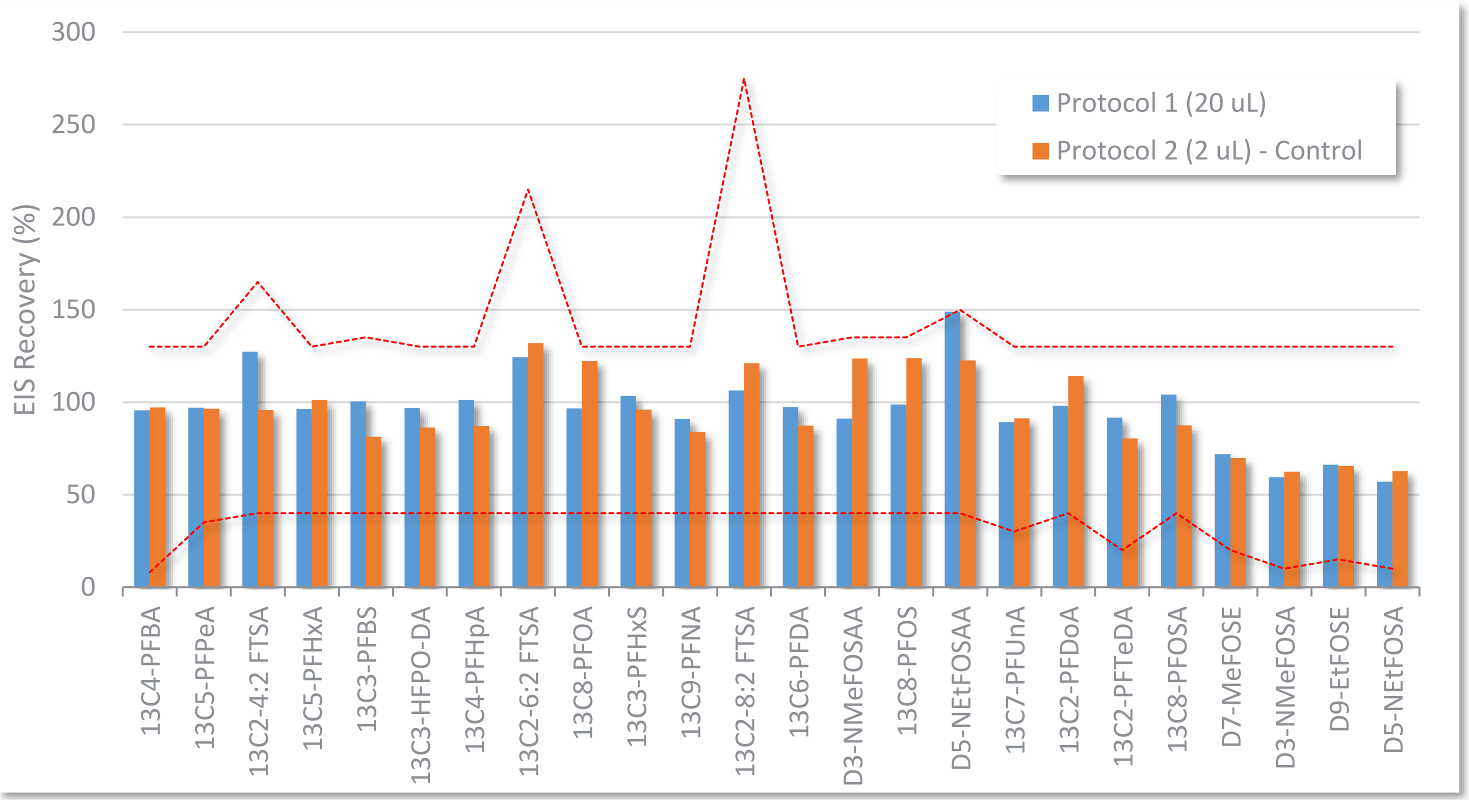
Estimated composition
- 45-50% inorganic matter - mixture of sand, silt and clay
- 1-10% organic matter – decomposed flora and fauna
- 20-30% water

Protocol 1

- Spiked **0.8 grams** of topsoil with EIS mix (0.5 to 10 ng)
- Extracted with blended Bond Elut PFAS 200 mg WAX/50 mg Carbon S
- Final extraction volume 5 mL
- **20 µL** injection volume

Protocol 2 (Control)

- Spiked **8 grams** of topsoil with EIS mix (0.5 to 10 ng)
- Extracted with layered 50 mg GCB/200 mg WAX
- Final extraction volume 5 mL
- **2 µL** injection volume



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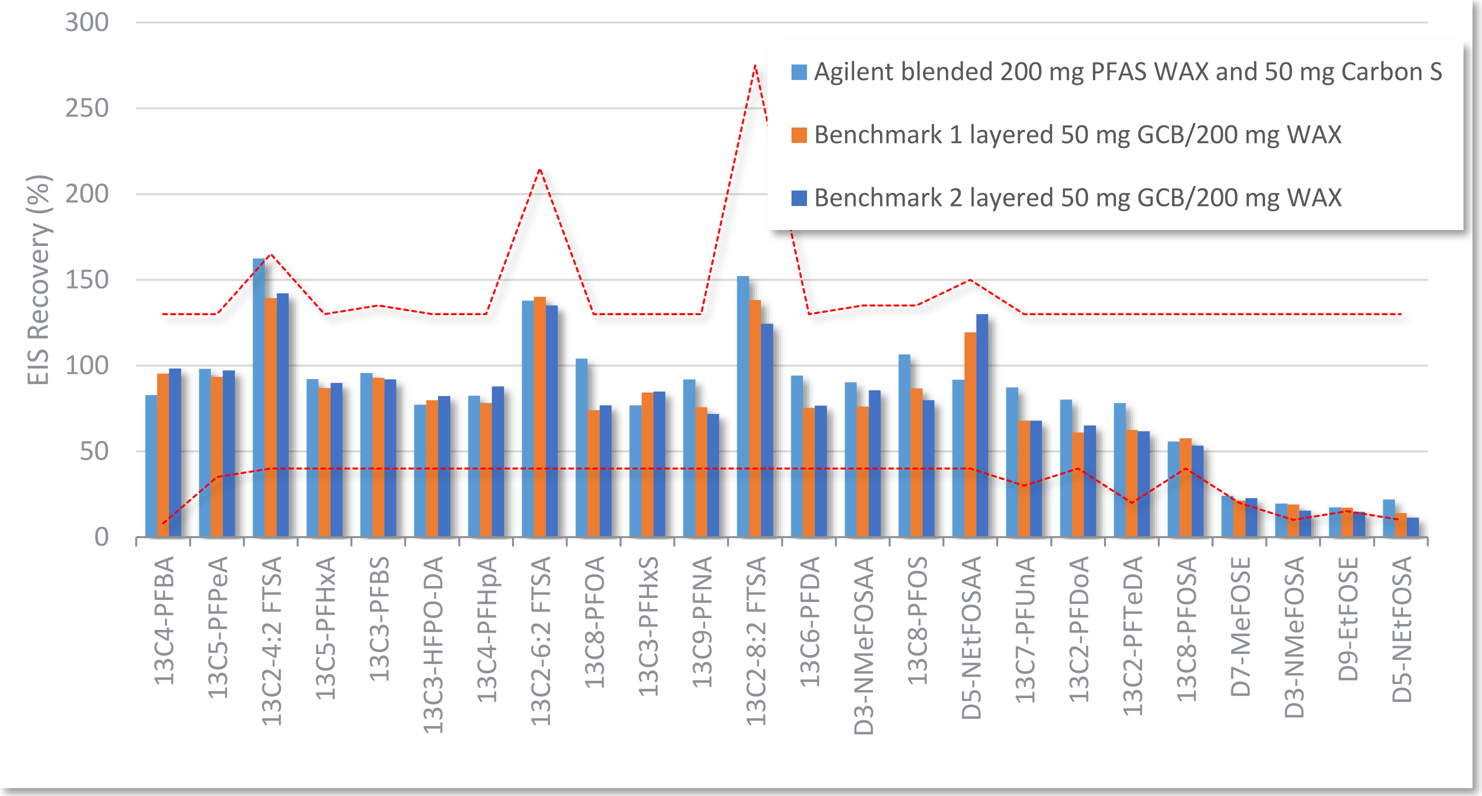
Sample Prep Method Development

Topsoil (easy matrix)

Estimated composition

- 45-50% inorganic matter - mixture of sand, silt and clay
- 1-10% organic matter – decomposed flora and fauna
- 20-30% water

What if 20 µL of 8 g of extract is injected?



Sample Prep Method Development

Reed Sedge Peat (semi-challenging matrix)

Estimated composition

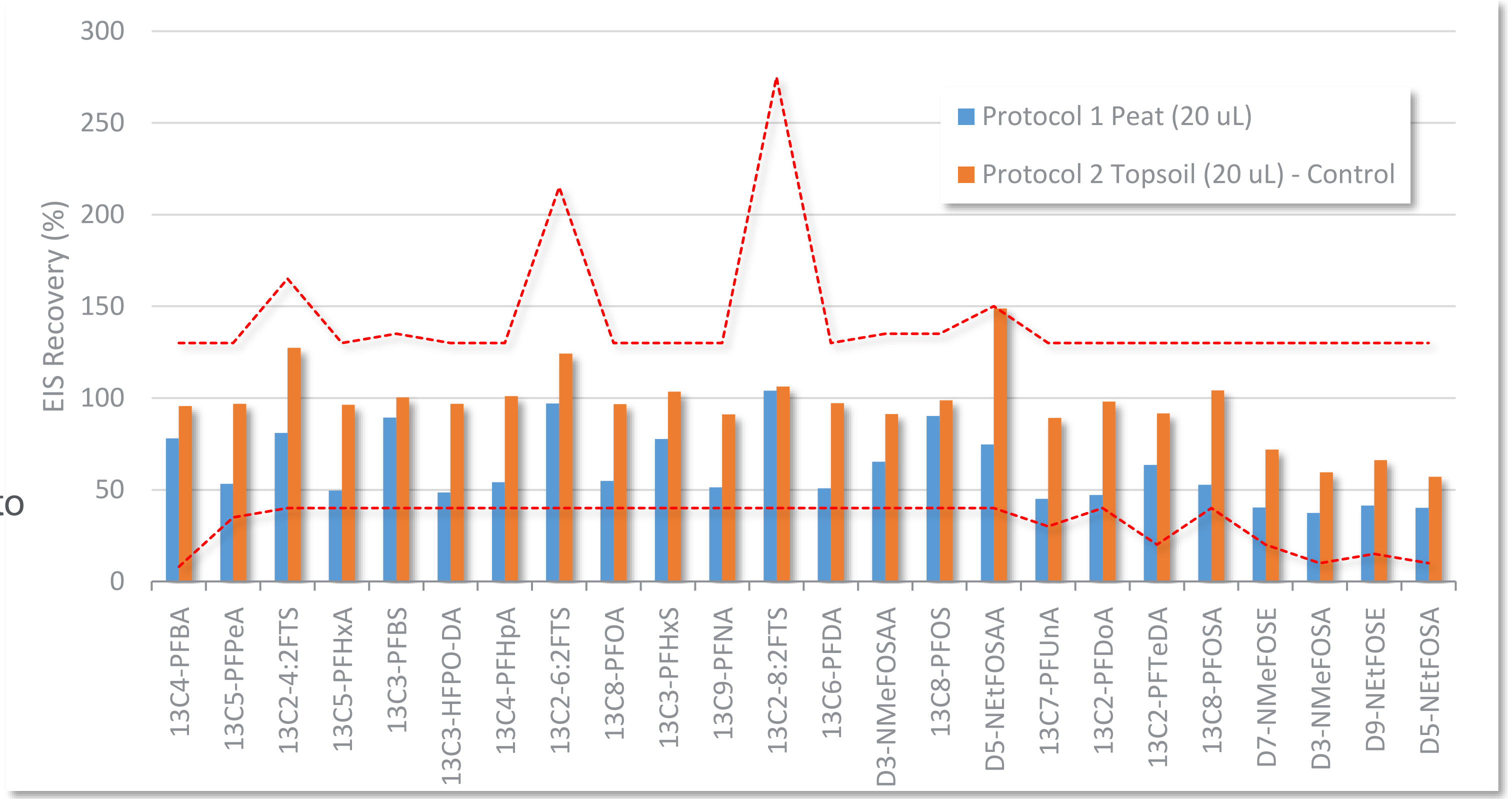
- 5-20% inorganic matter - mixture of sand, silt and clay
- 80-95% organic matter – humic acid, fulvic acids and humin
- 10-30% water – can be high

Protocol 1

- Spiked **0.8 grams of peat** with EIS mix (0.5 to 10 ng)
- Extracted with blended Bond Elut PFAS 200 mg WAX/50 mg Carbon S
- Final extraction volume 5 mL and **20 µL** injection volume

Protocol 2 (Control)

- Compare to **0.8 g of topsoil** spiked with EIS mix (0.5 to 10 ng)
- Extracted with blended Bond Elut PFAS 200 mg WAX/50 mg Carbon S
- Final extraction volume 5 mL and **20 µL** injection volume



Sample Prep Method Development – Based on EPA Method 1633

0.5 g dry weight solid sample (spike with EIS)

Extract in 0.3% NH_4OH in MeOH

- Vortex 10 min
- Centrifuge 10 min
- Repeat 3x for 10, 15 and 5 mL for total of 30 mL

30 mL of extract in 0.3% NH_4OH in MeOH

- Evaporate down to 7.5 -10 mL
- Bring up to 50 mL with water

Agilent Blended Bond Elut 200 mg PFAS WAX/50 mg Carbon S

- Wash 5 mL of 1% NH_4OH in MeOH
- Condition with 5 mL 0.3M formic acid in water
- Load sample 5 mL/min
- Rinse 1:1 MeOH:0.1M formic acid in water
- Elute 5 mL of 1% NH_4OH in MeOH

Agilent Bond Elut Carbon S for PFAS 250 mg

- Acidify extract
- Pass through cleanup
- (Replace syringe filtration step)

Agilent 1290 Infinity II
Agilent 6475 LC/TQ

Sample Prep Method Development

Reed Sedge Peat (semi-challenging matrix)

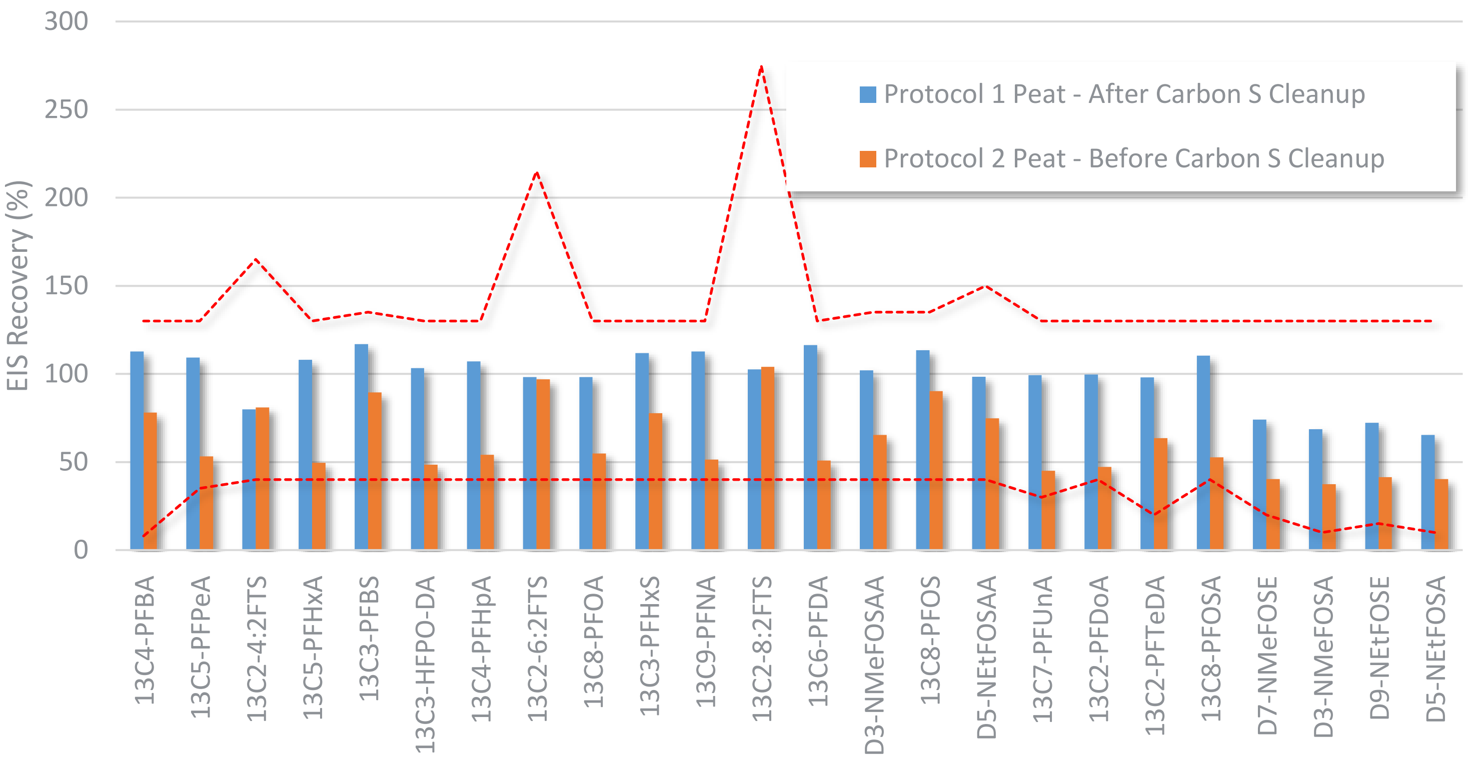
Estimated composition
- 5-20% inorganic matter - mixture of sand, silt and clay
- 80-95% organic matter – humic acid, fulvic acids and humin
- 10-30% water – can be high

Protocol 1

- Spiked **0.8 grams of peat** with EIS mix (0.5 to 10 ng)
- Extracted with blended Bond Elut PFAS 200 mg WAX/50 mg Carbon S
- Pass through cleanup using Bond Elut Carbon S for PFAS 250 mg
- Final extraction volume 5 mL and **20 µL** injection volume

Protocol 2

- Compare to **0.8 g of peat** spiked with EIS mix before pass-through cleanup with Carbon S



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Sample Prep Method Development

Biosolids (difficult matrix)

NIST Standard Reference Material®
2781Domestic Sludge

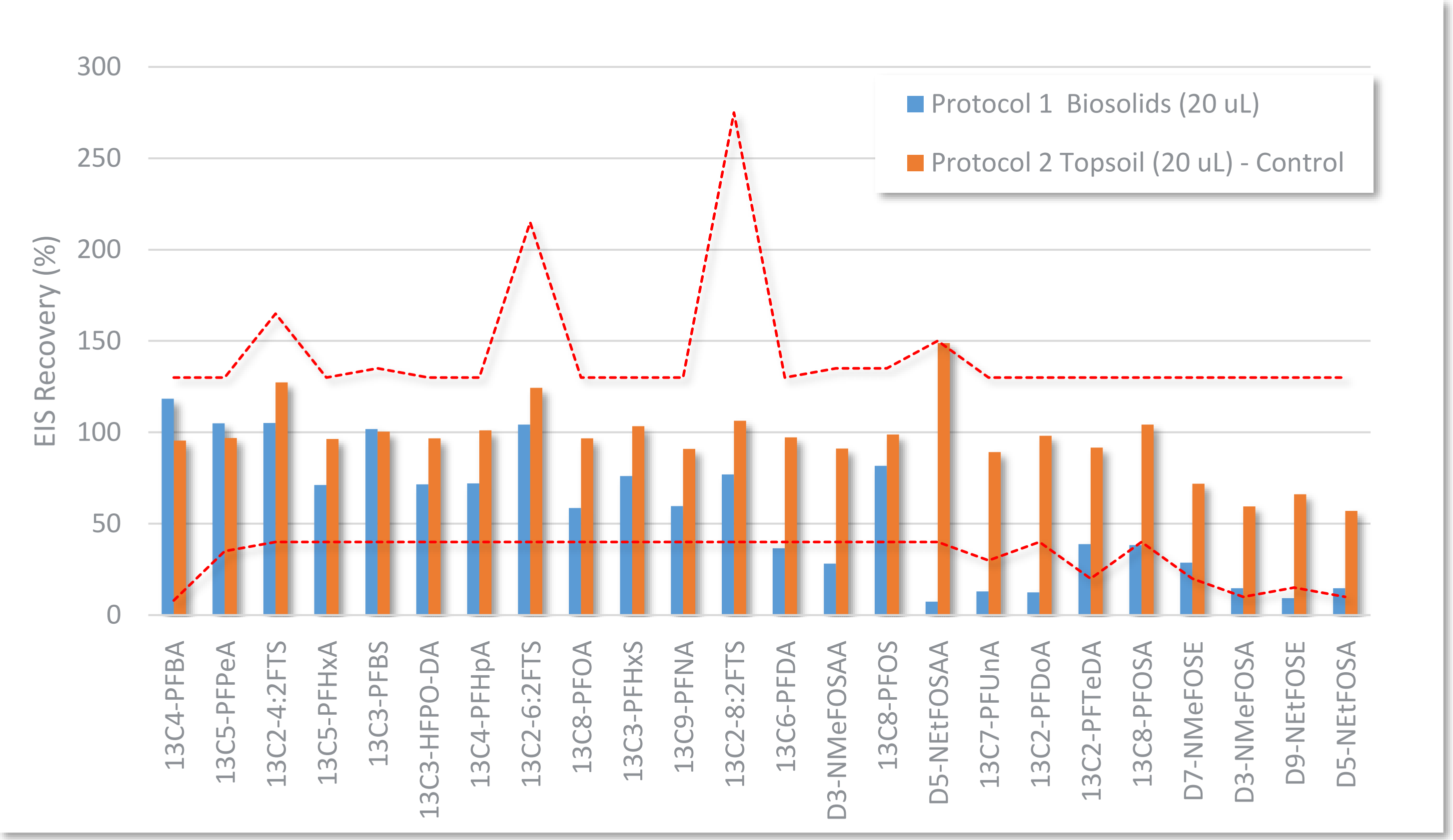
Estimated composition (doi: 10.3390/ijerph20064804)
- 40% carbohydrates
- 30% proteins
- 30% lipids

Protocol 1

- Spiked **0.05 grams** of biosolids with EIS mix (0.5 to 10 ng)
- Extracted with blended Bond Elut PFAS 200 mg WAX/50 mg Carbon S
- Final extraction volume 5 mL
- **20 µL** injection volume

Protocol 2 (Control)

- Compare to **0.8 g of topsoil** spiked with EIS mix (0.5 to 10 ng)
- Extracted with blended Bond Elut PFAS 200 mg WAX/50 mg Carbon S
- Final extraction volume 5 mL and **20 µL** injection volume



Sample Prep Method Development – Based on EPA Method 1633

0.05 g dry weight solid sample (spike with EIS)

Extract in 0.3% NH_4OH in MeOH

- Vortex 10 min
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30 mL of extract in 0.3% NH_4OH in MeOH

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Agilent Blended Bond Elut 200 mg PFAS WAX/50 mg Carbon S

- Wash 5 mL of 1% NH_4OH in MeOH
- Condition with 5 mL 0.3M formic acid in water
- Load sample 5 mL/min
- Rinse 1:1 MeOH:0.1M formic acid in water
- Elute 5 mL of 1% NH_4OH in MeOH

Agilent Captiva EMR PFAS Food II

- Acidify extract
- Pass through cleanup
- (Replace syringe filtration step)

Agilent 1290 Infinity II
Agilent 6475 LC/TQ

Sample Prep Method Development

Biosolids (difficult matrix)

NIST Standard Reference Material®
2781Domestic Sludge

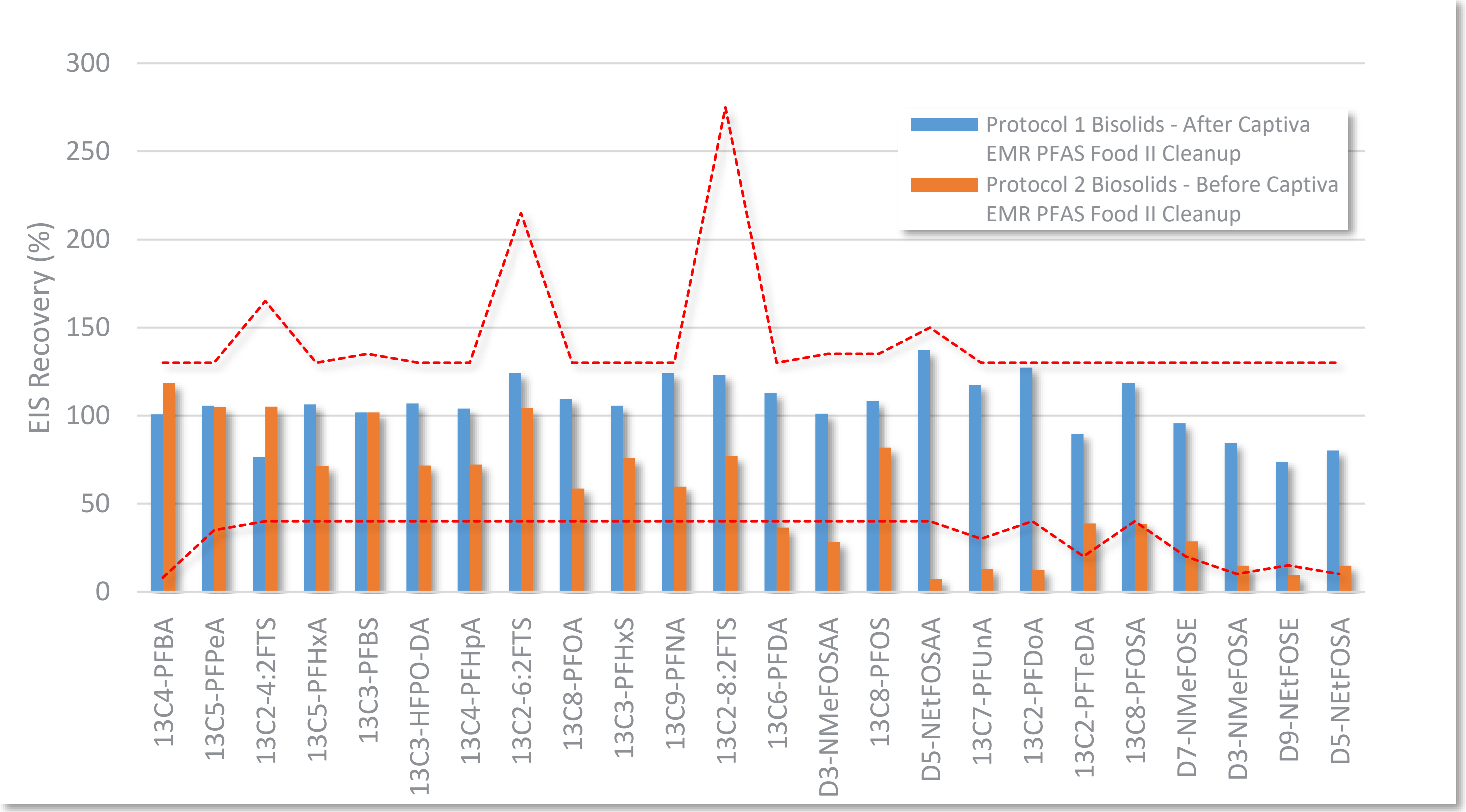
Estimated composition (doi: 10.3390/ijerph20064804)
- 40% carbohydrates
- 30% proteins
- 30% lipids

Protocol 1

- Spiked **0.05 grams of biosolids** with EIS mix (0.5 to 10 ng)
- Extracted with blended Bond Elut PFAS 200 mg WAX/50 mg Carbon S
- Pass through cleanup using Captiva EMR PFAS Food II
- Final extraction volume 5 mL and **20 μL** injection volume

Protocol 2

- Compare to **0.05 g of biosolids** spiked with EIS mix before pass-through cleanup with Captiva EMR PFAS Food II



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Conclusions

- Equivalent results achieved using two-step SPE and bulk carbon, one-step layered SPE, and blended Bond Elut PFAS WAX/Carbon S
- For difficult matrices, using blended SPE and reducing sample size can lower matrix interferences and improve recoveries
- For very difficult matrices, replacing post-extraction syringe filtration with pass-through cleanup can remove matrix interferences

Application notes:

- Automated Solid Phase Extraction of PFAS from Aqueous Samples
  Using dual-phase Agilent Bond Elut PFAS WAX/Carbon S SPE cartridges for US EPA Method 1633
  https://www.agilent.com/cs/library/applications/an-1633-automated-spe-wax-carbon-s-5994-8289en-agilent.pdf

- Comparison of Dual Sorbent Solid Phase Extraction for PFAS Applications
  Using dual-phase Agilent Bond Elut PFAS WAX/ Carbon S SPE cartridges for US EPA Method 1633
  https://www.agilent.com/cs/library/applications/an-1633-wax-carbon-s-spe-comparison-5994-8291en-agilent.pdf