Method Performance using dual WAX/GCB and GCB/WAX SPE Formats for Draft EPA Method 1633

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Global Market Development – Food and Environmental

phenomenex®

PFAS Methods Waters, Soils, Biosolids, Tissues

Drinking Water

- US EPA 537.1 – Internal Standard, 18 analytes
- US EPA 533 – Isotope Dilution, 25 analytes

Groundwater/wastewater/biosolids

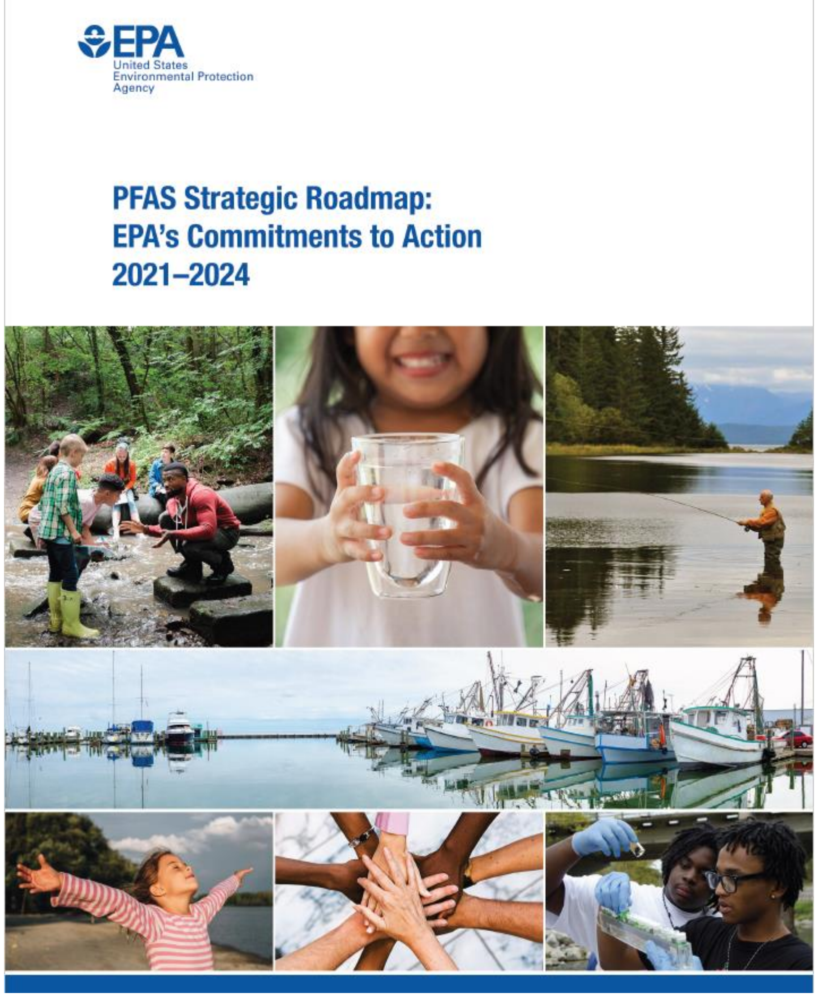
- DOD QSM 5.3- Isotope Dilution
- EPA 1633 –Isotope dilution (Draft)
- US EPA 8327 – External standard, 24 analytes
- ASTM D7979-17 – isotope dilution, 21 analytes
- ASTM D8421- 44 analytes

Soils

- EPA 1633 – Isotope dilution (Draft)
- US EPA 8327 – External standard, 24 analytes
- ASTM D7968-17a – isotope dilution, 21 analytes

Wastewater

- EPA 1621 Absorbable Organic Fluoride (AOF) – combustion ion chromatography (Draft)



EPA United States Environmental Protection Agency

PFAS Strategic Roadmap: EPA's Commitments to Action 2021–2024

Goals and Objectives

EPA's comprehensive approach to addressing PFAS is guided by the following goals and objectives.

RESEARCH

Invest in research, development, and innovation to increase understanding of PFAS exposures and toxicities, human health and ecological effects, and effective interventions that incorporate the best available science.

Objectives

- Build the evidence base on individual PFAS and define categories of PFAS to establish toxicity values and methods.
- Increase scientific understanding on the universe of PFAS, sources of environmental contamination, exposure pathways, and human health and ecological effects.
- Expand research on current and emerging PFAS treatment, remediation, destruction, disposal, and control technologies.
- Conduct research to understand how PFAS contribute to the cumulative burden of pollution in communities with environmental justice concerns.

RESTRICT

Pursue a comprehensive approach to proactively prevent PFAS from entering air, land, and water at levels that can adversely impact human health and the environment.

Objectives

- Use and harmonize actions under all available statutory authorities to control and prevent PFAS contamination and minimize exposure to PFAS during consumer and industrial uses.
- Place responsibility for limiting exposures and addressing hazards of PFAS on manufacturers, processors, distributors, importers, industrial and other significant users, dischargers, and treatment and disposal facilities.
- Establish voluntary programs to reduce PFAS use and release.
- Prevent or minimize PFAS discharges and emissions in all communities, regardless of income, race, or language barriers.

REMEDIATE

Broaden and accelerate the cleanup of PFAS contamination to protect human health and ecological systems.

Objectives

- Harmonize actions under all available statutory authorities to address PFAS contamination to protect people, communities, and the environment.
- Maximize responsible party performance and funding for investigations and cleanup of PFAS contamination.
- Help ensure that communities impacted by PFAS receive resources and assistance to address contamination, regardless of income, race, or language barriers.
- Accelerate the deployment of treatment, remediation, destruction, disposal, and mitigation technologies for PFAS, and ensure that disposal and destruction activities do not create new pollution problems in communities with environmental justice concerns.

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EPA Announces First Validated Laboratory Method to Test for PFAS in Wastewater, Surface Water, Groundwater, Soils

Draft Method 1633 for 40 PFAS Compounds

EPA's Office of Water, in partnership with the Department of Defense's (DoD) Strategic Environmental Research and Development Program,

- Single-laboratory validated method
- 40 PFAS compounds
- Wastewater, surface water, groundwater, soil, biosolids, sediment, landfill leachate, and fish tissue.
- Can be used in various applications, including National Pollutant Discharge Elimination System (NPDES) permits.
- tested in a wide variety of wastewaters and contains required quality control procedures for a CWA.
- Not nationally required until promulgated, it is recommended now for use in individual permits.

3^{rd} draft

Full Validation expected in 2023

EPA 1633 Method Aspects Relevant to dGCB

1.5 *This method is "**performance-based**," which means that modifications may be made without additional EPA review to improve performance (e.g., overcome interferences, or improve the sensitivity, accuracy, or precision of the results) provided that all performance criteria in this method are met.*

2.1 Extraction
2.1.1 *Aqueous samples are spiked …and undergo cleanup using carbon before analysis.*

12.2.3 *Add 25 µL of concentrated acetic acid …. Add **10 mg of carbon to each** sample and batch QC extract, using a 10-mg scoop. Hand-shake occasionally for no more than 5 minutes. **It is important to minimize the time the sample extract is in contact with the carbon.** Immediately vortex (30 seconds) and centrifuge at 2800 rpm for 10 minutes.*

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2.1 Extraction

***2.1.1** Aqueous samples are spiked …and undergo cleanup using carbon before analysis.*

*Note: **Carbon cleanup is required**. Carbon cleanup may remove analytes if the sample has a very low organic carbon content (this is unusual for non-drinking water environmental samples). … If the laboratory can demonstrate that the carbon cleanup is detrimental to the sample analysis (by comparing results when skipping the carbon cleanup during reanalysis), then the carbon cleanup **may be skipped** for that specific sample.*

EPA 1633 SPE Procedure Summary

12.1 All sample matrices

12.1.2 Set up the vacuum manifold with one **WAX SPE** cartridge plus a reservoir and reservoir adaptor for each cartridge for each sample and QC aliquot.

12.1.3 …washing them with 15 mL of 1% methanolic ammonium hydroxide …followed by 5 mL of 0.3M formic acid

12.1.4 Pour the sample into the reservoir... Adjust the vacuum

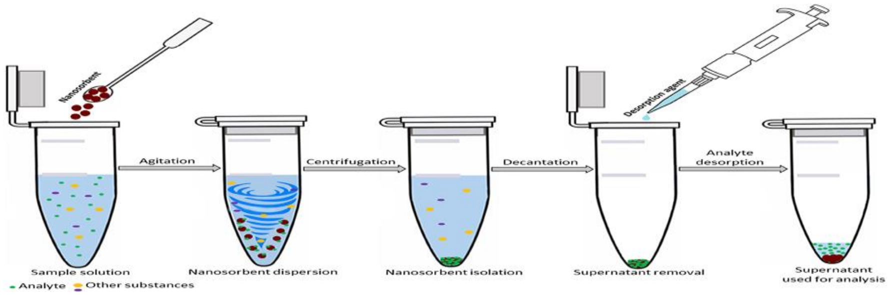
12.1.5 Dry the cartridge by pulling air through

12.2 Elution and Extract Concentration of Aqueous Samples

12.2.3 Add 25 µL of concentrated acetic acid …. Add **10 mg of carbon to each** sample and batch QC extract, using a 10-mg scoop. Hand-shake occasionally for no more than 5 minutes. **It is important to minimize the time the sample extract is in contact with the carbon.** Immediately vortex (30 seconds) and centrifuge at 2800 rpm for 10 minutes.

12.2.4 Add NIS solution …syringe filter Vortex to mix and transfer a portion of the extract into a 1-mL polypropylene microvial for LC-MS/MS analysis.

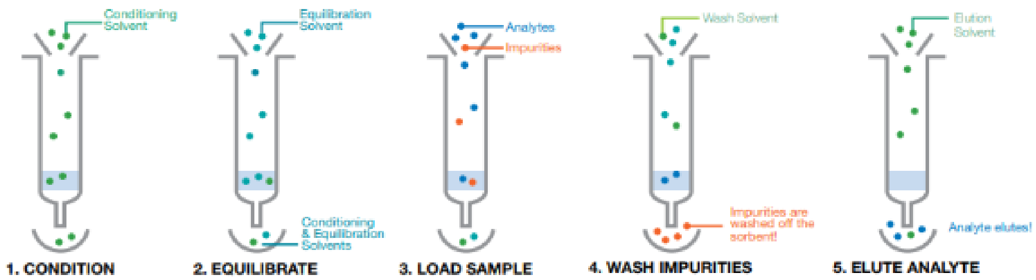
Downside of Dispersive GCB



- Time – additional 45-60 minutes per batch of samples
- Precision – more sample manipulation = more variability
- Messy – Loose GCB requires use of PPE and ventilation
- Recovery – potential loss of long chain compounds (remember warning in EPA method!)
- Potential clogging of LC or MS from contamination with GCB from extract

Downside of separate GCB tubes

Graphitized Carbon Black (GCB) Method Protocol.



- Additional Time – approximately 15 minutes per batch of samples
- Cost – solvent and tube ($5-7 per sample)

SPE for PFAS

EPA 533 and 537.1

- Drinking water method
- polystyrenedivinylbenzene (SDVB)
- SPE sorbent WAX (weak anion exchange)

DOD method 5.4 / EPA 1633

- Quality systems manual for environmental laboratories (Guidance Document) solid samples, soils, biota, sediments, or non-drinking water samples.
- Step 1: SPE sorbent
- Step 2: Sample cleanup with graphitized carbon black (GCB)
    - Dispersive
    - Or
    - Cartridge

WAX
- Developed for short chain PFAS

Or

SDVB
- Longer chain PFAS

WAX
- Developed for short chain PFAS

+

GCB
- Clean up

or

dGCB
- Clean up

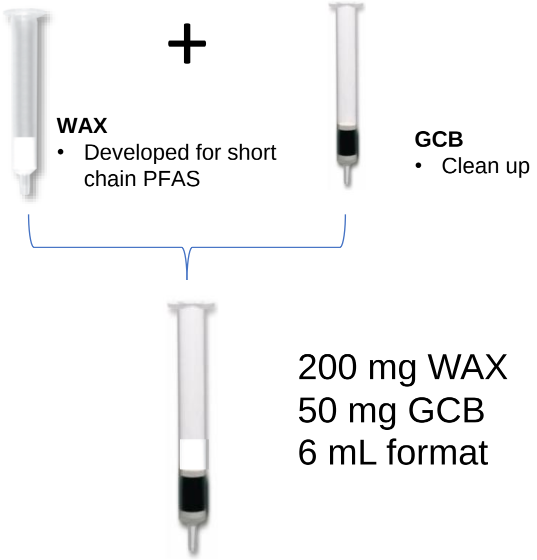
Dual SPE WAX / GCB for PFAS Analysis

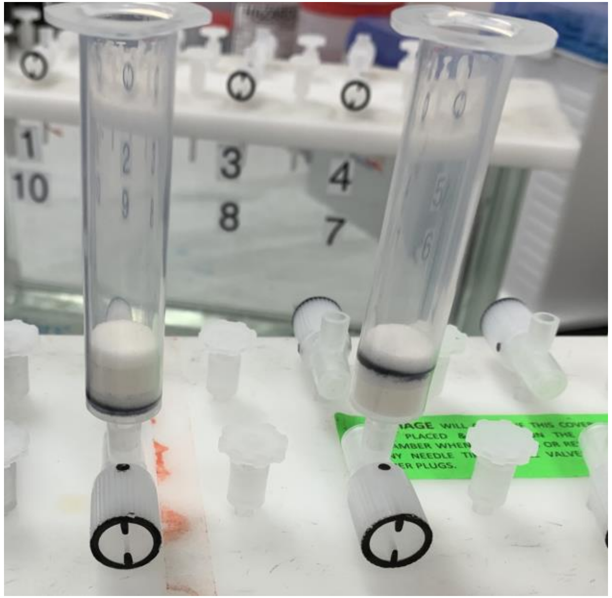
DOD method 5.4 / EPA 1633

- Quality systems manual for environmental laboratories (Guidance Document) solid samples, soils, biota, sediments, or non-drinking water samples.
- Step 1: SPE sorbent
- Step 2: Sample cleanup with graphitized carbon black (GCB)

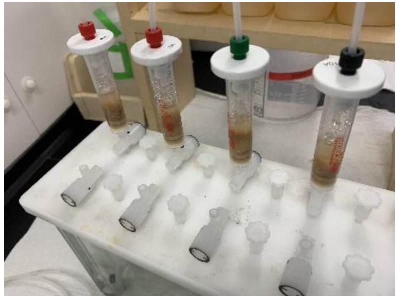
Q: How can we simplify SPE and sample cleanup to save time and possible errors?

A: Develop a cartridge with both phases!





- Stacked Cartridges for Aqueous and Soil samples
- 6ml SPE Tube Format
- 200 mg WAX
- 50 mg GCB
- Separated by a PP frit



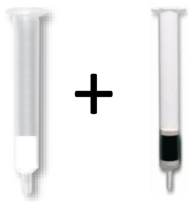
Extraction of wastewater samples

Instrumentation

LC System:	Sciex Exion LC™
Column:	Luna Polar C18 (100 x 2.1mm, 3um)
Guard Column:	Phenomenex SecurityGuard Ultra EVO-C18 (AJ0-9296)
Delay column:	Luna™ 5 µm C18(2) 30 x 3 mm, 00A-4250-Y0)
Temp:	40^{0}C
Injection:	2.0 µL
Eluent A:	2 mM Ammonium Acetate in 95:5 water/acetonitrile
Eluent B:	Acetonitrile
Run Time:	12 min.

Time (min)	**% A**	**% B**	**Flow Rate (mL/min)**
0	98	2	0.35
0.2	98	2	0.35
4	70	30	0.4
7	45	55	0.4
9	25	75	0.4
10	5	95	0.4
10.4	98	2	0.4
11.8	98	2	0.4
12	98	2	0.35

Mass analyzer	Sciex 5500+ (MS/MS)
Ion source	TurboV ™ Electro spray ionization (ESI)
Polarity	Negative
Scan type	MRM
Capillary voltage	2000
Nebulizer pressure (psi)	25
Gas temperature	120
Gas flow (L/min)	11
Sheath gas heater temperature	300
Sheath gas flow	11
Cell accelerator voltage	4
Collision energy (CE)	Compound dependent



GCB
- Clean up

WAX
- Developed for short chain PFAS

- Lab Control Sample

Table 2. Recovery Comparison of WAX + dGCB SPE and Strata PFAS from LCS Samples

		WAX SPE + dGCB SPE			Strata PFAS-WAX/GCB		
	Analyte	Spike Conc. (ng/L)	% Rec	RSD	Spike Conc. (ng/L)	% Rec	RSD
	10:2 FTS	50.00	80%	6.2%	20.00	94%	11.5%
	11Cl-PF3OUdS	50.00	85%	23.6%	20.00	93%	7.0%
	3:3 FTCA	50.00	89%	11.6%	20.00	86%	4.2%
	4:2 FTS	50.00	100%	2.9%	20.00	103%	2.9%
	5:3 FTCA	50.00	86%	0.6%	20.00	94%	3.0%
	6:2 FTS	50.00	98%	5.0%	20.00	109%	4.5%
	7:3 FTCA	50.00	79%	12.6%	20.00	90%	5.3%
	8:2 FTS	50.00	97%	5.8%	20.00	105%	3.4%
	9Cl-PF3ONS	50.00	94%	18.6%	20.00	95%	5.9%
	ADONA	50.00	99%	3.2%	20.00	100%	3.4%
	EtFOSA	50.00	109%	9.6%	20.00	104%	11.3%
	EtFOSE	50.00	92%	11.8%	20.00	92%	7.1%
	HFPO-DA	50.00	110%	6.9%	20.00	102%	9.9%
	MeFOSA	50.00	108%	6.6%	20.00	102%	16.7%
	MeFOSE	50.00	93%	11.2%	20.00	109%	8.4%
	N-MeFOSAA	50.00	103%	9.7%	20.00	99%	12.1%
	PFBA	50.00	96%	1.4%	20.00	96%	0.6%
	N-EtFOSAA	50.00	96%	6.1%	20.00	101%	11.2%
	PFBS	50.00	97%	3.2%	20.00	98%	4.7%
	PFDA	50.00	101%	4.3%	20.00	97%	6.1%
>	PFDoDA	50.00	100%	1.7%	20.00	98%	3.6%
	PFDS	50.00	85%	21.5%	20.00	96%	6.9%
	PFHpA	50.00	99%	2.8%	20.00	97%	3.2%
	PFHpS	50.00	102%	1.9%	20.00	92%	6.1%
>	PFHxA	50.00	96%	2.3%	20.00	100%	5.4%
	PFHxDA	50.00	73%	15.6%	20.00	97%	1.0%
	PFHxS	50.00	97%	0.8%	20.00	95%	7.3%
	PFNS	50.00	97%	10.5%	20.00	95%	3.7%
	PFOA	50.00	106%	8.0%	20.00	101%	3.8%
>	PFOcDA	50.00	32%	23.8%	20.00	87%	2.5%
	PFOS	50.00	96%	12.5%	20.00	98%	5.0%
	PFPeA	50.00	96%	3.6%	20.00	98%	4.0%
	PFPeS	50.00	95%	4.2%	20.00	95%	5.7%
>	PFTeDA	50.00	100%	2.6%	20.00	100%	4.2%
>	PFTrDA	50.00	96%	12.5%	20.00	94%	2.2%
	PFUndA	50.00	104%	5.9%	20.00	97%	0.8%
	Average (n=4)		94%	8%		98%	6%

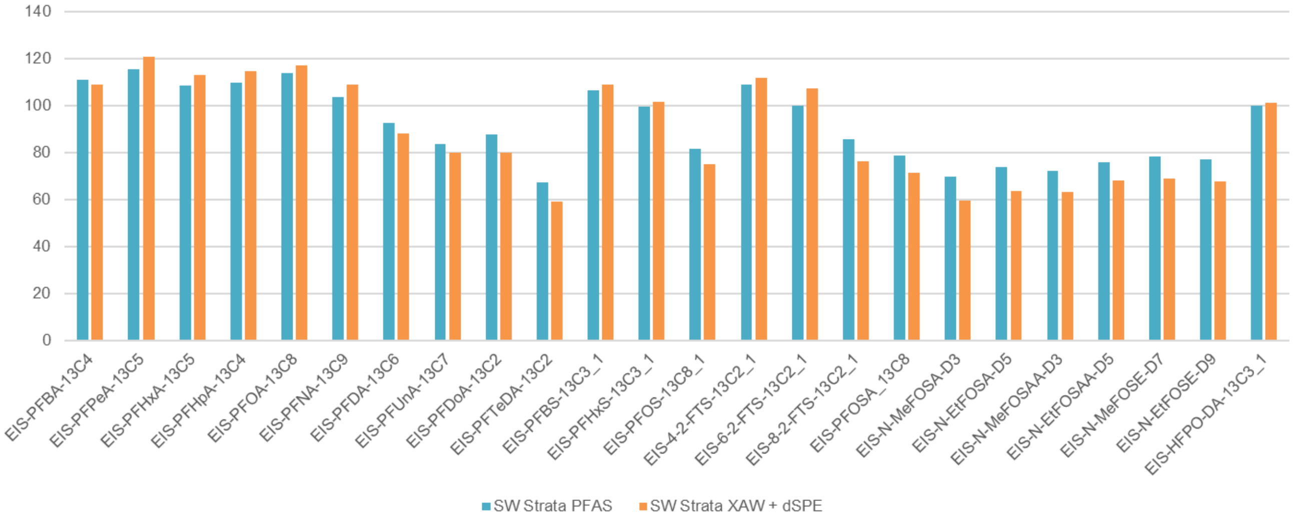
WAX/GCB
- Clean up

- Equivalent Recoveries

Data courtesy of Babcock Laboratories

PFAS Isotope Spike Recovery Comparison

Surface water samples

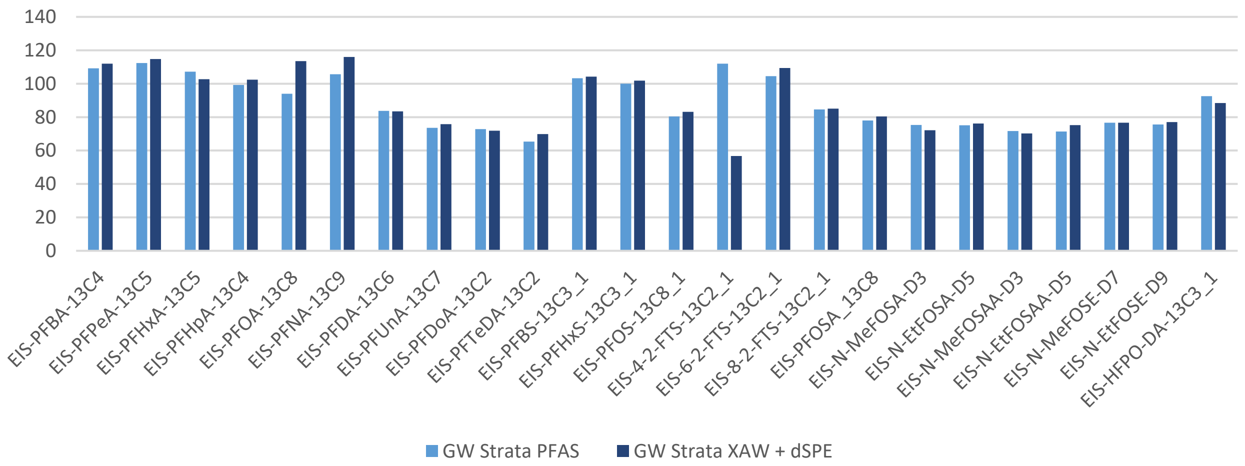


- Single sample, pond

Data courtesy of Alpha Analytical

PFAS Isotope Spike Recovery Comparison

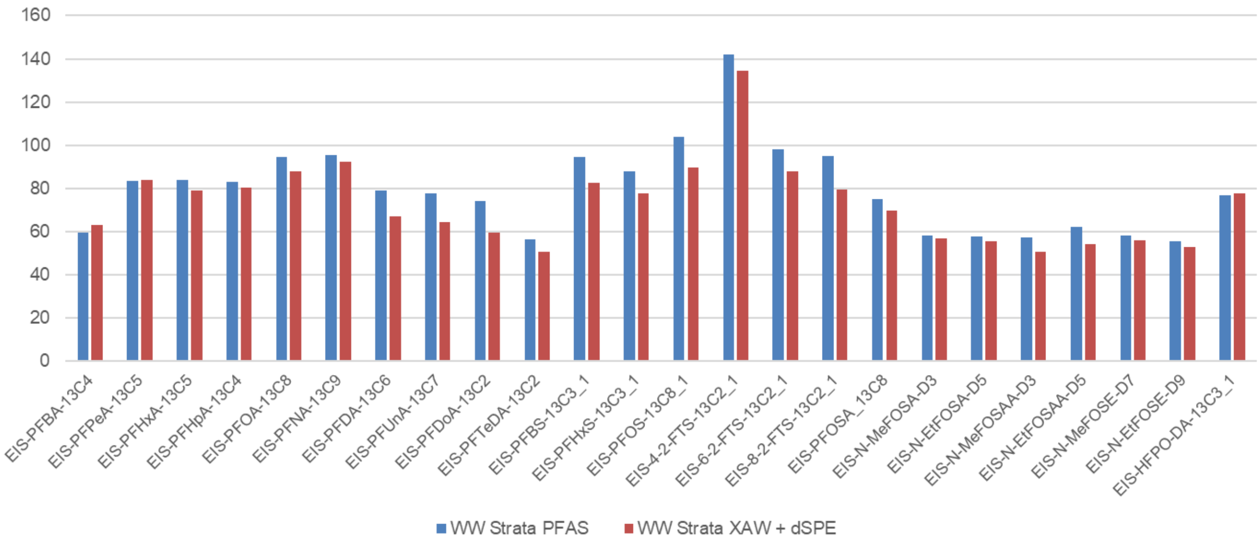
Groundwater samples



Data courtesy of Alpha Analytical

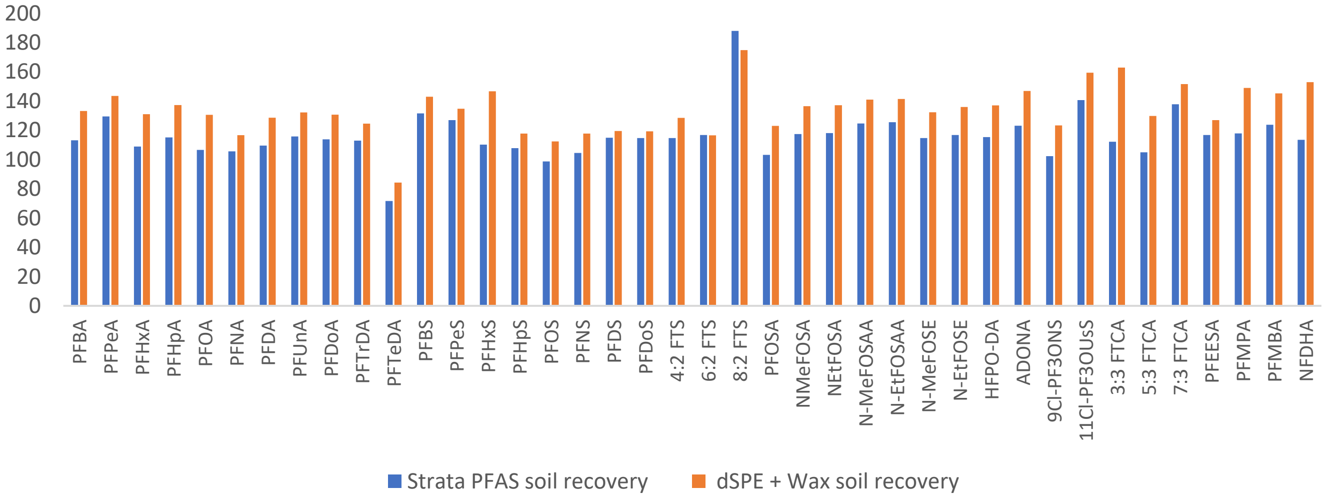
PFAS Isotope Spike Recovery Comparison

Wastewater sample



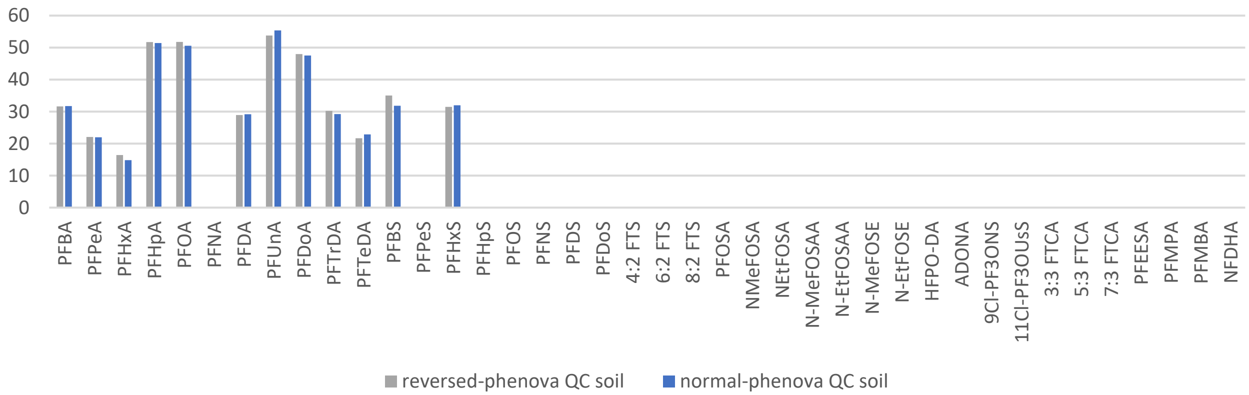
Data courtesy of Alpha Analytical

PFAS Soil Spike Recovery Comparison

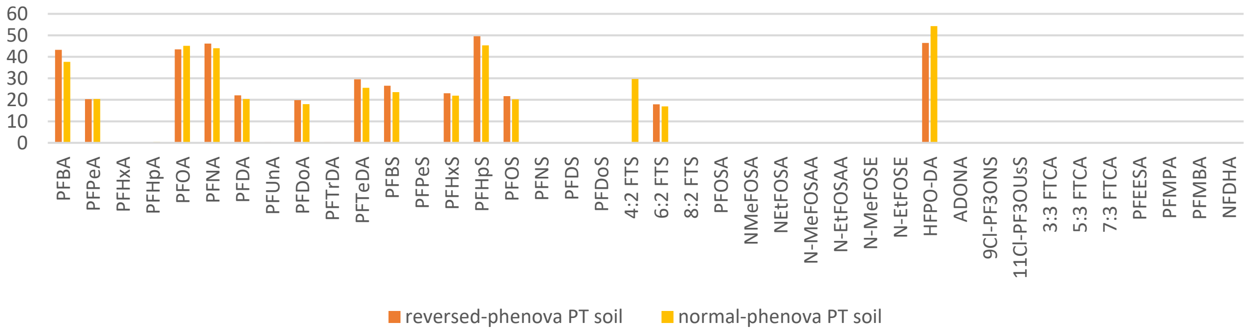


Data courtesy of Alpha Analytical

PFAS QC Soil Recovery Comparison



PFAS PT Soil Recovery Comparison



Data courtesy of Alpha Analytical

Final Conclusions

- Stacked media perform at least equivalent to loose GCB clean-up
- Stacked media save at a minimum 30 minutes per extraction batch
- Utilization of stacked media consume less lab consumables while eliminating contamination from loose GCB dust spreading throughout the lab.
- More consistency using a pre-packaged consumable than rough estimating 10 mg GCB.

PFAS consumables

Purpose	Description	Part Number
Delay Column	Luna 5µm C18(2) 30 x 3mm	00A-4252-Y0
Analytical Column (>100 µL injection volume)	Gemini 3µm C18 100 x 3mm	00D-4439-Y0
Analytical Column	Gemini 3µm C18 50 x 3mm	00B-4439-Y0
Analytical Column (improved lmw acids)	Luna Omega 3µm PS C18 50 x 3mm	00B-4758-Y0
Analytical Column (UHPLC)	Luna Omega 1.6µm 50 x 2.1mm	00B-4752-AN
Security Link	4x3.0/10 pack for ID: 3.2-8.0 mm	AJ0-7606
	4x2.0/10 pack for ID: 2.0-3.0mm	AJ0-7605
	3 pack for ID: 2.1mm	AJ0-7608
Polypropylene cap and vial kit – limited volume	Polypropylene, 300uL + Polyethylene Starburst Cap	AR0-9995-13-C
Polypropylene vials	Vial 9mm Screw Thd PP 2mL , 1000 pk.	AR0-89P6-13-C
Vial cap	Verex™ Cert+ Cap (one-piece), 9mm, PE w/ Starburst preSlit, nat	AR0-89C7-13
SPE cartridge (EPA 537.1)	Strata SDB-L 500mg/6cc tubes	8B-S014-HCH
SPE cartridge (EPA 533)	Strata™-X-AW 33 µm Polymeric Weak Anion, 500 mg / 6 mL, Tubes , 30/Pk	8B-S038-HCH
SPE tubes (reversed phase - high performance)	Strata-XL 500mg/6cc tubes	8B-S043-HCH
SPE tubes (ion-exchange - DOD QSM 5.1)	Strata-XL-AW 500mg/6cc tubes	8B-S051-HCH
Graphitized Carbon Black tubes (DOD QSM 5.1)	Strata GCB 250mg/6cc tubes	8B-S528-FCH
SPE Cartridge (DOD QSM 5.1)	Strata PFAS (WAX/GCB), 200mg/50mg/6mL, 30/Pk	CS0-9207
Large Volume SPE	Adapter Cap	AH0-7191
SPE Sample Reservoir	75 mL Sample Reservoir	AH0-7005

Questions?
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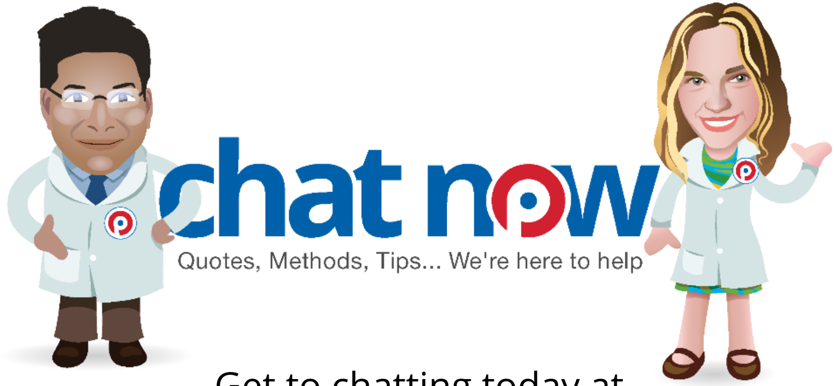
Chat Now, our free online service, connects you nearly instantly with one of our Technical Specialists, who can assist with:

- Any Chromatographic Inquiry
- Method Optimization
- Product Recommendations
- Provide quotes for easy purchasing
- And so much more!



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THANK YOU