Considerations for Improved SPE for EPA Method 1633 for the Analysis of PFAS in a Production Laboratory Environment

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Introduction

We will demonstrate that Strata PFAS single tube WAX/GCB sample preparation provides LC-MS/MS recovery and precision for non-drinking water PFAS analysis that is equivalent to WAX followed by dispersed GCB, thereby meeting DoD QSM 5.4 and the recent draft EPA 1633 requirements. The analysis of non-drinking water samples, such as treated wastewater, untreated wastewater, and stormwater runoff, is much more challenging. QSM 5.4 and EPA 1633 specify a two-step sample preparation step utilizing WAX followed by graphitized carbon black (GCB) for the analysis of all non-drinking water matrices. Initially, laboratories applied the WAX + GCB procedures sequentially by adding finely powdered GCB to the WAX treated eluent, thereby resulting in a dispersion (dGCB). The dGCB must then be removed by centrifugation and filtration and separately eluted to recover the adsorbed PFAS analytes. This time consuming and imprecise procedure was later improved by placing the GCB in a separate SPE tube. This results in a sequential, two-tube procedure (WAX followed by GCB) that is less error prone than WAX followed by dGCB. However, this two-step preparation process is still time consuming and increases laboratory cost through the addition of a second cartridge. A final improvement came when the WAX and GGB were combined in a single tube (Strata PFAS) to offer equivalent analytical performance, but with additional improvements in lower cost and higher laboratory productivity. Furthermore, owing to reduced sample handling, the single tube WAX/GCB sample preparation format reduces sample preparation time, material cost, and labor cost, thereby increasing laboratory productivity and sample throughput as compared to the traditional two-step sample preparation process.

Exhibit 1

Recovery of QSM 5.3 Target Analytes from a Laboratory Control Sample using Strata^{R} PFAS SPE (WAX/GCB) (Data provided by Eurofins Lancaster Laboratories)

SPE Conditions

Cartridge: Strata PFAS (WAX/GCB)
Dimensions: 200 mg/50 mg/6 mL
Part No.: CSO-9207
Sample pH: Adjust to pH 6-7 with 1M Phosphate Buffer
Conditioning: 1: 10 mL 0.1 % Ammonium Hydroxide in Methanol
2: 10 mL Methanol
3: 10 mL Phosphate Buffer, pH = 7
Load: 250 mL of sample
Wash: 5 mL 0.1 % Formic Acid in 50:50 Water/Methanol
Dry: 2 mins
Elute: 4 mL 0.1 % Ammonium Hydroxide in Methanol
Soak: 2 mins
Evaporate: Using Nitrogen, evaporate to below 2 mL
Adjust to 2 mL final volume using 100 % Methanol

Results

Table 1. Recovery of QSM 5.3 Target Analytes from a Typical Laboratory Control Sample

		Using Strata PFAS SPE (WAX/GCB)			
Analyte	Actual Conc.	Sample Result	% Recovery	Method Limits	Pass/Fail
PFBA	25.600	22.640	88	84-135	Pass
PFPeA	25.600	22.157	87	75-138	Pass
PFBS	22.640	22.300	99	81-133	Pass
4:2-FTS	23.920	22.078	92	64-134	Pass
PFHxA	25.600	24.644	96	80-137	Pass
PFPeS	24.000	21.699	90	82-132	Pass
HFPODA	25.600	26.336	103	70-130	Pass
PFHpA	25.600	27.018	106	80-140	Pass
PFHxS	24.200	24.713	102	71-131	Pass
DONA	24.120	26.083	108	70-130	Pass
6:2-FTS	24.280	24.217	100	51-155	Pass
PFHpS	24.360	23.015	94	80-129	Pass
PFOA	25.600	25.043	98	83-138	Pass
PFOS	24.480	22.492	92	54-139	Pass
PFNA	25.600	25.872	101	73-140	Pass
9Cl-PF3ONS	23.840	21.863	92	70-130	Pass
PFNS	24.560	21.993	90	71-121	Pass
8:2-FTS	24.520	22.231	91	62-133	Pass
PFOSA	25.600	25.714	100	73-121	Pass
PFDS	24.640	22.873	93	69-124	Pass
PFUnDA	25.600	26.353	103	70-134	Pass
11Cl-PF3OUdS	24.120	22.625	94	70-130	Pass
PFDoDA	25.600	27.710	108	75-139	Pass
10:2-FTS	24.680	26.626	108	50-124	Pass
NMeFOSSA	25.600	29.745	121	38-153	Pass
PFDoS	24.800	21.509	87	39-121	Pass
NEtFOSAA	25.600	25.846	112	36-156	Pass
PFTrDA	25.600	25.814	101	67-144	Pass
PFTeDA	25.600	25.446	99	79-134	Pass
PFHxDA	25.600	29.662	116	36-136	Pass
PFOcDA	25.600	27.373	107	10-124	Pass

Recovery Range: 87.0 % - 116.0 %
Average Recovery: 98.8 %
Mean Recovery: 99.0 %

Exhibit 2

Comparison of Strata PFAS and Sequential WAX and dGCB Sample Preparation for Laboratory Control Samples
(Data provided by Babcock Laboratories)

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

	Sequential WAX and dGCB			Strata PFAS WAX-GCB		
Analyte	Spike Conc. (ng/L)	% Recovery	% RSD	Spike Conc. (ng/L)	% Recovery	% 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 %

Results

The Strata PFAS recovery and precision results for this 36 analyte PFAS panel presented in Table 2 are within the recommended ranges and are comparable to (but on average slightly better than) those of sequential WAX and dGCB, thereby demonstrating both compliance and equivalency. Note, however, that the dGCB LCS samples were spiked at 50 ng/L whereas the Strata PFAS LSCs were spiked at 20 ng/L, which provided a greater challenge to the equivalency demonstration.

Exhibit 3

Comparison of Strata PFAS and Sequential WAX and dGCB Sample Preparation for Laboratory Control Samples
(Data provided by Eurofins TestAmerica)

	Strata PFAS		WAX + dGCB	
Analyte	% Recovery	% RSD	% Recovery	% RSD
Perfluoro(2-propoxypropanoic) acid	107.1	4.11	106.7	4.58
Perfluorobutanesulfonic acid	108.9	2.07	109.0	3.76
Perfluorobutanoic acid	127.6	2.68	124.6	2.14
Perfluorodecanesulfonic acid	103.4	4.74	105.6	10.1
Perfluorodecanoic acid	103.6	6.18	102.4	5.96
Perfluorododecanesulfonic acid (PFDoS)	91.90	14.8	96.76	8.60
Perfluorododecanoic acid	110.7	5.65	105.9	5.55
Perfluoroheptanesulfonic acid	109.6	4.82	111.7	4.20
Perfluoroheptanoic acid	112.2	5.12	109.1	5.47
Perfluorohexadecanoic acid	106.9	6.37	106.8	6.58
Perfluorohexanesulfonic acid	117.1	7.21	113.5	3.28
Perfluorohexanoic acid	115.1	2.38	114.9	3.51
Perfluorononanesulfonic acid	105.1	4.13	105.9	6.51
Perfluorononanoic acid	119.9	4.71	113.4	4.37
Perfluorooctadecanoic acid	101.2	8.33	93.00	12.7
Perfluorooctanesulfonamide	117.6	4.30	115.1	3.41
Perfluorooctanesulfonic acid	111.7	4.90	110.0	3.78
Perfluorooctanoic acid	121.2	4.79	113.5	5.05
Perfluoropentanesulfonic acid	107.7	4.82	107.0	3.92
Perfluoropentanoic acid	114.9	3.68	112.4	6.02
Perfluorotetradecanoic acid	110.4	6.05	114.6	8.56
Perfluorotridecanoic acid	113.1	10.0	109.0	6.87
Perfluoroundecanoic acid	101.8	6.66	100.8	7.86
1H,1H,2H,2H-perfluorodecanesulfonic acid (8:2)	113.9	2.81	113.6	5.32
1H,1H,2H,2H-perfluorododecanesulfonic acid (10:2)	98.37	5.29	104.6	8.33
1H,1H,2H,2H-perfluorooctanesulfonic acis (6:2)	118.5	5.22	119.6	6.81
2(N-ethylperfluoro-1-octanesulfonamido) ethanol	121.9	6.52	126.5	10.9
2(N-methylperflouro-1-octanesulfonamido) ethanol	116.6	8.99	115.1	8.15
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	105.5	4.17	111.5	5.33
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	98.56	7.12	100.5	5.41
N-ethylperfluoro-1-octanesulfonamide	104.9	7.59	95.36	8.61
N-ethylperfluorooctanesulfonamidoacetic acid	111.9	6.77	108.9	7.55
N-methylperfluoro-1-octanesulfonamide (NMeFOSA)	99.50	8.51	99.57	4.14
(NH4+) 4,8-dioxa-3H-perfluorononanoate (ADONA)	121.8	3.59	119.3	5.27
4,8-dioxa-3H-perfluorononanoate (DONA)	121.7	3.64	119.3	5.34
Average	111 %	5.80 %	110 %	6.12 %

Results

The data in Exhibit 3 were taken from an MDL study for 35 PFAS analytes spiked into 7 reagent water samples at the 2 ng/L level. These data directly compare the analyte recoveries for Strata PFAS with those of WAX followed by dGCB

SPE Procedure for SPE comparisons in Exhibits 2 and 3

Strata SPE PFAS Conditions

Cartridge: Strata PFAS (WAX/GCB)
Dimensions: 200 mg/50 mg/6 mL
Part No.: CSO-9207
Conditioning: 1: 10 mL 0.1 % Ammonium Hydroxide in Methanol
2: 10 mL Methanol
3: 10 mL Phosphate Buffer, pH = 7
Load: 250 mL of sample
Wash: 5 mL 0.1 % Formic Acid in 50:50 Water/Methanol
Dry: 2 mins
Elute: 4 mL 0.1 % Ammonium Hydroxide in Methanol
Soak: 2 mins
Evaporate: Using Nitrogen, evaporate to below 2 mL
Adjust to 2 mL final volume using 100 % Methanol

Sequential WAX and dGCB Conditions

WAX Conditions

Cartridge: Strata X-AW
Dimensions: 200 mg/6 mL
Part No.: 8B-S035-FCH
Conditioning: 1: 10 mL 0.1 % Ammonium Hydroxide in Methanol
2: 10 mL Methanol
3: 10 mL Phosphate Buffer, pH = 7
Load: 250 mL of sample
Wash: 5 mL 0.1 % Formic Acid in 50:50 Water/Methanol
Dry: 2 mins
Elute: 4 mL 0.1 % Ammonium Hydroxide in Methanol
Soak: 2 mins
Evaporate: Using Nitrogen, evaporate to below 2 mL
Adjust to 2 mL final volume using 100 % Methanol

dGCB Conditions

Sample: 2 mL WAX eluent
Sorbent: 50 mg ENVI-Carb™
Vortex: 30 sec
Centrifuge: 3000 rpm for 1 min
Syringe Filter: CLARIFY™-PP (polypropylene) 0.45 µm,13 mm (AFB-7101-12)

Discussion and Conclusion

The data presented in this technical note demonstrate that the Strata® PFAS single tube WAX/GCB sample preparation procedure is in all cases equivalent to — and in some cases better than — the two step procedure employing SPE-WAX and dispersive GCB. Therefore, we conclude that the use of Strata PFAS is compliant with DoD QSM 5.3 and can be effectively applied to the analysis of PFAS in non-drinking water samples from DoD facilities as well as labs trying to fulfill EPA 1633 compliance. At this time, EPA 1633 is a draft guidance method. While not discussed in this technical note, but demonstrated
through the analysis of many thousands of PFAS samples in commercial laboratories — Strata PFAS also offers significant operational and economic benefits over the traditional sample preparation approach. These benefits include:

- Lower reagent consumption and disposal cost
- Lower sample preparation labor cost
- Lower materials cost
- Higher sample throughput
- High process robustness
- Greater laboratory productivity

This combination of high-quality data and favorable analytical economics has the potential to favorably advance public and private assessment and remediation of PFAS contamination.

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References

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https://phenomenex.blob.core.windows.net/documents/60ac48b0-0cf4-4b2f-b688-9bfaeb17ef08.pdf

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