Evaluation of New Anion Exchange and Synthetic Carbon Sorbents for the Determination of PFAS in Solid Samples Following EPA Method 1633

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Introduction

US EPA draft method 1633 was developed to consolidate procedures for the extraction and quantitation of PFAS in aqueous (nonpotable water), solids (soil, biosolids, and sediment) and tissue samples.[1] Principally, the method utilizes polymeric weak anion exchange (WAX) solid phase extraction (SPE) for the selective extraction of target analytes in addition to matrix removal using graphitized carbon black (GCB). The target analytes are extracted along with isotopically labeled standards followed by separation and detection using liquid chromatography/tandem quadrupole (LC/TQ) mass spectrometry. To date, the draft method contains validation results for solids based on a single laboratory study for a total of 40 target PFAS across nine compound classes.

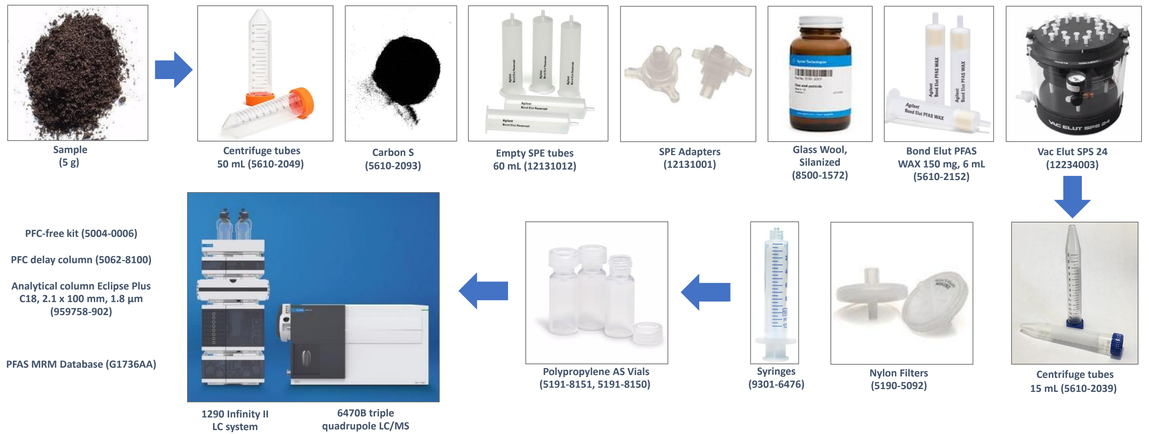
The draft method contains rigorous quality control procedures to ensure optimal data reliability. The requirements are described in Section 9[1] and include: the initial demonstration of precision, accuracy, and method detection limits; the recovery of extracted internal standards and non-extracted internal standards; method blank determination; instrument calibration verification and maintenance; laboratory duplicates; analysis of field replicates when necessary; and analysis of matrix spikes when necessary

The performance of the extraction and analysis procedures for solid matrices was verified following the draft method quality control protocols using Bond Elut PFAS WAX SPE cartridges, Carbon S (Figure 1) as a replacement for GCB, and the Agilent Infinity II 1290 LC and Agilent 6470B triple quadrupole LC/MS. The results were compared to the US EPA draft method 1633 for the single lab validation study.[2]

Figure 1. Agilent Bond Elut PFAS WAX and Carbon S

Experimental

Sample Workflow



Sample Preparation Procedure

Sample Preparation
- Solid sample size: 5 g in 50 mL centrifuge tube
- Add DI water (to reagent sand only)
- Add EIS directly to sample
- (Spike with targets)

Extraction
- Add 10 mL of 0.3% ammonium hydroxide in methanol to each sample. Vortex for 10 min, centrifuge 2800 rpm for 10 min and decant into another tube, repeat with another 15 and 5 mL of solvent. Combine extracts.
- Add 10 mg Agilent Carbon S to each extract, shake for 5, centrifuge, decant into another tube
- Concentrate extracts at 55 °C to 10 mL final volume
- Add 40 mL of reagent water and vortex (bring up to volume to 50 mL). Check pH 6.5 +/- 0.5.

Condition SPE
- Packed glass wool to half height of Agilent Bond Elut PFAS WAX SPE (150 mg, 6 mL) cartridge
- Add adapters and large volume reservoirs
- Rinse with 5 mL 1% ammonium hydroxide in methanol
- Rinse with 2 x 5 mL volumes 0.3M formic acid in water

Load Sample
- Pour samples into reservoir
- Pass through cartridge at 5 mL/min

Rinse Reservoir
- Rinse sample containers and cartridges with 2 x 5 mL reagent water
- Rinse containers and cartridges with 5 mL 1:1 0.1M formic acid in water:methanol
- Dry under vacuum for 15 seconds.

Internal Standard
- Add NIS to a clean collection tube (15 mL centrifuge tube)

Elution
- Rinse sample bottle with 5 mL 1% methanolic ammonium hydroxide
- Transfer to SPE cartridge
- Collect eluate, adjust pH with acetic acid

Filter
- Install a Captiva Premium Nylon Syringe Filter on a 5 mL polypropylene syringe
- Decant sample supernatant into syringe barrel
- Collect filtered sample in polypropylene AS vial

Analysis
- Analyze by LCTQ

Results and Discussion

Initial Method Detection Limits

- Seven replicates Ottawa sand spikes

Analyte	Bond Elut PFAS WAX Initial MDL (ng/g)	EPA Draft 1633 Aq. MDL (ng/g)*
PFBA	0.111	0.401
PFPeA	0.022	0.021
PFHxA	0.037	0.020
PFHpA	0.039	0.029
PFOA	0.017	0.037
PFNA	0.021	0.086
PFDA	0.029	0.031
PFUnA	0.023	0.033
PFDoA	0.027	0.059
PFTrDA	0.031	0.038
PFTeDA	0.030	0.032
PFBS	0.034	0.014
PFPeS	0.051	0.015
PFHxS	0.030	0.018

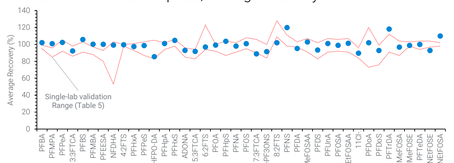
Analyte	Bond Elut PFAS WAX Initial MDL (ng/g)	EPA Draft 1633 Aq. MDL (ng/g)*
PFHpS	0.050	0.057
PFOS	0.033	0.067
PFNS	0.043	0.046
PFDS	0.040	0.040
PFDoS	0.064	0.038
4:2FTS	0.087	0.282
6:2FTS	0.239	0.116
8:2FTS	0.122	0.225
PFOSA	0.061	0.068
NMeFOSA	0.045	0.049
NEtFOSA	0.099	0.038
NMeFOSAA	0.039	0.030
NEtFOSAA	0.029	0.044
NMeFOSE	0.267	0.203

Analyte	Bond Elut PFAS WAX Initial MDL (ng/g)	EPA Draft 1633 Aq. MDL (ng/g)*
NEtFOSE	0.255	0.203
HFPO-DA	0.194	0.136
ADONA	0.084	0.057
PFMPA	0.040	0.033
PFMBA	0.033	0.029
NFDHA	0.067	0.084
9Cl-PF3ONS	0.020	0.038
11Cl-PF3OUdS	0.058	0.071
PFEESA	0.026	0.018
3:3 FTCA	0.066	0.060
5:3 FTCA	0.101	0.363
7:3 FTCA	0.283	0.308

* EPA 1633 3rd Draft – Table 6, single-lab validation results

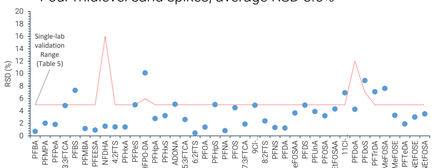
Accuracy

- Four midlevel sand spikes, average recovery 99.8%



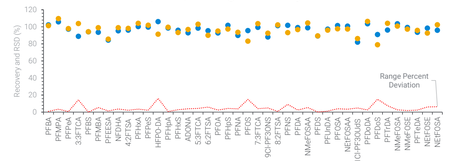
Precision

- Four midlevel sand spikes, average RSD 3.5%



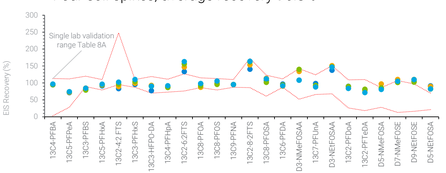
Topsoil Target Recovery

- Two midlevel soil spikes, average recovery 96.8%



Extracted Internal Standard Recovery

- Four soil spikes, average recovery 96.8%



Conclusions

- Fit for purpose consumables, supplies, hardware and instrumentation are the keys to successful PFAS analysis
- Agilent's Bond Elut PFAS WAX and Carbon S provide outstanding performance for PFAS application

References

1. 3rd Draft Method 1633, *United States Environmental Protection Agency*, December **2022**.

2. Giardina, M., Juck, M., Analysis of PFAS in Solid Samples, *Agilent Technologies application note*, publication number 5994-5667EN, **2023**.