Use of Carbon S for Matrix Cleanup in the Analysis of Per and Polyfluoroalkyl Substances (PFAS)

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Introduction

Background

Soil is a complex mixture of organic and inorganic compounds.[1] Many of these organic compounds are co-extracted into the organic solvent along with the target analytes during the extraction process. Without the further removal of these co-extractives, direct injection of extracts can result in multiple matrix effects upon analysis, including matrix ion suppression or enhancement on LC/MS/MS, and accumulation of matrix deposits in the sample flow path and MS ion source. Therefore, it is important to apply a cleanup step to remove matrix co-extractives prior to instrument analysis, without affecting the recovery of the target compounds.

What is Carbon S?

Graphitized carbon black (GCB) has been used widely in sample preparation for efficient removal of pigments and other matrix interferences. However, GCB may cause the loss of some analytes. Carbon S is an advanced hybrid carbon material with optimized carbon content and pore structure. Compared to GCB, Carbon S provides equivalent or better pigment removal from sample matrices, while significantly improving recovery for some GCB selective analytes (such as planar pesticides). As a result, Carbon S sorbent provides a better balance between analyte recovery and matrix removal efficiency than traditional GCB sorbent.[2]

The Carbon S sorbent is applied in the same SPE cartridge format with the same bed mass as GCB SPE. The Carbon S SPE cartridges can be used as a replacement for the GCB cartridges for applications where SPE methodology is used (Figure 1).

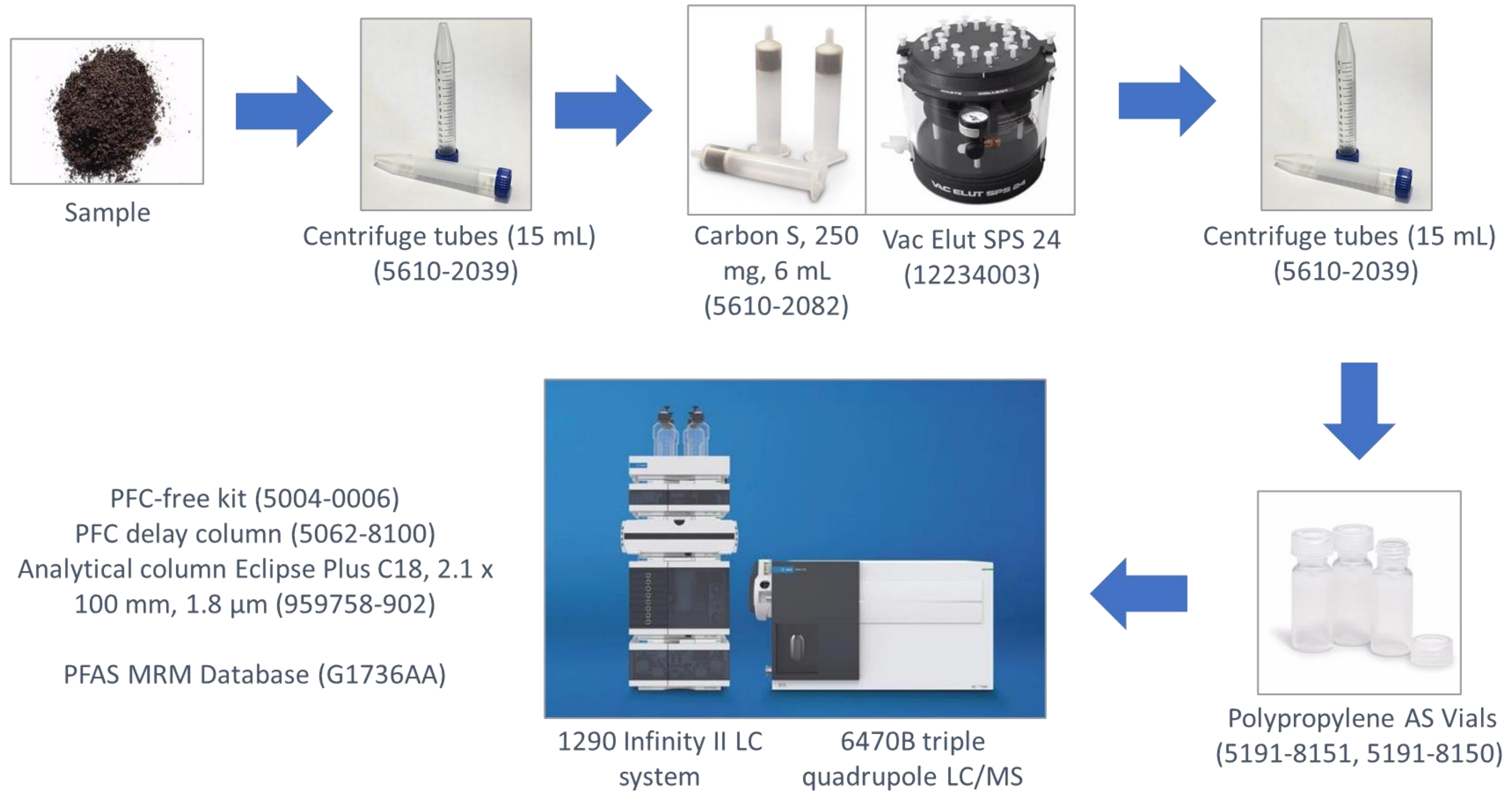
Figure 1. Carbon S SPE tubes

Experimental

Extraction Approach

- Modified ASTM D7968-17a
  - Determination of PFAS in Soil by LC/MS/MS – add Carbon S cleanup
- Targets
  - Select wide range of analytes encompassing multiple methods
- Quantitation
  - Isotope labeled internal standards
- Blank analysis
  - Determines minimum reporting limit (MRL) – MRL 3x blank at minimum
- Matrix spike recovery
  - Low level spike - 0.6 ng/g (most compounds) – check recovery 50-150%
  - High level spike – 6.0 ng/g (most compounds) – check recovery 70-130%
- Test commercial soil samples
  - Dark reed sedge peat
  - Topsoil

Sample Workflow



PFC-free kit (5004-0006)
PFC delay column (5062-8100)
Analytical column Eclipse Plus C18, 2.1 x 100 mm, 1.8 µm (959758-902)

PFAS MRM Database (G1736AA)

Extraction Procedure

1. Weigh 2 g of soil matrix to 15 mL centrifuge tube
2. Spike matrix with target spiking mix and/or isotope dilution analogue mix
3. Add 10 mL of 1% ammonia in methanol (v/v)
4. Tumble for 1 hour
5. Centrifuge at 1900 RPM for 10 min
6. Rinse **Bond Elut Carbon S SPE** with 10 mL methanol and discard
7. Decant extract into **Bond Elut Carbon S SPE**, elute under vacuum slight vacuum or gravity
8. Collect eluate into clean 15 mL centrifuge tube
9. Neutralize with 50 µL of acetic acid
10. Combine 790 µL of extract with 10 µL of internal standard and 200 µL of DI water

Target Compounds

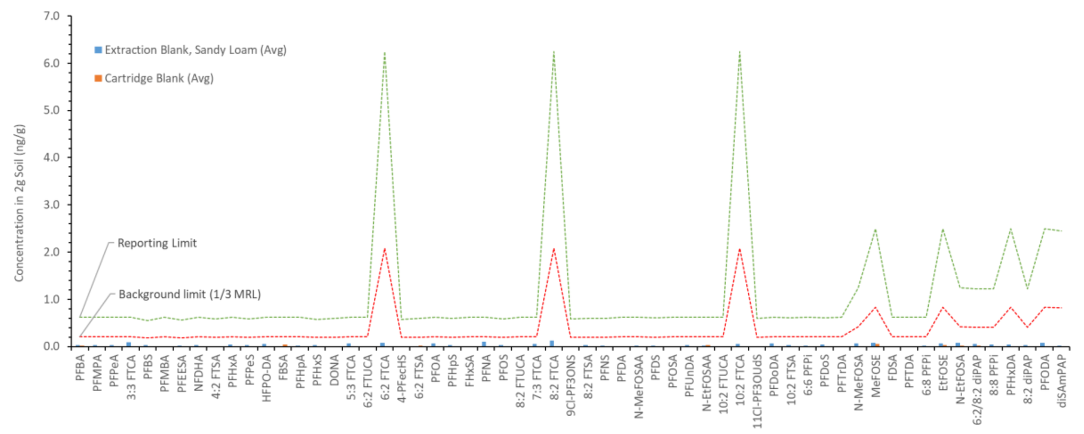
Acronym	ASTM D7968 (2017)	EPA 537.1 (2018)	ASTM D7979 (2019)	EPA 8327 (2019)	EPA 533 (2019)	ISO 21675 (2019)	CMA/3/D (2021)	EPA 1633 (2022 Draft)
10:2 FTCA	X		X					
10:2 FTSA								
10:2 FTUCA								
11Cl-PF3OUdS		X			X			X
3:3 FTCA	X							X
4:2 FTSA				X	X		X	X
4-PFecHS	X		X					
5:3 FTCA	X		X					X
6:2 FTCA	X		X					
6:2 FTSA				X	X	X	X	X
6:2 FTUCA								
6:2/8:2 diPAP								
6:6 PFPi								
6:8 PFPi								
7:3 FTCA	X		X					X
8:2 diPAP						X	X	
8:2 FTCA	X		X					
8:2 FTSA				X	X	X	X	X
8:2 FTUCA			X			X		
8:8 PFPi								
9Cl-PF3ONS		X			X	X		X
diSAmPAP								
DONA		X			X	X		X
EtFOSE								X
FBSA								
FDSA								
FHxSA								
HFPO-DA		X			X	X	X	X
MeFOSE								X
N-EtFOSA						X	X	X
N-EtFOSAA		X		X		X	X	X

Acronym	ASTM D7968 (2017)	EPA 537.1 (2018)	ASTM D7979 (2019)	EPA 8327 (2019)	EPA 533 (2019)	ISO 21675 (2019)	CMA/3/D (2021)	EPA 1633 (2022 Draft)
NFDHA					X			X
N-MeFOSA						X	X	X
N-MeFOSAA		X		X		X	X	X
PFBA	X		X	X	X	X	X	X
PFBS	X	X	X	X	X	X	X	X
PFDA	X	X	X	X	X	X	X	X
PFDoDA	X	X	X	X	X	X	X	X
PFDoS								X
PFDS				X		X	X	X
PFEESA					X			X
PFHpA	X	X	X	X	X	X	X	X
PFHpS				X	X	X	X	X
PFHxA	X	X	X	X	X	X	X	X
PFHxDA						X	X	
PFHxS	X	X	X	X	X	X	X	X
PFMBA					X			X
PFMPA					X			X
PFNA	X	X	X	X	X	X	X	X
PFNS				X			X	X
PFOA	X	X	X	X	X	X	X	X
PFODA						X		
PFOS	X	X	X	X	X	X	X	X
PFOSA				X		X	X	X
PFPeA	X		X	X	X	X	X	X
PFPeS				X	X		X	X
PFTDA	X	X	X	X		X	X	X
PFTrDA	X	X	X	X		X	X	X
PFUnDA	X	X	X	X	X	X	X	X
Totals: 59	21	18	21	24	25	30	30	40

Results and Discussion

Blank Analysis

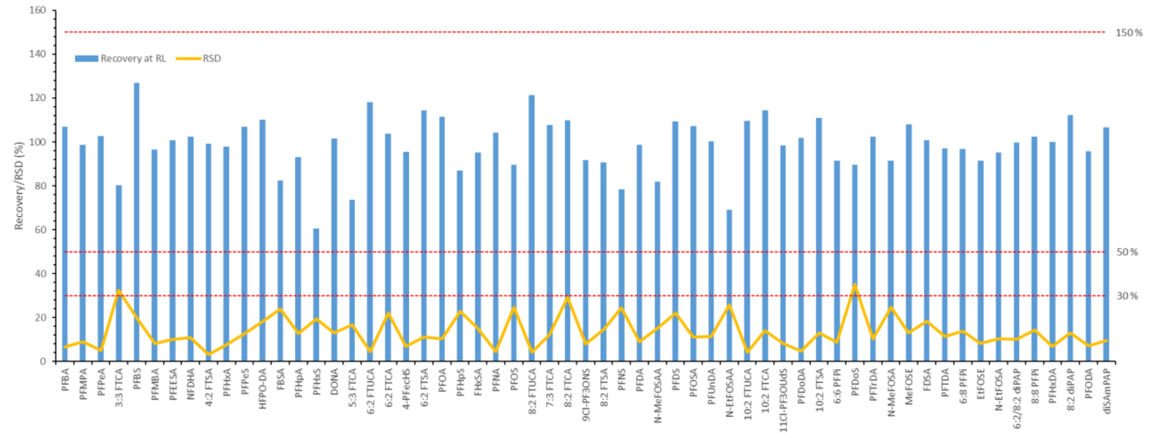
Target concentrations in blank < 1/3 MRL



Low Level Spike Recovery

Recovery at reporting limit (0.625 ng/g for most compounds)

- Within 50-150% accuracy, < 30% RSD precision
- Average recovery 99.9%, average RSD 13.5%



Soil Test Results

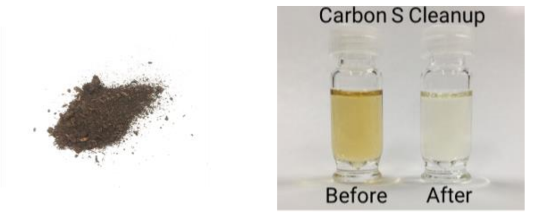
Acronym	Reed Sedge Peat	Topsoil
10:2 FTCA	< MRL	< MRL
10:2 FTSA	< MRL	< MRL
10:2 FTUCA	< MRL	< MRL
11Cl-PF3OUdS	< MRL	< MRL
3:3 FTCA	< MRL	< MRL
4:2 FTSA	< MRL	< MRL
4-PFecHS	< MRL	< MRL
5:3 FTCA	< MRL	< MRL
6:2 FTCA	< MRL	< MRL
6:2 FTSA	< MRL	< MRL
6:2 FTUCA	< MRL	< MRL
6:2/8:2 diPAP	< MRL	< MRL
6:6 PFPi	< MRL	< MRL
6:8 PFPi	< MRL	< MRL
7:3 FTCA	< MRL	< MRL
8:2 diPAP	< MRL	< MRL
8:2 FTCA	< MRL	< MRL
8:2 FTSA	< MRL	< MRL
8:2 FTUCA	< MRL	< MRL
8:8 PFPi	< MRL	< MRL
9Cl-PF3ONS	< MRL	< MRL
diSAmPAP	< MRL	< MRL
DONA	< MRL	< MRL
EtFOSE	< MRL	< MRL
FBSA	< MRL	< MRL
FDSA	< MRL	< MRL
FHxSA	< MRL	< MRL
HFPO-DA	< MRL	< MRL
MeFOSE	< MRL	< MRL
N-EtFOSA	< MRL	< MRL
N-EtFOSAA	< MRL	< MRL

Acronym	Reed Sedge Peat	Topsoil
NFDHA	< MRL	< MRL
N-MeFOSA	< MRL	< MRL
N-MeFOSAA	< MRL	< MRL
PFBA	4.5 ng/g	< MRL
PFBS	< MRL	< MRL
PFDA	< MRL	< MRL
PFDoDA	< MRL	< MRL
PFDoS	< MRL	< MRL
PFDS	< MRL	< MRL
PFEESA	< MRL	< MRL
PFHpA	0.83 ng/g	< MRL
PFHpS	< MRL	< MRL
PFHxA	< MRL	< MRL
PFHxDA	< MRL	< MRL
PFHxS	< MRL	< MRL
PFMBA	< MRL	< MRL
PFMPA	< MRL	< MRL
PFNA	< MRL	< MRL
PFNS	< MRL	< MRL
PFOA	< MRL	< MRL
PFODA	< MRL	< MRL
PFOS	< MRL	< MRL
PFOSA	< MRL	< MRL
PFPeA	2.98 ng/g	< MRL
PFPeS	< MRL	< MRL
PFTDA	< MRL	< MRL
PFTrDA	< MRL	< MRL
PFUnDA	< MRL	< MRL

Soil Samples

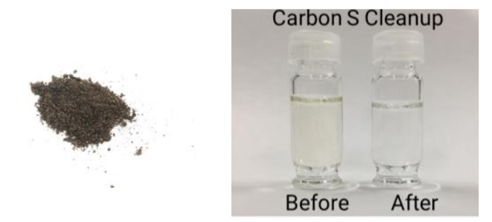
Reed Sedge Peat

- Decaying organic matter
- Rich in fulvic and humic acids
- High organic (~90%)



Topsoil

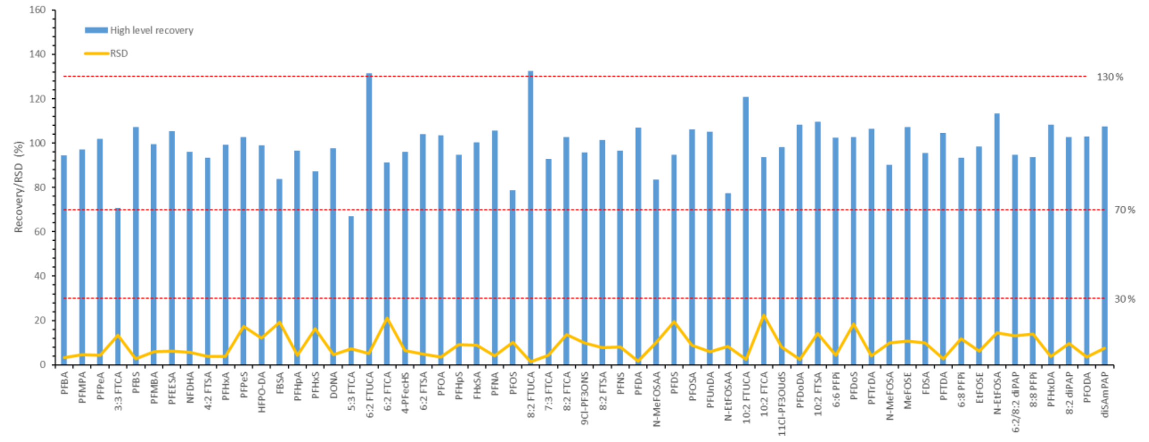
- Mixture of sand, silt and organic matter
- Low organic (~1-6%)



High Level Spike Recovery

Recovery at reporting limit (6.25 ng/g for most compounds)

- Within 70-130% accuracy, < 30% RSD precision
- Average recovery 99.8%, average RSD 8.5%



Conclusions

- Bond Elut Carbon S provides and efficient means of matrix removal for PFAS analysis in soil samples.
- Average recoveries for the 59 PFAS studied were in the 99% range with less than 30% RSD for sandy loam.
- For more information, refer to application note 5994-4770EN.

References

1. Weil, R. R.; Brady, N. C. Soil Architecture and Physical Properties. The Nature and Properties of Soils, 15th Ed. Pearson: Harlow, 2017, p. 122. Elements of the Nature and Properties of Soils, Prentice Hall 2017
2. Zhao, L.; Wei, T. Determination of Multiclass, Multiresidue Pesticides in Spring Leaf Mix by Captiva EMR−HCF Cleanup and LC/MS/MS, Agilent Technologies application note, publication number 5994-4765EN, 2022.