Extraction of ***PFAS from Soil*** Using EluCLEAN® PFAS SPE Columns (according to US EPA 1633^{4th} draft)

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Content

Key Features

- Excellent recovery rates and low standard deviations for 40 PFAS (plus 12 additional PFAS) analytes according to US EPA 1633 (4th draft)
- No detectable PFAS background contamination
- Only one SPE column for clean-up and enrichment needed
- EluCLEAN® PFAS – WAX/GCB SPE column can be used equivalently to the SPE cartridge + dispersive graphitized carbon black used in US EPA 1633 (4th draft)
- EluCLEAN® PFAS – WAX/GCB SPE column contains a weak anion exchanger, mixed-mode polymeric sorbent with an pKa above 8 with optimised parameters for PFAS enrichment, suitable for use in US EPA 1633 (4th draft) and DIN 38414-14
- EluCLEAN® PFAS – WAX/GCB SPE column with higher sorbent amount for samples with higher matrix load is also suitable for DoD/QSM 5.1/5.3 and DIN 38414-14

LCTech Products

SPE cartridges

Part No.: 20821, 20822, 20823

EluCLEAN® PFAS – WAX/GCB

Sorbent 1: Weak Anion Exchanger, Mixed-Mode Polymeric Sorbent (WAX),

Sorbent 2: Graphitized Carbon Black (GCB)

150/10 mg/6 mL

Part No.: 20831, 20832, 20833

EluCLEAN® PFAS – WAX/GCB

Sorbent1: Weak Anion Exchanger, Mixed-Mode Polymeric Sorbent (WAX)

Sorbent 2: Graphitized Carbon Black (GCB)

200/50 mg/6 mL

Other Relevant LCTech Application Notes and Product Information

AN0052 Analysis of PFAS from Drinking Water Using EluCLEAN® PFAS - SPE columns

AN0054 Analysis of PFAS from Drinking Water Using Automated FREESTYLE XANA-PFAS System and EluCLEAN® PFAS - SPE Columns

AN0045 D-EVA – Automated EVAporation of PFAS compliant to US-EPA 537.1

1. Introduction

Per- and polyfluorinated alkyl substances (PFAS) products have been in use for more than 60 years. They get into the environment during their manufacturing process, usages and disposal. Research has revealed the high toxicity of PFAS compounds and thus the resulting need to regulate the substances. Therefore the analytical interest in these compounds has rapidly increased in the last few years. The current and upcoming regulations in the EU and US make it necessary to test soil from various locations for PFAS content. Different methods for PFAS analysis in the EU and US exist. For example, DIN 38414-14, US-EPA 1633 (4th draft) [1] and DoD/QSM 5.1/5.3. All methods require solid phase extraction (SPE) prior to liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis. All methods apply SPE cartridges containing a weak anion exchanger, mixed-mode polymeric sorbent, whereas the US EPA 1633 (4th draft) and the DoD/QSM 5.1/5.3 additionally use a dispersive clean-up step depending on the type of matrices.

In this application note a new single SPE cartridge solution with a PFAS enrichment optimised polymeric sorbent is presented. The EluCLEAN® PFAS – WAX/GCB SPE column contains 200 mg of a weak anion exchanger, mixed-mode polymeric sorbent mixed with 50 mg of graphitized carbon black. The SPE cartridge shows excellent recovery rates in combination with low standard deviations and is therefore ideally suited for SPE of PFAS from soil and other environmental matrices. It can equivalently replace the dispersive clean-up step + WAX SPE cartridge used in US EPA 1633 (4th draft). The single cartridge solution saves time and costs in PFAS analysis.

Figure 1. Schematic workflow of extraction, clean-up, evaporation

2. Experimental

2.1 Sample Preparation

2.1.1 Sample Extraction

An aliquot of soil (5 g dry weight) was filled into a 50 mL polypropylene centrifuge tube. Then it was spiked with 40 PFAS (PFAC-MXF-J, Wellington Lab) plus 12 additional PFAS and 25 mass labelled extraction standard (PFAC-HIF-ES, Wellington Lab) with 3 mL reagent water. The resulting final concentration were 0.2 - 4 µg/kg soil. The spiked samples were incubated for 5 days in a refrigerator (4° C).

10 mL of 0.3 % ammonium hydroxide methanol were added to each centrifuge tube. The sample was vortexed and then shaken for 5 minutes at 800 rpm. After centrifugation at 2800 rpm for 10 minutes the supernatant was transferred into a clean 50 mL polypropylene centrifuge tube. The process was repeated two more times with 15 mL and 5 mL 0.3 % ammonium hydroxide methanol solution.
The samples were then diluted to 35 mL by adding 7.5 mL reagent water. After concentration and removal of most of methanol with the D-EVA Rotational Vacuum Concentrator, the concentrated final volume was approx. 10 mL per sample. The samples were then filled with reagent water to get a final volume of 45 mL. After vortexing the pH was measured and adjusted to 6.5 ± 0.5 with 50 % formic acid and/or 30 % aqueous ammonium hydroxide as required.

2.1.2 Solid Phase Extraction

EluCLEAN® PFAS – WAX/GCB (200/50 mg/6 mL) SPE cartridges were placed on an vacuum manifold and 25 mL reservoirs were placed on top of each cartridge. The cartridges were pre-conditioned with 15 mL of 1 % ammonium hydroxide methanol followed by 5 mL of 0.3 M formic acid (cartridges were not allowed to run dry). The samples were applied with approx. 5 mL/min (using vacuum). The cartridges and the reservoirs were washed with 5 mL reagent water (twice) followed by 5 mL of 1:1 0.1 M formic acid/methanol using vacuum. The cartridges were then dried with high vacuum for 15 sec. The 50 mL sample polypropylene centrifuge tube was rinsed using 5 mL of 1 % ammonium hydroxide methanol. Then the rinsate was transferred to the reservoir while washing the walls of the reservoir. Vacuum was slowly applied to pull the elution solvent through the cartridge into the 15 mL polypropylene centrifuge tubes.
25 µL of concentrated acetic acid and 10 µL NIS (MPFAC-HIF-IS) solution were added to each sample eluate and vortexed.

2.1.3 Evaporation/Concentration

All samples were evaporated to ~1 mL using D-EVA Rotational Vacuum Concentrator (using methanol program), transferred into a 1.5 mL polypropylene vial and kept at 0 – 4 °C for LC-MS/MS analysis.

2.2 Instrumentation

2.2.1 MS Conditions

Table 1. MS Conditions

Parameter	Value
MS	TSQ Quantis (Thermo)
Polarity	Negative
Spray voltage	2500 V
Sheath gas	50 Arb
Aux gas	10
CID gas	2 mTorr
Ion transfer tube temp	325 °C
Vaporizer temp	300 °C
Q1 resolution	0.7 FWHM
Q3 resolution	1.2 FWHM
Cycle time	0,5 sec
Chromatographic peak width	6 sec

2.2.2 LC Instrument Conditions

Table 2. LC Conditions

Parameter	Value	
LC	Thermo Scientific Vanquish Flex UHPLC system	
Analytical column	Accucore RP-MS, 2.1*100 mM, 2.6 µm	
Delay column	Agilent ZOBRAX Eclipse plus C18, 4.6*50 mm; 3.5 µm	
Column temperature	45 °C	
Injection volume	5 µL	
Mobile phase	A) 20 mM ammonium acetate H2O with 2 % MeOH and 0.1 % acetic acid B) 20 mM ammonium acetate MeOH with 2 % H2O and 0.1 % acetic acid	
Gradient flow rate	0.5 mL/min	
Gradient	Time (min) 0 1 6 13 14 17 20 22 25	% 0 30 45 80 95 95 95 0 0

3. Results

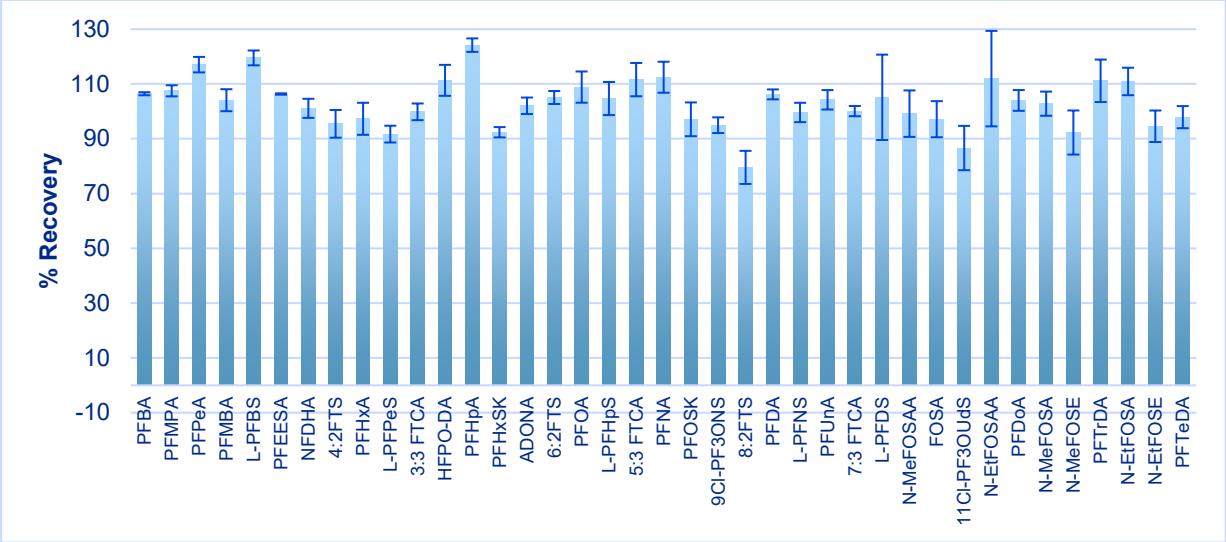

Figure 2. Recovery rates of 40 PFAS (listed in US EPA method 1633 4th draft) from soil matrix extracted with EluCLEAN® PFAS– WAX/GCB (200/50 mg) SPE column (n = 4, spiked concentration = 1-20 ng in 5,g soil spiked for 5 days)

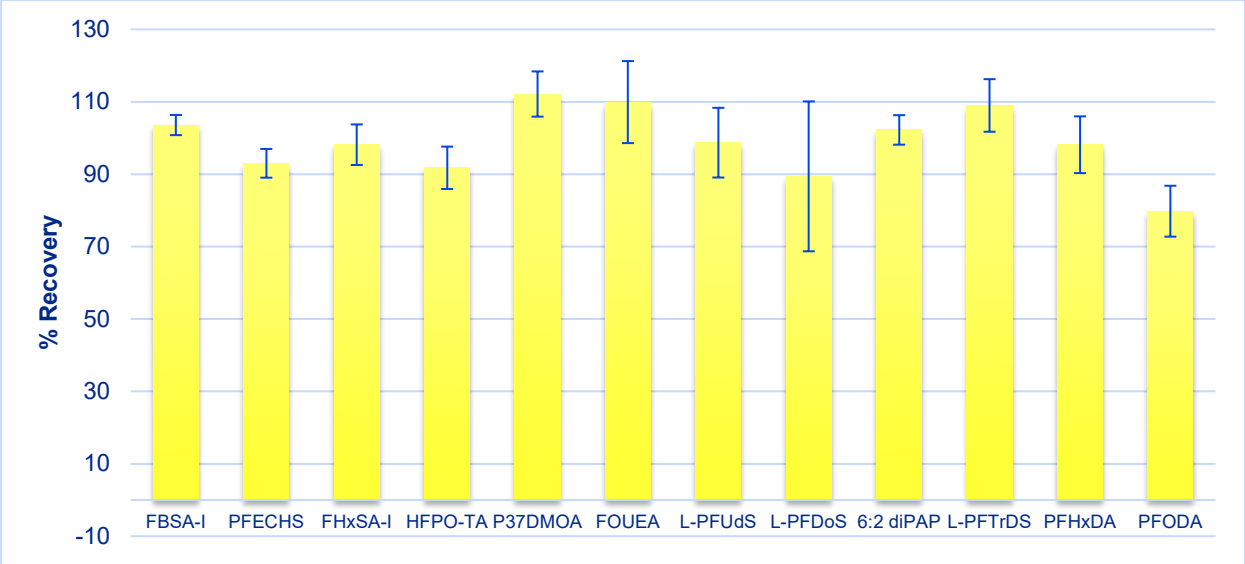

Figure 3. Recovery rates of 12 additional PFAS analytes from soil matrix extracted with EluCLEAN® PFAS– WAX/GCB SPE column (n = 4, spiked concentration = 1 - 20 ng in 5 g soil spiked for 5 days)

3.1 Analytes, their Retention Times and Corresponding Isotope Dilution Standard

Table 3. Overview retention times and corresponding isotope dilution standard

Analyte	Retention Time (min)	Isotope Dilution Standard
PFBA	2.80	MPFBA
PFMPA	3.33	M5PFPeA
PFPeA	4.51	M5PFPeA
PFMBA	5.21	M5PFPeA
L-PFBS	5.19	M3PFBS
PFEESA	6.14	MPFBS
NFDHA	6.55	MPFBS
4:2FTS	6.66	M2-4:2FTS
PFHxA	6.98	M5PFHxA
L-PFPeS	7.59	M5PFHxA
3:3 FTCA	7.93	M5PFHxA
HPFO-DA	7.78	M3HPFO-DA
PFHpA	9.30	M4PFHpA
PFHxSK	9.61	M3PFHxSK
ADONA	9.56	M4PFHpA
6:2FTS	10.71	M2-6:2FTS
PFOA	10.82	M8PFOA
L-PFHpS	10.97	M8PFOA
5:3 FTCA	11.74	M9PFNA
PFNA	11.96	M9PFNA
PFOSK	12.03	M8PFOS
9Cl-PF3ONS	12.51	M6PFDA
8:2FTS	12.81	M2-8:2FTS
PFDA	12.86	M6PFDA
L-PFNS	12.89	M7PFUnA
PFUnA	13.63	M7PFUnA
7:3 FTCA	13.73	M8FOSA
L-PFDS	13.63	d3-N-MeFOSAA
N-MeFOSAA	13.60	d3-N-MeFOSAA
FOSA	13.77	M8FOSA
11Cl-PF3OUdS	13.98	d5-N-EtFOSAA
N-EtFOSAA	14.04	d5-N-EtFOSAA
PFDoA	14.28	MPFDoA
N-MeFOSA	14.67	d-N-MeFOSA
N-MeFOSE	14.60	d7-N-MeFOSE
L-PFDoS	14.77	MPFDoA
PFTrDA	14.82	M2PFTeDA
N-EtFOSA	15.05	d-N-EtFOSA
N-EtFOSE	14.97	d9-N-EtFOSE
PFTeDA	15.15	MPFTeDA
FBSA-I	7.79	M5PFHxA
PFECHS	10.19	M8PFOA
FHXSA-I	11.39	M8PFOS
HFPO-TA	12.10	M8PFOS
P37DMOA	11.96	M8PFOS
FOUEA	12.03	M8PFOS
L-PFUdS	13.93	D9-EtFOSE
L-PFDoS	14.50	MPFDoA
6:2 diPAP	15.08	M4 8:2diPAP
L-PFTrDS	14.95	M2PFHxDA
PFHxDA	15.43	M2PFHxDA
PFODA	15.7	d-N-EtFOSA

3.2 Recovery Rates and RSD % of 40 + 12 PFAS

Table 4. Recovery rates and RSD

Analytes	Recovery Rate (%)	RSD (%)
PFBA	106	1
PFMPA	107	2
PFPeA	117	3
PFMBA	104	4
L-PFBS	120	3
PFEESA	106	1
NFDHA	101	3
4:2FTS	95	5
PFHxA	97	6
L-PFPeS	92	3
3:3 FTCA	100	3
HPFO-DA	111	6
PFHpA	124	2
PFHxSK	92	2
ADONA	102	3
6:2FTS	105	2
PFOA	109	6
L-PFHpS	105	6
5:3 FTCA	112	6
PFNA	112	6
PFOSK	97	6
9Cl-PF3ONS	95	3
8:2FTS	80	6
PFDA	106	2
L-PFNS	100	4
PFUnA	100	4
7:3 FTCA	100	2
L-PFDS	105	16
N-MeFOSAA	99	8
FOSA	97	7
11Cl-PF3OUdS	87	8
N-EtFOSAA	112	17
PFDoA	104	4
N-MeFOSA	103	4
N-MeFOSE	92	8
L-PFDoS	94	8
PFTrDA	111	8
N-EtFOSA	111	5
N-EtFOSE	95	6
PFTeDA	98	4
FBSA-I	104	3
PFECHS	93	4
FHXSA-I	98	6
HFPO-TA	92	6
P37DMOA	112	6
FOUEA	110	11
L-PFUdS	99	10
L-PFDoS	94	8
6:2 diPAP	102	4
L-PFTrDS	109	7
PFHxDA	98	9
PFODA	80	7

4. Conclusion

EluCLEAN® PFAS – WAX/GCB cartridges have no detectable PFAS background contamination. The cartridge EluCLEAN® PFAS – WAX/GCB 200/50 mg is fulfilling the required performance of US EPA 1633 (4th draft). Recoveries for 0.2 - 4 µg/kg soil samples with a range of 80 - 124 % were very well in between the acceptable criteria of 70 - 130 %. Therefore, the desired accuracy is given. Precision, measured by % RSD of replicate extracts, was also well within the range of requirements, with all RSDs below 20 %.

EluCLEAN® PFAS – WAX/GCB cartridges are therefore ideally suited to be used for the enrichment and clean-up of PFAS from soil and other environmental matrices. It can replace the dispersive carbon clean-up + WAX cartridge or other two cartridge solutions with only one column. This is the time and cost saving alternative for every laboratory.

5. References

[1] 4th Draft Method 1633*: Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS; EPA Document No. EPA 821-D-23-001, July 2023. *Finalized for the Aqueous Matrices: Wastewater, Surface water and Groundwater

Any Questions?
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