

Analysis of *PFAS from Drinking Water* Using EluCLEAN PFAS SPE Columns

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Key Features

- Excellent recovery rates and low standard deviations for 18 PFAS analytes according to US EPA 537.1 and 25 PFAS analytes according to US EPA 533
- No detectable PFAS background contamination
- EluCLEAN PFAS - SDVB column is an equivalent to the SPE cartridge mentioned in US EPA 537.1
- EluCLEAN PFAS - WAX SPE column contains a weak anion exchanger, mixed-mode polymeric sorbent with an pKa above 8, suitable for use in ISO 21675, ISO 25101, DIN 38407-42, US EPA 533

LCTech Products

SPE cartridges

Part No.:20801, 20802, 20803

EluCLEAN PFAS – SDVB

Sorbent: Poly(Styrene-Co-Divinylbenzene) Polymer (SDVB)

500 mg/6 mL

Part No.:20811, 20812, 20813

EluCLEAN PFAS – WAX

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

500 mg/6 mL

Other Relevant LCTech Application Notes and Product Information

AN0053 Analysis of PFAS from Soil 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 and also during their use and disposal. The analytical interest in these compounds has rapidly increased in the last few years. Research has revealed the high toxicity of PFAS compounds and thus the resulting need to regulate the substances. The current and upcoming regulations in the EU and US make it necessary to test drinking water for PFAS content. Different methods for PFAS analysis in the EU and US exist. For example ISO 21675, ISO 25101, DIN 38407-42, US EPA 533 [1] and US EPA 537.1 [2]. All methods require solid phase extraction (SPE) prior to liquid chromatography-tandem mass spectrometry (LC-MS/MS). The European methods and US EPA 533 are using SPE cartridges containing a weak anion exchanger, mixed-mode polymeric sorbent, whereas the US EPA 537.1 calls for a styrene divinylbenzene polymer (SDVB).

In this application note two new SPE cartridges with for PFAS enrichment optimised polymeric sorbents are presented. The EluCLEAN PFAS - SDVB SPE column is a 500 mg containing SDVB based sorbent which is used for US EPA 537.1. The EluCLEAN PFAS - WAX SPE column is a 500 mg containing weak anion exchanger, mixed-mode polymeric sorbent which is used for US EPA 533. Both SPE cartridges show excellent recovery rates in combination with low standard deviations and are therefore ideally suited for SPE of PFAS from drinking water matrices.

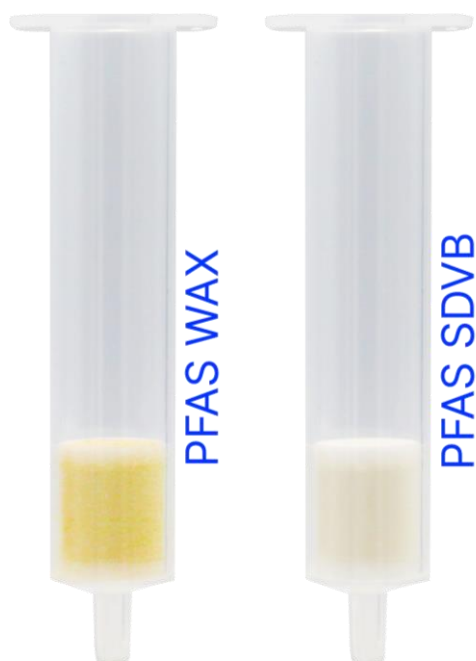


Figure 1. EluCLEAN PFAS - SPE Columns



2. Experimental

2.1 Sample Preparation

2.1.1 Sample Pre-Treatment

a) According to US EPA 537.1

250 mL of drinking water is collected from tap in a 250 mL PE bottles. No further treatment was applied. 18 native PFAS (ES 5631, Cambridge Isotope lab) and 4 surrogate standards (ES-5632, Cambridge Isotope lab) were spiked to get the final concentrations of 40 ng/L and 80 ng/L, respectively.

b) According to US EPA 533

250 mL of drinking water is collected from tap in a 250 mL PE bottles. Ammonium acetate was added to achieve a 1 g/L concentration. 25 native PFAS (EPA-533PAR, Wellington Lab) and 16 isotope dilution standards (EPA-533ES, Wellington Lab) were spiked to get the final concentration of 20 ng/L and 20 - 80 ng/L, respectively.

2.1.2 Solid Phase Extraction

SPE columns were placed on an EluVac SPE vacuum manifold. EluVac was connected with a vacuum with a waste bottle in between (cartridges were not allowed to run dry during conditioning and sample extraction).

a) According to US EPA 537.1

The columns were each conditioned (gravitation) with 3 x 5 mL methanol. Afterwards, each cartridge was rinsed with 3 x 5 mL and 1 x 3 mL of reagent water. 4 mL of reagent water was added on the cartridges and transfer tubes were attached to the cartridges. 250 mL of the spiked drinking water was slowly sucked over the column with a flow rate of 10 - 15 mL/min set with the vacuum through the transfer tube. After passing the entire sample through the cartridge, the sample bottle was rinsed two times with 7.5 mL aliquots of reagent water and each aliquot was drawn through the sample transfer tubes to the cartridges. The cartridges were dried for 5 min at high vacuum. The vacuum pump was turned off and the vacuum was released. Vacuum manifold top was lifted and a rack inserted with collection tubes placed inside the extraction tank to collect the extracts as they are eluted from the cartridges. Sample bottles were rinsed with 4 mL of methanol, which was sucked through the sample transfer tubes into the cartridges to elute analytes. A low vacuum was used so that the solvent exits the cartridge in a dropwise fashion. The elution was conducted with the 4 mL sample bottle rinse and with a second 4 mL aliquot of methanol to get the final volume of 8 mL.



b) **According to US EPA 533**

The columns were each rinsed (gravitation) with 10 mL of methanol. Afterwards cartridges were rinsed with 10 mL of aqueous 0.1 M phosphate buffer without allowing the water to drop below the edge of the upper frit of the cartridges. The valve was closed and 2 - 3 mL of phosphate buffer was added to the cartridge reservoir and the remaining volume was filled with reagent water. The sample transfer tubes were attached. 250 mL of the spiked drinking water was slowly sucked over the column with a flow rate of 5 mL/min set with the vacuum through the transfer tube. After the entire sample has passed through the cartridge, the sample bottle was rinsed with a 10 mL aliquot of 1 g/L ammonium acetate in reagent water. The rinsate was drawn through the sample transfer tubes into the cartridges. Furthermore, 1 mL of MeOH was added to the sample bottle and drawn through the transfer tube into SPE cartridge. The cartridges were dried for 5 min at high vacuum. Vacuum pump was turned off and the vacuum was released. Vacuum manifold top was lifted and a rack inserted with collection tubes placed inside the extraction tank to collect the extracts as they are eluted from the cartridges. Sample bottles were rinsed with 5 mL of 2 % ammonium hydroxide methanol (v/v) which was sucked through the sample transfer tubes into the cartridges to eluate analytes. A low vacuum was used so that the solvent exits the cartridge in a dropwise fashion. The elution was conducted with the sample bottle rinse and with a second 5 mL aliquot of 2 % ammonium hydroxide in methanol to get the final volume of 10 mL.

2.1.3 Evaporation/Concentration

All samples were evaporated to dryness using D-EVA Rotational Vacuum Concentrator (temperature: 45°C, vacuum: 20 mbar).

2.1.4 Reconstitution

a) **According to US EPA 537**

Appropriate amount of 96:4% (vol/vol) methanol:water solution was added to bring the volume to 1 mL (2 x 500 uL extraction: 500 uL MeOH + 460 uL MeOH and 40 uL H₂O) and transferred into a 1.5 mL PP vial.

b) **According to US EPA 533:**

Sample was reconstituted in 1 mL of 20% reagent water in methanol (v/v) and into a 1.5 mL PP vial.

10 uL of respective isotopic dilution standards were added and vortexed. The vial was closed with a PP cap and stored at 0 - 4°C for LC-MS/MS.



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 ZOBAX 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 H ₂ O with 2 % MeOH and 0.1 % acetic acid B) 20 mM ammonium acetate MeOH with 2 % H ₂ O and 0.1 % acetic acid	
Gradient Flow rate	0.5 mL/min	
Gradient	Time (min)	% B
	0	0
	1	30
	6	45
	13	80
	14	95
	17	95
	20	95
	22	0
	25	0



3. Results

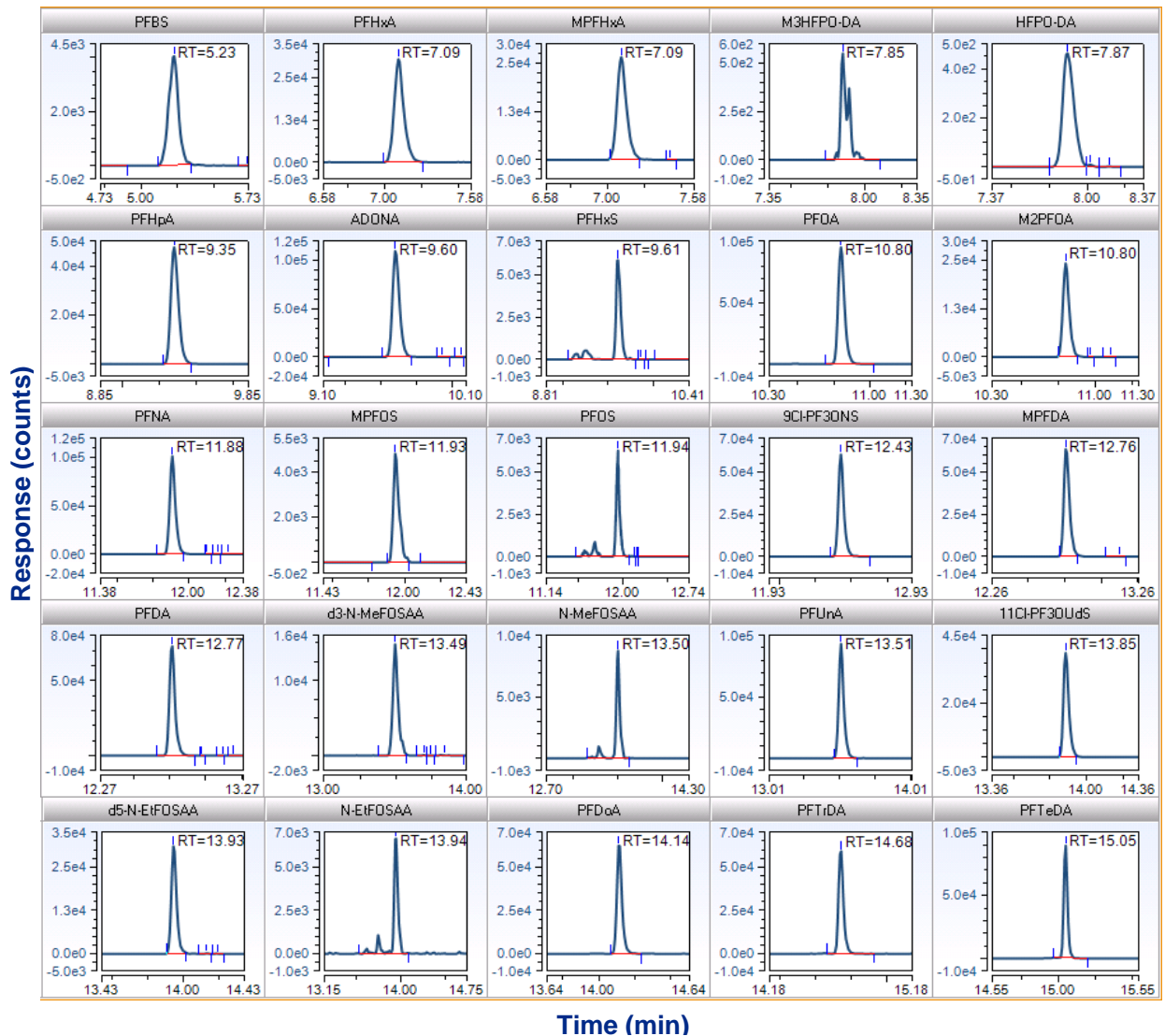


Figure 2. Chromatogram of 18 PFAS, its 4 surrogate standards (listed in US EPA method 537.1) and 3 internal standards after extraction with EluCLEAR PFAS – SDVB cartridges, spiked concentration: 40 ng/L for native PFAS and 80 ng/L for surrogate standard)

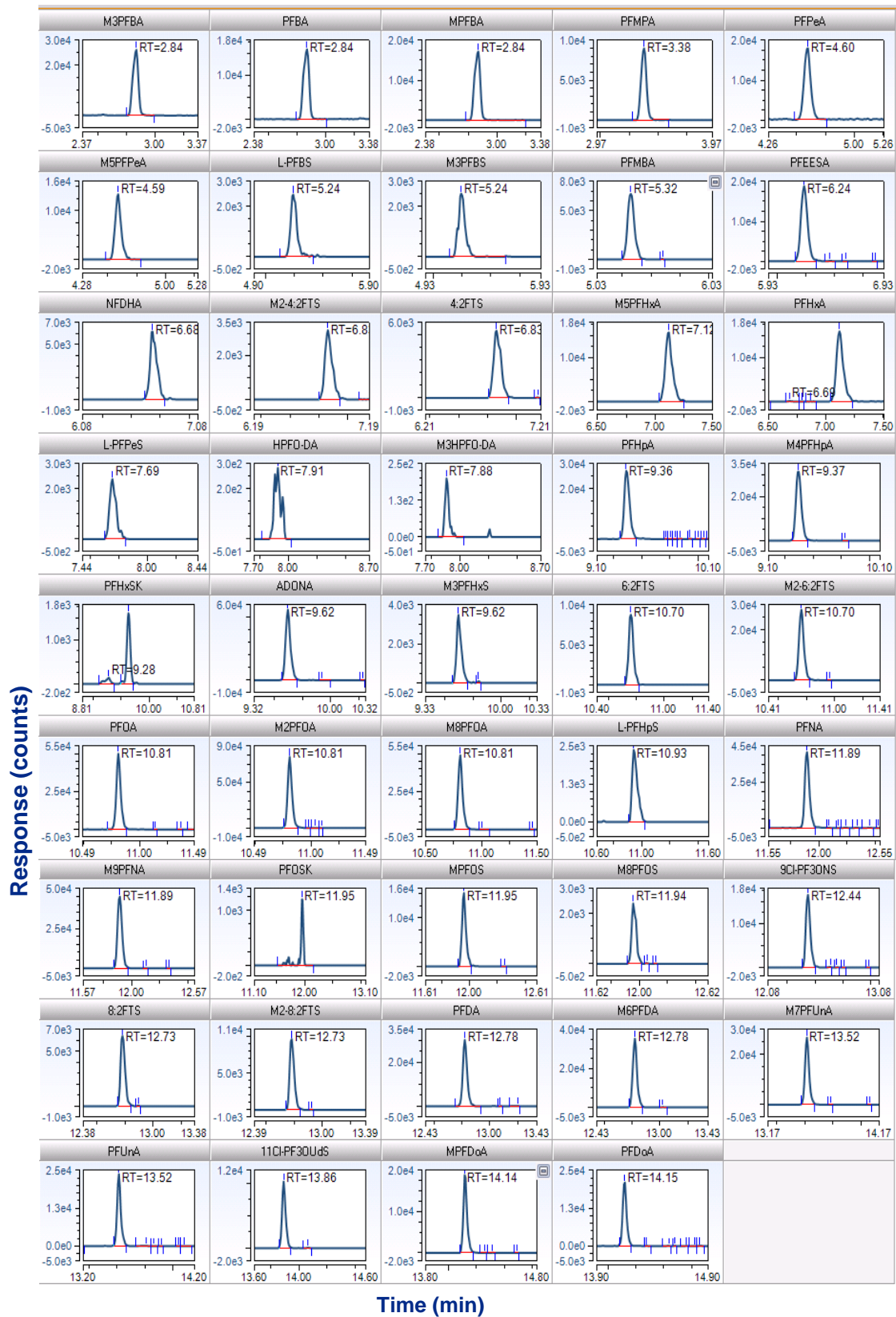


Figure 3. Chromatogram of 25 PFAS, 16 isotopic dilution standard (listed in US EPA method 533) and 3 isotopic standard after extraction with EluCLEAN PFAS – WAX cartridges, spiked concentration = 20 ng/L



Table 3. Recovery rates of native PFAS for both methods

Drinking water				
Analyte	EPA 533		EPA 537.1	
	Recovery rates in %	RSD in %	Recovery rates in %	RSD in %
PFBA	72	6	-	-
PFMPA	93	3	-	-
PFPeA	101	7	-	-
L-PFBS	103	8	105	1
PFMBA	93	7	-	-
PFEESA	94	6	-	-
NFDHA	95	8	-	-
4:2FTS	99	5	-	-
PFHxA	97	4	106	2
L-PFPeS	96	11	-	-
HPFO-DA	94	6	100	8
PFHpA	95	4	107	2
PFHxSK	101	8	103	4
ADONA	96	7	106	3
6:2FTS	101	7	-	-
PFOA	100	5	107	2
L-PFHpS	92	5	-	-
PFNA	97	3	106	2
PFOSK	94	10	98	3
9Cl-PF3ONS	95	4	100	1
8:2FTS	98	3	-	-
PFDA	95	5	103	3
PFUnA	92	3	93	3
11Cl-PF3OUdS	90	6	85	4
PFDaA	93	4	89	5
N-MeFOSAA	-	-	92	7
N-EtFOSAA	-	-	95	4
PFTrDA	-	-	84	8
PFTeDA	-	-	83	6



Table 4. Recovery rates of labelled PFAS (used as surrogates and isotopic dilution standard) for both methods

Drinking water				
Analyte	EPA 533		EPA 537.1	
	Recovery rates [%]	RSD in %	Recovery rates [%]	RSD [%]
MPFBA	73	9	-	-
M5PFPeA	99	3	-	-
M3PFBS	98	9	-	-
M2-4:2FTS	99	5	-	-
M5PFHxA	103	6	-	-
MPFHxA	-	-	106	1
M3HPFO-DA	98	6	101	8
M4PFHpA	102	5	-	-
M3PFHxS	95	7	-	-
M2-6:2FTS	103	6	-	-
M8PFOA	100	4	-	-
M9PFNA	110	3	-	-
M8PFOS	106	6	-	-
M2-8:2FTS	100	5	-	-
M6PFDA	99	5	-	-
MPFDA	-	-	102	2
M7PFUnA	99	6	-	-
MPFDoA	96	6	-	-
d5-N-EtFOSAA	-	-	90	6

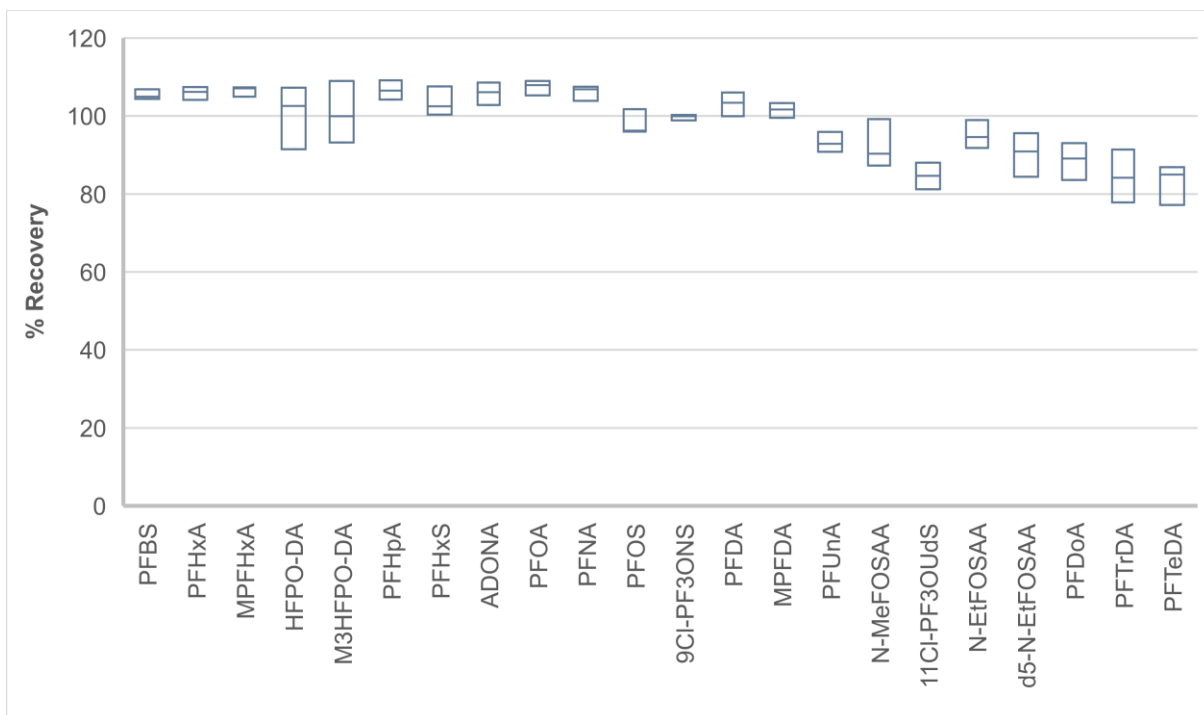


Figure 4. Recovery rates of 18 PFAS (listed in US EPA method 537.1) + 4 surrogates from drinking water with EluCLEAR SDVB columns (n = 4, c = 40 ng/L for native PFAS and 80 ng/L for surrogates)

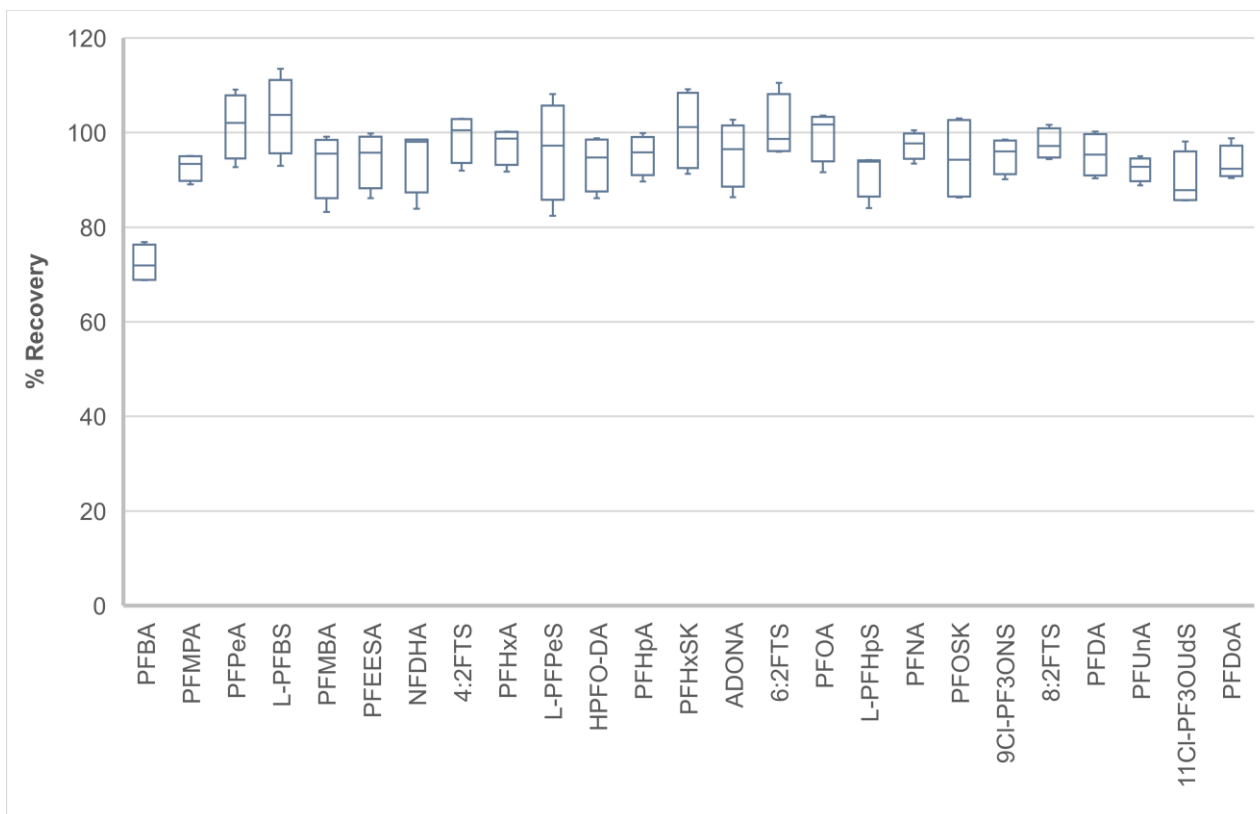


Figure 5. Recovery rates 25 PFAS (listed in US EPA method 533) from drinking water with EluCLEAR-WAX Column (n = 4, c = 20 ng/L)

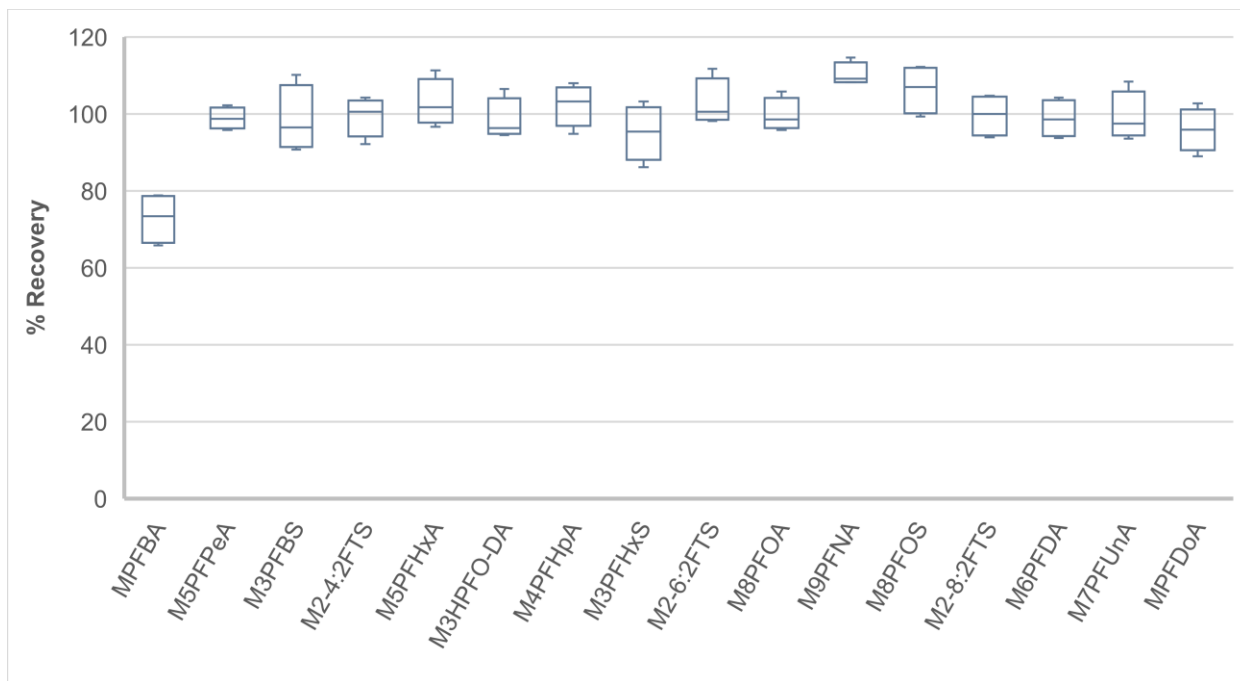


Figure 6. Recovery rates 16 Isotope dilution PFAS standard (listed in US EPA method 533) from drinking water with EluCLEAN-WAX Column n = 4, c = 20-80 ng/L)



4. Conclusion

EluCLEAN PFAS – SPE cartridges have no detectable PFAS background contamination. Both cartridges are fulfilling the required performance of US EPA 537.1 (SDVB) and US EPA 533 (WAX). Recoveries for 20 ng/L and 40 ng/L samples, respectively, were in a range of 72 - 110%, and thus fit very well to the acceptance 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 12 %.

EluCLEAN PFAS – SDVB and WAX cartridges are therefore ideally suited to be used for the enrichment of PFAS from drinking water.

5. References

[1] METHOD 533: DETERMINATION OF PER- AND POLYFLUOROALKYL SUBSTANCES IN DRINKING WATER BY ISOTOPE DILUTION ANION EXCHANGE SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY; EPA Document No. 815-B-19-020, December 2019.

[2] METHOD 537.1 DETERMINATION OF SELECTED PER- AND POLYFLUORINATED ALKYL SUBSTANCES IN DRINKING WATER BY SOLID PHASE EXTRACTION AND LIQUID CHROMATOGRAPHY/TANDEM MASS SPECTROMETRY (LC/MS/MS), EPA Document No.: EPA/600/R-20/006, Version 2.0, March 2020

Any Questions?
Do not hesitate to contact us: