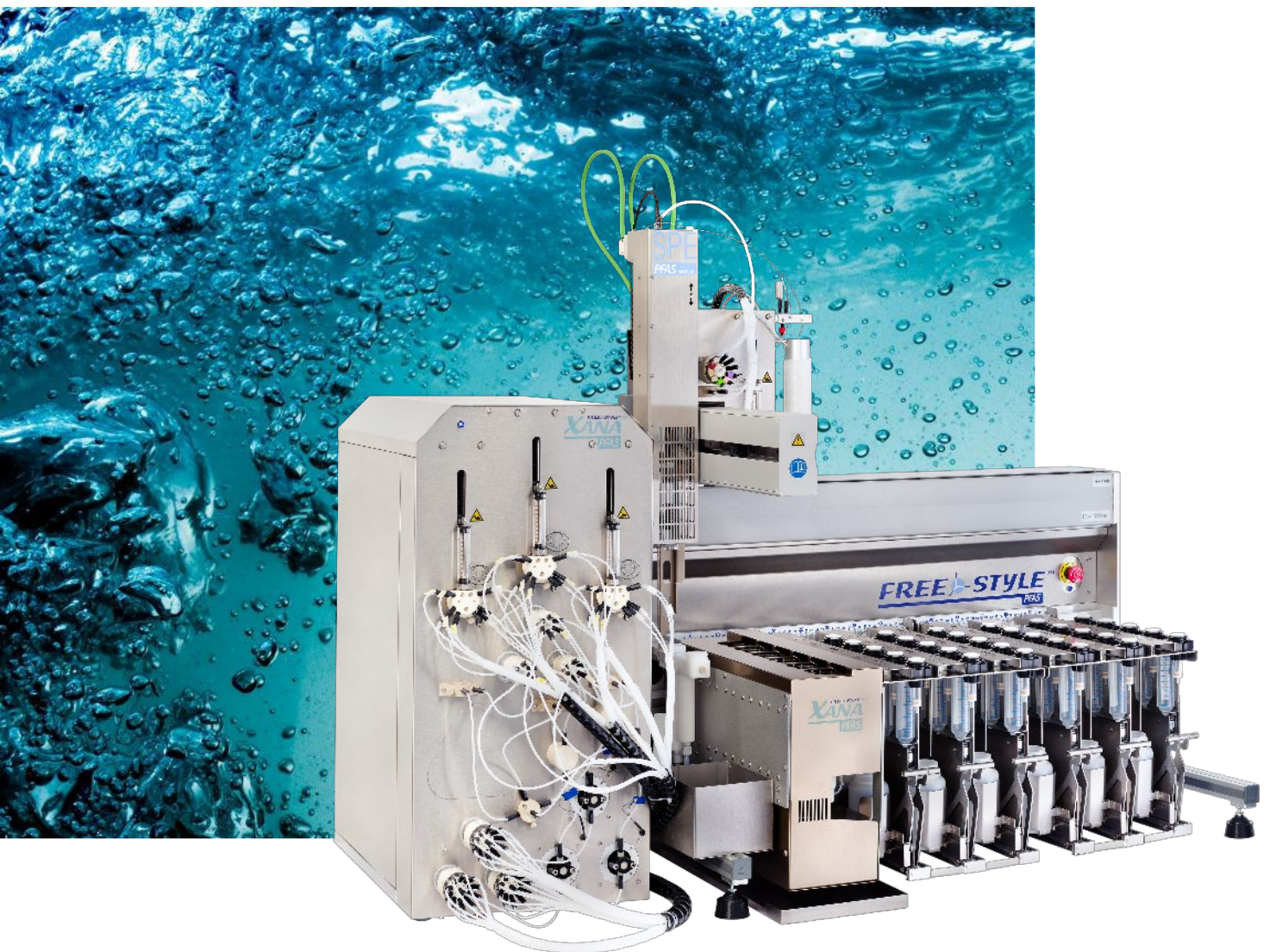


Analysis of *PFAS from Drinking Water* Using Automated FREESTYLE XANA PFAS TableTop System and EluCLEAR[®] PFAS SPE Columns

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Content

Key Features	3
LC Tech Products	3
Other Relevant LC Tech Application Notes and Product Information	4
1. Introduction	6
2. Experimental	7
Sample Preparation	7
Sample Pre-Treatment	7
Solid Phase Extraction	7
Evaporation/Concentration	8
Reconstitution	8
Instrumentation	9
3. Results	10
4. Conclusion	16
5. References	17



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
- EluCLEAR® PFAS - SDVB column is an equivalent to the SPE cartridge mentioned in US EPA 537.1
- EluCLEAR® 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
- Reliable and robust automation with FREESTYLE XANA-PFAS TableTop
- Fully automated processing of up to 30 samples in one sequence
- Parallel processing of up to 6 samples
- No detectable PFAS background contamination

LCTech Products

SPE cartridges

Part No.:20801, 20802, 20803 EluCLEAR® PFAS – SDVB

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

500 mg/6 mL

Part No.:20811, 20812, 20813 EluCLEAR® PFAS – WAX

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

500 mg/6 mL

Part No.:20871, 20872, 20873 EluCLEAR® PFAS – WAX

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

200 mg/6 mL

FREESTYLE XANA PFAS TableTop

Part No.: 20600 FREESTYLE XANA-PFAS TableTop (30 positions)

Part No.: 19372 SPE column adapters for elution into 50 mL Falcon tubes (12 pcs.)

Part No.: 14923-PFAS Caps for 6 mL SPE PFAS cartridges, reusable (25 pcs.)

Part No.: 13156 Solvent bottle rack, 6 x 1 L

Part No.: 12709 Overflow Sensor for Waste Level Control, with GL 45 Cap



Other Relevant LCTech Application Notes and Product Information

[AN0052 Analysis of PFAS from Drinking Water Using EluCLEAN PFAS SPE Columns](#)

[AN0053 Analysis of PFAS from Soil Using EluCLEAN PFAS SPE Columns](#)

[AN0045 D-EVA – Automated EVaporation of PFAS compliant to US-EPA 537.1](#)

[AN0058 Automated Evaporation of PFAS samples](#)

[AN0060 Analysis-PFAS-1633- Drinking water-EluCLEAN-PFAS-SPE-Column](#)



Figure 1. FREESTYLE XANA PFAS TableTop with EluCLEAN® PFAS – SPE columns



Figure 2. Equipping the bottle rack of the FREESTYLE XANA PFAS TableTop

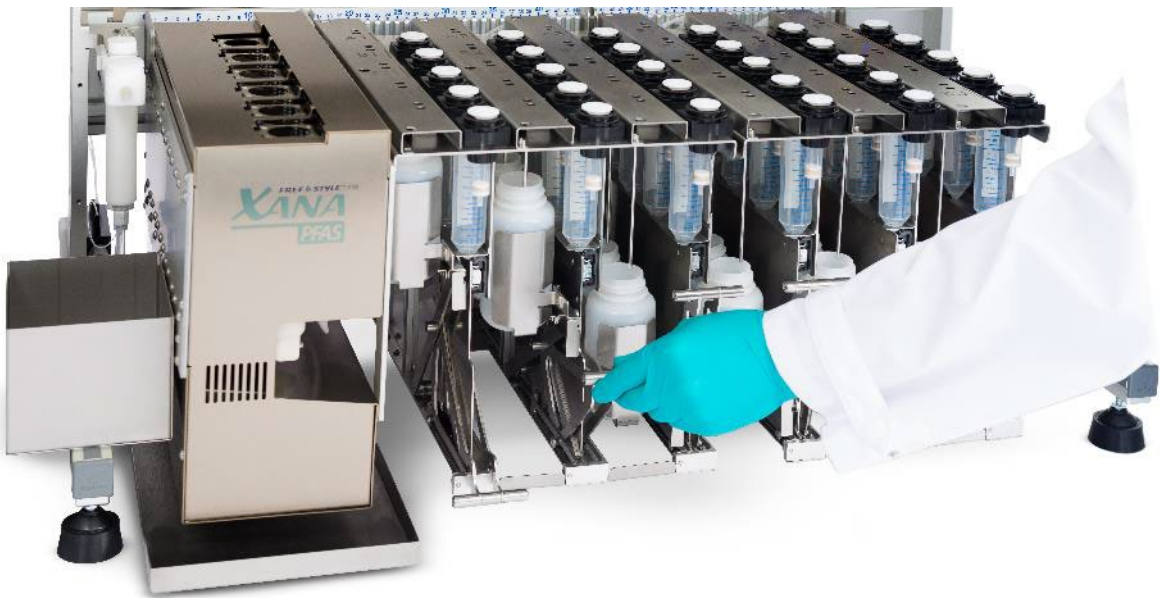


Figure 3. Loading the bottles of the FREESTYLE XANA PFAS TableTop



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 liquid chromatography-tandem mass spectrometry (LC-MS/MS). The European methods and US EPA 533 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).

The following application note shows how water samples can be prepared fully automated for LC-MS/MS analysis by applying SPE with the FREESTYLE XANA-PFAS TableTop robotic system according to US EPA 537.1 and US EPA 533. By the application of fully automated parallel sample preparation, multiple samples can be processed at the same time. Thus, a high sample throughput at low demand of personnel resources is obtained. The FREESTYLE XANA-PFAS TableTop robotic system is a solution especially for PFAS applications by avoiding fluorine-containing plastics such as PTFE and is thus solving the challenge: No blank values from the system were measurable.

The FREESTYLE XANA-PFAS Tabletop robotic system was used in combination with two newly introduced SPE cartridges containing optimised polymeric sorbents for PFAS enrichment. 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 200 or 500 mg containing weak anion exchanger, mixed-mode polymeric sorbent which is used for US EPA 533.

For both methods excellent recovery rates in combination with low standard deviations were achieved.



2. Experimental

Sample Preparation

Sample Pre-Treatment

a) According to US EPA 537.1

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

b) According to US EPA 533

250 mL of drinking water is collected from tap in 250 mL PE bottles. Ammonium acetate was added to achieve a 1 g/L concentration. 25 Native PFAS (EPA-533PAR, Wellington Laboratories) and 16 isotope dilution standard (EPA-533ES, Wellington Laboratories) were spiked to get the final concentration of and 4 ng/L, respectively.

Solid Phase Extraction

SPE columns were placed on a SPE rack of the FREESTYLE system. Sample bottles were placed in the TableTop bottle rack. Solvent bottles were connected with respective ports. The fully automated method (see below) was applied and the eluate was collected for subsequent evaporation.

a) According to US EPA 537.1

The method was designed to comply with the SPE procedure described in US EPA 537.1 method.

Table 1. FREESTYLE XANA-PFAS TableTop conditions according to US EPA 537.1

LCTech FreeStyle - Report on Methods: WAT		Type PFAS - EPA			
Name: 537_1.wat					
Column:	LCTech_6ml.col	Extension cannula:	yes		
Conditioning 1:	ON	Dispensing Speed:	5 ml / min		
Volume:	15 ml	Waiting time:	2 min	Port : W4 MeOH	
Suction Speed:	15 ml / min				
Conditioning 2:	ON	Dispensing Speed:	5 ml / min		
Volume:	20 ml	Waiting time:	2 min	Port : W10 Water	
Suction Speed:	20 ml / min				
Conditioning 3:	OFF				
Load 1:	ON	Typ:	empty		
Number of bottles:	1	Transfer Speed	5 ml / min		
1. rinsing cycle					
1x Rinsing volume:	7.5 ml	Suction Speed:	20 ml / min		
Dispensing Speed:	5 ml / min	Port : 7 Water			
Washing 1:	OFF				
Washing 2:	OFF				
Drying 1:	ON	stay on actual position			
Time:	45 min				
PFAS RinsElution	ON	Dispensing Speed:	3 ml / min		
1x Volume:	8 ml	Waiting time:	0 min	Port : 1 MeOH	
Suction Speed:	10 ml / min				



b) According to US EPA 533

The method was designed to comply with the SPE procedure described in US EPA 533 method.

Table 2. FREESTYLE XANA-PFAS conditions according to US EPA 533

Name: 533.wat		LCTech FreeStyle - Report on Methods: WAT Type PFAS - EPA		
Column:	LCTech_6ml.col	Extension cannula:	yes	
Conditioning 1:	ON	Dispensing Speed:	5 ml / min	Port : W4 MeOH
Volume:	10 ml	Waiting time:	0 min	
Suction Speed:	15 ml / min			
Conditioning 2:	ON	Dispensing Speed:	5 ml / min	Port : W1 0.1M Phosphate buffer
Volume:	13 ml	Waiting time:	0 min	
Suction Speed:	15 ml / min			
Conditioning 3:	OFF			
Load 1:	ON	Typ:	empty	
Number of bottles:	1	Transfer Speed	5 ml / min	
1. rinsing cycle		Suction Speed:	15 ml / min	Port : 8 1g/L AA aq.
1x Rinsing volume:	10 ml			
Dispensing Speed:	5 ml / min			
2. rinsing cycle		Suction Speed:	15 ml / min	Port : 1 MeOH
1x Rinsing volume:	1 ml			
Dispensing Speed:	40 ml / min			
Washing 1:	OFF			
Washing 2:	OFF			
Drying 1:	ON	stay on actual position		
Time:	45 min			
PFAS RinsElution	ON	Dispensing Speed:	3 ml / min	Port : 9 2% NH4OH MeOH
1x Volume:	10 ml	Waiting time:	0 min	
Suction Speed:	15 ml / min			

Evaporation/Concentration

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

Reconstitution

a) According to US EPA 537.1

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

10 µL 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.



Instrumentation

MS Conditions

Table 3. 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

LC Instrument Conditions

Table 4. 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

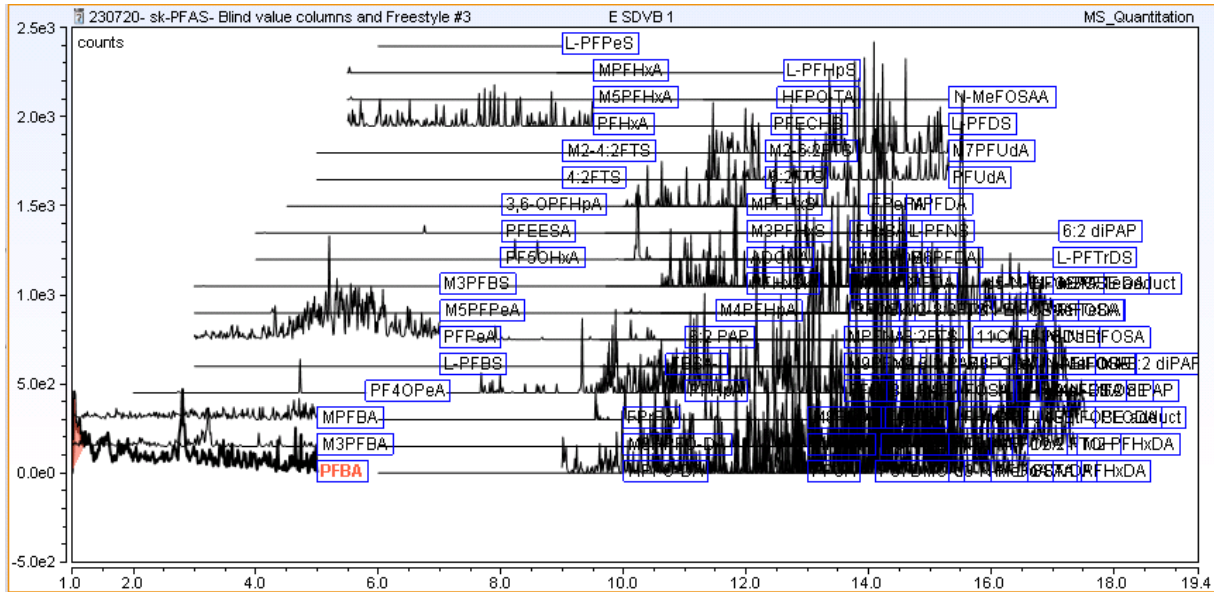


Figure 4. Chromatogram demonstrating EluCLEAR® PFAS - SDVB columns (used in US EPA 537.1 method) are free of blind value when screened for 55 PFAS analytes

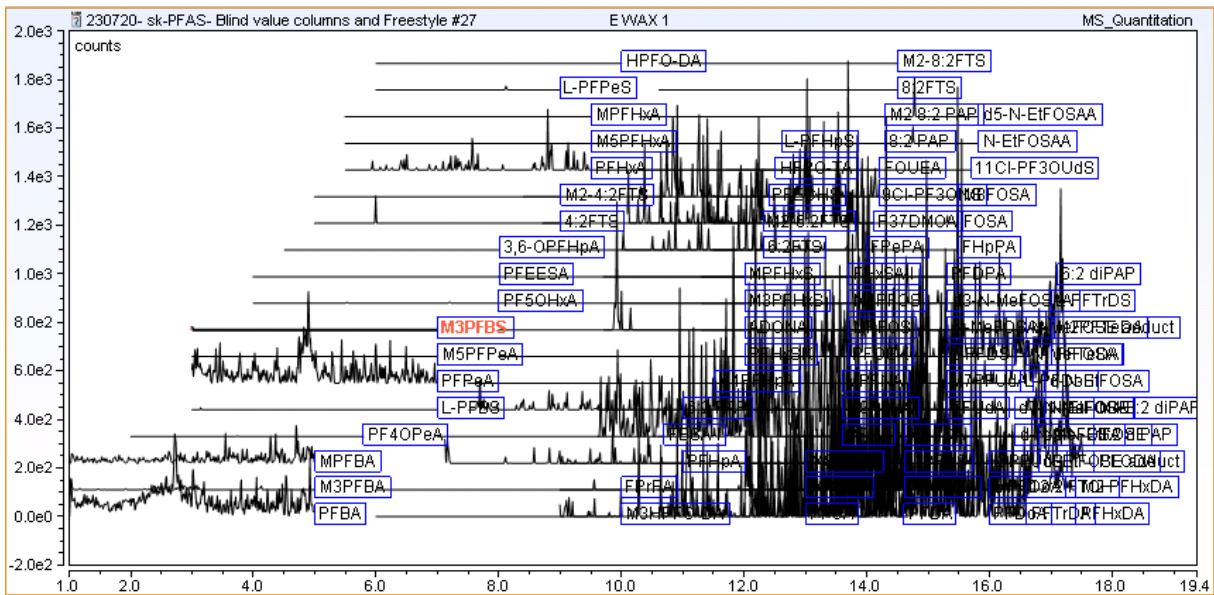


Figure 5. Chromatogram demonstrating EluCLEAR® PFAS- WAX columns (200 mg) (used in US EPA 533 method) are free of blind value when screened for 55 PFAS analytes



Table 5. Recovery rates and RSD 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	102	10	-	-
PFMPA	105	11	-	-
PFPeA	104	12	-	-
L-PFBS	105	14	104	5
PFMBA	99	11	-	-
PFEESA	97	9	-	-
NFDHA	112	8	-	-
4:2FTS	98	7	-	-
PFHxA	109	8	100	5
L-PFPeS	96	11	-	-
HPFO-DA	104	12	100	9
PFHpA	99	12	105	4
PFHxSK	107	14	98	4
ADONA	110	14	109	3
6:2FTS	97	10	-	-
PFOA	112	13	117	2
L-PFHpS	92	9	-	-
PFNA	100	12	111	3
PFOSK	85	13	102	6
9Cl-PF3ONS	98	12	89	4
8:2FTS	95	14	-	-
PFDA	91	9	101	4
PFUnA	87	11	87	6
11Cl-PF3OUdS	87	16	82	7
PFDaA	88	9	85	2
N-MeFOSAA	-	-	91	5
N-EtFOSAA	-	-	84	4
PFTTrDA	-	-	79	5
PFTeDA	-	-	79	5



Table 6. Recovery rates and RSD of labelled PFAS for both methods

Drinking water				
Analyte	EPA 533		EPA 537.1	
	Recovery rates [%]	RSD [%]	Recovery rates [%]	RSD [%]
MPFBA	105	5	-	-
M5PFPeA	102	10	-	-
M3PFBS	112	8	-	-
M2-4:2FTS	116	12	-	-
M5PFHxA	93	5	-	-
MPFHxA	-	-	109	5
M3HPFO-DA	99	11	85	9
M4PFHpA	112	11	-	-
M3PFHxS	102	15	-	-
M2-6:2FTS	110	3	-	-
M8PFOA	103	5	-	-
M9PFNA	107	10	-	-
M8PFOS	102	11	-	-
M2-8:2FTS	93	8	-	-
M6PFDA	87	7	-	-
MPFDA	-	-	98	5
M7PFUnA	89	10	-	-
MPFDoA	83	7	-	-
d5-N-EtFOSAA	-	-	86	7

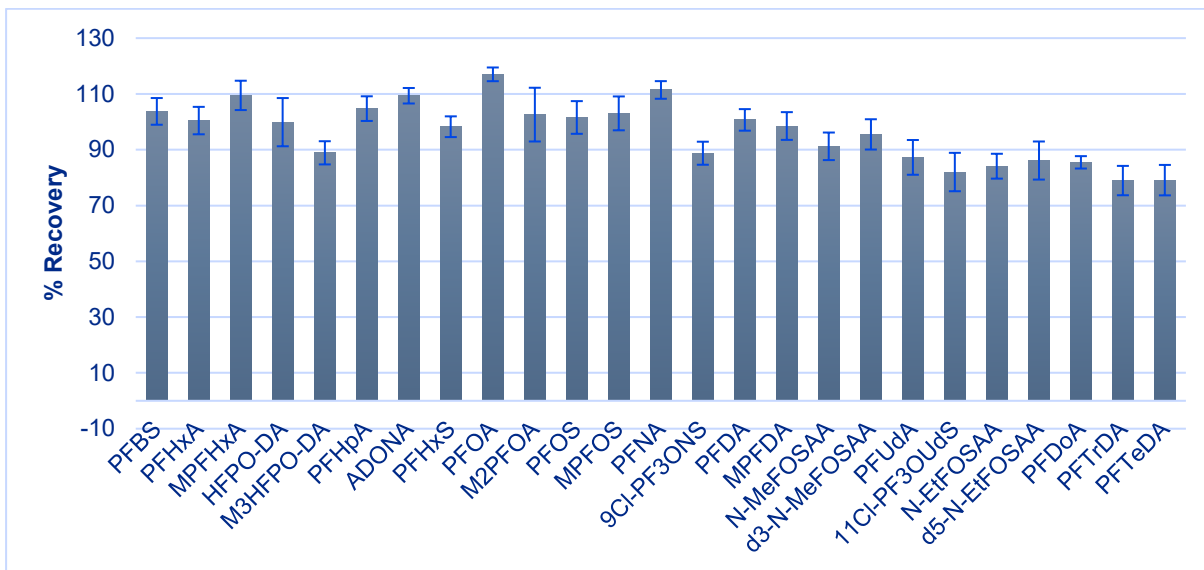


Figure 7. Recovery rates of 18 PFAS (listed in US EPA method 537.1) + 4 surrogates from drinking water with EluCLEAR PFAS - SDVB columns (n=5, c=4 ng/L) using FREESTYLE XANA PFAS TableTop automated SPE

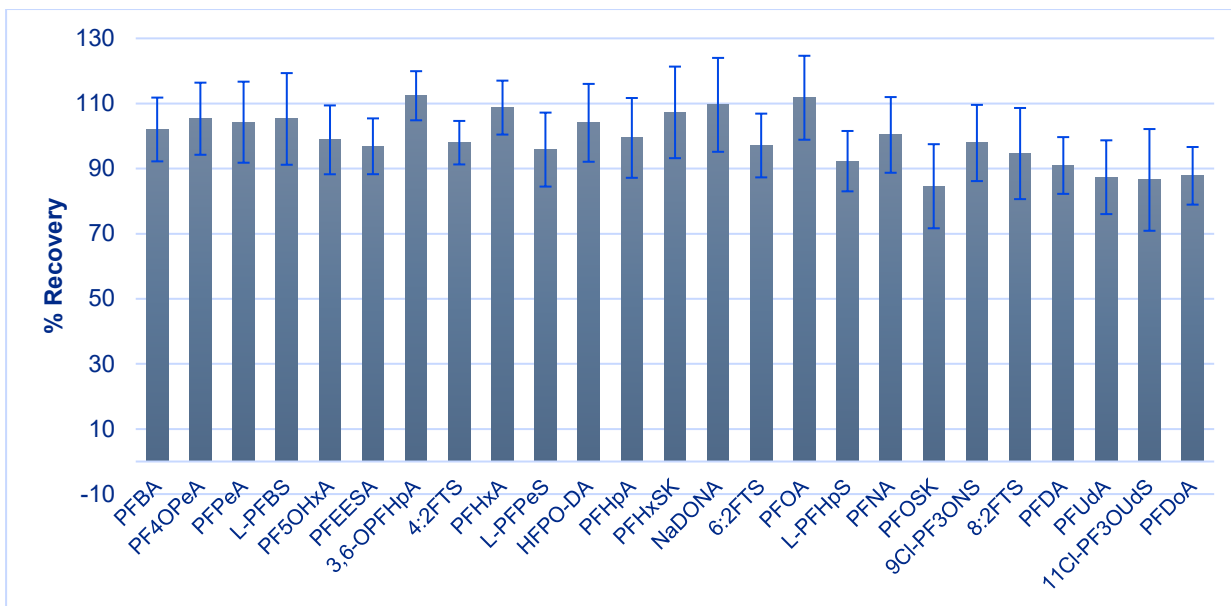


Figure 8. Recovery rates 25 PFAS (listed in US EPA method 533) from drinking water with EluCLEAR® - WAX (200 mg) Column (n=6, c=4 ng/L) using FREESTYLE XANA PFAS TableTop automated SPE

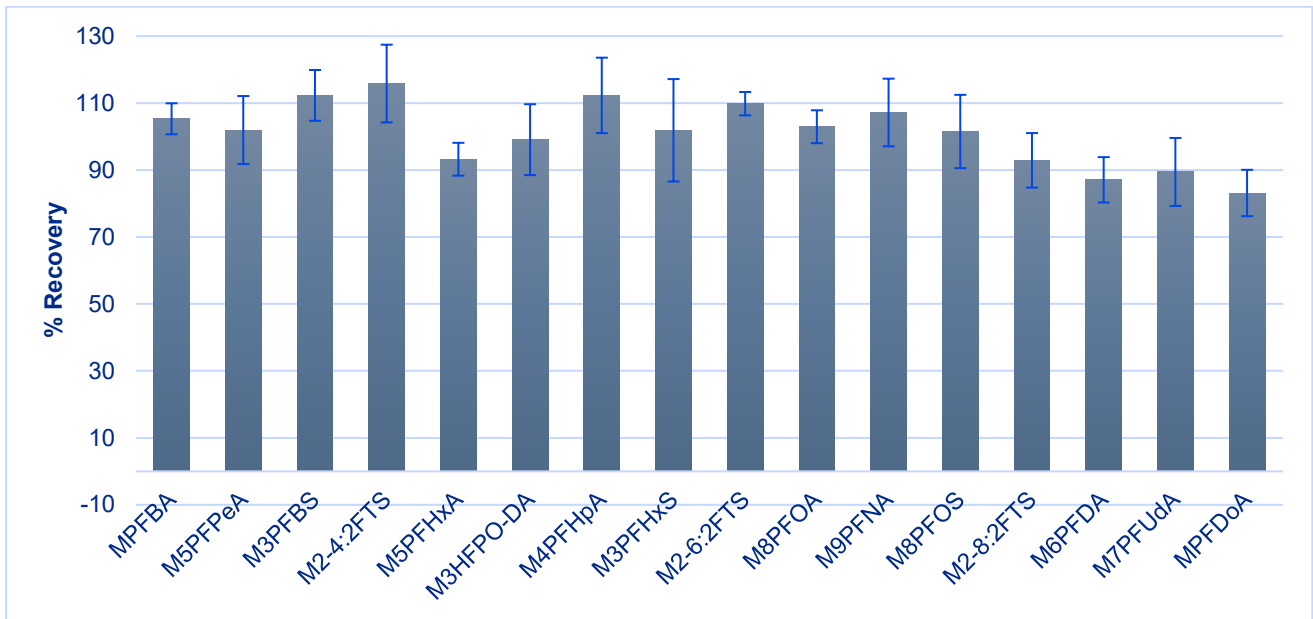


Figure 9. Recovery rates 16 isotope dilution PFAS standards (listed in US EPA method 533) from drinking water with EluCLEAR[®] PFAS – WAX (200 mg) Column (n=6, c=4-16 ng/L) using FREESTYLE XANA PFAS TableTop automated SPE



4. Conclusion

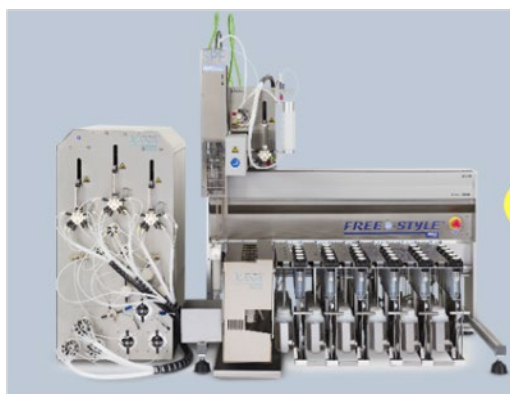
Due to the specifically designed PFAS system, which is virtually free of fluorocarbon compounds, any blank values stemming from the system are minimised, which was shown by PFAS background measurements (see Fig 6). In addition, EluCLEAR[®] PFAS SPE cartridges have no detectable PFAS background contamination (Fig 4 & 5).

The analytical targets of the US EPA 537.1 (with EluCLEAR[®] PFAS-SDVB) and US EPA 533 (with EluCLEAR[®] PFAS-WAX) method were successfully fulfilled. Recoveries for samples with a concentration of 4 ng/L for US EPA 537.1 with a range of 85 - 112 % and recoveries for samples for US EPA 533 with a range of 79-117 % 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 at 15 % or below.

The results show that a reliable and robust PFAS analysis can be processed via a fully automated sample preparation on FREESTYLE XANA-PFAS TableTop robotic system in combination with EluCLEAR[®] PFAS SPE cartridges.

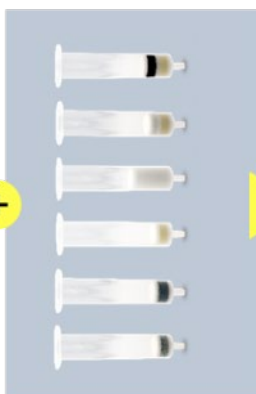
FREESTYLE™ XANA PFAS TableTop

For clean-up of up to 250 mL



EluCLEAR[®] PFAS

SPE columns



D-EVA Concentration

For the sensor controlled evaporation to a few µL





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: