

PFAS Analysis According to EPA 537.1

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Abstract

This application note describes the determination of per- and polyfluoroalkyl substances (PFAS) according to EPA directive 537.1. It demonstrates the enrichment of PFAS using the SPE column CHROMABOND® HR-X and subsequent chromatographic separation on a NUCLEODUR® PFAS analytical HPLC column.

To protect human health, EPA recommends two methods to detect PFAS from drinking water by solid phase extraction (SPE) and liquid chromatography/tandem mass spectrometry (LC/MS/MS) [2, 3].

This work presents the analysis of PFAS from drinking water according to directive EPA method 537.1. It shows high recoveries using a spherical, hydrophobic polystyrene-divinylbenzene resin in SPE columns for the enrichment of PFAS from water samples. The extracts are finally analyzed by HPLC-MS/MS.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a large class of persistent and bioaccumulative anthropogenic pollutants characterized by a linear aliphatic backbone, a high degree of fluorination and often feature a carboxylic or sulfonic acid functionality. PFAS present numerous analytical challenges, including their widespread presence in a variety of environmental samples, occurrence of isomers for some compounds, and precursor transformations that may occur during preservation and storage of the samples. There is also evidence that exposure to PFAS can lead to adverse human health effects. This is the reason why, in the US, authorities published variety of laws and regulations to protect public health and the environment [1]:

- Safe Drinking Water Act
- Toxic Substances Control Act (TSCA)
- Comprehensive Environmental Response, Compensation and Liability Act
- Clean Air Act

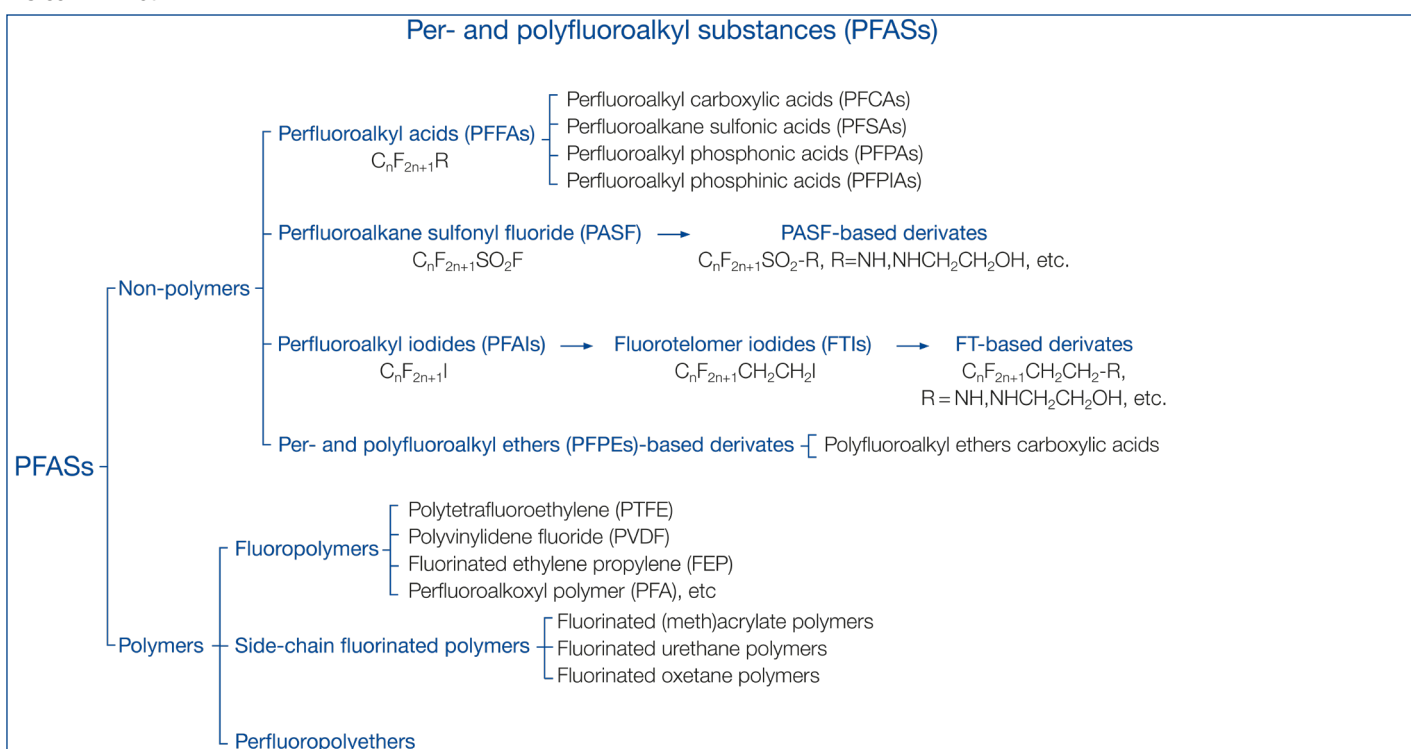


Figure 1: General structure of various per- and polyfluoroalkyl compounds (PFAS)

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Sample pretreatment for solid phase extraction (SPE)

- Samples are preserved, collected and stored as presented in polypropylene bottles.
- Add the dechlorinating agent (5.0 g/L) to the sample.
- Verify that the sample pH is 7 ± 0.5 . Control pH of the water sample (it should be between 6 and 8).
- Add 20 μL organic standard solution* ($\beta = 25.0 \text{ ng/mL}$ in methanol for each compound) to the 250 mL water sample
* Contains native and isotopically labeled per- and polyfluoroalkyl substances.

Solid phase extraction

Column: CHROMABOND® HR-X, 85 μm , 6 mL, 500 mg, (REF 730939) or
CHROMABOND® HR-X, 45 μm , 3 mL, 200 mg, (REF 730931P45)

Conditioning: 15 mL methanol, 18 mL water

Sample application: Add 2 mL of water to each cartridge, attach the reservoir cartridges, turn on the vacuum, and begin adding the 250 mL water sample with a flow rate of 10–15 mL/min to the cartridge. Do not allow the cartridge to run dry before all the sample has passed through.

Sample bottle and cartridge rinse: After the entire sample has passed through the cartridge, rinse the sample bottles and the transfer cartridges with two 7.5-mL aliquots of water and draw each aliquot through the SPE columns. Draw air or nitrogen through the cartridge for 5 min at high vacuum (10–15 inches Hg).

Sample bottle and cartridge elution: Rinse the sample bottles and the transfer cartridge with 4 mL of methanol and elute the analytes from the cartridges by pulling the 4 mL of methanol through the SPE column. Use a low vacuum such that the solvent exits the cartridge in a dropwise fashion. Repeat sample bottle rinse and cartridge elution with a second 4 mL aliquot of methanol.

Eluent exchange: Evaporate eluate to dryness at 40 °C under a stream of nitrogen and dissolve residue in 0.5 mL methanol.

Analysis by HPLC-MS/MS

Chromatographic conditions:

Delay column: EC 50/2 NUCLEODUR® PFAS Delay , 5 μm (REF 760673.20)

Analytical column: EC 100/2 NUCLEODUR® PFAS, 3 μm (REF 760666.20)

Eluent A: 5 mM ammonium acetate in water

Eluent B: 5 mM ammonium acetate in methanol

Gradient: hold 40 % B for 1.0 min, in 8 min from 40 % B to 95 % B, hold 95 % B for 3.0 min, in 0.1 min to 40 % B, hold 40 % B for 2.9 min

Flow rate: 0.3 mL/min

Temperature: 40 °C

Injection volume: 2 μL

Sample solution: Mixture of PFAS in methanol, concentration 1 ng/mL for each compound

MS conditions :

AB Sciex QTRAP 5500

Acquisition mode: SRM	Ion spray voltage: – 4500 V
Interface: ESI	Temperature: 400 °C
Polarity: negative	Ion source gas 1: 50 psig
Curtain gas: 30 psig	Ion source gas 2: 60 psig
Collision Gas: medium	Detection window: 60 s



PFAS Analysis According to EPA 537.1

MRM transitions

Abbreviation	Analyte	CASRN	Q ₁ Mass (DA)	Q ₃ Mass (DA)	RT (min)
HFPO-DA	Hexafluoropropylene oxide dimer acid	13252-13-6	284.991	168.7	5.77
PFBS	Perfluorobutanesulfonic acid	375-73-5	298.933	98.9	4.20
PFHxA	Perfluorohexanoic acid	307-24-4	312.911	268.8	5.40
PFHpA	Perfluoroheptanoic acid	375-85-9	362.931	318.8	6.45
ADONA	4,8-Dioxa-3H-perfluorononanoic acid	919005-14-4	376.901	250.7	6.58
PFHxS	Perfluorohexanesulfonic acid	355-46-4	398.942	79.8	6.49
PFOA	Perfluorooctanoic acid	335-67-1	412.910	369.0	7.26
PFNA	Perfluorononanoic acid	375-95-1	462.893	418.9	7.92
PFOS	Perfluorooctanesulfonic acid	1763-23-1	498.836	79.9	7.89
PFDA	Perfluorodecanoic acid	335-76-2	512.841	468.9	8.49
9Cl-PF ₃ ONS	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	756426-58-1	530.752	350.7	8.25
PFUnA	Perfluoroundecanoic acid	2058-94-8	562.801	518.9	8.95
NMeFOSAA	<i>N</i> -methyl perfluorooctanesulfonamidoacetic acid	2355-31-9	569.801	418.9	8.78
NEtFOSAA	<i>N</i> -ethyl perfluorooctanesulfonamidoacetic acid	2991-50-6	583.809	418.8	9.02
PFDoA	Perfluorododecanoic acid	307-55-1	612.787	568.9	9.33
11Cl-PF ₃ OUdS	11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	763051-92-9	630.738	451.0	9.15
PFTTrDA	Perfluorotridecanoic acid	72629-94-8	662.767	618.9	9.66
PFTA	Perfluorotetradecanoic acid	376-06-7	712.774	668.8	9.94

Table 1: MRM transitions and retention times of PFAS according to EPA 537.1.

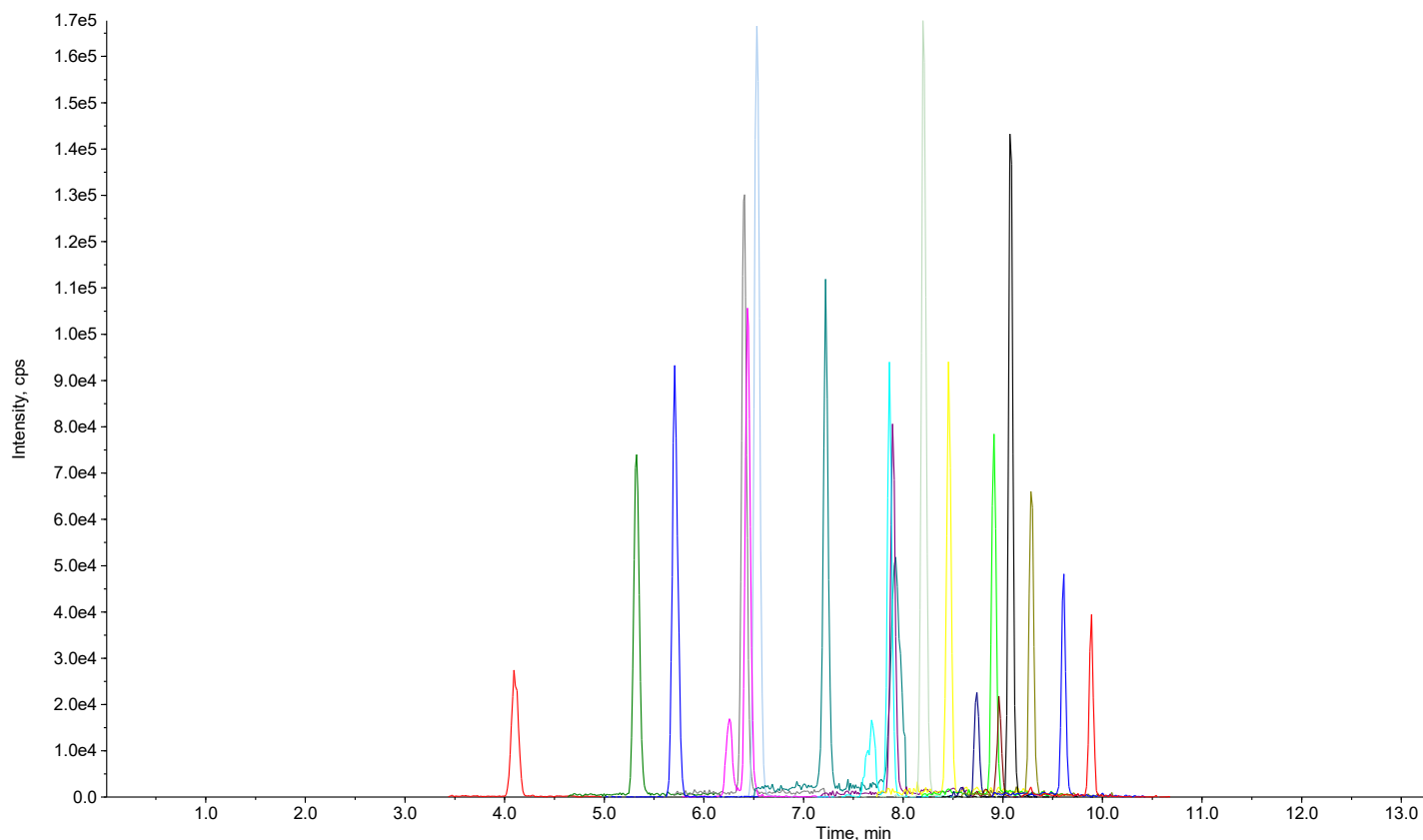


Figure 2: Chromatogram of PFAS according to EPA 537.1 on NUCLEODUR® PFAS EC 100/2 mm column ($\beta = 1.0$ ng/mL for each compound).

PFAS Analysis According to EPA 537.1

Recovery rates

Native Analyte	Abbreviation	CHROMABOND® HR-X, 45 µm, 3 mL/200 mg		CHROMABOND® HR-X, 85 µm, 6 mL/500 mg	
		Mean %	RSD %	Mean %	RSD %
Hexafluoropropylene oxide dimer acid	HFPO-DA	102.0	3.9	107.9	2.4
Perfluorobutanesulfonic acid	PFBS	111.5	5.8	107.0	5.3
Perfluorohexanoic acid	PFHxA	111.6	3.1	103.8	6.1
Perfluoroheptanoic acid	PFHpA	106.9	3.2	112.1	4.0
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	104.4	4.0	103.1	6.4
Perfluorohexanesulfonic acid	PFHxS	113.9	2.9	99.1	2.0
Perfluorooctanoic acid	PFOA	107.6	5.4	114.1	2.0
Perfluorononanoic acid	PFNA	114.3	4.5	110.9	6.7
Perfluorooctanesulfonic acid	PFOS	101.1	8.5	106.9	5.6
Perfluorodecanoic acid	PFDA	119.6	6.1	119.6	6.1
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF ₃ ONS	103.3	3.9	94.4	4.8
Perfluoroundecanoic acid	PFUnA	117.5	6.4	130.9	7.9
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	118.1	8.0	116.1	7.6
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	108.9	5.4	106.8	7.6
Perfluorododecanoic acid	PFDoA	116.5	7.9	126.6	8.4
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF ₃ OUdS	104.8	4.8	94.4	6.1
Perfluorotridecanoic acid	PFTrDA	111.8	12.3	124.4	6.3
Perfluorotetradecanoic acid	PFTA	117.8	5.8	124.5	6.8
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	110.3	4.1	112.3	6.0
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	110.2	19.2	93.8	4.6
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	102.4	6.0	102.6	11.1
Perfluoro-1-octanesulfonamide	FOSA	94.1	7.4	87.0	12.1
Perfluoro-1-nonanesulfonate	PFNS	103.0	6.6	87.0	6.6
Perfluoropentanesulfonic acid	PFPeS	104.0	4.6	96.6	6.1
Perfluoro-1-decanesulfonate	PFDS	108.2	4.7	87.1	4.9
Perfluoroheptanesulfonic acid	PFHpS	104.0	4.1	99.7	3.7
Perfluoropentanoic acid	PFPeA	103.7	4.0	100.1	5.3

Internal Standards	Abbreviation	Mean %	RSD %	Mean %	RSD %
Sodium perfluoro-1-[2,3,4- ¹³ C ₃]-butanesulfonate	M3PFBS	110.0	3.4	108.1	3.9
Perfluoro- <i>n</i> -[1,2,3,4,6- ¹³ C ₅]hexanoic acid	M5PFHxA	111.0	3.9	111.1	4.2
Perfluoro- <i>n</i> -[1,2,3,4- ¹³ C ₄]heptanoic acid	M4PFHpA	114.5	4.0	113.5	5.7
Sodium perfluoro-1-[1,2,3- ¹³ C ₃]-hexanesulfonate	M3PFHxS	104.6	5.2	101.1	5.0
Perfluoro- <i>n</i> -[¹³ C ₈]octanoic acid	M8PFOA	112.4	4.1	115.3	5.0
Perfluoro- <i>n</i> -[¹³ C ₉]nonanoic acid	M9PFNA	115.2	5.9	116.3	5.1
Sodium perfluoro-1-[¹³ C ₈]-octanesulfonate	M8PFOS	105.3	5.6	93.6	9.8
Perfluoro- <i>n</i> -[1,2,3,4,5,6- ¹³ C ₆]decanoic acid	M6PFDA	114.4	7.7	113.2	12.1
Perfluoro- <i>n</i> -[1,2,3,4,5,6,7- ¹³ C ₇]undecanoic acid	M7PFUnA	110.0	14.1	124.0	6.6
N-methyl- <i>d</i> ₃ -perfluoro-1-octanesulfonamidoacetic acid	<i>d</i> ₃ -NMeFOSAA	109.3	9.4	124.6	13.5
N-ethyl- <i>d</i> ₅ -perfluoro-1-octanesulfonamidoacetic acid	<i>d</i> ₅ -NEtFOSAA	121.5	4.6	114.3	23.1
Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]dodecanoic acid	MPFDoA	113.5	8.7	125.8	5.6
Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]tetradecanoic acid	M2PFTA	116.6	10.0	125.2	7.6
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2- ¹³ C ₂]-hexane sulfonate (4:2)	M2-4:2FTS	104.0	6.4	114.1	4.8
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2- ¹³ C ₂]-octane sulfonate (6:2)	M2-6:2FTS	105.2	5.1	109.1	5.9
Sodium 1H,1H,2H,2H-perfluoro-1-[1,2- ¹³ C ₂]-decane sulfonate (8:2)	M2-8:2FTS	118.9	5.0	105.6	6.3
Perfluoro-1-[¹³ C ₈]octanesulfonamide	M8FOSA	97.0	5.5	94.5	10.0
Perfluoro- <i>n</i> -[¹³ C ₅]pentanoic acid	M5PFPeA	109.1	3.5	107.7	5.5

Table 2: Recovery rates for the presented SPE method for drinking water using SPE column, CHROMABOND® HR-X, 45 µm, 3 mL/200 mg and SPE columns, CHROMABOND® HR-X, 85 µm, 6 mL/500 mg.

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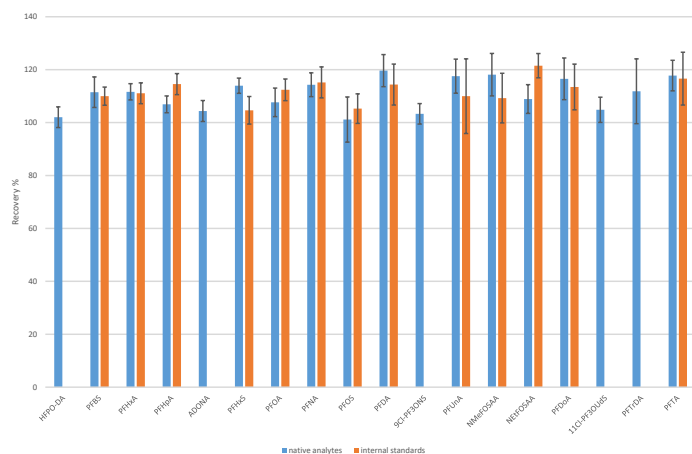


Figure 3: Recovery rates of PFAS according to EPA 537.1 method for drinking water using SPE column, CHROMABOND® HR-X, 45 µm, 3 mL/200 mg (spiked with 0.5 ng for each compound in 0.25 L water).

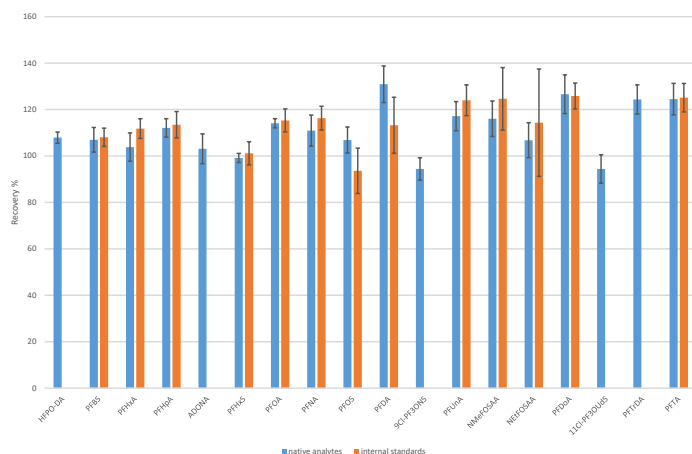


Figure 4: Recovery rates of PFAS according to EPA 537.1 method for drinking water using SPE column, CHROMABOND® HR-X, 85 µm, 6 mL/500 mg (spiked with 0.5 ng for each compound in 0.25 L water).

Conclusion

This application note presents the reliable and successful determination of per- and polyfluoroalkyl substances (PFAS) from drinking water according to EPA method 537.1. By using CHROMABOND® HR-X SPE columns, it was possible to achieve high recovery rates for PFAS from drinking water with good reproducibility. The used SPE phase, a spherical, hydrophobic polystyrene-divinylbenzene resin shows effective analyte enrichment with hydrophobic interaction mechanism for a broad spectrum of PFAS.

The work shows that both tested SPE column dimensions, CHROMABOND® HR-X, 45 µm, 3 mL/200 mg and CHROMABOND® HR-X, 85 µm, 6 mL/500 mg, fulfill the analytical requirements of this EPA method. Most of the PFAS show recovery rates between 90 % and 120 %.

The chromatographic separation of PFAS was performed by using NUCLEODUR® PFAS HPLC column. This phase is specially suitable for the analysis of PFAS compounds. It shows high retention for polar PFAS, high MS intensity and excellent batch-to-batch reproducibility. Contaminants from an LC system, especially PFOA, are separated from sample analytes by implementing an isolator column, NUCLEODUR® PFAS Delay.

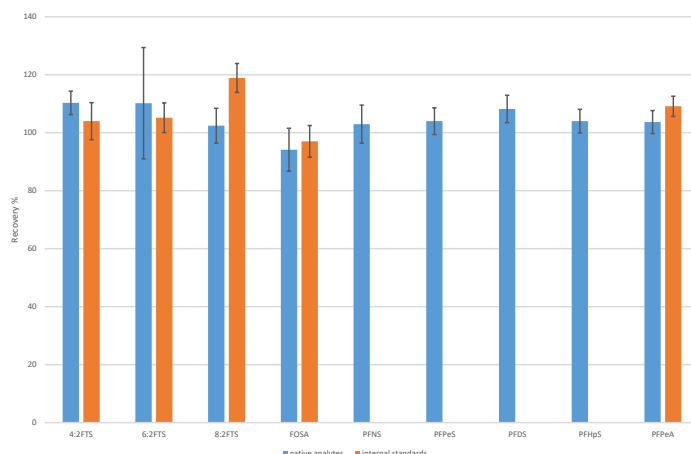


Figure 5: Recovery rates of further PFAS* according to EPA 537.1 method for drinking water using SPE column, CHROMABOND® HR-X, 45 µm, 3 mL/200 mg (spiked with 0.5 ng for each compound in 0.25 L water). * not specified in EPA method 537.1

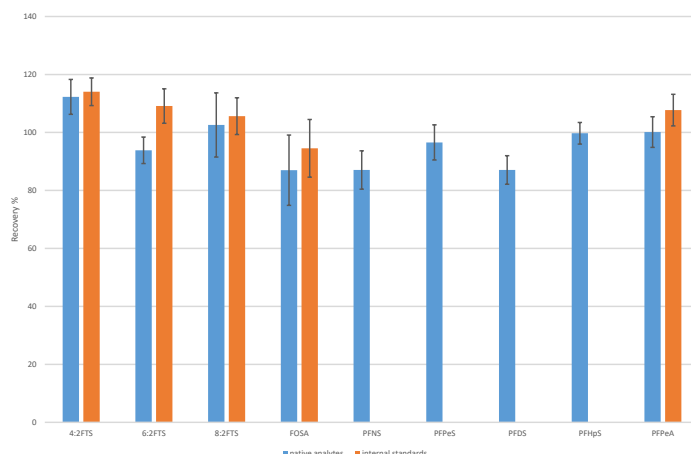


Figure 6: Recovery rates of further PFAS* according to EPA 537.1 method for drinking water using SPE column, CHROMABOND® HR-X, 85 µm, 6 mL/500 mg (spiked with 0.5 ng for each compound in 0.25 L water). * not specified in EPA method 537.1

In summary, the presented application shows that the utilized SPE and HPLC products allow a reliable and successful determination of per- and polyfluoroalkyl substances (PFAS) from drinking according to EPA method 537.1.

References

- [1] United States Environmental Protection Agency, PFAS Laws and Regulations, <https://www.epa.gov/pfas/pfas-laws-and-regulations>
- [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). U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, DC, 2018.
- [3] 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. U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington, DC, 2019.

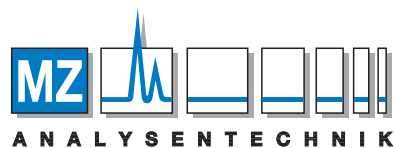
PFAS Analysis According to EPA 537.1

Product information

The following MACHEREY-NAGEL products have been used in this application note:

REF 760673.20	EC 50/2 NUCLEODUR® PFAS Delay
REF 760666.20	EC 100/2 NUCLEODUR® PFAS
REF 730931P45	SPE columns, CHROMABOND® HR-X, 45 µm, 3 mL/200 mg
REF 730939	SPE columns, CHROMABOND® HR-X, 85 µm, 6 mL/500 mg
REF 730382	Reservoir columns, 70 mL with adaptor for 1, 3, 6 mL CHROMABOND® SPE PP columns
REF 702402	Screw closure, N 9, PP, blue, c. hole, Sili. w./ Polyimide orange, 1.0 mm, flourine-free.
REF 702009	Screw neck vial, N 9, 11.6 x 32.0 mm, 0.3 mL, inner cone, PP tr.

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