Chromatography

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Robust determination of PFAS substances in drinking water using SPE and HPLC-MS/MS according to EPA 537.1

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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

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.

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* (β = 25.0 ng/mL in methanol for each compound) to the 250 mL water sample.

*Contains native and isotopically labeled per- and polyfluoroalkyl substances.

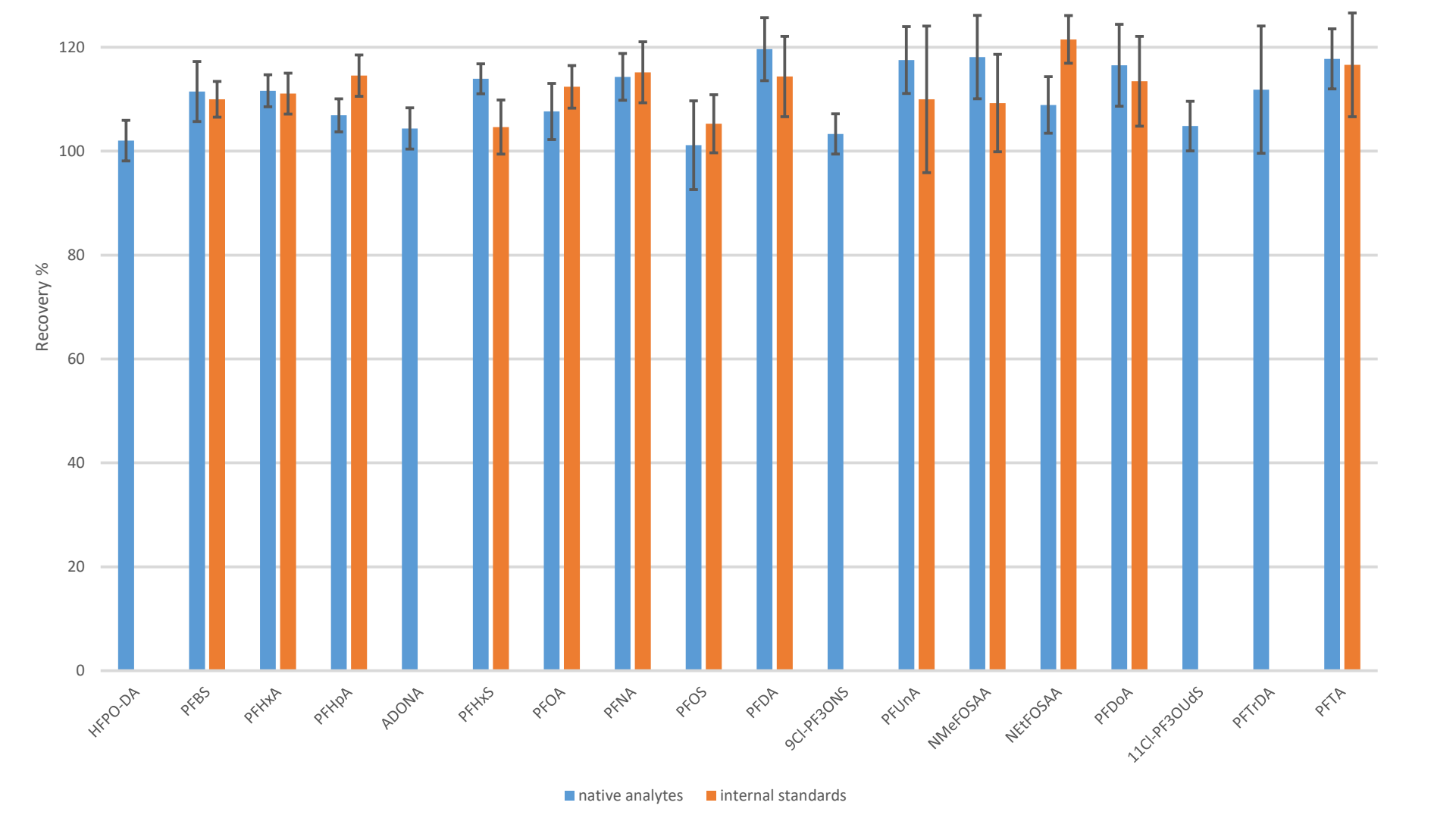

Figure 1: Recovery rates of PFAS according to EPA 537.1 method for drinking water using SPE column, CHROMABOND® HR-X, 45 µm, 3 mL/200 mg (spiked with 0.5 ng for each compound in 0.25 L water, n=5).

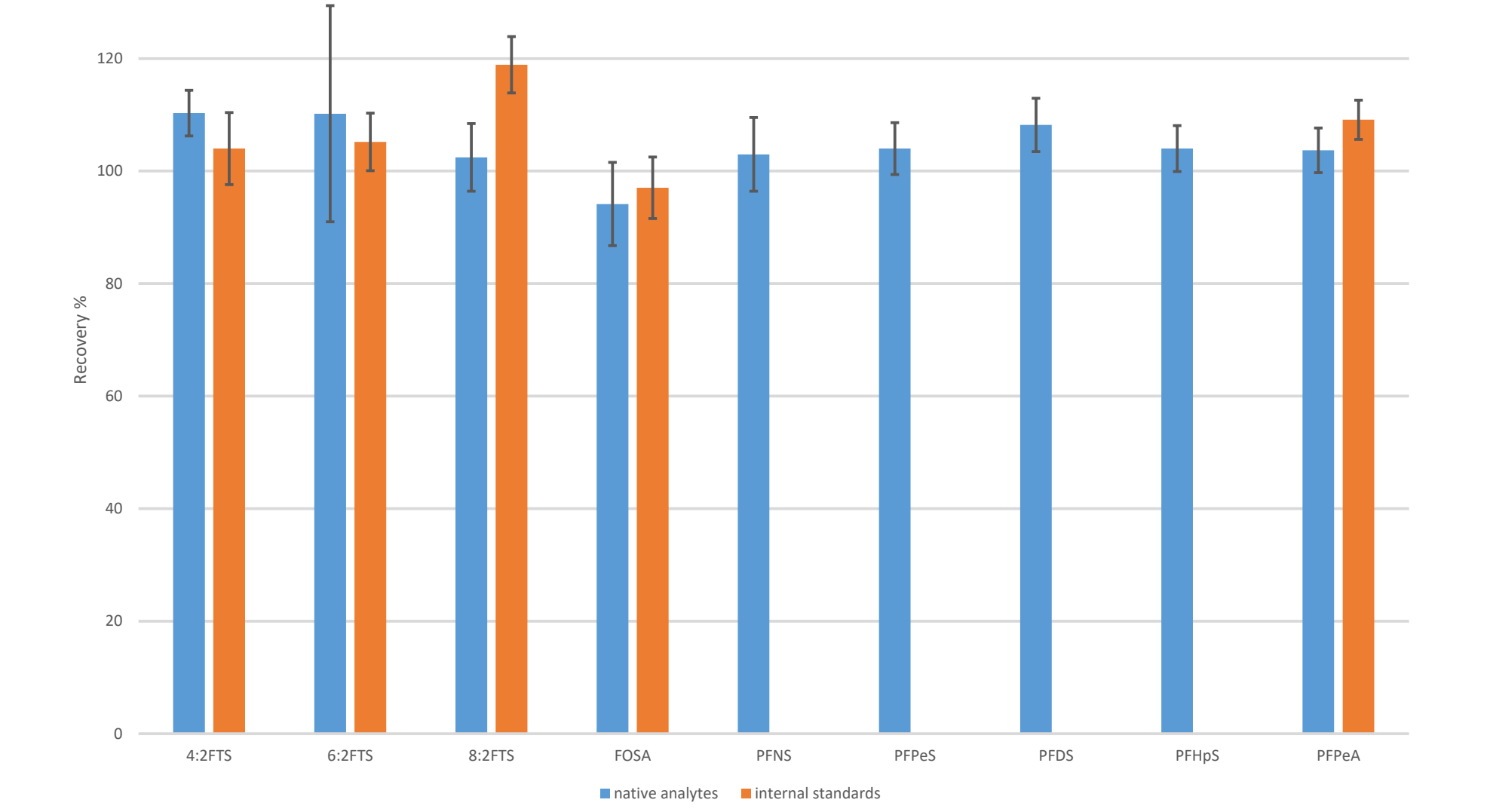

Figure 3: Recovery rates of further PFAS* according to EPA 537.1 method for drinking water using SPE column, CHROMABOND® HR-X, 45 µm, 3 mL/200 mg (spiked with 0.5 ng for each compound in 0.25 L water, n=5).
* not specified in EPA method 537.1

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.

Sample bottle and cartridge elution: Rinse the sample bottles and the transfer cartridge with 5 mL of methanol with 2 % ammonium hydroxide (v/v) and elute the analytes from the cartridges by pulling the 5 mL of methanol with 2 % ammonium hydroxide (v/v) 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 5 mL aliquot of methanol with 2 % ammonium hydroxide (v/v).

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

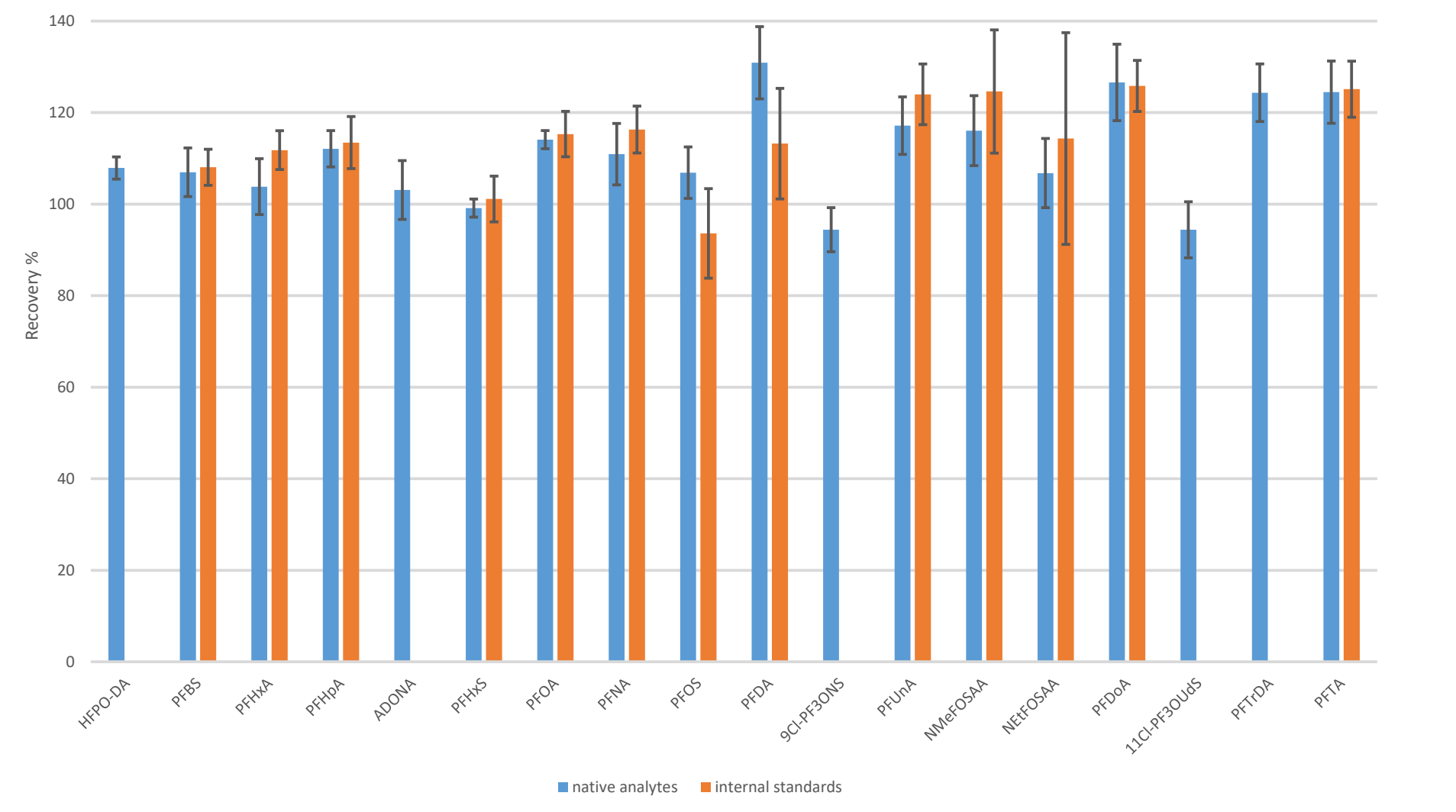

Figure 2: Recovery rates of PFAS according to EPA 537.1 method for drinking water using SPE column, CHROMABOND® HR-X, 85 µm, 6 mL/500 mg (spiked with 0.5 ng for each compound in 0.25 L water, n=5).

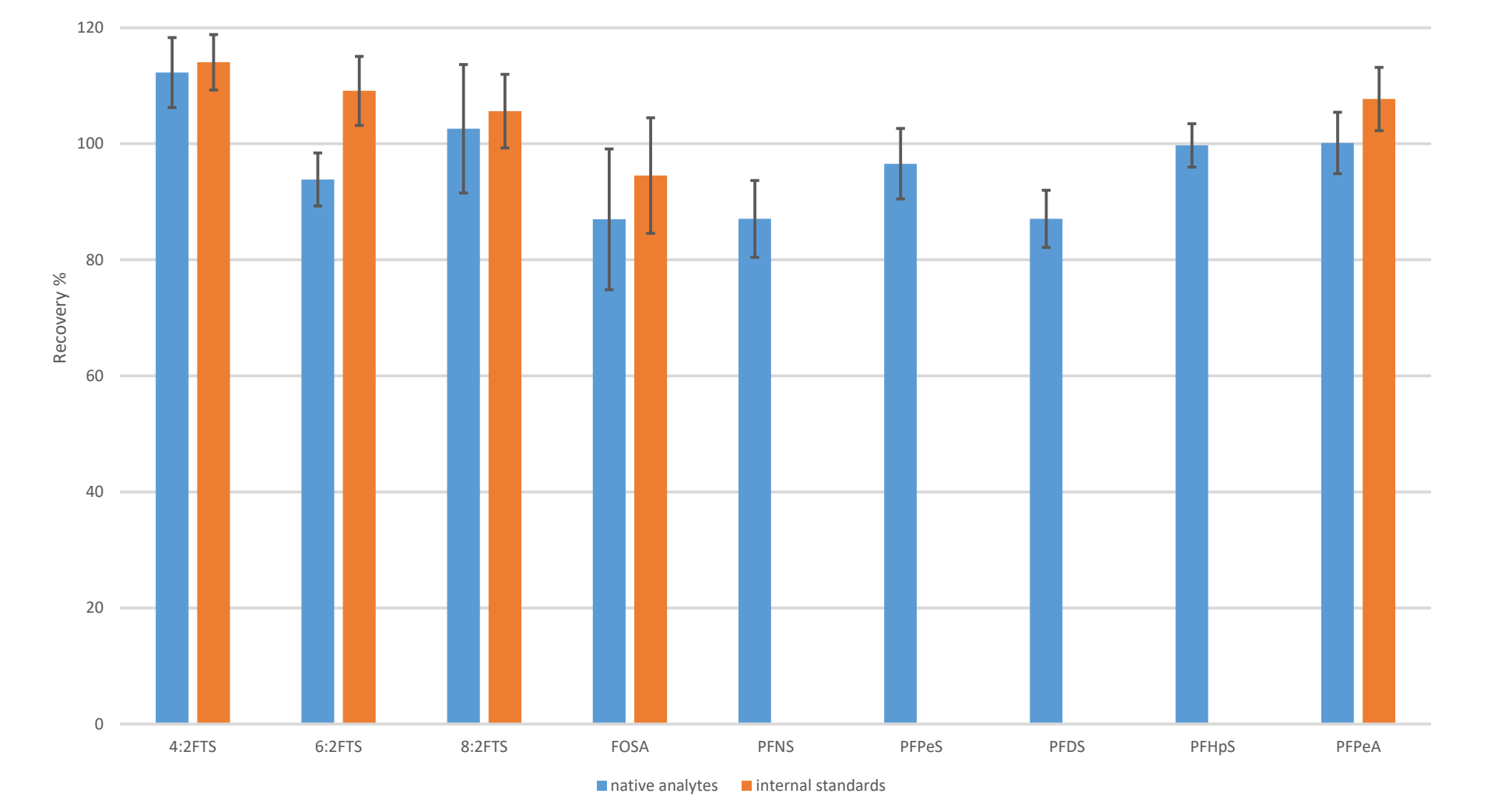

Figure 4: Recovery rates of further PFAS* according to EPA 537.1 method for drinking water using SPE column, CHROMABOND® HR-X, 85 µm, 6 mL/500 mg (spiked with 0.5 ng for each compound in 0.25 L water, n=5).
* not specified in EPA method 537.1

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
Sample solution	Mixture of PFAS in methanol, concentration 1 ng/mL for each compound
Flow rate	0.3 mL/min
Temperature	40 °C
Injection volume	2 µL

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.

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 water according to EPA method 537.1.

To see complete application note, please scan the following QR-code:

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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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.

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Poster PFAS analysis according to EPA 533 en1 / 0 / 0 / 08.2021

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