MACHEREY-NAGEL

Analysis of PFAS from water samples

Hans Rainer, Wollseifen[1], Lukas Emmerich[2]

[1] MACHEREY-NAGEL GmbH & Co. KG, Dueren, Germany, hwollseifen@mn-net.com

[2] MACHEREY-NAGEL GmbH & Co. KG, Dueren, Germany

Introduction

The new EU Directive 2020/2184 came into force on January 12th, 2021 and had to be be implemented into national law by January 12th, 2023. [1] The objectives of this Directive are to protect human health from the adverse effects of any contamination of water intended for human consumption by ensuring that it is wholesome and clean, and to improve access to water intended for human consumption. By January 12th, 2024, the Commission shall establish technical guidelines regarding methods of analysis for the monitoring of per- and polyfluoroalkyl substances including detection limits, parametric values and frequency of sampling. The directive defines the following parameters: 'PFAS Total' and 'Sum of PFAS'. The parameter 'PFAS Total' means the totality of per- and polyfluoroalkyl substances. The parameter 'Sum of PFAS' means the sum of 20 per- and polyfluoroalkyl substances:

- Perfluorobutanoic acid (PFBA)
- Perfluoropentanoic acid (PFPA)
- Perfluorohexanoic acid (PFHxA)
- Perfluoroheptanoic acid (PFHpA)
- Perfluorooctanoic acid (PFOA)
- Perfluorononanoic acid (PFNA)
- Perfluorodecanoic acid (PFDA)
- Perfluoroundecanoic acid (PFUnDA)
- Perfluorododecanoic acid (PFDoDA)
- Perfluorotridecanoic acid (PFTrDA)
- Perfluorobutane sulfonic acid (PFBS)
- Perfluoropentane sulfonic acid (PFPS)
- Perfluorohexane sulfonic acid (PFHxS)
- Perfluoroheptane sulfonic acid (PFHpS)
- Perfluorooctane sulfonic acid (PFOS)
- Perfluorononane sulfonic acid (PFNS)
- Perfluorodecane sulfonic acid (PFDS)
- Perfluoroundecane sulfonic acid (PFUDS)
- Perfluorododecane sulfonic acid (PFDoS)
- Perfluorotridecane sulfonic acid (PFTrDS)

Those substances shall be monitored when the risk assessment and risk management of the catchment areas for abstraction points carried out conclude that those substances are likely to be present in a given water supply.

In this word, a SPE method for the parameter 'Sum of PFAS' using the CHROMABOND® PFAS is presented. The effects of adding methanol to the sample solution on the recovery rates for ionic PFAS are described. In the work high recovery rates with very good reproducibility are achieved for the listed PFAS analytes. Finally, the extracts are analyzed using HPLC-MS/MS on a NUCLEODUR® PFAS column.

Sample pretreatment

Solid phase extraction

Sample preparation

1. The pH value of the sample shall be adjusted to the pH value of 3 with acetic of ammonia solution, if necessary.
2. Add the spiking solution containing the internal standard substances to the water sample in the sample bottle [adding 0.5 ng of each (5813/20 PFAS Native Solution/Mixture)] and mix throroughly by shaking.
3. Adjust methanol content of sample solution [0 %, 5 % and 10 % (percent by volume)]
4. Zentrifugieren: 10 min, 20 °C, 4500 rpm

SPE method

1. Column: CHROMABOND® PFAS, 3 mL 120 mg (REF 7300009)
2. Conditioning: Add 4 mL of 0.1 % NH_3 in methanol solution, 4 mL of methanol and 4 mL of water to the cartridge.
3. Sample application: Add 200 mL water sample with a flow rate of 5 mL/min to the cartridge. (Do not let the sorbent material in the cartridge go dry and ensure it is immersed in water at all times).
4. Bottle Rinse: Rinse the sample bottle wall and reservoir column with 4 mL of 0.1 % NH_3 in methanol solution.
5. Washing step: Add 4 mL of water and 4 mL of acetate buffer solution to the cartridge and discrad the eluate.
6. Drying step: Dry the cartridge for 2 min with vacuum and centrifuge the cartridge at 1500 g for about 2 min.
7. Elution: Add 4 mL of 0.1 % NH_3 in methanol solution with a flow rate of 3 mL/min and collect the eluate into the sample tubes.
8. 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 (REF 760673.20)
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 min, in 8 min from 40 % B to 95 % B, hold 95 % B for 3 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	1 µL

MS conditions

Acquisition mode	SRM	Ionspray Voltage	-4500 V
Interface	ESI	Temperature	400 °C
Polarity	negative	Ion Source Gas 1	50
Curtain Gas	30	Ion Source Gas 2	60
Collision Gas	medium	Detection Window	60 sec

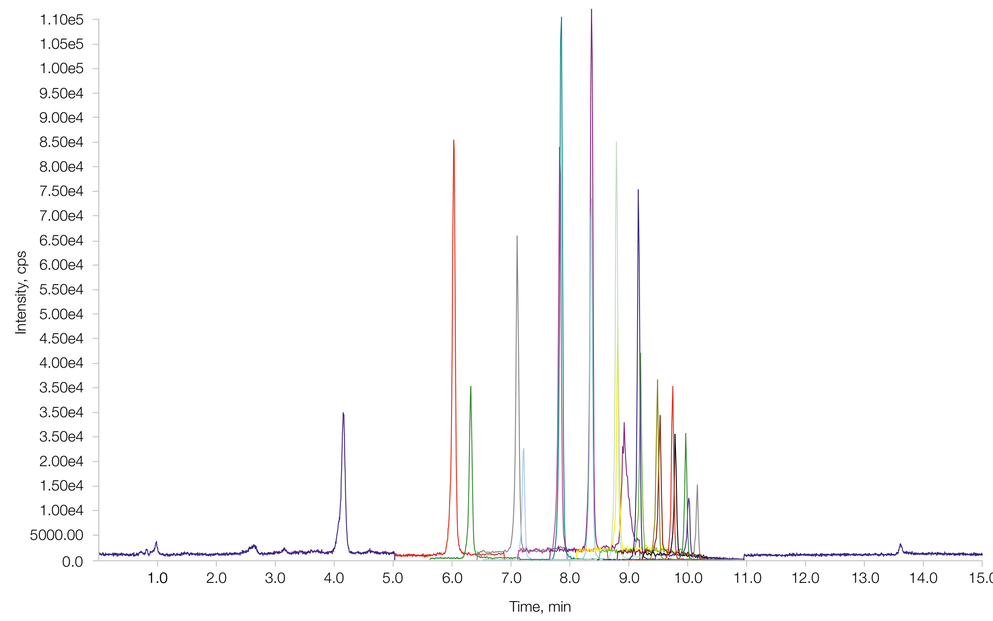
MRM transitions

Analyte	Abbreviation	CAS number	Q1 mass [Da]	Q3 mass [Da]	Retention time [min]
Perfluoro-*n*-butanoic acid	PFBA	375-22-4	212.904	168.8	2.01
Perfluoro-*n*-pentanoic	PFPeA	2706-90-3	262.880	219.0	3.90
Perfluoro-*n*-hexanoic acid	PFHxA	307-24-4	312.911	268.8	5.40
Perfluoro-*n*-heptanoic acid	PFHpA	375-85-9	362.931	318.8	6.45
Perfluoro-*n*-octanoic acid	PFOA	335-67-1	412.910	369.0	7.26
Perfluoro-*n*-nonanoic acid	PFNA	375-95-1	462.893	418.9	7.92
Perfluoro-*n*-decanoic acid	PFDA	335-76-2	512.841	468.9	8.49
Perfluoro-*n*-undecanoic acid	PFUdA	2058-94-8	562.801	518.9	8.95
Perfluoro-*n*-dodecanoic acid	PFDoA	307-55-1	612.787	568.9	9.33
Perfluoro-*n*-tridecanoic acid	PFTrDA	72629-94-8	662.767	618.9	9.66
Perfluoro-*n*-butanesulfonic acid	PFBS	375-73-5	298.933	98.9	4.20
Perfluoropentansulfonic acid	PFPes	2706-91-4	348.850	80.0	5.54
Perfluoro-*n*-hexanesulfonic acid	PFHxS	355-46-4	398.942	79.8	6.49
Perfluoro-*n*-heptanesulfonic acid	PFHpS	375-92-8	448.929	79.8	7.26
Perfluoro-*n*-octanesulfonic acid	PFOS	1763-23-1	498.836	79.9	7.89
Perfluoro-*n*-nonanesulfonic acid	PFNS	68259-12-1	548.808	79.9	8.45
Perfluoro-*n*-decanesulfonic	PFDS	335-77-3	598.790	79.9	8.90
Perfluoro-*n*-undecanesulfonic	PFUdS	749786-16-1	648.850	80.0	9.30
Perfluorododecanesulfonic acid	PFDoS	79780-39-5	698.720	80.0	9.70
Perfluoro-*n*-tridecanesulfonic	PFTrDS	791563-89-8	748.846	79.8	9.87

MRM transitions and retention times of native PFAS analytical standards.

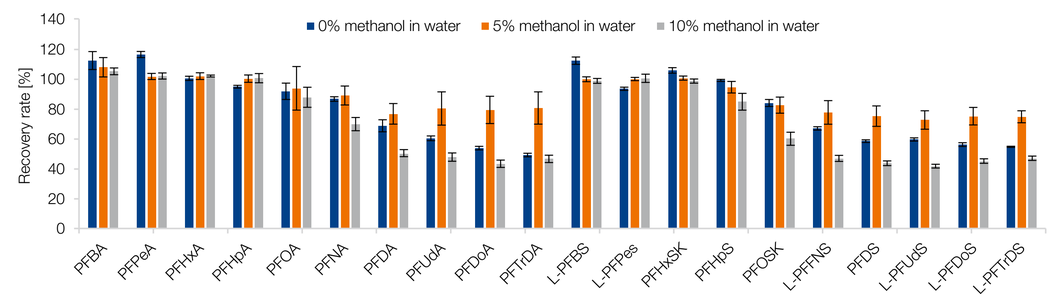
Chromatogram

Figure 1:



Chromatogram of a sample eluate (concentration sample β = 0.5 ng/mL, methanol content of water sample 5 %

Recovery rates



Recovery rates for the presented SPE method using CHROMABOND® PFAS, 3 mL, 120 mg.

Conclusion

This application note presents the reliable and successful determination of 20 PFAS according to EU Directive 2020/2184 for the parameter 'Sum of PFAS' from drinking water. By using CHROMABOND® PFAS, a double-layer SPE column, it was possible to achieve high recovery rates with good reproducibility. By the combination of different SPE sorbents in a multi-layer column it is possible to use various interaction types like ionic, hydrophobic, hydrogen bonds and dipole-dipole interactions for the enrichment of a broad spectrum of PFAS. In this way, a SPE method could be developed with the strength of two sorbents.

The methanol content in the sample solution helps to reduce adsorption effects of long-chain perfluoroalkyl substances and leads to better recovery rates. Most of the PFAS show recovery rates between 75 % and 110 %.

However, if neutral PFAS are the focus of the analysis, adding methanol to the sample solution can have a negative impact on the recovery rates. In addition, the SPE methodology should include a methanolic elution step as described in application note 10/2022 [2].

This work shows an accurate and robust method for the parameter 'Sum of PFAS'. The identification and the quantification of PFAS in water were finally carried out by ESI mass spectrometry on a NUCLEODUR® PFAS column.

References

[1] DIRECTIVE (EU) 2020/2184 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 16 December 2020 on the quality of water intended for human consumption.

[2] Determination of Per- and Polyfluoroalkyl Substances from water samples according to ISO 21675:2019.