Determination of perfluorinated alkyl substances in water with SPE and HLPC-MS / MS detection

H. R. Wollseifen, Düren/D, T. Kretschmer, Düren, A. Mengus-Kaya, Düren/D, M. Arens, Düren/D
Dr. H. R. Wollseifen, MACHEREY-NAGEL GmbH & Co. KG · Valencienner Str. 11 · 52355 Düren/D

Introduction

Perfluorinated alkyl substances are widespread in environment because of their use for over sixty years. These substances are highly stable and are discovered in human blood samples due to food intake. Their toxicity and potential health hazards are shown in several studies indicating that PFOA and PFOS can cause reproductive and developmental, liver and kidney, and immunological effects in laboratory animals. For protecting human health, there is an increasing demand for sensitive and efficient analysis of perfluorinated alkyl substances that are described in DIN and EPA regulations. It consists of a solid phase extraction step and determination and quantification prior HPLC-MS / MS [1, 2].

Subsequently, a sensitive solid phase extraction method for perfluorinated alkyl substances in water samples was developed. The solid phase extraction was performed for water samples with a special SPE-cartridge CHROMABOND® PFC according to the requirements of DIN 38407-42. The sorbent of this cartridge was optimized to the analytical requirements of the SPE achieving high recovery of perfluorinated alkyl compounds.

Fig. 1: Mühlenteich

Solid phase extraction (SPE)

Column	A) **CHROMABOND® PFC**, 300 mg, 3 mL B) **CHROMABOND® HR-XAW**, 85 µm, 60 mg, 3 mL
Conditioning	2 mL 0.1 % ammonium hydroxide in methanol, 2 mL methanol, 2 mL water
Sample application	50 mL water sample spiked with PFC standard mixture (β = 0.5 ng/mL for each analyt), adjusted to pH value 7–8
Washing step 1	2 mL water
Washing step 2	2 mL 1.0 % formic acid in acetone-acetonitrile mixture (50:50, v/v)
Washing step 3	2 mL methanol
No drying step	
Elution	2.4 mL of 0.1 % ammonium hydroxide in methanol
Eluent exchange	Evaporate eluate to dryness at 40 °C under a stream of nitrogen and reconstitute in 0.5 mL water / methanol (40:60, v/v)

Subsequent analysis HPLC-MS / MS

Chromatographic Conditions

Column:	EC 100/2 **NUCLEOSHELL® Bluebird RP 18**, 2.7 µm, (REF 763433.20)
Eluent A:	5 mM ammonium acetate in water
Eluent B:	5 mM ammonium acetate in methanol
Gradient:	hold 20 % B for 1 min, from 20 % B to 95 % B in 8.0 min, hold 95 % B for 3 min, from 95 % B to 20 % in 0.1 min, hold 20 % B for 4.9 min
Flow rate:	0.33 mL/min
Temperature:	40 °C
Injection volume:	10 µL
MS conditions:	API 5500, ion source ESI, negative ionization mode, scan type MRM Curtain gas 30 psig, ion spray voltage -4500 V, temperature 400 °C, nebulizer gas 50 psig, turbo gas 60 psig, CAD medium

MRM Transitions

Analyt	RT [min]	$[M-H]^-$	Q1 (Quantifier)	Q2 (Qualifier)
PFBA	2.57	212.9	168.8	-
PFPeA	4.68	262.9	219.0	-
PFHxA	5.88	312.9	268.7	119.0
PFHpA	6.65	362.9	318.6	168.8
PFOA	7.23	412.9	368.8	168.8
PFNA	7.70	462.9	418.9	218.9
PFDA	8.10	512.8	468.9	218.8
PFUdA	8.43	562.8	518.9	268.8
PFDoA	8.73	612.8	568.8	318.8
PFTrDA	8.98	662.8	618.8	318.8
PFTeDA	9.20	712.8	668.9	219.0
PFHxDA	9.56	812.9	768.8	369.0
PFODA	9.82	912.9	368.9	868.9
PFBS	5.02	298.9	79.9	98.9
PFHxS	6.69	398.9	79.8	98.8
PFHpS	7.24	448.9	79.8	98.9
PFOS	7.69	498.9	79.9	98.9
PFDS	8.40	598.8	79.9	98.9
FOSA	8.46	497.9	77.8	63.9
N-MeFOSAA	8.28	569.8	418.8	511.8
N-EtFOSAA	8.46	583.8	418.9	525.9
4-2 FTS	5.78	326.9	306.9	286.8
6-2 FTS	7.20	426.9	406.9	386.8
8-2 FTS	8.09	526.8	506.8	486.7
M4-PFBA	2.56	216.9	171.9	-
M4-PFOA	7.23	416.9	371.8	-
M2-PFHxA	5.88	314.9	269.9	-
M4-PFHXS	6.69	402.9	83.9	-
M5-PFNA	7.70	467.9	422.8	-
M4-PFOS	7.68	502.8	79.9	-
M2-PFDA	8.09	514.9	469.9	-
M2-PFUdA	8.42	564.8	519.9	-
M2-PFDoA	8.72	614.9	569.8	-

Chromatograms

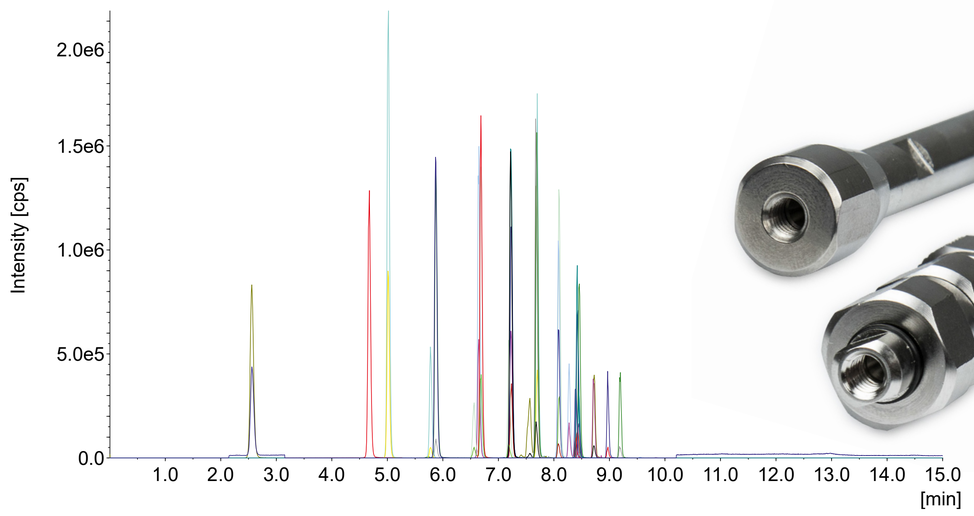

Fig. 2: Chromatogram of a standard mixture of perfluorinated alkyl substances (β = 10 ng/mL for each compound in water / methanol (40:60, v/v))

Recovery rates

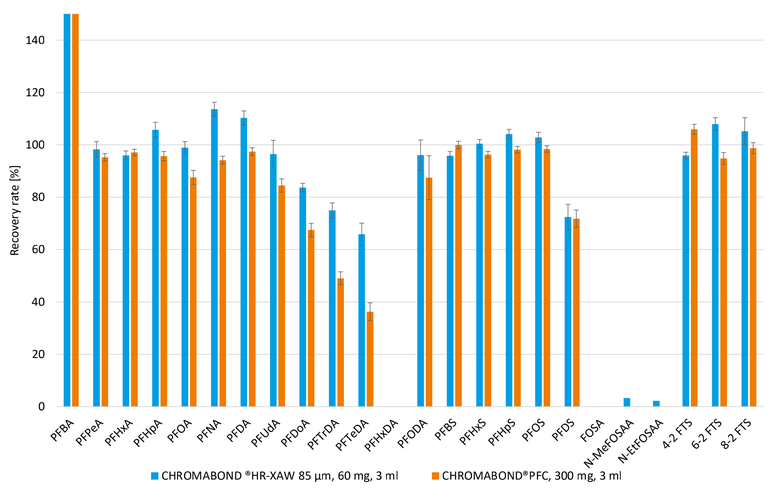

Fig. 3: Comparison of recovery rates of perfluorinated alkyl substances using CHROMABOND® PFC or CHROMABOND® HR-XAW in water.

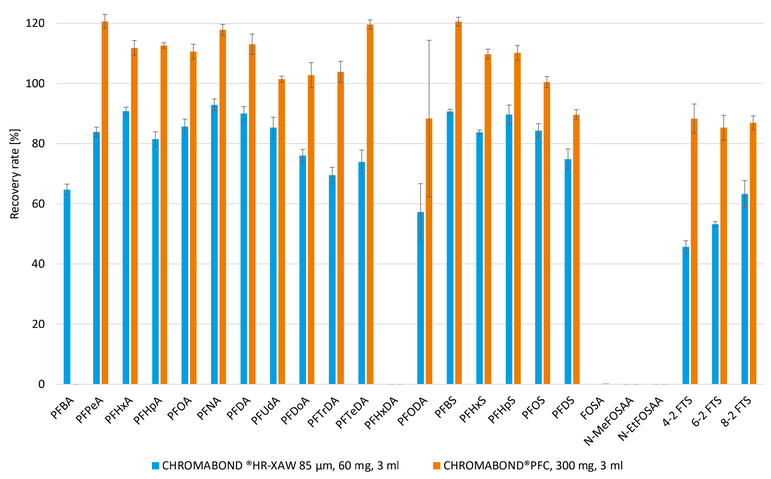

Fig. 4: Comparison of recovery rates of perfluorinated alkyl substances using CHROMABOND® PFC or CHROMABOND® HR-XAW in seawater.

Conclusion

The results show that the determination of perfluorinated alkyl substances from water and seawater could be carried out successfully with the tested products as presented in figure 3 and 4. By using SPE with CHROMABOND® PFC it was possible to achieve higher recovery rates for perfluorinated alkyl substances from seawater with good reproducibility. Regarding the different types of perfluorinated alkyl substances two groups, in particular the perfluorooctanesulfonamides and the perfluorooctanesulfonamidoacedic acids show low recovery rates. It is assumed that their interactions (ionic or/and hydrophobic) with the solid phase sorbent are too weak. These compounds do not stay on column during sample application or they get loose by organic washing step. In generally, the solid phase methodology does work with the group of perfluoroalkylcarboxylic acids very well. The low/high recovery rates of PFBA, PFODA and PFHxDA are probably caused by detection problems with mass spectrometry for instance bad signal to noise value for small molecules or bad ionizability or blind values.

The identification and quantification of perfluorinated alkyl substances in the solid phase extracts were carried out by ESI mass spectrometry on an EC 100/2 NUCLEOSHELL® Bluebird RP 18 column. The chromatogram in figure 2 shows the results of standard mixture with β = 10 ng/mL for each analyt.

In summary, the presented application describes a quick and convenient method for the determination of most of the tested perfluorinated alkyl substances from water samples with a SPE procedure according to DIN 30407-42.

References

[1] EPA Drinking Water Laboratory Method 537 Q&A.

[2] German standard methods for the examination of water, waste water and sludge - Jointly determinable substances (group F) - Part 42: Determination of selected polyfluorinated compounds (PFC) in water - Method using high performance liquid chromatography and mass spectrometric detection (HPLC/MS-MS) after solid-liquid extraction (F 42), 2011-03.

Product information

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

REF 763433.20, EC 100/2 NUCLEOSHELL® Bluebird RP 18, 2.7 µm
REF 730747, CHROMABOND® HR-XAW, 85 µm, 60 mg, 3 mL
CHROMABOND® PFC, 300 mg, 3 mL, order on request.