MACHEREY-NAGEL
Chromatography application note

MN application note 07/2020

Solid phase extraction of per- and polyfluoroalkyl substances (PFAS) from contaminated soils

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Abstract

This application note describes the determination of per- and polyfluoroalkyl substances (PFAS) from contaminated soils. It demonstrates the extraction of PFAS from soil samples using CHROMABOND® PFAS column, a special SPE combination phase, for the methodology described in DIN 38407-42. The eluates are finally analyzed by HPLC-MS / MS.

Introduction

Per- and polyfluoroalkyl substances (PFAS) have been manufactured since the 1940s and have been used for various applications due to their unique chemical properties. PFAS are used as additives for example in:

- Fire-fighting foam
- Fiber coating
- Textile coating, e. g. seat covers, carpets, outdoor clothing
- Cookware
- Paper finishing
- Food packaging, e. g. pizza cartons, paper cups
- Building material, e. g. water resistant lacquer.

This broad use, appearance and their persistency leads to the fact that PFAS are now abundant in the environment. From fire-fighting foams, textiles and food-packaging PFAS blaze their trail into soil and from there into ground water. During this distribution, degradation processes can also take place leading to several PFAS by-products. From the ground water, PFAS and their degradation products are being further transported to other locations in the environment. Unfortunately, many of the PFAS are toxic. Therefore, monitoring these substances is important.

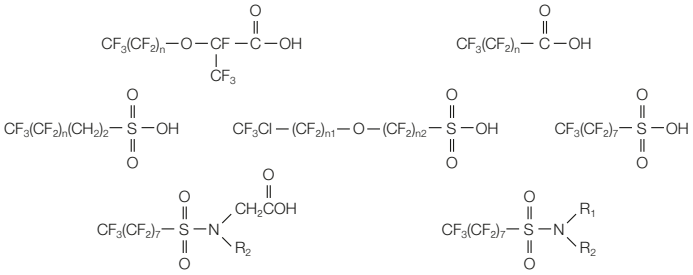

Figure 1: General structure of various per- and polyfluoroalkyl compounds (PFAS).

In a previous application note [1], we presented a solution for the analysis of PFAS from water. CHROMABOND® PFAS solid phase extraction columns showed excellent recovery rates and reproducibility for 30 PFAS. This present application note describes the use of CHROMABOND® PFAS for the enrichment of several PFAS from different types of soil according to DIN 38414-14 [2]. In addition to the 10 analytes mentioned in DIN 38414-14, the note even describes the enrichment of a total of 40 PFAS. The extracts are analyzed by HPLC-MS / MS.

Sample pretreatment for solid phase extraction (SPE)

Weigh out 2.5 g of homogenized sample (dried) into a 50 mL centrifuge tube

- Add 62.5 µL of standard solution (β = 0.2 µg/mL for each compound in methanol) for determining recovery rate
- Add 25 mL methanol and shake
- Place centrifuge tube for 10 min in a ultra-sonic bath
- Shake the tube and repeat 5 times
- Centrifuge the mixture at 4500 rpm, for 10 min at 25 °C
- Take 2.5 mL of the centrifugate and dilute it with 2.5 mL of water
- Use the mixture for solid phase extraction

Solid phase extraction

Column:	CHROMABOND® PFAS, 6 mL, 300 mg, (REF 730283)
Conditioning:	10 mL 0.1 % NH_3 in methanol, 10 mL methanol, 10 mL water
Sample application:	5 mL of mixture with a flow rate of 2–3 mL/min
Washing:	5 mL of 25 mM ammonium acetate buffer (pH 4.0) with a flow rate of 3 mL/min
Drying:	1 min with vacuum
Elution:	7.5 mL 0.1 % NH_3 in methanol
Eluent exchange:	Evaporate eluate to dryness at 40 °C under a stream of nitrogen and dissolve residue in 0.5 mL water / methanol (20:80, v/v)

Subsequent analysis: HPLC-MS / MS

Chromatographic conditions:

Column:	EC 50 / 2 NUCLEOSHELL® RP 18plus, 2.7 µm (REF 763232.20)
Eluent A:	5 mM ammonium acetate in water
Eluent B:	5 mM ammonium acetate in methanol
Gradient:	hold 40 % B for 0.5 min, in 4 min from 40 % B to 95 % B, hold 95 % B for 1.5 min, in 0.05 min to 40 % B, hold 40 % B for 1.45 min
Flow rate:	0.3 mL/min
Temperature:	40 °C

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Solid phase extraction of per- and polyfluoroalkyl substances (PFAS)

Injection volume: 2 µL

MS conditions: AB Sciex QTRAP 5500

Acquisition mode: SRM

Interface: ESI

Polarity: negative

Curtain gas: 30

Collision gas: medium

Ionspray voltage: -4500 V

Temperature: 400 °C

Ion source gas 1: 50

Ion source gas 2: 60

Detection window: 60 sec

MRM transitions

Abbreviation	Compound	Q_1	Q_3 (quan.)	Q_3 (qual.)	RT (min)
3,6-OPFHpA	Perfluoro-3,6-dioxaheptanoic acid	200.9	85.0	134.9	2.18
PFBA	Perfluoro-*n*-butanoic acid	212.9	168.8	88.9	0.78
PF4OPeA	Perfluoro-4-oxapentanoic acid	228.9	84.9	197.0	0.93
PFPeA	Perfluoro-*n*-pentanoic acid	262.9	219.0	68.7	1.47
PF5OHxA	Perfluoro-5-oxahexanoic acid	279.1	85.0	229.0	1.74
FBSA	Perfluoro-1-butanesulfonamide	297.9	77.9	183.9	2.48
L-PFBS	Perfluoro-1-butanesulfonate	298.9	79.9	98.9	1.64
PFHxA	Perfluoro-*n*-hexanoic acid	312.9	268.8	119.0	2.29
PFEESA	Perfluoro(2-ethoxyethane)sulfonate	315.1	135.1	69.1	2.00
4:2FTS	1H,1H,2H,2H-Perfluoro-1-hexanesulfonate	326.9	306.9	81.0	2.22
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid	328.9	284.8	169.0	2.49
L-PFPeS	Perfluoro-1-pentanesulfonate	348.9	79.9	98.9	2.36
PFHpA	Perfluoro-*n*-heptanoic acid	362.9	318.7	169.0	2.86
NaDONA	Sodium dodecafluoro-3H-4,8-dioxanonanoate	376.9	250.7	85.0	2.94
FHEA	2-Perfluorohexyl ethanoic acid	377.0	292.8	95.0	2.96
FHxSA	Perfluoro-1-hexanesulfonamide	398.0	78.0	96.9	3.55
PFHxSK	Perfluoro-1-hexanesulfonate	398.9	79.8	98.9	2.89
PFOA	Perfluoro-*n*-octanoic acid	412.9	369.0	169.0	3.27
6:2FTS	1H,1H,2H,2H-Perfluoro-1-octanesulfonate	426.9	406.9	79.9	3.25
L-PFHpS	Perfluoro-1-heptanesulfonate	448.9	79.8	98.9	3.28
PFNA	Perfluoro-*n*-nonanoic acid	462.9	418.9	169.0	3.61
FOEA	2-Perfluorooctyl ethanoic acid	476.9	392.8	412.9	3.72
FOSA	Perfluoro-1-octanesulfonamide	497.9	77.8	63.9	4.17
PFOSK	Perfluorooctanesulfonate	498.8	79.9	99.0	3.60
PFDA	Perfluoro-*n*-decanoic acid	512.8	468.9	219.1	3.89
8:2FTS	1H,1H,2H,2H-Perfluoro-1-decanesulfonate	526.8	506.8	81.0	3.87
9Cl-PF3ONS	9-Chlorohexadecafluoro-3-oxanonane-1-sulfonate	530.8	350.7	82.8	3.78
L-PFNS	Perfluoro-1-nonanesulfonate	548.8	79.9	98.8	3.87
PFUdA	Perfluoro-*n*-undecanoic acid	562.8	518.9	169.1	4.12
N-MeFOSAA	*N*-Methylperfluoro-1-octanesulfonamidoacetic acid	569.8	418.9	168.9	4.01
FDEA	2-Perfluorodecyl-ethanoic acid	576.9	493.0	512.8	4.22
N-EtFOSAA	*N*-Ethylperfluoro-1-octanesulfonamidoacetic acid	583.8	418.8	168.9	4.13
L-PFDS	Perfluoro-1-decanesulfonate	598.8	79.9	98.9	4.09
PFDoA	Perfluoro-*n*-dodecanoic acid	612.9	568.9	169.0	4.32
11Cl-PF3OUdS	11-Chloroeicosafluoro-3-oxaundecane-1-sulfonate	630.7	451.0	82.8	4.25
PFTrDA	Perfluoro-*n*-tridecanoic acid	662.8	618.9	169.0	4.50
PFTeDA	Perfluoro-*n*-tridecanoic acid	712.7	668.8	168.9	4.65
6-2diPAP	(1H,1H,2H,2H-Perfluorooctyl)phosphate	788.9	97.0	78.9	4.63
6-2-8-2diPAP	(1H,1H,2H,2H-Perfluorooctyl-1H,1H,2H,2H-perfluorodecyl)phosphate	888.9	442.8	97.1	4.84
8-2diPAP	(1H,1H,2H,2H-Perfluorodecyl)phosphate	988.9	96.9	78.8	5.01
MPFBA	Perfluoro-*n*-($^{13}C_4$)butanoic acid	216.9	171.9	-	0.75

Solid phase extraction of per- and polyfluoroalkyl substances (PFAS)

Abbreviation	Compound	Q_1	Q_3 (quan.)	Q_3 (qual.)	RT (min)
M5PFPeA	Perfluoro-*n*-($^{13}C_5$)pentanoic acid	267.9	222.9	-	1.47
M3PFBS	Perfluoro-1-(2,3,4-$^{13}C_3$)butanesulfonate	301.9	98.9	-	1.64
M5PFHxA	Perfluoro-*n*-(1,2-$^{13}C_2$)hexanoic acid	314.9	269.8	-	2.29
M2-4FTS	1H,1H,2H,2H-Perfluoro-1-(1,2-$^{13}C_2$)hexanesulfonate	328.9	81.0	-	2.21
M4PFHpA	Perfluoro-*n*-(1,2,3,4-$^{13}C_4$)heptanoic acid	366.9	321.8	-	2.85
MFHEA	2-Perfluorohexyl-(1,2-$^{13}C_2$)ethanoic acid	379.1	293.8	-	2.96
M3PFHxS	Perfluoro-1-(1,2,3-$^{13}C_3$)hexanesulfonate	401.9	79.9	-	2.88
M8PFOA	Perfluoro-*n*-($^{13}C_8$)octanoic acid	420.9	376.0	-	3.27
M2-6:2FTS	1H,1H,2H,2H-Perfluoro-1-(1,2-$^{13}C_2$)octanesulfonate	428.9	81.0	-	3.25
M9PFNA	Perfluoro-*n*-($^{13}C_9$)nonanoic acid	471.9	427.0	-	3.61
MFOEA	2-Perfluorooctyl-(1,2-$^{13}C_2$)ethanoic acid	478.9	394.0	-	3.73
M8FOSA	Perfluoro-1-($^{13}C_8$)octanesulfonamide	505.9	77.9	-	4.17
M8PFOS	Perfluoro-1-($^{13}C_8$)octanesulfonate	506.9	98.9	-	3.60
M6PFDA	Perfluoro-*n*-(1,2,3,4,5,6-$^{13}C_6$)decanoic acid	518.9	474.0	-	3.88
M2-8:2FTS	1H,1H,2H,2H-Perfluoro- 1-(1,2-$^{13}C_2$)decanesulfonate	528.9	80.9	-	3.88
M7PFUdA	Perfluoro-*n*-(1,2,3,4,5,6-$^{13}C_7$)undecanoic acid	569.9	525.0	-	4.12
d3-*N*-MeFOSAA	*N*-Methyl-d_3-perfluoro-1-octanesulfonamidoacetic acid	572.9	419.0	-	4.01
MFDEA	2-Perfluorodecyl-(1,2-$^{13}C_2$)ethanoic acid	578.9	493.8	-	4.23
d5-*N*-EtFOSAA	*N*-Ethyl-d_5-perfluoro-1-octanesulfonamidoacetic acid	588.8	418.8	-	4.14
MPFDoA	Perfluoro-*n*-(1,2-$^{13}C_2$)dodecanoic acid	614.9	569.8	-	4.33
M2PFTeDA	Perfluoro-*n*-(1,2-$^{13}C_2$)tridecanoic acid	714.9	670.0	-	4.66

Table 1: MRM transitions and retention times of PFAS.

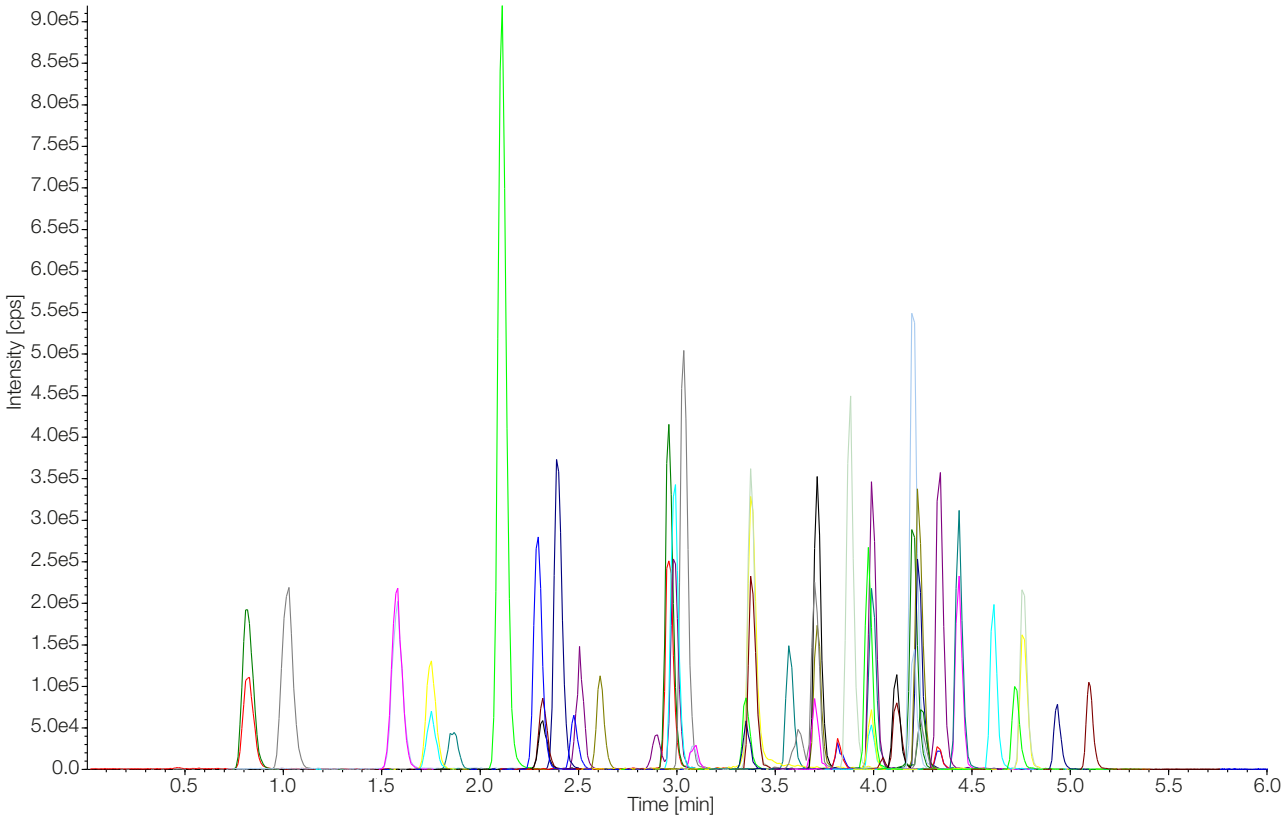

Figure 2: Chromatogram of PFAS standard solution after eluent exchange procedure on NUCLEOSHELL® RP 18plus column (β = 2.5 ng/mL for each compound).

Solid phase extraction of per- and polyfluoroalkyl substances (PFAS)

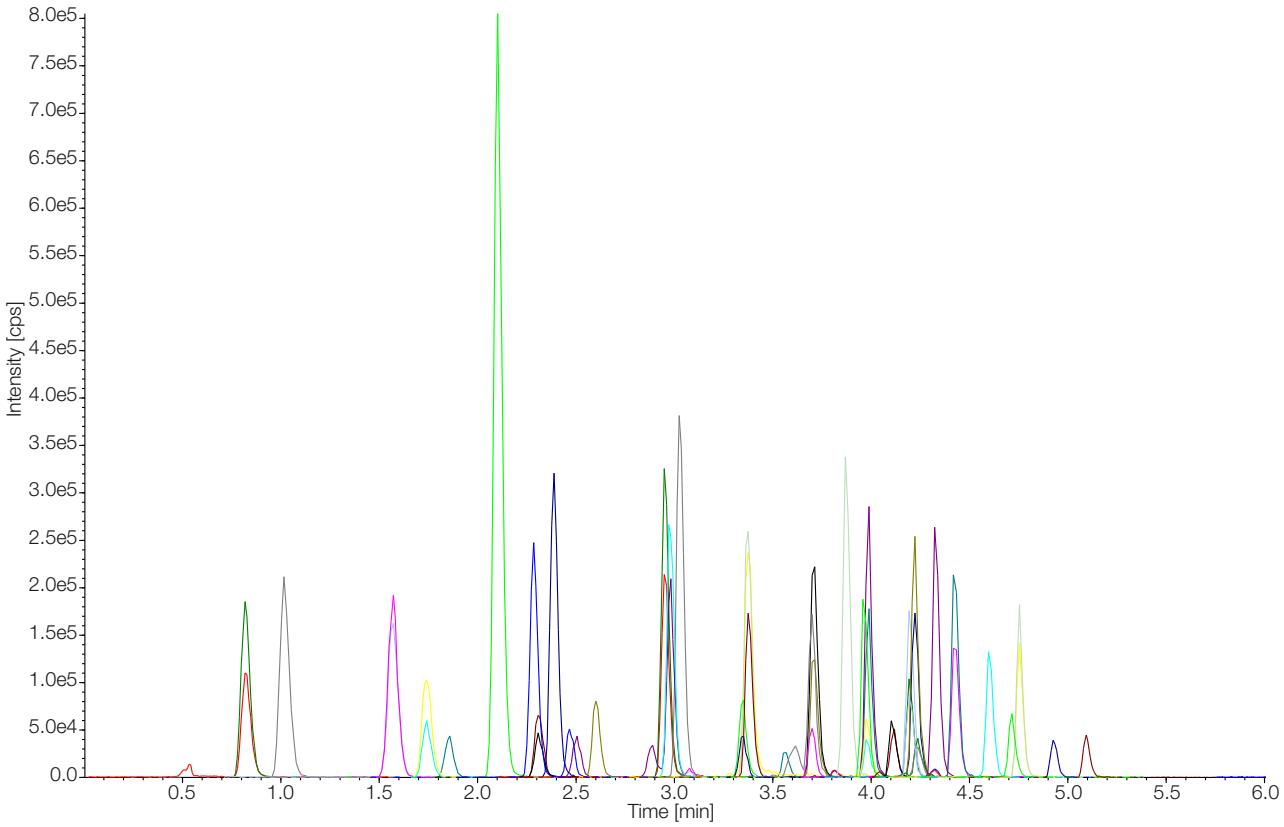

Figure 3: Chromatogram of PFAS extract from sample matrix sand on NUCLEOSHELL® RP 18plus column (β = 2.5 ng/mL for each compound).

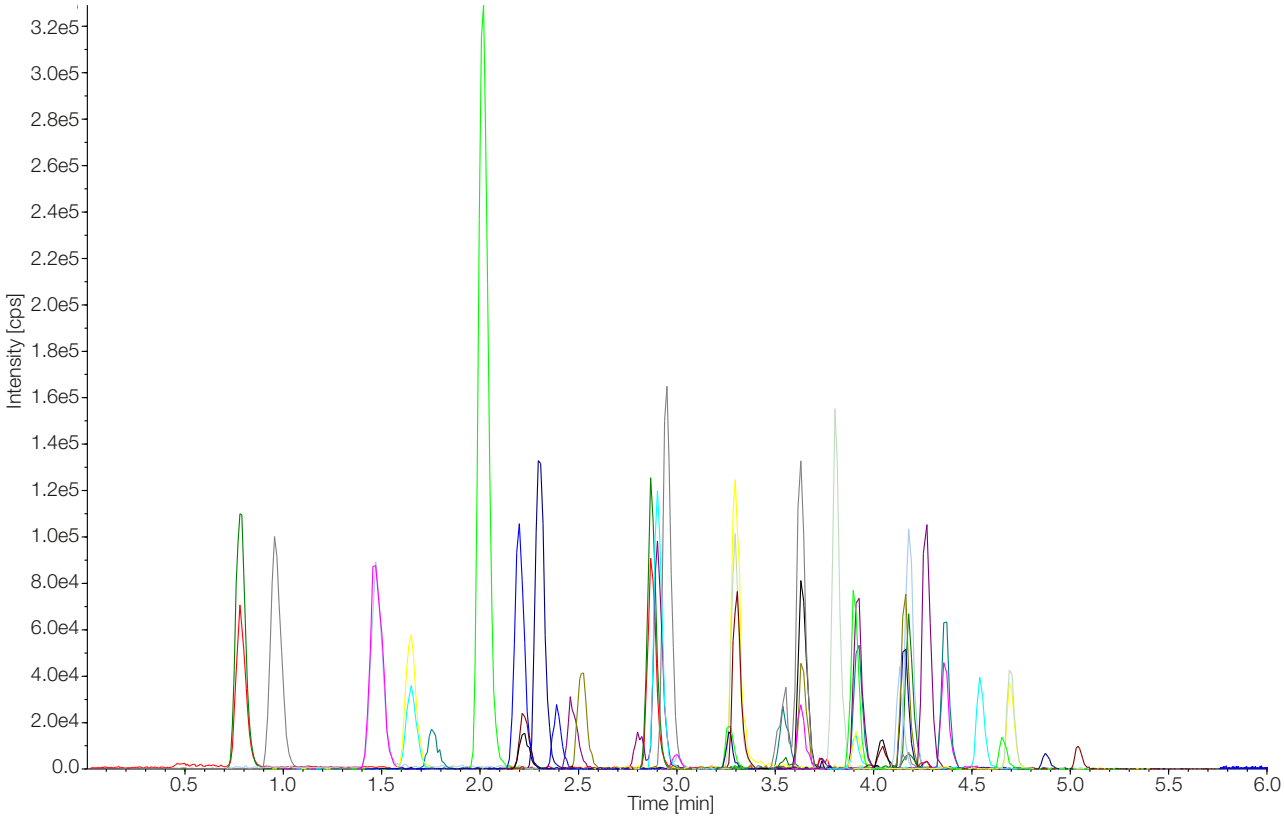

Figure 4: Chromatogram of PFAS from sample matrix soil on NUCLEOSHELL® RP 18plus column (β = 2.5 ng/mL for each compound).

Solid phase extraction of per- and polyfluoroalkyl substances (PFAS)

Calibration and Recovery rates

Abbreviation	% Recovery (sand)	% RSD	% Recovery (soil)	% RSD	R_2
11Cl-PF3OUdS	84.6	3.5	64.2	2.4	0.995
3.6-OPFHpA	92.9	3.2	81.0	6.8	0.993
4:2FTS	91.3	4.7	71.2	5.1	0.995
6:2FTS	133.9	33.7	58.5	9.3	0.996
6-2-8-2diPAP	74.1	8.2	29.5	7.8	0.994
6-2diPAP	84.4	8.8	39.5	8.1	0.996
8:2FTS	90.4	3.9	58.1	12.5	0.997
8-2diPAP	64.2	11.1	29.3	10.1	0.993
9Cl-PF3ONS	86.2	5.1	66.6	4.1	0.997
FBSA	38.9	15.4	29.7	52.7	0.992
FDEA	46.2	6.5	34.3	21.3	0.995
FHEA	29.9	12.5	42.8	7.3	0.991
FHxSA	20.7	11.8	28.9	38.3	0.993
FOEA	27.4	12.4	30.6	6.6	0.994
FOSA	46.2	10.8	31.9	27.5	0.996
HFPO-DA	85.0	4.5	82.0	7.4	0.994
L-PFBS	93.9	3.4	85.7	5.3	0.993
L-PFNS	87.5	1.5	62.3	3.7	0.997
L-PFPeS	90.0	3.7	80.6	2.2	0.994
NaDONA	85.3	4.0	70.1	3.5	0.995
N-EtFOSAA	73.0	6.9	33.1	7.7	0.996
N-MeFOSAA	69.3	4.7	30.1	10.9	0.994
PF4OPeA	89.2	4.3	79.8	2.3	0.993
PF5OHxA	87.1	7.5	79.9	3.9	0.993
PFBA	88.5	3.8	82.2	2.6	0.994
PFDA	87.1	5.2	55.7	4.5	0.996
PFDoA	89.8	2.6	52.8	4.5	0.995
L-PFDS	81.2	6.1	59.6	5.5	0.995
PFEESA	93.2	2.8	84.6	1.9	0.995
PFHpA	90.2	2.2	71.1	3.7	0.993
L-PFHpS	85.5	3.9	72.5	7.0	0.995

Abbreviation	% Recovery (sand)	% RSD	% Recovery (soil)	% RSD	R_2
PFHxA	84.6	3.7	75.2	4.2	0.992
PFHxSK	90.5	2.3	74.4	3.6	0.995
PFNA	85.1	4.3	58.4	8.8	0.996
PFOA	73.5	3.4	48.2	1.9	0.994
PFOSK	86.3	3.0	74.4	7.9	0.997
PFPeA	90.7	3.2	80.6	6.3	0.994
PFTeDA	89.8	3.4	45.0	6.2	0.994
PFTrDA	84.8	3.0	49.0	6.1	0.996
PFUdA	84.0	3.2	55.4	5.1	0.995
d3-*N*-MeFOSAA	66.7	7.3	29.0	6.5	0.993
d5-*N*-EtFOSAA	70.3	15.0	35.1	9.9	0.995
M2-4FTS	89.0	5.3	72.5	5.2	0.991
M2-6:2FTS	99.6	7.6	60.8	9.3	0.994
M2-8:2FTS	97.3	5.8	53.2	8.8	0.996
M2PFTeDA	89.2	4.4	47.0	4.8	0.995
M3PFBS	92.3	3.9	84.5	2.9	0.994
M3PFHxS	90.3	3.8	73.6	5.8	0.994
M4PFBA	89.5	2.8	85.3	3.0	0.994
M4PFHpA	88.7	3.7	70.4	1.9	0.996
M5PFHxA	90.6	2.9	77.4	3.9	0.994
M5PFPeA	92.8	3.7	81.5	2.0	0.992
M6PFDA	90.3	4.2	56.1	6.0	0.996
M7PFUdA	88.3	2.6	55.1	5.4	0.994
M8FOSA	42.5	11.1	30.1	26.6	0.997
M8PFOA	86.9	3.1	66.4	3.0	0.994
M8PFOS	82.9	5.0	61.4	11.4	0.997
M9PFNA	88.4	6.1	60.5	2.6	0.996
MFDEA	44.9	13.4	31.4	9.7	0.997
MFHEA	31.5	8.8	39.6	17.3	0.989
MFOEA	30.1	12.3	34.3	8.3	0.997
MPFDoA	89.3	4.1	53.1	4.3	0.997

Table 2: Recovery rates for the presented SPE method for contaminated soils. Correlation coefficient is given for all compound from calibration curves, determined of 7 levels between 0.1 ng/mL and 10.0 ng/mL for each compound.

Solid phase extraction of per- and polyfluoroalkyl substances (PFAS)

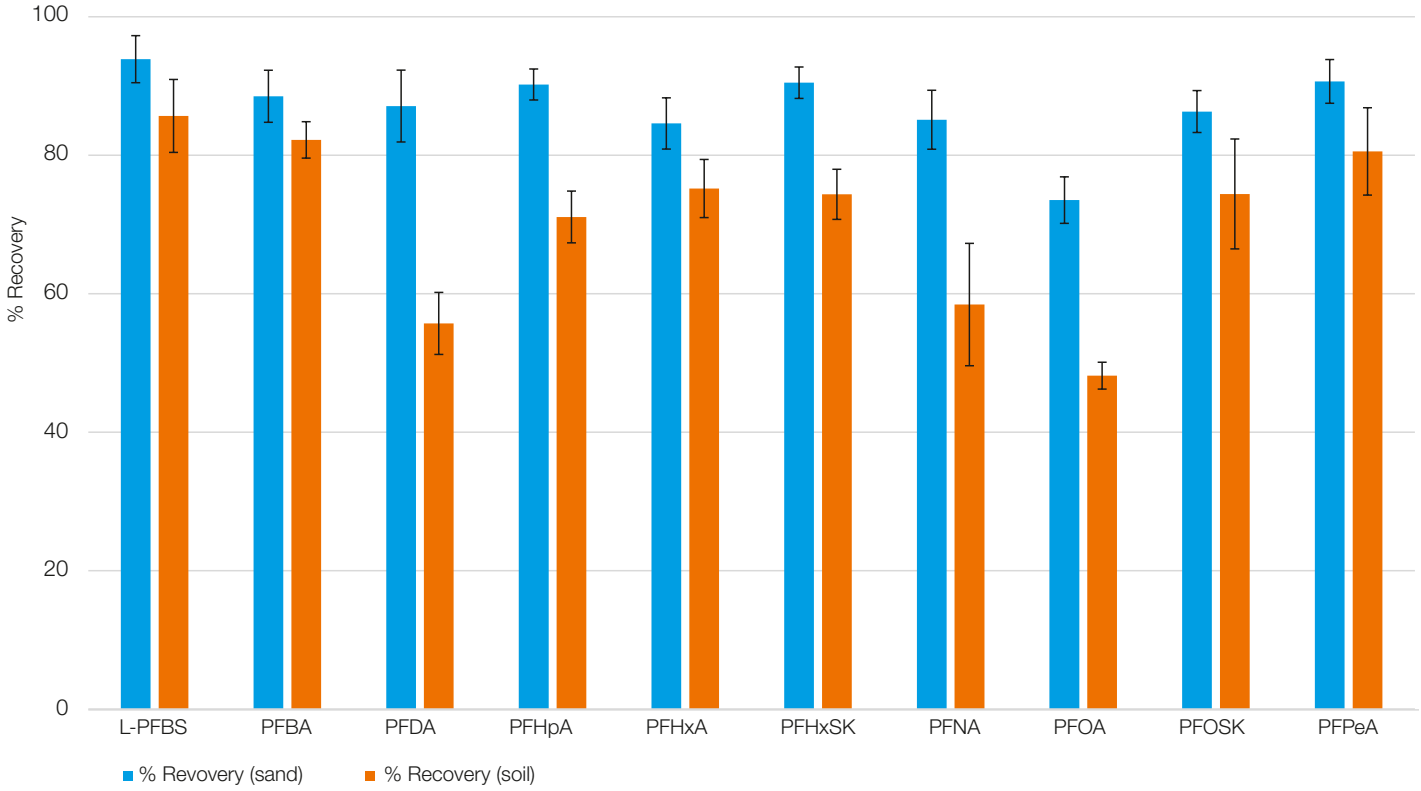

Figure 5: Recovery rates of PFAS from contaminated soils (spiked with 5 ng/g sample for each compound) according to DIN 3814-14.

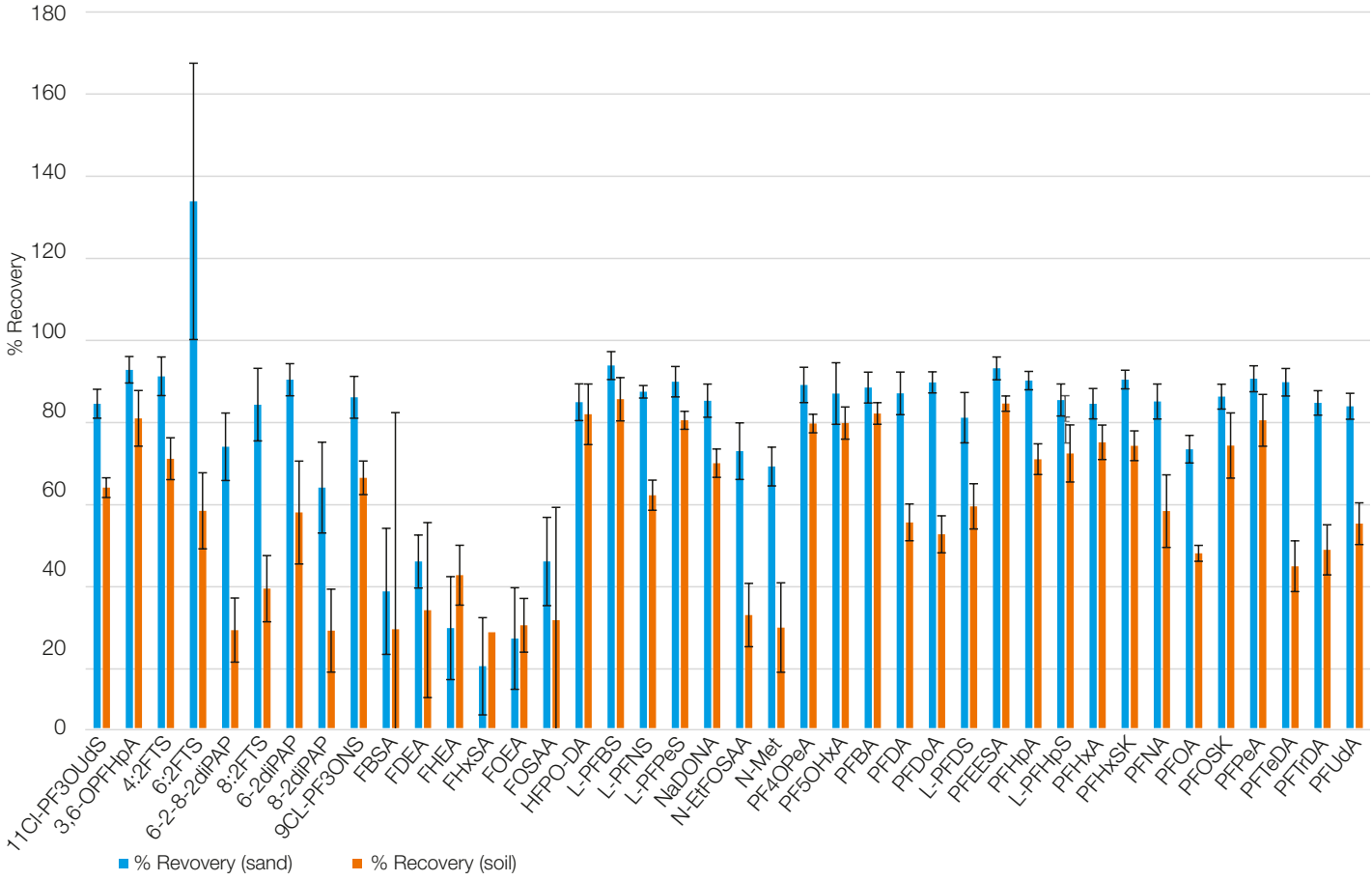

Figure 6: Recovery rates of 40 PFAS from contaminated soils (spiked with 5 ng/g sample for each compound).

Solid phase extraction of per- and polyfluoroalkyl substances (PFAS)

Conclusion

This application note shows the reliable and successful determination of per- and polyfluoroalkyl substances (PFAS) from sediments like sand and soil with an optimized SPE method. The successful determination of 40 PFAS was successfully carried out with the special CHROMABOND® PFAS column. In this way, the combination of different SPE sorbents in a multi-layer column allows to use various of interaction types like ionic, hydrophobic, hydrogen bonds, dipole-dipole and π-π interactions for the enrichment of a broad spectrum of PFAS in a single enrichment procedure.

With the presented methodology good recovery rates for PFAS from matrices like sand and sufficient recovery rates from soil with good reproducibility could be achieved. Figure 5 shows that high recovery rates for PFAS analysis according to DIN could be obtained. More results for the additional 30 PFAS are presented in table 2 and figure 6.

The investigation of the extraction procedure described in DIN shows that the efficiency of the extraction of PFAS depends on different parameters like polarity and adsorption effects. These effects lead to losses of PFAS before the SPE enrichment procedure. Probably a second extraction step with a mixture of methanol and water could lead to better extraction efficiency of more PFAS.

The chromatographic separation of PFAS was performed by using core-shell particles that are well known for fast and high-efficient separations combined with a reasonably low backpressure. In this work, subsequent analysis was developed on a NUCLEOSHELL® RP 18plus column as shown in figure 2. The chromatographic results provide a good correlation for all PFAS compounds as presented in table 2.

In summary, the presented application describes a quick and convenient method for the determination of various PFAS from sediment samples with a SPE procedure using the extraction mechanisms of DIN 30407-42.

References

[1] Solid phase extraction of per- and polyfluoroalkyl substances (PFAS) from drinking water, MN application note 05/2020

[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 application note:

REF 763232.20	EC 50 / 2 HPLC column (analytical), NUCLEOSHELL® RP 18plus, 2.7 µm
REF 730283	CHROMABOND® PFAS, 6 mL, 300 mg
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, 11.6x32.0 mm, 0.3 mL, inner cone, PP tr.