MACHEREY-NAGEL
Chromatography application note

MN application note 06/2020

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

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Abstract

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

Introduction

More than 4730 compounds belong to the group of PFAS (which stands for per- and polyfluoroalkyl substances) which have been manufactured since the 1940s. All of them are non-natural but man-made. Their unique chemical properties provide them with water and dirt repellent characteristics, which makes them ideal for the daily use in (waterproof) textile coatings e.g. carpets, *t*-shirts, jeans and outdoor jackets. During the fabrication process of such textiles and their daily use, PFAS are emitted into the environment (water, air, soil). Since they are non-biodegradable ("persistent"), PFAS can accumulate in the environment and food chain. Despite their unique advantageous properties, there is the drawback of toxicity of many PFAS. Therefore, there are now several official regulations (US EPA, DIN, ASTM) for monitoring PFAS in water. For textiles itself, there is currently no official regulation. The market has given itself voluntary regulations for testing the contamination of PFAS in the field of textile and leather, for example Standard 100 from OEKO-TEX® [1, 2].

In this application note we present a solution for the enrichment of 40 PFAS from several textile types on the basis of the methodology of DIN [3]. The combination of MACHEREY-NAGEL's special solid phase extraction column, CHROMABOND® PFAS, with subsequent HPLC-MS/MS analysis provides a robust method with excellent recovery rates and short run times to monitor these analytes. By analyzing PFAS in textiles prior to sale or trade, their distribution into the environment can be reduced or even avoided.

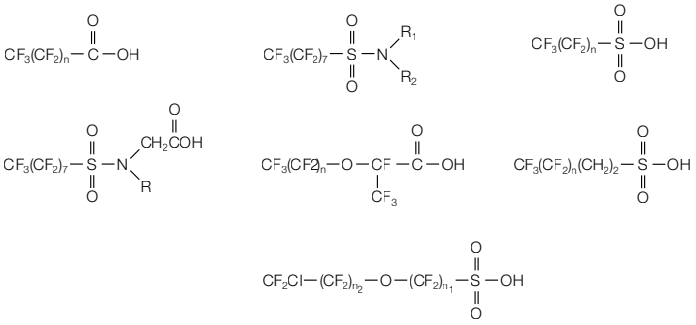

Figure 1: General structure of various per- and polyfluoroalkyl compounds (PFAS)

Sample pretreatment for solid phase extraction (SPE)

- Weigh out 1.0 g of homogenized sample (dried) into a 50 mL centrifuge tube
- Add 50 µL of standard solution (β = 0.2 µg/mL for each compound in methanol) for determining recovery rates
- Add 25 mL methanol and shake
- Place centrifuge tube for 10 min in an ultra-sonic bath
- Shake the tube and repeat 5 times
- Centrifuge the mixture at 4500 rpm, for 10 min at 25 °C
- Take 5.0 mL of the centrifugate and dilute it with 5.0 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:	10 mL of mixture sample 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:	10 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 1.0 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 5 % B for 1.45 min
Flow rate:	0.3 mL/min
Injection volume:	2 µL
Temperature:	40 °C

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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

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
M5PFPeA	Perfluoro-*n*-($^{13}C_5$)-pentanoic acid	267.9	222.9	–	1.47

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Abbreviation	Compound	Q_1	Q_3 (quan)	Q_3 (qual)	RT (min)
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

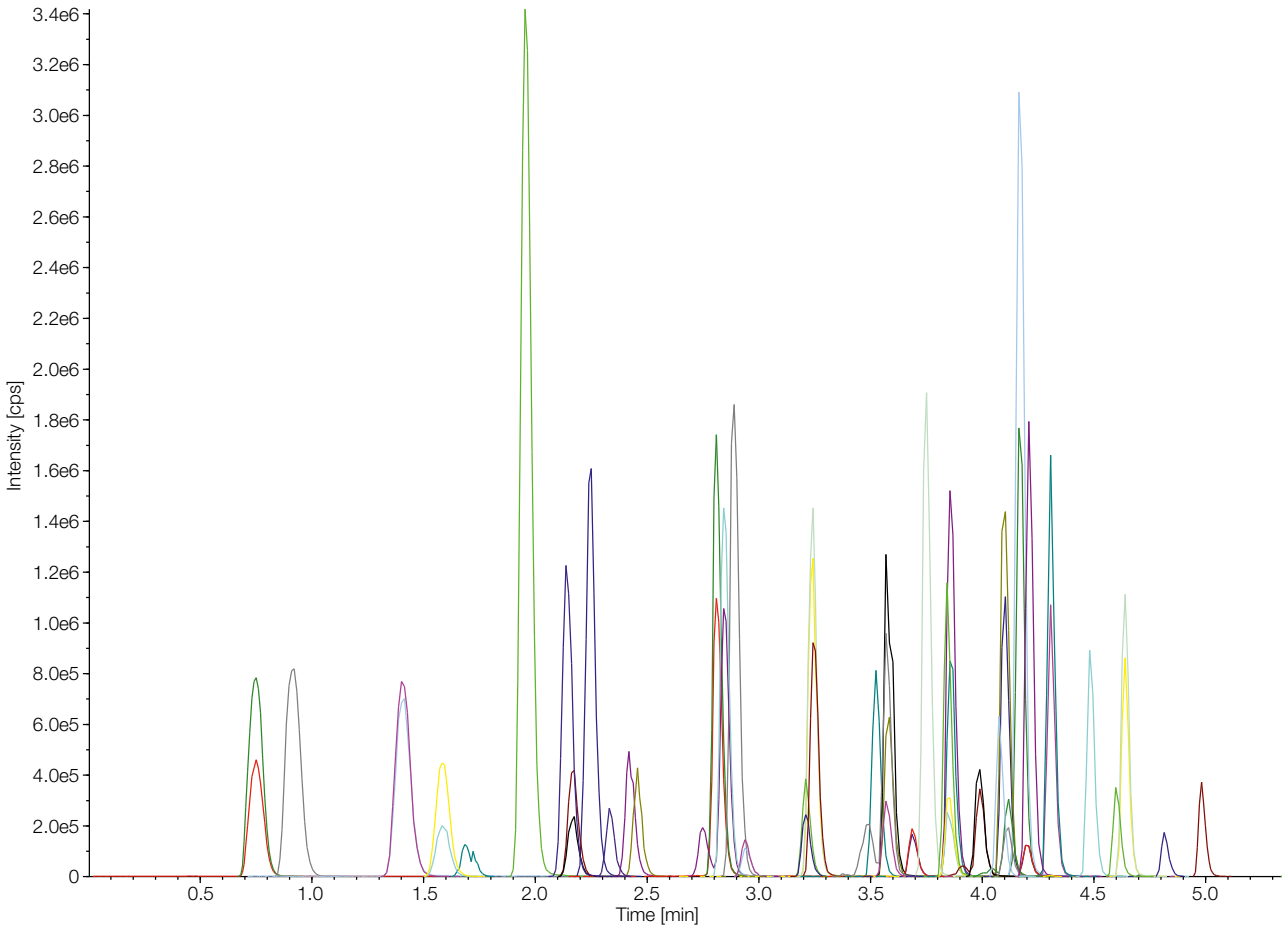

Figure 2: Chromatogram of PFAS standard solution after eluent exchange procedure on NUCLEOSHELL® RP 18plus column (β = 10 ng/mL for each compound).

SPE of PFAS from clothing

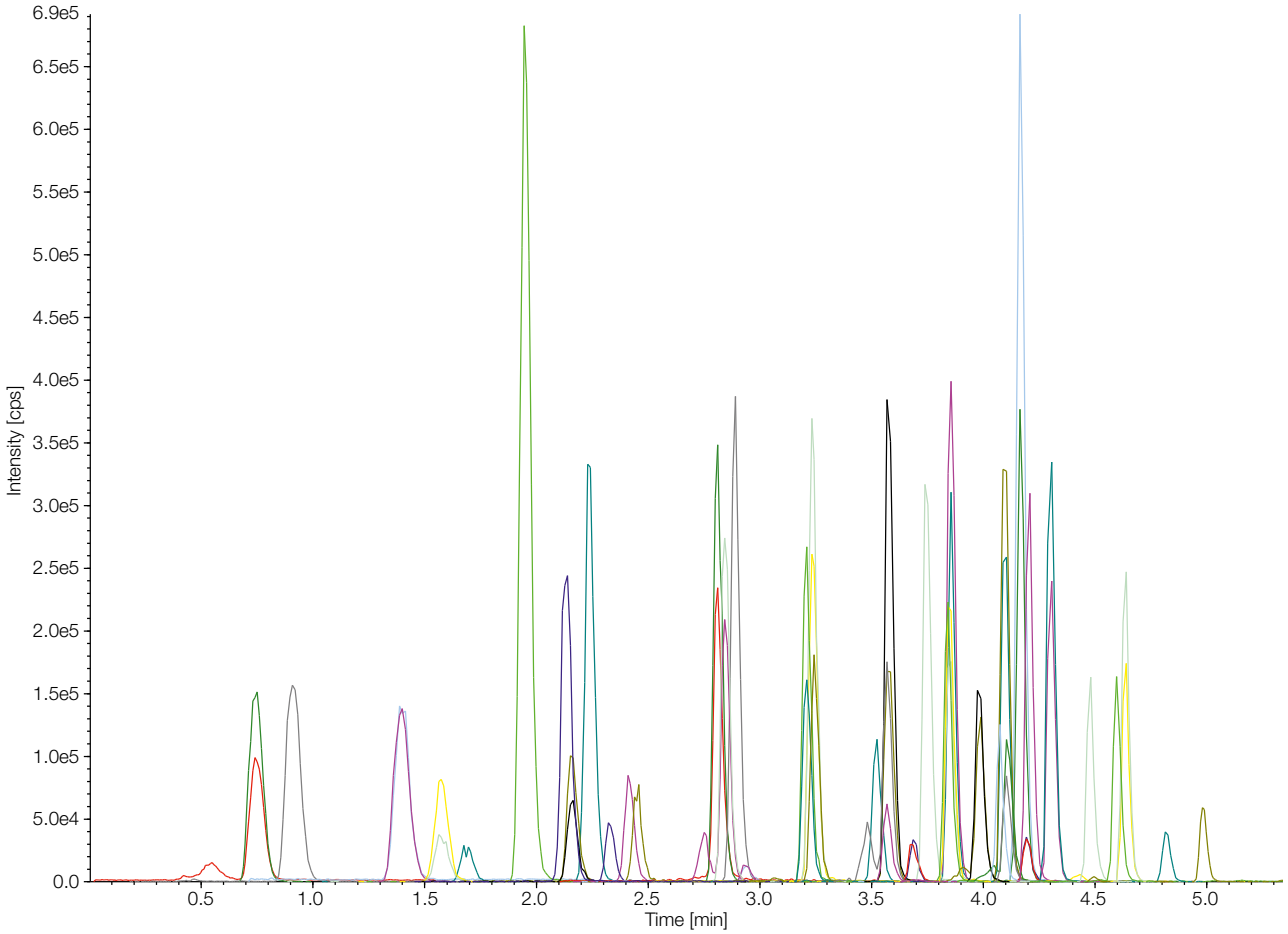

Figure 3: Chromatogram of PFAS extract from clothing matrix blouse on NUCLEOSHELL® RP 18plus column (β = 2.0 ng/mL for each compound).

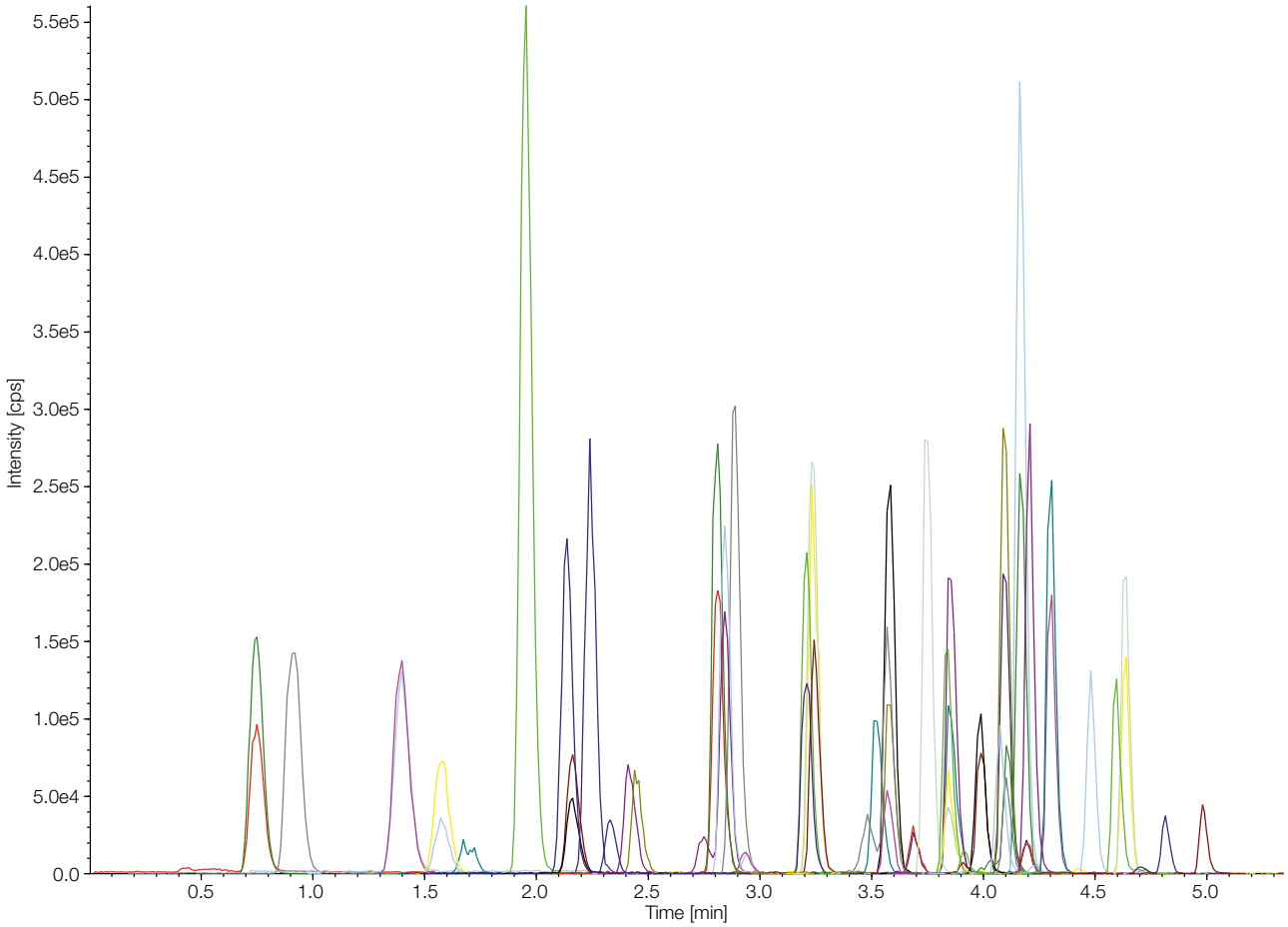

Figure 4: Chromatogram of PFAS from clothing matrix shirt on NUCLEOSHELL® RP 18plus column (β = 2.0 ng/mL for each compound).

SPE of PFAS from clothing

Calibration and Recovery rates

Abbreviation	% Recovery (blouse)	% Recovery (shirt)	R_2
11Cl-PF3OUdS	86.1	95.7	0.995
3.6-OPFHpA	102.7	96.1	0.993
4:2FTS	127.1	115.3	0.995
6:2FTS	362.1	315.9	0.996
6-2-8–2diPAP	129.8	97.6	0.994
6–2diPAP	235.4	154.4	0.996
8:2FTS	330.7	93.1	0.997
8–2diPAP	87.9	62.8	0.993
9Cl-PF3ONS	91.2	99.1	0.997
FBSA	93.4	87.5	0.992
FDEA	135.8	75.4	0.995
FHEA	57.9	49.7	0.991
FHxSA	78.2	82.4	0.993
FOEA	92.2	72.7	0.994
FOSA	101.8	88.4	0.996
HFPO-DA	102.7	102.6	0.994
L-PFBS	96.8	100.7	0.993
L-PFNS	101.4	79.7	0.997
L-PFPeS	97.5	92.0	0.994
NaDONA	97.5	99.8	0.995
N-EtFOSAA	195.8	122.0	0.996
N-MeFOSAA	182.5	119.0	0.994
PF4OPeA	94.7	92.5	0.993
PF5OHxA	98.1	85.1	0.993
PFBA	108.6	120.1	0.994
PFDA	146.9	70.9	0.996
PFDoA	123.4	108.0	0.995
L-PFDS	95.6	96.0	0.995
PFEESA	98.1	96.7	0.995
PFHpA	110.9	109.8	0.993
L-PFHpS	99.5	99.7	0.995

Abbreviation	% Recovery (blouse)	% Recovery (shirt)	R_2
PFHxA	102.8	92.6	0.992
PFHxSK	101.3	107.0	0.995
PFNA	146.9	102.0	0.996
PFOA	111.3	111.8	0.994
PFOSK	104.6	102.3	0.997
PFPeA	100.9	96.9	0.994
PFTeDA	101.8	95.5	0.994
PFTrDA	88.7	85.8	0.996
PFUdA	122.1	106.0	0.995
d3-*N*-MeFOSAA	172.0	120.3	0.993
d5-*N*-EtFOSAA	196.1	118.1	0.995
M2–4FTS	143.1	114.5	0.991
M2–6:2FTS	337.1	303.5	0.994
M2–8:2FTS	336.8	92.8	0.996
M2PFTeDA	106.1	97.5	0.995
M3PFBS	94.3	99.2	0.994
M3PFHxS	98.5	102.4	0.994
M4PFBA	96.0	97.1	0.994
M4PFHpA	106.5	103.9	0.996
M5PFHxA	107.1	98.6	0.994
M5PFPeA	95.8	97.7	0.992
M6PFDA	125.3	74.8	0.996
M7PFUdA	117.0	105.1	0.994
M8FOSA	106.1	89.7	0.997
M8PFOA	122.2	112.8	0.994
M8PFOS	101.9	96.6	0.997
M9PFNA	139.7	99.9	0.996
MFDEA	124.9	76.3	0.997
MFHEA	49.3	54.9	0.989
MFOEA	83.9	75.0	0.997
MPFDoA	117.8	96.3	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.

SPE of PFAS from clothing

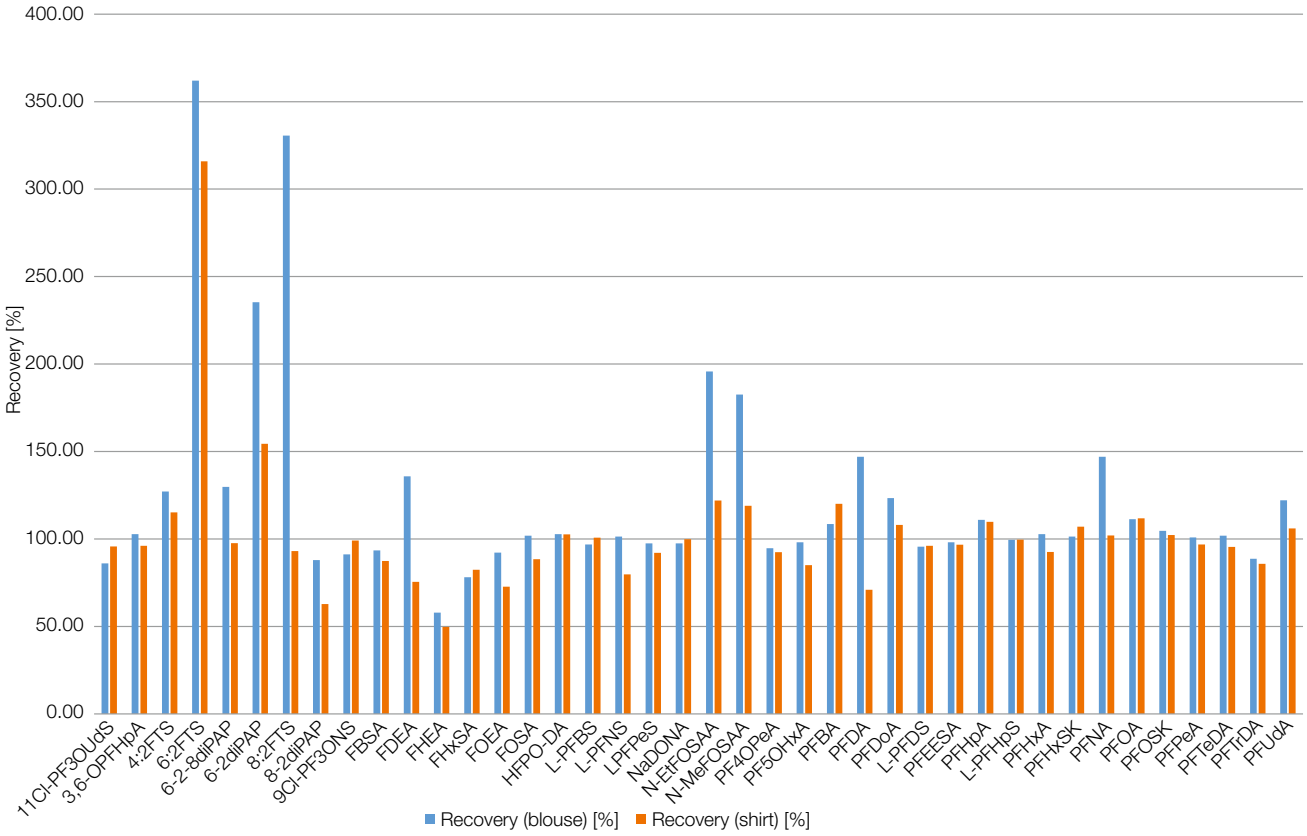

Figure 5: Recovery rates of PFAS from contaminated clothes (spiked with 10 ng/g sample for each compound).

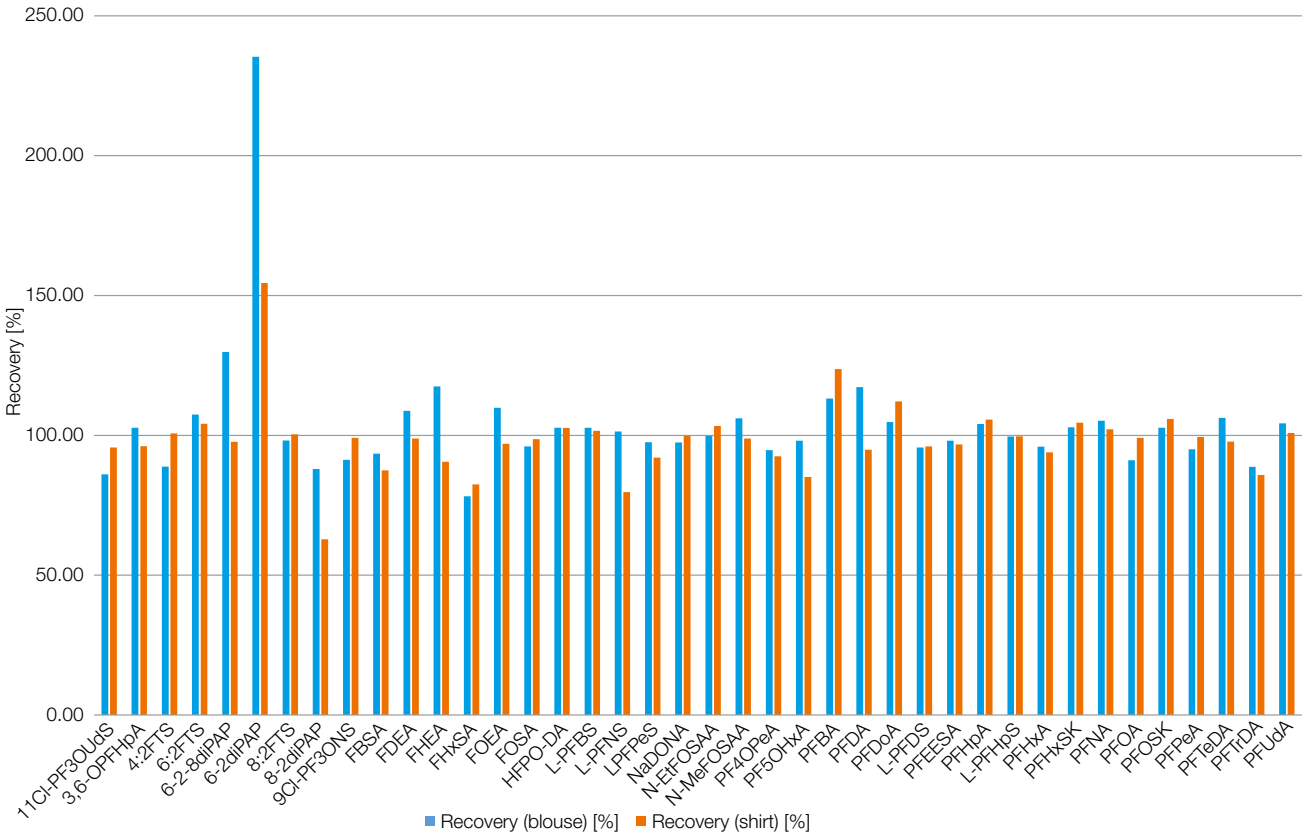

Figure 6: Recovery rates of PFAS from contaminated clothes (spiked with 10 ng/g sample for each compound). Internal standards are used to correct high results.

SPE of PFAS from clothing

Conclusion

This application note shows the reliable and successful determination of per- and polyfluoroalkyl substances (PFAS) from clothing with an optimized SPE method. It was possible to achieve high recovery rates for 40 PFAS from clothes by using the special CHROMABOND® PFAS cartridge. In this way, the combination of various of interaction types like ionic, hydrophobic, hydrogen bonds, dipole-dipole and π-π interactions allows to enrich a broad spectrum of PFAS.

Most of the PFAS show recovery rates between 80 % to 100 % for both sample materials as presented in table 2 and figures 5 and 6. Most of the results with a recovery higher than 120 % could be successfully corrected with internal standards (shown in figure 6).

Problems caused by solubility or adsorption effects on surface materials in aqueous mixtures are successfully reduced by working with solutions containing higher organic solvents (more than 50 %).

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 application note, we use a NUCLEOSHELL® RP 18plus column as shown in figures 2–4. The runtime could be reduced to 7.5 minutes with a fast gradient and a column length of 50 mm. 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 40 PFAS from textiles with a special CHROMABOND® PFAS cartridge.

References

[1] Testing Methods, STANDARD 100 by OEKO-TEX® - International Association for Research and Testing in the Field of Textile and Leather Ecology. Edition 01.2018

[2] Standard, STANDARD 100 by OEKO-TEX® - International Association for Research and Testing in the Field of Textile and Leather Ecology, Edition 03.2020

[3] 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, 11.6 x 32.0 mm, 0.3 mL, inner cone, PP tr.