

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

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Abstract

This application note describes the determination of per- and polyfluoroalkyl substances (PFAS) from drinking water. It demonstrates the extraction of PFAS from drinking water samples using CHROMABOND® PFAS column, a special SPE combination phase, for the methodology described in EPA 537.1, 533 and DIN 38407-42. The eluates are finally analyzed by HPLC-MS/MS.

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group 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 are common to consumer and industrial processes around the globe. They are introduced to the environment through a variety of sources such as food contact materials, manufacturing or industrial applications. Because of the accumulation of PFAS in water, soil and living organisms and the well-known health risks associated with PFAS exposure it is important to ensure proper worldwide monitoring of these chemicals.

Authorities of various countries published several methods, such as US EPA, ASTM, DIN and other standard methods for PFAS [1, 2, 3]. Further regulations are expected to be enacted.

This work presents a method for the simultaneous analysis of 32 PFAS from drinking water including a solid phase extraction method. It combines successful types of retention mechanisms of several directives like EPA method 537.1, EPA 533 and DIN 38407-42 method to ensure the best enrichment of PFAS from water samples using a multi-layer SPE column. The extracts are finally analyzed by HPLC-MS/MS.

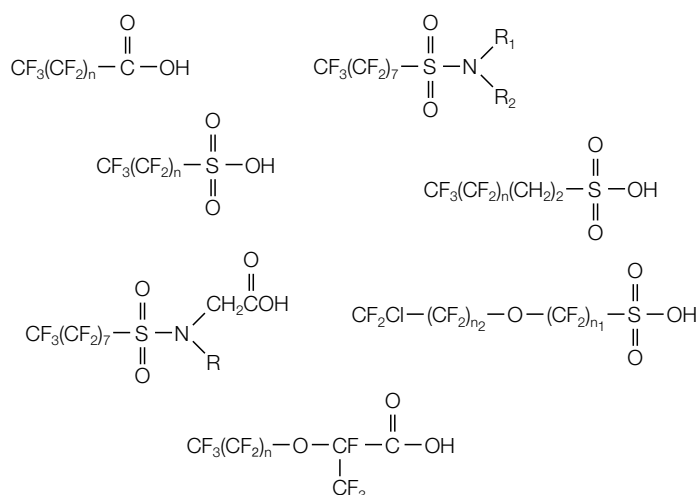


Figure 1: General structure of various per- and polyfluoroalkyl substances (PFAS)

Sample pretreatment for solid phase extraction (SPE)

- Control pH of water sample (it should be between 6 and 8)
- Add 25 µL organic standard solution* ($\beta = 20$ ng/mL in methanol for each compound) to 150 mL water sample
 - * Contains native and isotopically labeled per- and polyfluoroalkyl substances.

Solid phase extraction

- Column:** CHROMABOND® PFAS, 6 mL, 300 mg, (REF 730283)
- Conditioning:** 10 mL 0.1 % NH₃ in methanol, 10 mL methanol, 10 mL water
- Sample application:** 150 mL water sample with a flow rate of 5 mL/min
- Washing:** 5 mL of 25 mM ammonium acetate buffer (pH 4.0) water with a flow rate of 3 mL/min
- Drying:** 1 min with vacuum
- Elution:** 10 mL 0.1 % NH₃ 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 (40:60, v/v)

Subsequent analysis: HPLC-MS / MS

Chromatographic conditions:

- Column:** EC NUCLEOSHELL® RP 18plus, 100x2.0 mm, 2.7 µm (REF 763234.20)
- 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
- Flow rate:** 0.3 mL/min
- Injection volume:** 5 µL
- Temperature:** 40 °C

MS conditions:

- AB Sciex QTRAP 5500
- Acquisition mode:** SRM
- Interface:** ESI
- Polarity:** negative
- Curtain gas:** 30 psig
- Collision Gas:** medium
- Ion spray voltage:** - 4500 V
- Temperature:** 400 °C
- Ion source gas 1:** 50 psig
- Ion source gas 2:** 60 psig
- Detection window:** 60 s

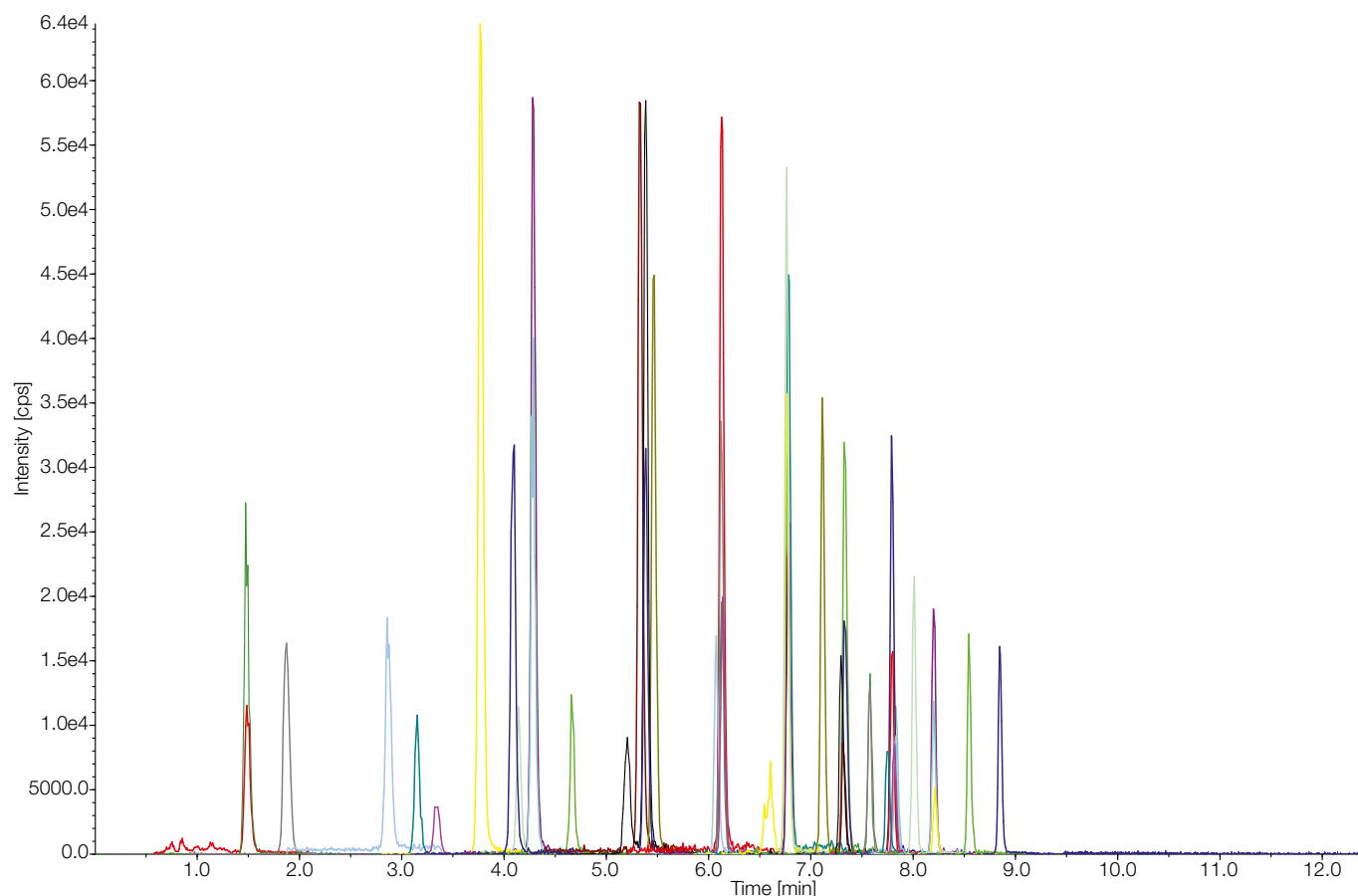
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MRM transitions

Abbreviation	Compound	Q ₁	Q ₃ (quan)	Q ₃ (qual)	RT (min)
MPFBA	Perfluoro- <i>n</i> -[¹³ C ₄]butanoic acid	216.9	171.9	95.7	1.32
PFBA	Perfluoro- <i>n</i> -butanoic acid	212.9	168.8	88.9	1.33
PF ₄ OPeA	Perfluoro-4-oxapentanoic acid	228.9	84.9	197.0	1.67
PFPeA	Perfluoro- <i>n</i> -pentanoic acid	262.9	219.0	68.7	2.63
L-PFBS	Perfluoro-1-butanedisulfonate	298.9	79.9	98.9	2.94
PF ₅ OHxA	Perfluoro-5-oxahexanoic acid	279.1	85.0	229.0	3.11
PFEESA	Perfluoro(2-ethoxyethane)sulfonate	315.0	135.0	69.1	3.56
3,6-OPFHpA	Perfluoro-3,6-dioxaheptanoic acid	201.0	85.0	134.9	3.88
4:2FTS	1H, 1H, 2H, 2H-perfluoro-1-hexanesulfonate	326.9	306.9	81.0	3.94
MPFHxA	Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]hexanoic acid	314.9	269.8	119.5	4.08
PFHxA	Perfluoro- <i>n</i> -hexanoic acid	312.9	268.8	119.0	4.09
L-PFPeS	Perfluoro-1-pentanesulfonate	348.9	79.9	98.9	4.4
HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)-propanoic acid	328.9	284.8	169.0	4.47
M ₃ HFPO-DA	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)- ¹³ C ₃ -propanoic acid	331.9	286.6	169.0	4.47
PFHpA	Perfluoro- <i>n</i> -heptanoic acid	362.9	318.7	169.0	5.15
MPFHxS	Perfluoro-1-hexane[¹⁸ O ₂]sulfonate	402.9	103.0	83.9	5.21
PFHxSK	Perfluoro-1-hexanesulfonate	398.9	79.8	98.9	5.22
NaDONA	Sodium dodecafluoro-3H-4,8-dioxanonoate	376.9	250.7	85.0	5.29
MPFOA	Perfluoro- <i>n</i> -[1,2,3,4- ¹³ C ₄]octanoic acid	417.0	371.8	169.1	5.91
6:2FTS	1H, 1H, 2H, 2H-perfluoro-1-octanesulfonate	426.9	406.9	79.9	5.91
M ₂ PFOA	Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]octanoic acid	415.0	369.8	169.4	5.96
PFOA	Perfluoro- <i>n</i> -octanoic acid	412.9	369.0	169.0	5.97
L-PFHpS	Perfluoro-1-heptanesulfonate	448.9	79.8	98.9	5.98
PFOSK	Perfluorooctanesulfonate	498.8	79.9	99.0	6.61
MPFOS	Perfluoro- <i>n</i> -[1,2,3,4- ¹³ C ₄]octanesulfonate	502.9	98.9	79.9	6.61
PFNA	Perfluoro- <i>n</i> -nonanoic acid	462.9	418.9	169.0	6.62
MPFNA	Perfluoro- <i>n</i> -[1,2,3,4,5- ¹³ C ₅]nonanoic acid	468.0	422.8	169.0	6.62
9Cl-PF ₃ ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	530.8	350.7	82.8	6.96
L-PFNS	Perfluoro-1-nonanesulfonate	548.8	79.9	98.8	7.15
8:2FTS	1H, 1H, 2H, 2H-perfluoro-1-decanesulfonate	526.8	506.8	81.0	7.16
PFDA	Perfluoro- <i>n</i> -decanoic acid	512.8	468.9	219.1	7.18
MPFDA	Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]decanoic acid	514.8	469.7	219.1	7.18
d ₃ -N-MeFOSAA	<i>N</i> -methyl-d ₃ -perfluoro-1-octanesulfonamidoacetic acid	572.9	419.0	169.0	7.42
N-MeFOSAA	<i>N</i> -methylperfluoro-1-octanesulfonamidoacetic acid	569.8	418.9	168.9	7.43
L-PFDS	Perfluoro-1-decanesulfonate	598.8	79.9	98.9	7.6
FOSA	Perfluoro-1-octanesulfonamide	497.9	77.8	63.9	7.65
PFUdA	Perfluoro- <i>n</i> -undecanoic acid	562.8	518.9	169.1	7.65
MPFUdA	Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]undecanoic acid	564.8	519.9	169.1	7.65
d ₅ -N-EtFOSAA	<i>N</i> -ethyl-d ₅ -perfluoro-1-octanesulfonamidoacetic acid	588.8	418.8	169.0	7.66
N-EtFOSAA	<i>N</i> -ethylperfluoro-1-octanesulfonamidoacetic acid	583.8	418.8	168.9	7.67
11Cl-PF ₃ OUdS	11-chloroeicosfluoro-3-oxaundecane-1-sulfonate	630.7	451.0	82.8	7.87
PFDoA	Perfluoro- <i>n</i> -dodecanoic acid	612.8	568.9	169.0	8.06
MPFDoA	Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]dodecanoic acid	614.9	569.8	168.9	8.06
10:2FTS	1H, 1H, 2H, 2H-perfluoro-1-dodecanesulfonate	626.9	606.9	81.0	8.07
PFTriDA	Perfluoro- <i>n</i> -tridecanoic acid	662.8	618.9	169.0	8.41
PFTeDA	Perfluoro- <i>n</i> -tetradecanoic acid	712.8	668.8	168.9	8.72

Table 1: MRM transitions and retention times of PFAS.

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Figure 2: Chromatogram of PFAS on NUCLEOSHELL® RP 18plus column ($\beta = 1$ ng/mL for each compound).

Calibration and Recovery rates

Compound	%Recovery	% RSD	R_2
3–6-OPFHpA	86.6 %	2.6 %	1.000
M ₂ PFOA	89.5 %	3.0 %	0.999
MPFBA	85.7 %	1.4 %	1.000
MPFDA	89.5 %	0.7 %	0.999
MPFDoA	80.5 %	1.7 %	0.998
MPFHxA	88.8 %	4.7 %	0.999
MPFNA	88.8 %	2.0 %	0.999
MPFOA	90.2 %	3.0 %	1.000
MPFUdA	84.1 %	3.5 %	0.999
PF ₄ OPeA	86.4 %	0.6 %	0.999
PF ₅ OHxA	89.5 %	3.2 %	0.999
PFBA	81.1 %	1.8 %	0.994
PFDA	90.9 %	1.7 %	1.000
PFDoA	79.1 %	1.4 %	0.998
PFHpA	89.1 %	1.0 %	0.999
PFHxA	86.0 %	0.3 %	0.999
PFNA	89.9 %	3.5 %	0.999
PFOA	89.3 %	3.7 %	0.999
PFPeA	88.4 %	2.4 %	1.000
PFTeDA	72.1 %	4.4 %	0.997
PFTrDA	77.4 %	2.7 %	0.999
PFUdA	85.7 %	3.8 %	1.000
L-PFBS	89.2 %	2.8 %	0.999

Compound	%Recovery	% RSD	R_2
L-PFDS	89.6 %	3.8 %	0.996
L-PFHpS	89.0 %	1.6 %	0.999
L-PFNS	84.7 %	3.3 %	0.999
MPFHxS	89.0 %	3.0 %	1.000
MPFOS	87.0 %	2.5 %	0.999
PFEESA	87.6 %	2.1 %	1.000
PFHxSK	88.5 %	1.4 %	0.999
PFOSK	86.4 %	2.3 %	0.999
10:2FTS	80.8 %	3.8 %	0.997
4:2FTS	87.2 %	2.3 %	0.999
6:2FTS	92.2 %	10.3 %	0.998
8:2FTS	92.7 %	4.4 %	1.000
d ₃ -N-MeFOSAA	82.1 %	9.9 %	0.999
d ₅ -N-EtFOSAA	83.9 %	2.8 %	0.993
N-EtFOSAA	85.2 %	4.8 %	0.995
N-MeFOSAA	87.3 %	3.2 %	0.999
FOSA	42.0 %	1.9 %	0.999
NaDONA	86.7 %	1.8 %	1.000
11Cl-PF ₃ OUdS	84.3 %	0.5 %	0.999
9Cl-PF ₃ ONS	89.9 %	4.4 %	0.999
HFPO-DA	89.1 %	3.2 %	0.999
M ₃ HFPO-DA	92.1 %	2.6 %	0.996

Table 2: Recovery rates for presented SPE method for drinking water. Correlation coefficient is given for all compound from calibration curves, determined of 5 levels between 0.1 ng/mL and 1.0 ng/mL for each compound.

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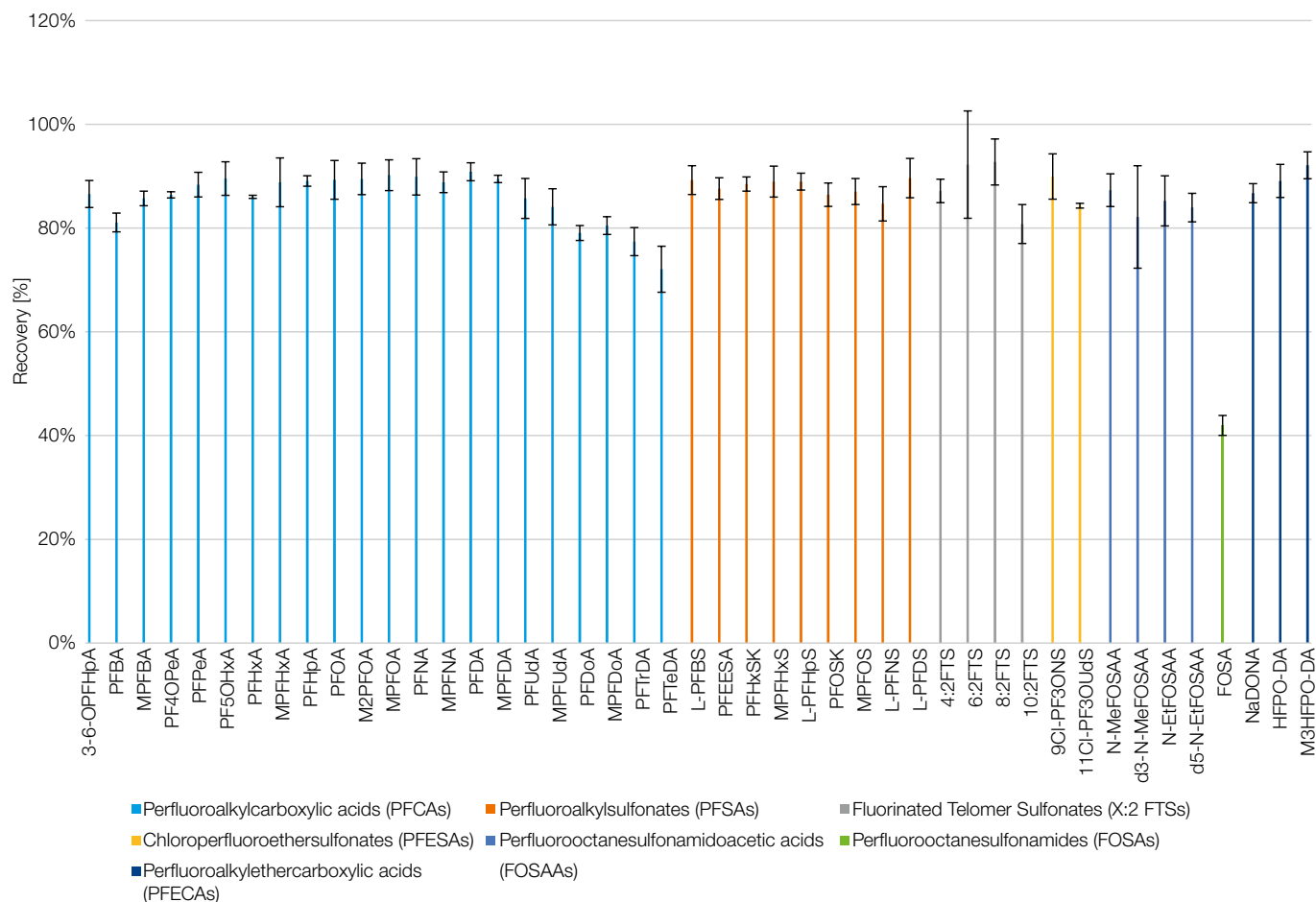


Figure 3: Recovery rates of PFAS from a water sample (spiked with 0.5 ng for each compound in 0.15 L water).

Conclusion

This application note shows the reliable and successful determination of per- and polyfluoroalkyl substances (PFAS) from drinking water with an optimized SPE method. By using CHROMABOND® PFAS it was possible to achieve high recovery rates for PFAS from drinking water 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 several directives EPA 537.1, EPA 533 and DIN 38407-42.

Most of the PFAS show recovery rates between 80 % to 100 %. Regarding the different types of perfluoroalkyl substances, the perfluorooctanesulfonamide (FOSA) and three perfluoroalkylcarboxylic acids with long carbon chain (PFTrDA, PFTeDA, PFDaA) show lower recovery rates. This result depends on the high polarity and less ionic interaction of FOSA with the SPE sorbent. Lower recovery for PFTrDA, PFTeDA and PFDaA can probably be explained by solubility problems and adsorption effects on surface materials.

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 back pressure. In this work, a 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 water samples with a SPE procedure using the extraction mechanisms of DIN 30407-42 and EPA Methods 537.1 and 533.

References

- [1] 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.
- [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.
- [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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Product information

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

REF 763234.20	EC HPLC column (analytical), NUCLEOSHELL® RP 18plus, 2.7 µm, 100x2 mm
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, fluorine-free
REF 702009	Screw neck vial, N 9, 11.6 x 32.0 mm, 0.3 mL, inner cone, PP transparent

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