PFAS

Application Note

Trace analysis of 29 perfluorinated compounds (PFAS) in sediments using AttractSPE® PFAS GCB-WAX

Sediments

Introduction

This application note describes an efficient solid phase extraction (SPE) method for the cleanup and trace analysis of 29 perfluorinated compounds (PFAS) in sediments. The method relies on AttractSPE® PFAS GCB-WAX, a bi-layer SPE cartridge to catch perfluorinated compounds in complex matrices prior to their analysis by LC-MSMS. The method is based on and compatible with EPA 1633 (January 2024).

Perfluorinated compounds (PFAS or PFCs) are a large family of molecules consisting of varying lengths of fluorocarbons chains with a functional group such as carboxylic or sulfonic acids attached. They have been widely used for more than 50 years in various products, such as firefighting foams, hydrophobic and nonstick coatings, or surfactants to cite a few examples. Their nature makes them particularly chemically inert and very resistant to degradation in environment. Some PFAS are classified as persistent organic pollutants (POPs) and are strongly associated with a variety of human disorders such as neurotoxicity, immune deficiency, and cancer[1].

Solid phase extraction allows to purify and concentrate samples prior to analysis, which is particularly important to reach low concentrations or in complex matrices. **AttractSPE® PFAS GCB-WAX** for PFAS analysis brings cleaner extracts than with regular WAX SPE cartridges.

Table 1. List of the 29 tested PFAS

Compound	Abbrevation	CAS Number
Perfluorobutanoic acid	PFBA	375-22-4
Perfluoropentanoic acid	PFPeA	2706-90-3
Perfluorohexanoic acid	PFHxA	307-24-4
Perfluoroheptanoic acid	PFHpA	375-85-9
Perfluorooctanoic acid	PFOA	335-67-1
Perfluorononanoic acid	PFNA	375-95-1
Perfluorodecanoic acid	PFDA	335-76-2
Perfluoroundecanoic acid	PFUnA	2058-94-8
Perfluorododecanoic acid	PFDoA	307-55-1
Perfluorotridecanoic acid	PFTrDA	72629-94-8
Perfluorotetradecanoic acid	PFTeDA	376-06-7
Perfluorohexadecanoic acid	PFHxDA	67905-19-5
Perfluorooctadecanoic acid	PFODA	16517-11-6
Perfluorobutanesulfonic acid	PFBS	375-73-5
Perfluoropentanesulfonic acid	PFPeS	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	355-46-4

Perfluoroheptanesulfonic acid	PFHpS	375-92-8
Perfluorooctanesulfonic acid	PFOS	1763-23-1
Perfluorononanesulfonic acid	PFNS	68259-12-1
Perfluorodecanesulfonic acid	PFDS	335-77-3
Perfluoroundecanesulfonic acid	PFUdS	749786-16-1
Perfluorododecanesulfonic acid	PFDoS	79780-39-5
Perfluorotridecanesulfonic acid	PFTrDS	791563-89-8
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2 FTS	27619-97-2
N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6
Perfluorooctanesulfonamide	FOSA	754-91-6
N-methyl perfluorooctanesulfonamide	MeFOSA	31506-32-8
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4

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Proceeding of the experiment

Sample preparation:

Four samples of sediments (taken from Le Cailly river, Le Houlme, France) were spiked with 29 PFAS at 0.4-2µg/Kg (detailed concentrations table 3). A non-spiked sediment sample was also extracted as a blank to measure the initial presence of PFAS.

The method of extraction is adapted from the solid sample procedure on EPA 1633 (January 2024):

1. Weight 5g of homogenized sediments into a 50mL centrifuge tube. Add 10mL 0.3% NH3 (in methanol), vortex and shake for 30 min. Centrifuge at 2800rpm for 10 minutes. Collect the supernatant into another tube.
2. Add another 15mL 0.3% NH3 (in methanol) to the same sediments, vortex and shake for 30 min. Centrifuge at 2800rpm for 10 minutes. Collect the supernatant and add it to the first supernatant fraction.
3. Add another 5mL 0.3% NH3 (in methanol) to the same sediments and shake by hand. Centrifuge at 2800rpm for 10 minutes. Collect the supernatant and add it to the first and second supernatant fraction.
4. Concentrate the solution obtained to around 5-10mL using nitrogen evaporation at 55°C. Adjust to ~48mL with ultrapure water and vortex. Adjust pH at 6-7 with formic acid or 3% NH3 to form the loading solution prior to SPE.

PURIFICATION WITH A 6mL ATTRACTSPE® PFAS GCB-WAX – 50mg/200mg CARTRIDGE WITH 60mL RESERVOIR AND ADAPTER

Conditioning/Equilibration

1. 15mL 1% NH_3 in methanol
2. 5mL 0.3M formic acid in water

Loading

1. ~48mL of loading solution

Washing

1. *2x5mL ultrapure water
2. *5mL 0.05M formic acid in 50/50 water/methanol (v/v)
3. Dry cartridge for 15 seconds by applying full vacuum

Elution

1. *5mL 1% NH_3 in methanol

Analysis

Add 25µL of acetic acid to the elution and homogenize prior LC-MS/MS analysis

*Prior to washing/elution, rinse the walls of sample container with the solution then pass through the cartridge. For the elution step, also rinse the walls of the reservoir prior passing through the cartridge.

2 Conditions of analysis

Some molecules of interest are ubiquitous and so likely to be found in mobile phase or LC parts, leading to contamination during LC-MS/MS analysis. Fitting **SilactHPLC Delay – PFAS** as a delay column upstream of the injector (Figure 1) shifts the contaminant retention time, allowing the analyte of interest to be measured in the sample without contamination (Figure 2). This solution, in comparison with the monitoring of contamination from the LC device, is very easy to implement and is cost effective.

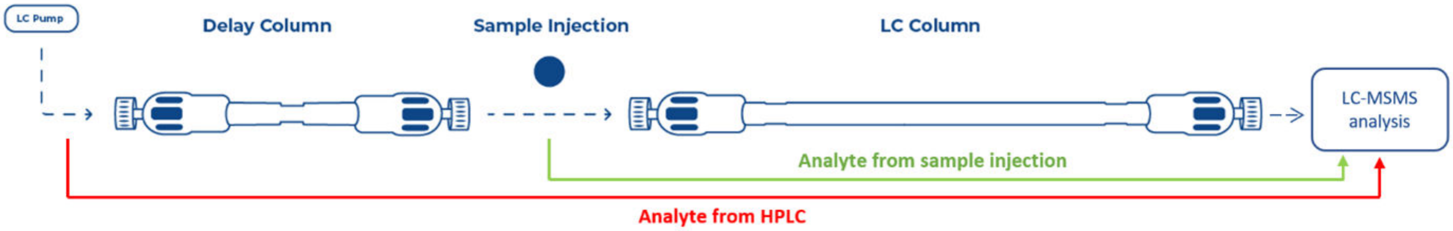


Figure 1. Installation of Delay column for LC analysis

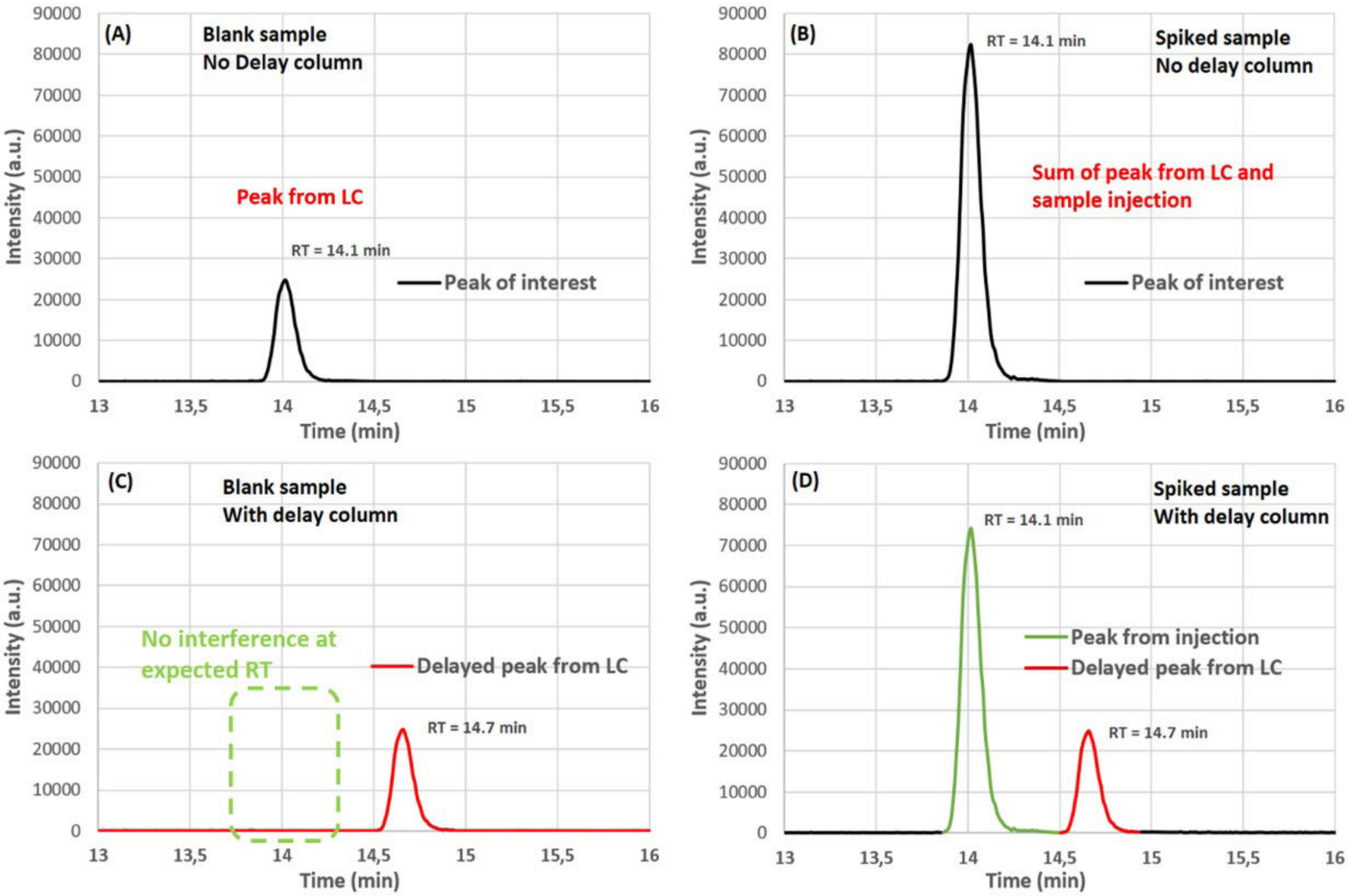


Figure 2. Effects of a delay column on samples. A: Blank sample without delay column. B: Spiked sample without delay column. C: Blank sample with delay column. D: Spiked sample with delay column.

Table 2. LC-MS/MS conditions of analysis

LC Conditions	MS/MS Conditions
LC Dionex U3000	Qtrap 4000 ESI- MS/MS
Column : Siliachrom dtC18 150*2.1mm at 40°C Delay column : SilactHPLC Delay-PFAS 50*2.1mm	Curtain gas : 30
	CAD : High
Injection volume : 5µL	IS : -4500V
T° sampler : 10°C	Temperature : 550°C
Flow rate : 0.25mL/min	GS1/GS2 : 50/50

Time (min)	10mM Ammonium Acetate (in water)	Methanol	Analyte	Retention time (min)	Q1 (m/z)	Q3 (m/z)	CE (V)
0	60%	40%	PFBA	3.2	213.0	168.8	-14
			PFPeA	4.9	263.0	218.8	-12
1	60%	40%	PFHxA	10.1	313.0	268.9	-14
			PFHpA	13.0	363.0	318.8	-16
20	10%	90%	PFOA	15.0	413.1	368.9	-14
			PFNA	16.7	463.0	418.9	-16
30	10%	90%	PFDA	18.1	513.0	469.0	-18
			PFUnA	19.3	563.1	519.0	-16
31	60%	40%	PFDoA	20.3	613.1	569.1	-18
			PFTrDA	21.1	663.1	619.0	-18
35	60%	40%	PFTeA	22.0	712.9	668.9	-18
			PFHxDA	23.2	813.0	769.0	-20
			PFODA	24.3	913.0	869.0	-22
			PFBS	6.2	299.0	79.8	-52
			PFPeS	10.6	349.0	79.9	-68
			PFHxS	13.2	399.0	79.9	-74
			PFHpS	15.1	448.9	80.0	-90
			PFOS	16.7	499.0	80.1	-84
			PFNS	18.1	549.0	80.0	-94
			PFDS	19.2	599.0	79.8	-110
			PFUdS	20.3	649.0	79.9	-116
			PFDoS	21.1	699.0	79.8	-130
			PFTrDS	21.9	749.0	80.0	-130
			HFPO-DA	11.1	285.1	168.7	-12
			6:2 FTS	14.9	427.1	406.8	-34
			N-EtFOSAA	19.4	584.1	418.8	-30
			FOSA	19.7	498.1	77.8	-70
			MeFOSA	22.1	512.1	168.8	-38
			ADONA	13.3	377.0	250.9	-18

3 Results

The analytes were simultaneously analysed by LC-MS/MS. The results obtained are presented in the table below.

Table 3. Recovery obtained for tested analytes (ND : not detected)

Compound	Sediments spiked at (µg/kg)	Sediments		
		[C] in blank (µg/kg)	% Recovery	% RSDr (n=4)
PFBA	0.40	ND	111%	5%
PFPeA	0.40	ND	109%	5%
PFHxA	0.40	0.01	110%	3%
PFHpA	0.40	0.03	110%	5%
PFOA	0.40	0.03	114%	5%
PFNA	0.40	0.01	97%	7%
PFDA	0.40	0.01	109%	7%
PFUnA	0.40	ND	110%	7%
PFDoA	0.40	0.02	98%	3%
PFTrDA	0.40	ND	108%	6%
PFTeA	0.40	ND	128%	6%
PFHxDA	0.40	ND	97%	6%
PFODA	0.40	ND	106%	5%
PFBS	0.40	ND	111%	0%
PFPeS	0.40	ND	110%	2%
PFHxS	0.40	0.01	112%	2%
PFHpS	0.40	ND	107%	3%
PFOS	0.40	0.11	111%	6%
PFNS	0.40	ND	109%	2%
PFDS	0.40	ND	107%	4%
PFUdS	0.40	ND	107%	2%
PFDoS	0.40	ND	104%	4%
PFTrDS	0.40	ND	102%	4%
HFPO-DA	0.40	ND	95%	2%
6:2 FTS	2.00	0.03	99%	2%
N-EtFOSAA	0.80	ND	112%	6%
FOSA	0.40	0.01	108%	2%
MeFOSA	0.80	ND	90%	5%
ADONA	0.40	ND	108%	2%

Perfluorooctadecanoic acid (PFODA) and heavier PFAS may have difficulty to be eluted as it adsorbs strongly to GCB. So, for the heaviest PFAS (with chains over 18 carbon), it is recommended to use stronger eluting solvents or **AttractSPE® PFAS.**

CONCLUSION

AttractSPE® PFAS GCB-WAX has been successfully used for the enrichment and cleanup of 29 perfluorinated compounds in sediments. The method has shown excellent performances with recoveries from **95%** to **128%** and a very good repeatability.

Furthermore, the use of **SilactHPLC DELAY - PFAS** as delay column allows to avoid any PFAS interference during LC-MS/MS analysis. Particular attention must be paid to check that the laboratory environment does not contaminate samples and lead to false positives. Some simple precautionary steps are described in the application note (e.g., the use of a delay column). For routine analysis, the use of internal standards to correct the potential matrix effects and adsorption of the largest PFAS is advised.

References

1. **Impact of Perfluorinated Compounds on Human Health, 2014 Academy for Environment and Life Sciences.**

Product references:

***AttractSPE® PFAS GCB-WAX 6mL - 50mg/200mg**

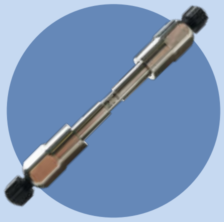
Quantity : 50/pk

PFAS-GW-50.S.6.50.200

***AttractSPE® PFAS 6mL - 200mg**

Quantity : 50/pk

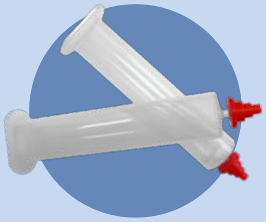
PFAS-50.S.6.200



SilactHPLC DELAY - PFAS 50*2.1mm (5µm) for PFAS analysis

Quantity : 1 unit

DELAY-PFAS-50.2.1



kit of 12 reservoirs 60ml and adapters for use with 1,3 & 6 mL columns

Quantity : 1 unit

ACC-AR1

SPE Vacuum Manifold 12-port model

Quantity : 1 unit

ACC-MAN2

***Other formats and sorbent volumes available in our catalogue**