affinisep

PFAS

Application Note

Analysis of 28 perfluorinated compounds (PFAS) in river water using AttractSPE® Disks WAX

Water analysis

Introduction

This application note describes an efficient solid phase extraction (SPE) method for the cleanup and trace analysis of 28 perfluorinated compounds (PFAS) in large volumes of river water. The method relies on AttractSPE® Disks - WAX, a SPE disk to quickly concentrate PFAS from large water volumes prior to their analysis by LC-MSMS.

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 the 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].

AttractSPE® Disks are thin, dense, soft and uniform extraction SPE membranes that ensure reduced extraction time of large sample volumes thanks to a fast flow rate and without any channeling. They have a high surface area of exchange that allows the best interactions with analytes to obtain excellent recoveries. Several formats and chemistries are available to best suit each application.

Table 1. List of the 28 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
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 perfluorooctanesulfonamidoethanol	N-MeFOSE	24448-09-7
N-methyl perfluorooctanesulfonamide	MeFOSA	31506-32-8
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4

1 Proceeding of the experiment

Loading solution:

One liter of river water (Le Cailly river, Le Houlme, France) is spiked with 28 PFAS at 0,02-2 µg/L (detailed concentrations table 3). One liter of river water (not spiked) was also performed as a blank control.

PURIFICATION PROTOCOL

Place the AttractSPE® Disks WAX – 47mm on the SPE disk manifold.

Note: A glass microfiber (1 µm or 3 µm) can be added on top of the disk to prevent clogging from particulates in the water sample.

Conditioning/Equilibration

1. **20 mL 1%NH_3 in methanol (soak disk for 1 minute)**
2. **20 mL 0.3M formic acid in water**

Loading

1. **1 L at 50 mL/min**

Washing

1. ***20 mL ultrapure water**
2. ***10mL 0.05M formic acid in 50/50 water/methanol (v/v)**
3. **Dry disk 30 seconds under vacuum**

Elution

1. ***20 mL 1% NH_3 in methanol (soak disk for 1 minute)**

Analysis

Add 100µL of acetic acid to the elution and homogenize prior LC-MS/MS analysis

***Before washing/elution, rinse the walls of the sample container with the solution, then pass it through the disk. For the elution step, also rinse the walls of the glass funnel using a glass pipette before passing it through the disk.**

SPE disk manifold for AttractSPE® Disks

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** aas 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.

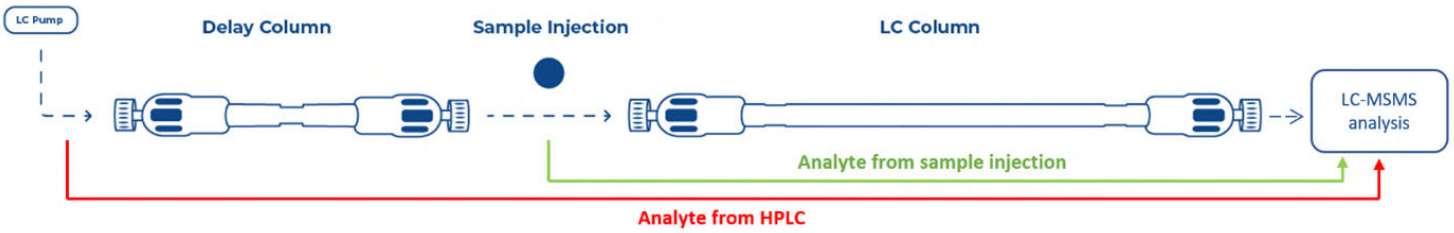

Figure 1. Installation of Delay column for LC analysis

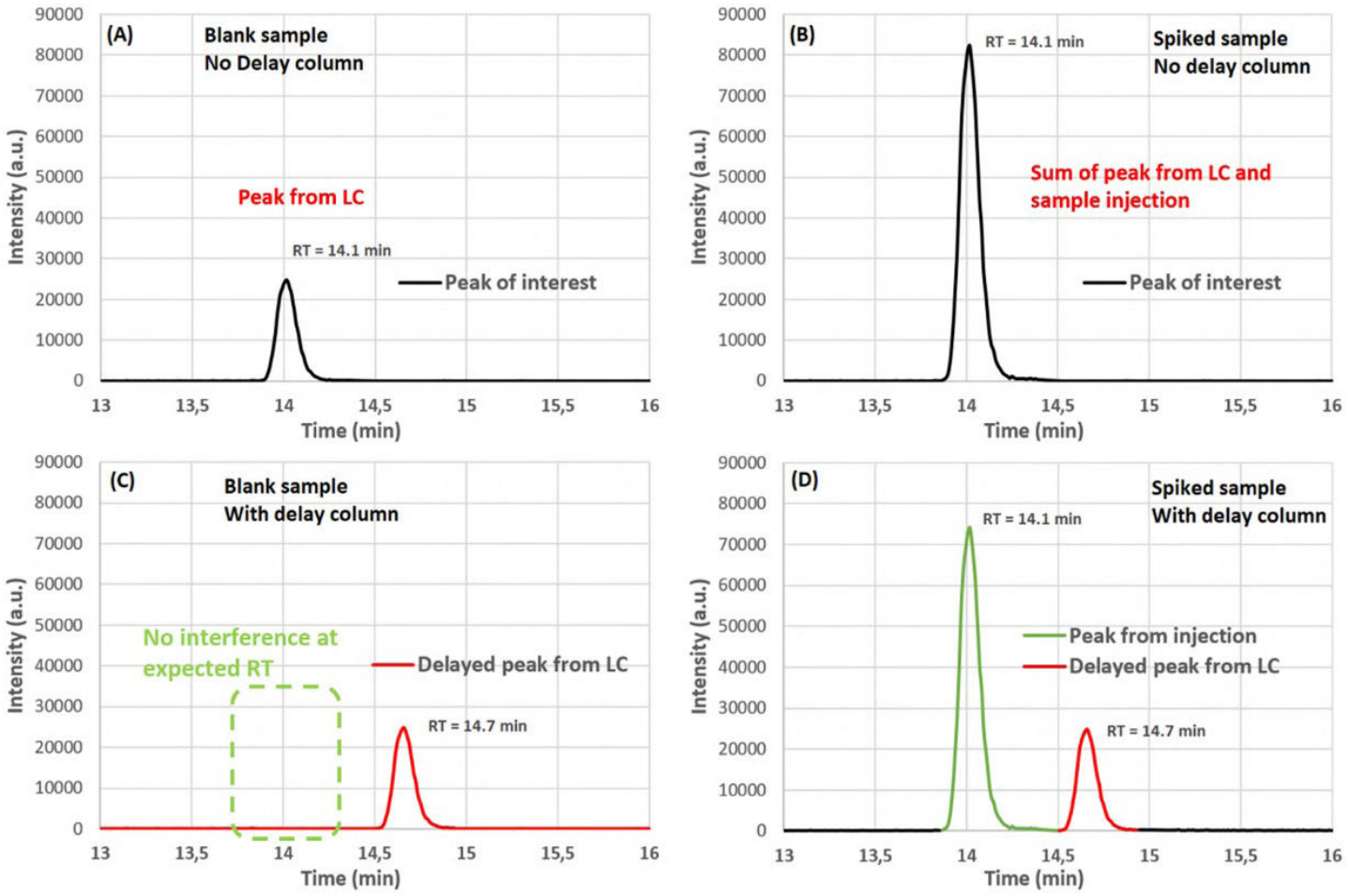

Figure 2. Effects of a delay column on samples. A: Blank sample without delay column. B: Spiked sample without delay column. C: Blank sample with delay column. D: Spiked sample with delay column.

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
			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
			N-MeFOSE	22.1	556.2	79.9	-92
			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	Water spiked at (µg/L)	River Water		
		[C] in blank (µg/L)	% Recovery	% RSDr (n=4)
PFBA	0.02	ND	126%	5%
PFPeA	0.02	ND	127%	7%
PFHxA	0.02	ND	113%	3%
PFHpA	0.02	ND	115%	2%
PFOA	0.02	ND	111%	4%
PFNA	0.02	ND	111%	2%
PFDA	0.02	ND	104%	3%
PFUdA	0.02	ND	118%	4%
PFDoA	0.02	ND	103%	8%
PFTrDA	0.02	ND	108%	8%
PFTeA	0.02	ND	107%	11%
PFBS	0.02	ND	110%	9%
PFPeS	0.02	ND	105%	3%
PFHxS	0.02	ND	109%	5%
PFHpS	0.02	ND	107%	5%
PFOS	0.02	ND	113%	4%
PFNS	0.02	ND	102%	4%
PFDS	0.02	ND	107%	4%
PFUdS	0.02	ND	106%	4%
PFDoS	0.02	ND	102%	2%
PFTrDS	0.02	ND	90%	4%
HFPO-DA	0.02	ND	105%	9%
6:2 FTS	0.1	ND	103%	6%
N-EtFOSAA	0.04	ND	105%	3%
FOSA	0.02	ND	102%	5%
N-MeFOSE	2	0.04	115%	6%
MeFOSA	0.04	ND	94%	6%
ADONA	0.02	ND	109%	5%

CONCLUSION

AttractSPE® Disks WAX has been successfully used for the enrichment and cleanup of 28 perfluorinated compounds in river water. The method has shown excellent performances with recoveries from **90%** to **127%** for river water and a 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® Disks WAX – 47mm
Quantity : 20/pk
SPE-Disks-WAX-47.T1.20

AttractSPE® Prefilter Glassfiber for 47mm disks
Quantity : 50/pk
1µm - PF-GF-50.T1.47.1
3µm - PF-GF-50.T1.47.3

SilactHPLC DELAY - PFAS 50*2.1mm (5µm) for PFAS analysis
Quantity : 1 unit
DELAY-PFAS-50.2.1

SPE Disks manifold 47mm (also available for 90mm) :
1 station - ACC-DISKSPE-G47-1
3 stations - ACC-DISKSPE-G47-3
6 stations - ACC-DISKSPE-G47-6