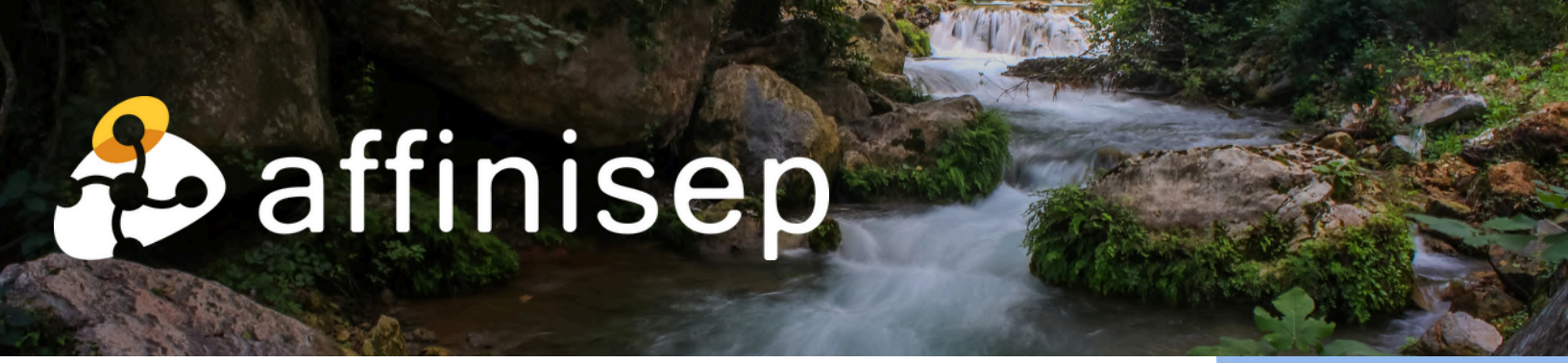

affinisep

PFAS

Application Note

Analysis of 30 perfluorinated compounds (PFAS) in river water and tap water using AttractSPE® PFAS

Water analysis

Introduction

This application note describes an efficient solid phase extraction (SPE) method for the cleanup and analysis of 30 perfluorinated compounds (PFAS) in river water and tap water. The method relies on **AttractSPE® PFAS** cartridges to catch perfluorinated compounds in water 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 describe 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]. The recast of the Drinking Water Directive (EU) 2020/2184, which took effect on 12 January 2021, includes a limit of 0.5 µg/l for all PFAS in European Union [2]. In the USA, April 10th, 2024, EPA announced the final National Primary Drinking Water Regulation (NPDWR) for six PFAS [3], establishing legally enforceable levels of 4.0 to 10 ng/L in drinking water.

Solid phase extraction allows to purify and concentrate samples prior analysis that is particularly important to reach low concentrations in complex matrices.

Compound	Abbreviation	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 perfluorooctanesulfonamidoethanol	N-MeFOSE	24448-09-7
N-methyl perfluorooctanesulfonamide	MeFOSA	31506-32-8
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4

Table 1. List of the 30 tested PFAS.

Proceeding of the experiment

Sample preparation

Four samples of 500mL of river water (Le Cailly river, Le Houlme, France) and four sample of 500mL of tap water (Le Houlme, France) were spiked with 30 PFAS at 4-400ng/L (detailed concentrations table 3) to form the loading solutions. 500mL non-spiked river water and tap water sample were also purified as a blank sample.

Purification with a 6 mL AttractSPE® PFAS – 200mg cartridge with a 60mL reservoir and adapter

CONDITIONING/EQUILIBRATION

1. 15 mL 1% NH4OH in methanol
2. 5 mL 0.3M formic acid in water

LOADING

500 mL of loading solution

WASHING

1. *2x5 mL 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

*5mL 1% NH4OH 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.

Conditions of analysis

During analyses, some analytes of interest are also likely to be found in mobile phase or LC parts and tubing. These analytes concentrate at the front of the LC column during each sample run, leading to the analysis of these interferences due to contamination. The change of LC parts and tubing or the control of solvents purity are very expensive and time consuming. Moreover, some contaminants may never be fully removed. The alternative solution is the use of a delay column.

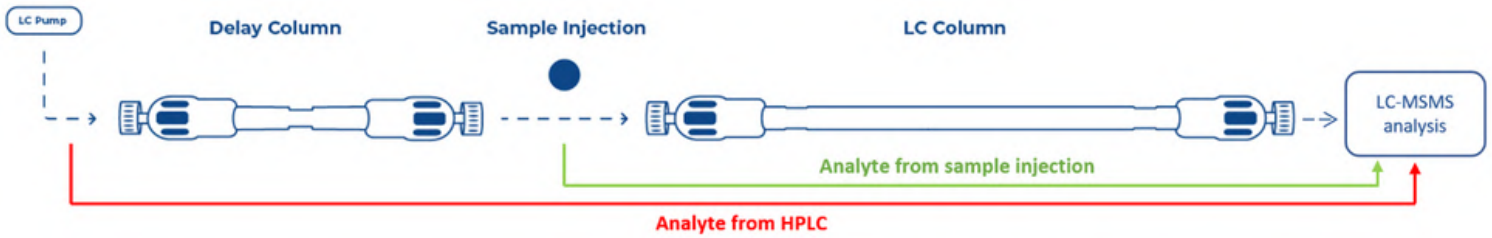

Figure 1. Installation of Delay column for LC analysis

A delay column is set between LC pumps and sample injection (Figure 1). It allows the analytes of interest coming from the LC devices to concentrate at the front of the delay column instead of LC column, while the analytes coming from sample injection will concentrate directly on the LC column. This will lead to a longer retention time for the analytes from LC device because it has to pass through the delay column first in addition to the LC column whereas the analyte from sample injection has to only pass through LC column (Figure 2). This solution is very easy to implement and is cost-effective.

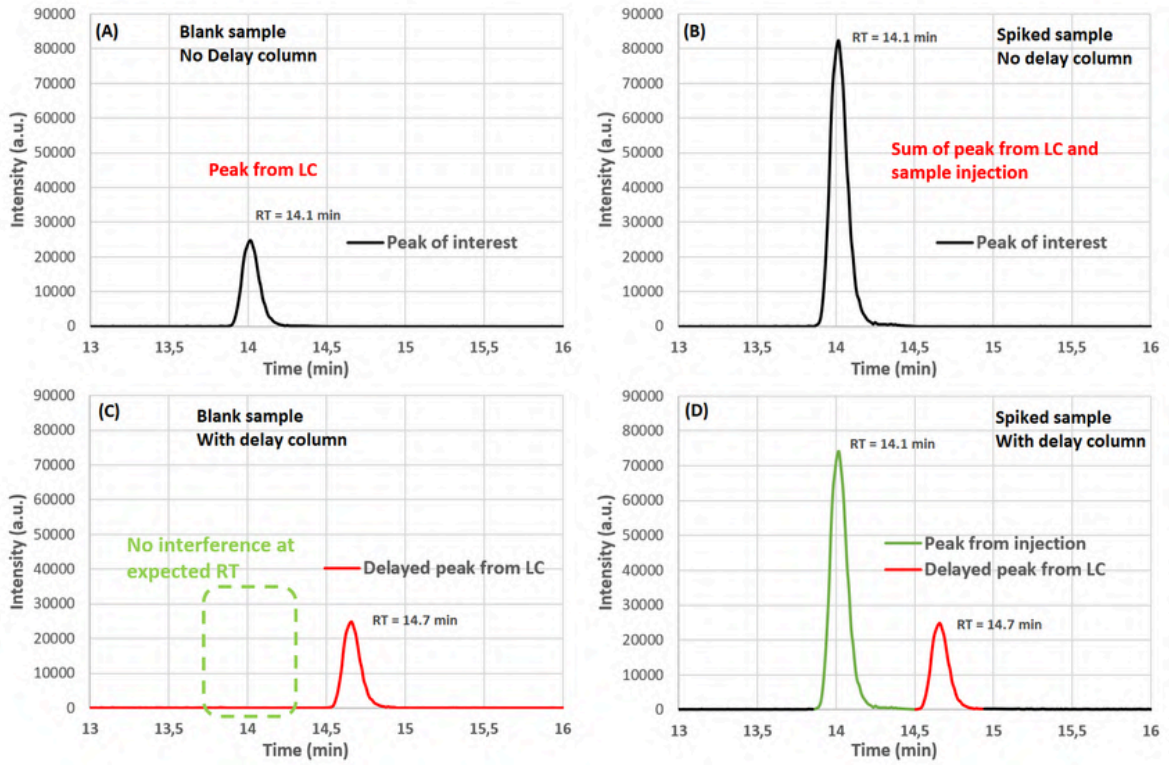

Figure 2. Effects of a delay column on samples. A: Blank sample without delay column. B: Spiked sample without delay column. C: Blank sample with delay column. D: Spiked sample with delay column.

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
0	60%	40%
1	60%	40%
20	10%	90%
30	10%	90%
31	60%	40%
35	60%	40%

Analyte	Retention time (min)	Q1 (m/z)	Q3 (m/z)	CE (V)
PFBA	3.2	213.0	168.8	-14
PFPeA	4.9	263.0	218.8	-12
PFHxA	10.1	313.0	268.9	-14
PFHpA	13.0	363.0	318.8	-16
PFOA	15.0	413.1	368.9	-14
PFNA	16.7	463.0	418.9	-16
PFDA	18.1	513.0	469.0	-18
PFUnA	19.3	563.1	519.0	-16
PFDoA	20.3	613.1	569.1	-18
PFTrDA	21.1	663.1	619.0	-18
PFTeDA	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
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

Table 2. LC-MS/MS conditions of analysis.

Results

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

Compound	Water spiked at (ng/L)	River water			Tap water		
		[C] in blank (ng/L)	% Recovery	% RSDr (n=4)	[C] in blank (ng/L)	% Recovery	% RSDr (n=4)
PFBA	4	0.4	102%	2%	0.5	112%	7%
PFPeA	4	ND	106%	9%	ND	108%	3%
PFHxA	4	0.4	105%	3%	0.5	101%	4%
PFHpA	4	ND	103%	3%	ND	98%	5%
PFOA	4	ND	101%	1%	ND	105%	4%
PFNA	4	ND	100%	7%	ND	106%	4%
PFDA	4	ND	94%	4%	ND	91%	8%
PFUnA	4	ND	106%	6%	ND	99%	9%
PFDoA	4	ND	95%	7%	ND	92%	8%
PFTrDA	4	ND	89%	9%	ND	97%	5%
PFTeDA	4	ND	98%	6%	ND	125%	6%
PFHxDA	4	ND	93%	6%	ND	98%	7%
PFODA	4	ND	100%	5%	ND	122%	12%
PFBS	4	ND	106%	4%	ND	102%	4%
PFPeS	4	ND	104%	5%	ND	102%	4%
PFHxS	4	ND	100%	5%	ND	98%	4%
PFHpS	4	ND	103%	4%	ND	99%	4%
PFOS	4	0.7	101%	3%	ND	100%	3%
PFNS	4	ND	101%	3%	ND	101%	3%
PFDS	4	ND	98%	1%	ND	97%	2%
PFUdS	4	ND	98%	2%	ND	100%	6%
PFDoS	4	ND	90%	5%	ND	95%	2%
PFTrDS	4	ND	91%	2%	ND	100%	3%
HFPO-DA	4	ND	94%	9%	ND	116%	5%
6:2 FTS	20	ND	98%	5%	ND	107%	7%
N-EtFOSAA	8	ND	97%	5%	ND	92%	8%
FOSA	4	ND	101%	3%	ND	96%	3%
N-MeFOSE	400	ND	88%	7%	ND	93%	4%
MeFOSA	8	ND	77%	4%	ND	66%	6%
ADONA	4	ND	102%	3%	ND	97%	2%

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

Conclusion

AttractSPE® PFAS has been successfully used for the enrichment and the cleanup of 30 perfluorinated compounds in river water and tap water. The method has shown excellent performances with recoveries higher than **88% and 90%** for 29 compounds in respectively tap and river waters. MeFOSA has shown lower but acceptable recoveries at respectively 77% and 66%. They all show an excellent repeatability.

Furthermore, the use of **SilactHPLC DELAY - PFAS** as delay column prevent the interference of PFAS generated by LC devices. Special 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 recommended.

References :

1. Impact of Perfluorinated Compounds on Human Health, 2014 Academy for Environment and Life Sciences.
2. http://data.europa.eu/eli/reg_del/2023/1608/oj
3. https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas

Product reference

- **AttractSPE® PFAS**

Catalog number: **PFAS-50.S.6.200** for 50 cartridges

- **SilactHPLC DELAY - PFAS** - 50x2,1mm (5µm) Delay column for PFAS analysis

Catalog number: **DELAY-PFAS-50.2.1** for 1 pc