



ENVIRONMENTAL MARKET

TRACE LEVEL DETERMINATION OF PER- AND POLYFLUOROALKYL SUBSTANCES (PFASs) IN WATER USING THE AGILENT 6460 LC/MS/MS

A method for the determination of per- and polyfluoroalkyl substances (PFASs) in various water types has been developed on the Agilent 6460 LC/MS/MS. Samples are prepared using solid phase extraction.



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ABSTRACT

A method for the determination of per- and polyfluoroalkyl substances (PFASs) in various water types has been developed on the Agilent 6460 LC/MS/MS. Samples are prepared using solid phase extraction. The analytical suite contains 26 PFASs including 4 perfluoroalkane sulfonates (PFASs) (PFBS, PFHxS, PFOS, PFDS), 13 perfluoroalkyl carboxylates (PFCAs) (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA, PFTrIDA, PFTeDA, PFHxDA, PFOcDA), 3 perfluorooctane sulfonamides (FOSAs) (FOSA, MeFOSA EtFOSA), 2 perfluorooctane sulfonamidoethanols (FOSEs) (MeFOSE, EtFOSE), 3 perfluorooctane sulfonamidoacetic acids (FOSAAAs) (FOSAA, MeFOSAA, EtFOSAA) and fluorotelomer carboxylate (6:2 FTSA). The range of application for this method is 0.05 – 40 ng/mL of concentrated extract, which is equivalent to 0.05 – 40 ng/L of unextracted water. Method detection limits are less than 2 ng/L for all compounds.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFASs), which are also commonly known as PFCs (per- and polyfluorinated chemicals), comprise a diverse group of man-made chemicals that are widely used as processing additives during fluoropolymer production and as surfactants in consumer applications, including surface coatings for textiles, furniture and paper products, as well as in some types of fire-fighting foam [1]. PFASs are known to be persistent, bioaccumulative and have possible adverse effects on humans and wildlife [2]. As a result, PFOS (perfluorooctane sulfonate) and its salts were added to the Stockholm Convention on Persistent Organic Pollutants (POPs) in May 2009 [3]. However, their homologues, neutral precursor compounds and new PFAS classes continue to be produced.

The Swedish Drinking Water Guideline includes 11 PFASs. These are perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, 6:2 fluorotelomer sulfonate (6:2 FTSA), perfluorobutanoate (PFBA), perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA) and perfluorodecanoate (PFDA). The action value for the sum of these 11 PFASs is 90 ng/L and the health risk limit is 900 ng/L (Swedish National Food Agency, 2015).

The analytical technique of choice for the determination of PFASs in water is high performance liquid chromatography coupled with tandem mass spectrometry using the Agilent 6460 (LC/MS/MS). This solution note outlines a robust, sensitive method that has been developed for the routine determination of 26 PFASs for a variety of water types, including marine water, surface water from lakes and streams, groundwater, wastewater (influent and effluent), landfill leachate, surface run-off, precipitation, snow and ice.

ANALYTICAL TECHNIQUE

Standards

- Calibration standards prepared in methanol containing 26 target compounds and 16 mass-labelled internal standards
- Concentration of calibration standards – 0.05, 0.25, 1, 4, 8 and 40 ng/mL
- Concentration of mass-labelled internal standards – 2 ng/mL
- Mass-labelled injection standard – 2 ng/mL

Sample Preparation

- 0.5 L of water sample extracted using solid phase extraction (SPE) and eluent concentrated to 1 mL

Instrumentation

- Agilent 1200 Series HPLC System
- Agilent 6460 Triple Quadrupole System

Agilent 1200/6460 LC/MS/MS Operating Conditions

LC Conditions	
Analytical Column	Betasil C18 50 x 2.1 mm, 5 µm
Guard Column	Hypersil Gold 10 x 2.1 mm, 5 µm
Column Temperature	25°C
Injection Volume	10 µL
Mobile Phase	A = MilliQ + 10 mM NH ₄ OH
	B = Methanol + 10 mM NH ₄ OH
Flow Rate	0.35 – 0.40 mL/min
Run Time	20 min
MS Conditions	
Acquisition Mode	MRM, ESI Negative
Gas Temperature	300°C
Gas Flow	7 L/min
Nebuliser Pressure	30 psi
Sheath Gas Temperature	250°C
Sheath Gas Flow	11 L/min
Capillary Voltage	3500 V
Nozzle Voltage	0 V

RESULTS AND DISCUSSIONS

An Agilent 6460 LC/MS/MS system was used to determine a group of 26 PFASs, consisting of 4 perfluoroalkane sulfonates (PFASs) (PFBS, PFHxS, PFOS, PFDS), 13 perfluoroalkyl carboxylates (PFCAs) (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), 3 perfluorooctane sulfonamides (FOSAs) (FOSA, MeFOSA, EtFOSA), 2 perfluorooctane sulfonamidoethanols (FOSEs) (MeFOSE, EtFOSE), 3 perfluorooctane sulfonamidoacetic acids (FOSAAAs) (FOSAA, MeFOSAA, EtFOSAA) and fluorotelomer carboxylate (6:2 FTSA) (Tables 1 and 2).

Class	Name
PFASs	perfluoroalkane sulfonates
PFCAs	perfluoroalkyl carboxylates
FOSAs	perfluorooctane sulphonamides
FOSEs	perfluorooctane sulfonamidoethanols
FOSAAAs	perfluorooctane sulfonamidoacetic acids
X:2 FTSAAs	X:2 fluorotelomer carboxylates

Table 1. Classes of Compounds within the PFAS Analytical Suite.

The mass-spectrometer was operated in MRM negative ionisation mode, and all compounds were determined in a single analytical run. Table 2 lists the compounds in the analytical suite, along with their retention times and method detection limits (MDLs) based on solid phase extraction (SPE) of 0.5 L of water and extract concentration to 1 mL.

Peak	RT (min)	Compound	Abbreviation	Class	MDLs (ng/L)
1	3.9	perfluorobutanoate	PFBA	PFCAs	0.25
2	5.3	perfluoropentanoate	PFPeA	PFCAs	0.03
3	5.6	perfluorobutane sulfonate	PFBS	PFSAAs	0.22
4	6.5	perfluorohexanoate	PFHxA	PFCAs	0.09
5	7.6	perfluoroheptanoate	PFHpA	PFCAs	0.05
6	7.7	perfluorohexane sulfonate	PFHxS	PFSAAs	0.15
7	8.6	6:2 fluorotelomer sulfonate	6:2 FTSA	X:2 FTSAAs	1.79
8	8.6	perfluorooctanoate	PFOA	PFCAs	0.40
9	9.6	perfluorononanoate	PFNA	PFCAs	0.08
10	9.6	perfluorooctane sulfonate	PFOS	PFSAAs	0.21
11	10.3	perfluorooctane sulfonamidoacetic acid	FOSAA	FOSAAAs	0.25
12	10.4	perfluorodecanoate	PFDA	PFCAs	0.19
13	10.7	N-methylperfluorooctane sulfonamidoacetic acid	N-MeFOSAA	FOSAAAs	0.25
14	10.8	perfluorooctane sulfonamide	FOSA	FOSAAs	0.11
15	11.1	perfluoroundecanoate	PFUnDA	PFCAs	0.16
16	11.1	N-ethylperfluorooctane sulfonamidoacetic acid	N-EtFOSAA	FOSAAAs	0.25
17	11.1	perfluorodecane sulfonate	PFDS	PFSAAs	0.25
18	11.7	perfluorododecanoate	PFDoDA	PFCAs	0.19
19	12.0	N-methylperfluorooctane sulfonamide	N-MeFOSA	FOSAAs	0.05
20	12.0	N-methylperfluorooctane sulfonamido-ethanol	N-MeFOSE	FOSEs	1.00
21	12.3	perfluorotridecanoate	PFTriDA	PFCAs	0.05
22	12.4	N-ethylperfluorooctane sulfonamide	N-EtFOSA	FOSAAs	0.05
23	12.4	N-ethylperfluorooctane sulfonamido-ethanol	N-EtFOSE	FOSEs	0.25
24	12.8	perfluorotetradecanoate	PFTeDA	PFCAs	0.05
25	13.5	perfluorohexadecanoate	PFHxDA	PFCAs	0.05
26	14.1	perfluorooctadecanoate	PF0cDA	PFCAs	0.25

Table 2. Retention Times for individual PFASs, Abbreviation, Compound Class and MDLs (see Figure 1 for the Chromatogram)

The calibration range for each compound was 0.05 – 40 ng/mL, with standards at 0.05, 0.25, 1, 4, 8 and 40 ng/mL. The internal standards were spiked into the standards and samples at a concentration of 2 ng/mL.

Figure 1 shows a typical chromatogram for a 16 ng/mL standard, and Figure 2 shows the compound information for PFOA (using $^{13}\text{C}_4$ PFOA as the internal standard) alongside a typical PFOA calibration curve.

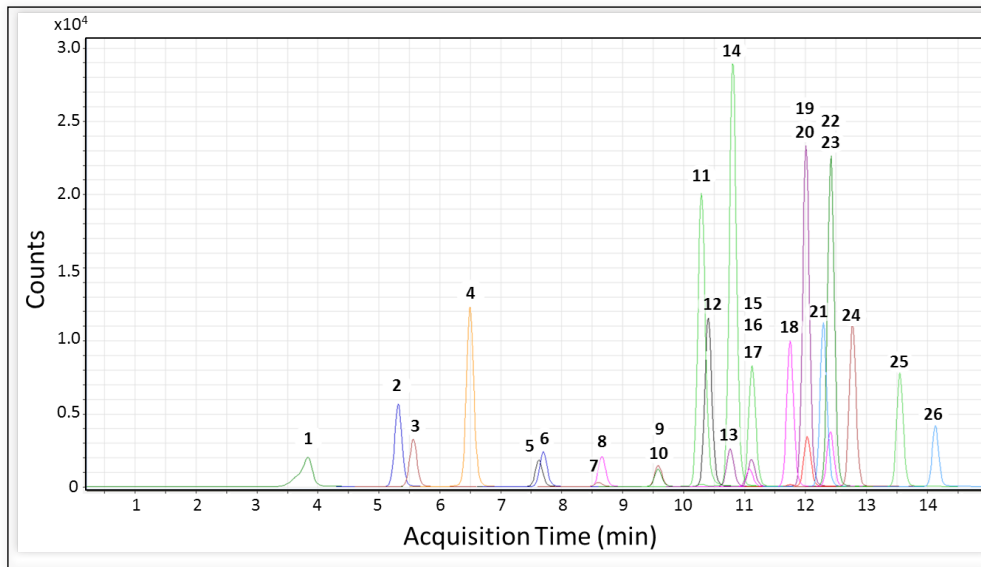


Figure 1. 16 ng/mL Standard Chromatogram (see Table 2 for the PFAS of the corresponding peak).

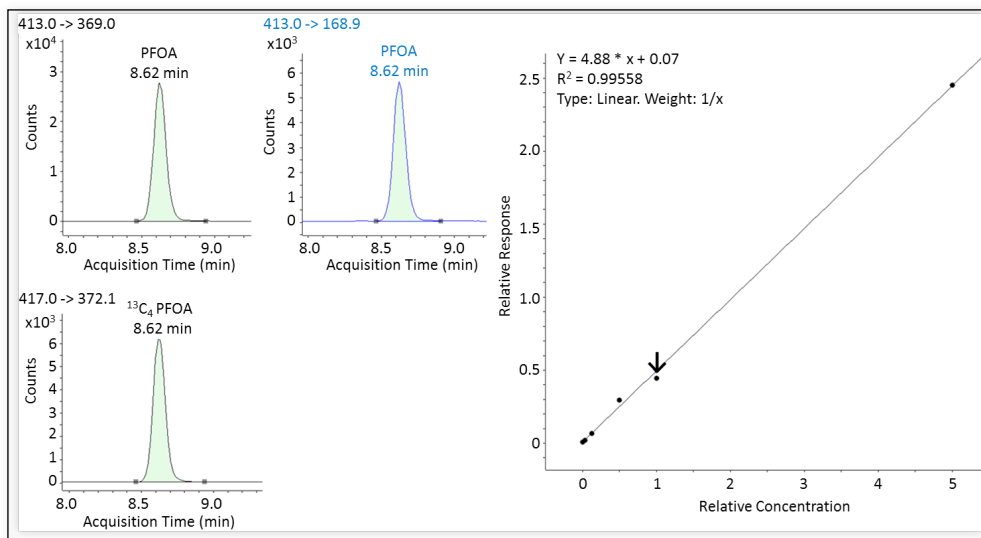


Figure 2. PFOA Compound Information and Calibration Curve (0.05 – 40 ng/mL).

A surface water sample chromatogram is shown in Figure 3. This sample contains a total of 10 different PFASs out of the 26 target compounds in this suite.

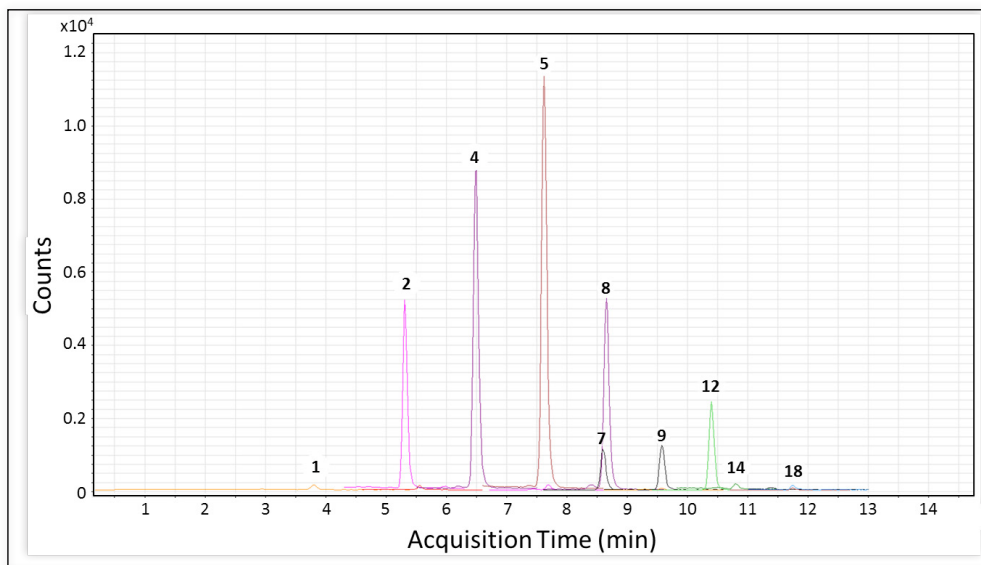


Figure 3. Surface Water Sample Chromatogram (see Table 2 for the PFAS of the corresponding peak).

CONCLUSIONS

A robust, sensitive method has been developed for the determination of 26 PFASs in water samples using SPE and analysis on the Agilent 6460 LC/MS/MS. This method demonstrates excellent linearity and sensitivity, with a calibration range of 0.05 – 40 ng/mL of concentrated extract, which is equivalent to 0.05 – 40 ng/L of unextracted water. The method achieves MDLs of less than 2 ng/L for all compounds.

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