

ENVIRONMENTAL ANALYSIS

TRACE LEVEL DETERMINATION OF PFOS, PFOA AND HBCD IN DRINKING WATER BY DIRECT AQUEOUS INJECTION ON THE AGILENT 6495 LC/MS/MS



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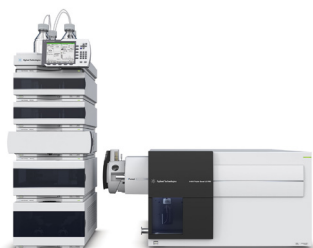
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ABSTRACT

A robust, sensitive method for the routine determination of PFOS, PFOA and HBCD in drinking water samples has been developed on the Agilent 6495 LC/MS/MS. Using direct aqueous injection, this method enables fast sample turnaround and reduces potential PFC and HBCD background contamination that can be an issue with conventional sample preparation techniques. The system comes equipped with an Agilent trapping column, further reducing any PFC and HBCD background that may be introduced through the LC system. This method achieves excellent linearity and precision over the calibration range of 0.25 – 50 ng/L.



INTRODUCTION

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) belong to a large group of manufactured chemicals called PFCs (perfluorinated chemicals), which are very persistent in the environment. PFOS has been used in a number of different industries, including the semiconductor and photographic industries, in some firefighting foams and in hydraulic fluids used in the aviation industry.

It has also been widely used in the past as a protective coating for materials such as carpets, textiles and leather, as well as in various household and industrial cleaning products. In the EU, the manufacture and use of PFOS is prohibited under Directive 2006/122/EC that came into force in June 2008 [1]. PFOA is still manufactured and is mainly used in the production of fluoropolymers, which are used in electronics, textiles and non-stick cookware.

Hexabromocyclododecane (HBCD) is a brominated flame retardant. Its main application is in expanded and extruded polystyrene insulation foam boards that are used for thermal insulation by the construction industry. It is also used in the back-coating of textiles, mainly for upholstered furniture. HBCD has undergone an EU risk assessment for environment and human health, which concluded that HBCD has Persistent, Bioaccumulative and Toxic (PBT) properties [2]. In May 2013, governments from around the world agreed to add HBCD to a list of 22 other substances that have been targeted for global elimination under the Stockholm Convention on Persistent Organic Pollutants [3]. It has also been identified as a substance of very high concern (SVHC) under the REACH procedure and from August 2015 its use will be restricted in the European Union [4].



These compounds may be released into the environment following their production or when products containing these chemicals are used by industry or consumers. They may also enter from landfill sites where products containing these chemicals have been sent for disposal.

This solution note gives an overview of a robust, sensitive method that was developed at the National Laboratory Service, Starcross and Agilent Technologies for the routine determination of trace levels of these compounds in drinking water, using direct aqueous injection on the Agilent 6495 Triple Quadrupole LC/MS.

ANALYTICAL TECHNIQUE

Sample Preparation

- Direct aqueous injection onto the Agilent Triple Quadrupole LC/MS

Instrumentation

- Agilent 1290 HPLC System
- Agilent 6495 LC/MS/MS with Jet Stream Interface

Agilent 1290 HPLC Operating Conditions

PFOS & PFOA Analytical Column	Agilent Eclipse Plus C18 2.1 x 100 mm, 1.8 µm
HBCD Analytical Column	Agilent Poroshell 120 Phenyl-Hexyl 2.1 x 100 mm, 2.7 µm
Trapping Column	Trapping Column – Agilent Poroshell 120 EC-C18 3 x 50 mm, 2.7 µm
Injection Volume	20 µL
Flow Rate	0.4 mL/min
Run Time	9.6 minutes

The trapping column was installed in place of the JetWeaver, located after the mixing point, to minimize delay volume increase and its purpose was to trap PFC/HBCD traces originating from the solvent system. Owing to this design the trapping column was regenerated from run to run avoiding the possible breakthrough of the trapped compounds over time. The introduced elution time delay between the interfering (higher RT) and target (lower RT) compounds allowed for the accurate determination of the target compounds.

RESULTS AND DISCUSSION

Direct Aqueous Injection

The use of direct aqueous injection eliminates the need for costly and time consuming sample preparation techniques. Smaller sample volumes are required to be taken and results can be obtained faster. The method should also be more reproducible as there are no extraction variables.

Another advantage is the reduction in PFC background contamination, as this can be introduced through extraction consumables, such as SPE cartridges. However, it should be noted that PFC background can also be introduced through the LC system and for this reason a trapping column was installed on the system.

PFOS and PFOA - Sensitivity, Linearity and Precision

The on-column sensitivity and linearity of the instrument were assessed by analysing PFOS and PFOA standards prepared in acetonitrile, with a calibration range of 0.25 – 50 ng/L. A large volume injection of 20 µL was used and the linearity was evaluated using the external standard calibration approach. The calibration curves for PFOS and PFOA are shown in Figure 1.

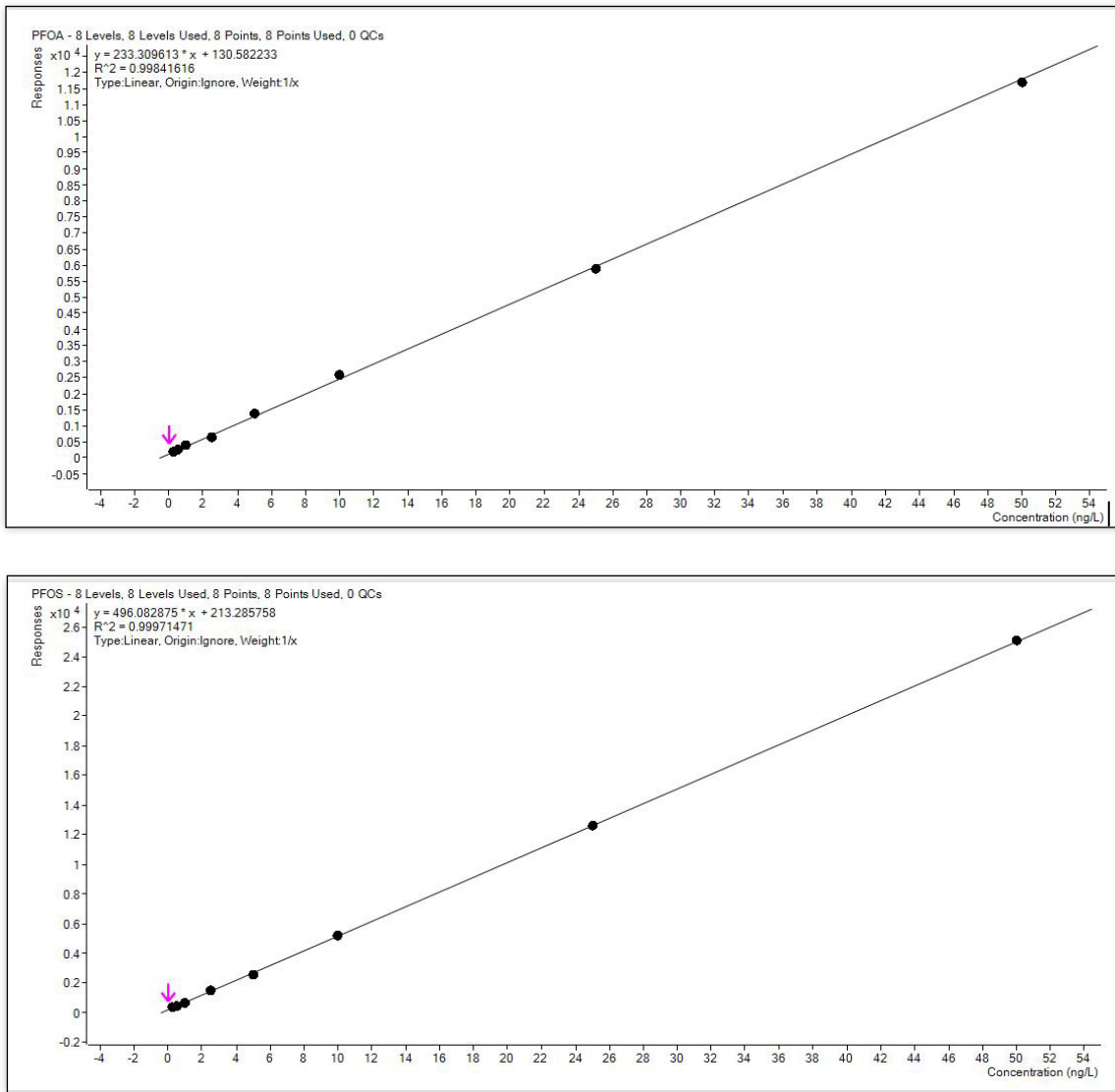


Figure 1. Calibration curves for PFOS and PFOA, standards at 0.25, 0.5, 1, 2.5, 5, 10, 25 and 50 ng/L.

Typical PFOS and PFOA chromatograms for the 1 ng/L standard are shown in Figure 2. The precision of the system was determined with seven replicate injections at low concentrations. The precision data for the 0.5 and 1.0 ng/L PFOS and PFOA standards are shown in Table 1.

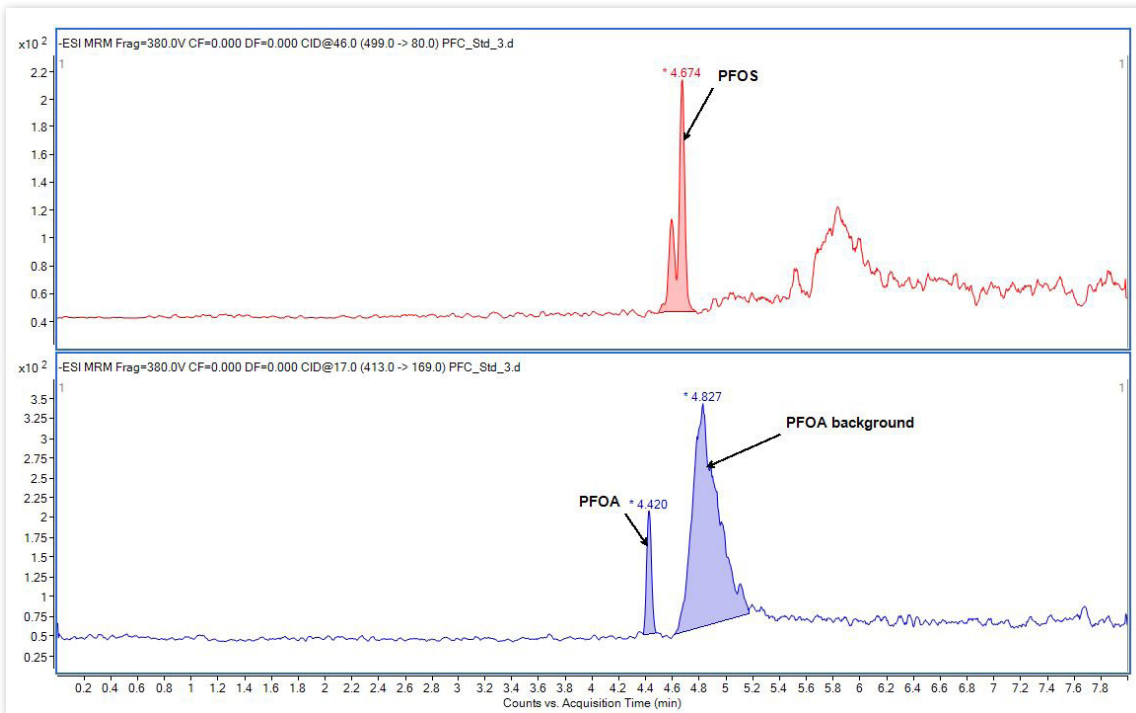


Figure 2. 1 ng/L PFOS and PFOA Standard Chromatograms showing separation of targets from background.

Compound	0.5 ng/L Standard		1.0 ng/L Standard	
	Average Area	% RSD	Average Area	% RSD
PFOS	423.3	5.3	668.3	4.9
PFOA	280.1	5.0	387.7	4.4

Table 1. PFOS and PFOA Precision Results.

HBCD - Sensitivity, Linearity and Precision

The on-column sensitivity and linearity of the instrument were assessed by analysing HBCD (alpha, beta and gamma isomers) standards prepared in acetonitrile, with a calibration range of 0.25 – 50 ng/L. A large volume injection of 20 μ L was used and the linearity was evaluated using the external standard calibration approach. The calibration curve for alpha-HBCD is shown in Figure 3. Those for beta-HBCD and gamma-HBCD are very similar, with correlation coefficients also greater than 0.995.

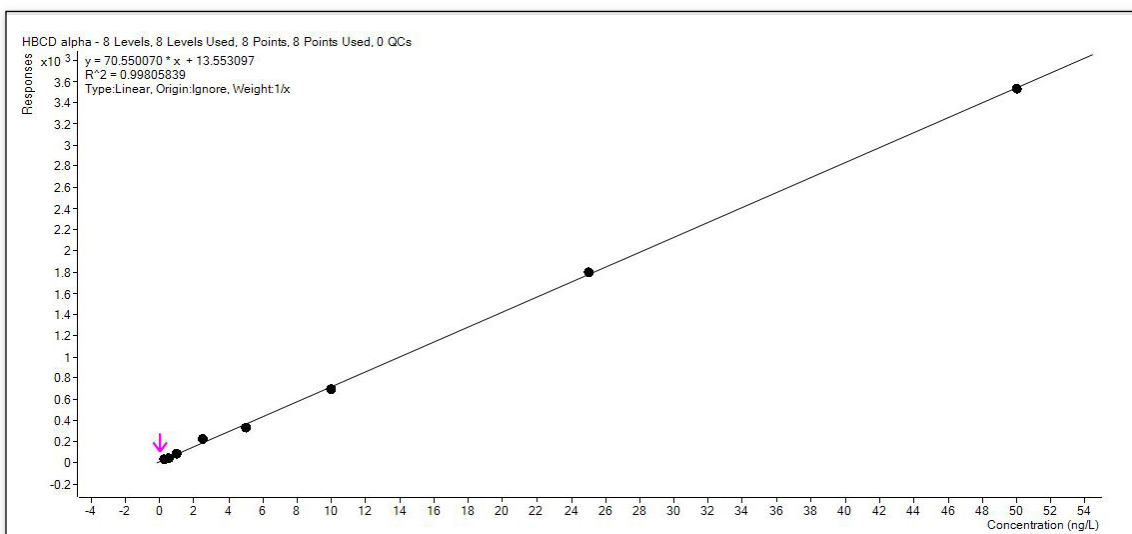


Figure 3: Calibration curve for alpha-HBCD, standards at 0.25, 0.5, 1, 2.5, 5, 10, 25 and 50 ng/L.

A typical chromatogram for the HBCD isomers at 1 ng/L is shown in Figure 4. The precision of the system was determined with seven replicate injections at low concentrations. The precision data for the 1 and 2.5 ng/L HBCD standards are shown in Table 2.

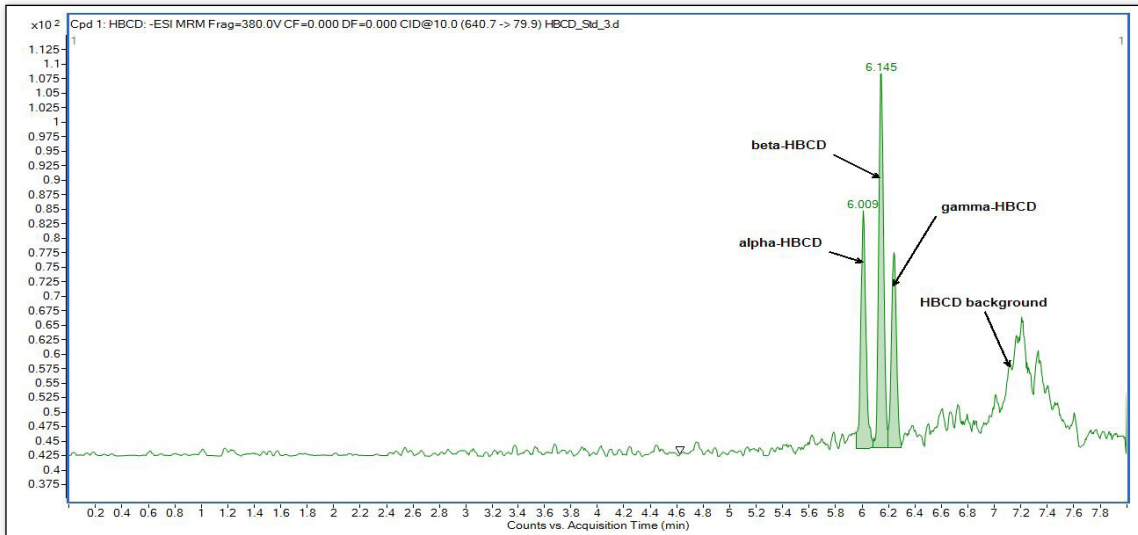


Figure 4. 1 ng/L HBCD Standard Chromatogram showing separation of targets from background.

Compound	1.0 ng/L Standard		2.5 ng/L Standard	
	Average Area	% RSD	Average Area	% RSD
Alpha HBCD	97.4	6.2	235.2	4.9
Beta HBCD	156.4	5.3	354.7	1.5
Gamma HBCD	94.8	10.4	185.2	4.5

Table 2. HBCD Precision Results.

CONCLUSIONS

A robust, sensitive method has been developed for the determination of PFOS, PFOA and HBCD in drinking waters using direct aqueous injection on the Agilent 6495 LC/MS/MS. Using an injection volume of 20 μ L, this method achieves excellent linearity and precision over the calibration range of 0.25 – 50 ng/L.

REFERENCES

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