

IMPROVED SENSITIVITY FOR THE DETECTION OF PER- AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS) USING DIRECT INJECTION METHOD ON THE WATERS XEVO™ TQ ABSOLUTE

INTRODUCTION

The determination of per- and polyfluorinated alkyl substances (PFAS) is an essential part of water analysis today. The requirements for sensitivity for the detection of PFAS are extremely demanding since the regulations in Europe for the quality of drinking water ground water and surface waters include mandatory parametric values and environmental quality standards for a selection of PFAS at extremely low concentrations (pg/L to ng/L). In the following article, we describe how highly sensitive LC-MS/MS technologies and mitigation of background contamination help to check for compliance with these challenging limits using a direct injection approach.

Regulatory framework for PFAS in water in Europe

In Directive (EU) 2020/2184 of 16 December 2020 on the quality of water intended for human consumption (the recast Drinking Waters Directive - DWD), new parameters were specified for the first time that defined limits for PFAS compounds in drinking water in Europe.¹ A parametric value of 0.1 µg/L was applied to the "sum of PFAS", a group of PFAS considered a concern as regards water intended for human consumption, namely 20 selected carboxylic and sulfonic acids with chain lengths from C4 to C13 listed in point 3 of Part B of Annex III. Preserving and improving the quality of surface water is a declared goal of the European Directive 2000/60/EC (the Water Framework Directive - WFD), which established a framework for Community action in the field of water policy.² Directive 2013/39/EU subsequently amended earlier legislation regarding priority substances and defined various types of Environmental Quality Standards (EQS) for PFOS and its derivatives.³ The term "derivatives" is used to refer to any or all of the substances which contain the PFOS moiety and may break down in the environment to give PFOS. The annual average (AA) EQS in freshwater is extremely low at 0.65 ng/L whereas the maximum allowable concentration (MAC) for PFOS for inland surface waters is much higher (36 µg/L). To check compliance with the limits and standards, sensitive, accurate and reliable methods are required.

Two analytical approaches have been used to reach detection limits low enough to check compliance with regulatory requirements: with and without a sample clean-up/analyte enrichment step. With the former, water samples can be subjected to solid-phase extraction (SPE), typically using a weak anion exchange sorbent (eg Oasis™ WAX). However, reliance on SPE for enhanced sensitivity has some disadvantages. It adds to the cost of the analysis in terms of the need for extra consumables and additional time. SPE can also be a source of PFAS contamination, concentrated by evaporation of the solvents and leaching from the sorbent, which has a negative impact on the performance of the method. The alternative to SPE is direct injection of the water sample on to the LC-MS/MS system, which avoids one source of contamination and results in a quicker overall method, and which could also lead to increased sample throughput as well as less solvent waste. However, the sensitivity of the LC-MS/MS system selected needs to be sufficient for the detection of PFAS at the extremely low levels without any enrichment or clean-up steps.

A direct injection method was developed for the practical implementation of this requirement, which achieves a limit of quantification of 0.001 µg/L for the individual substances. Various factors played a role in the development of the method in order to reach ultimate sensitivity in routine sample analysis.

Action to mitigate background contamination issues

PFAS from fluoropolymers and coating are ubiquitous in common

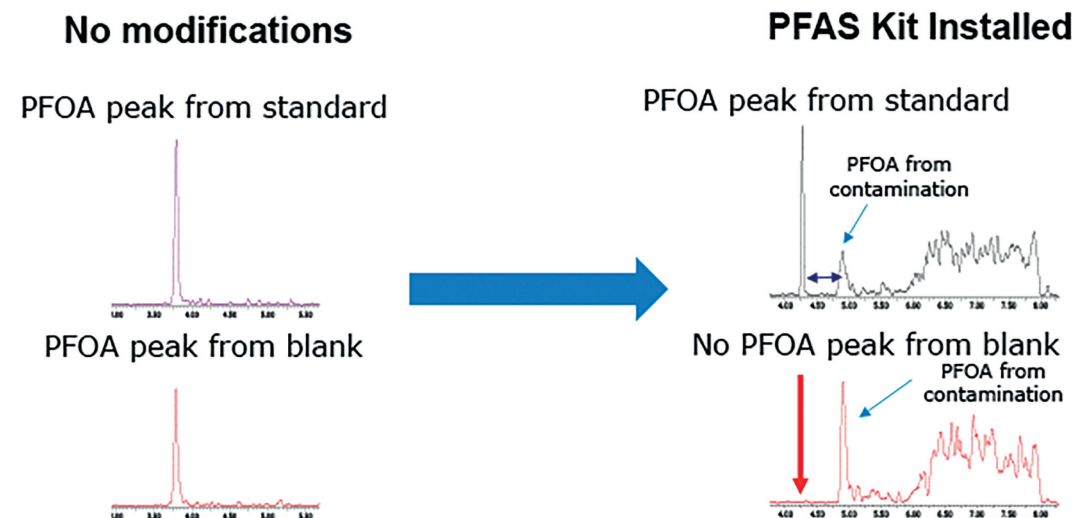


Figure 1: delay mechanism with the PFAS kit

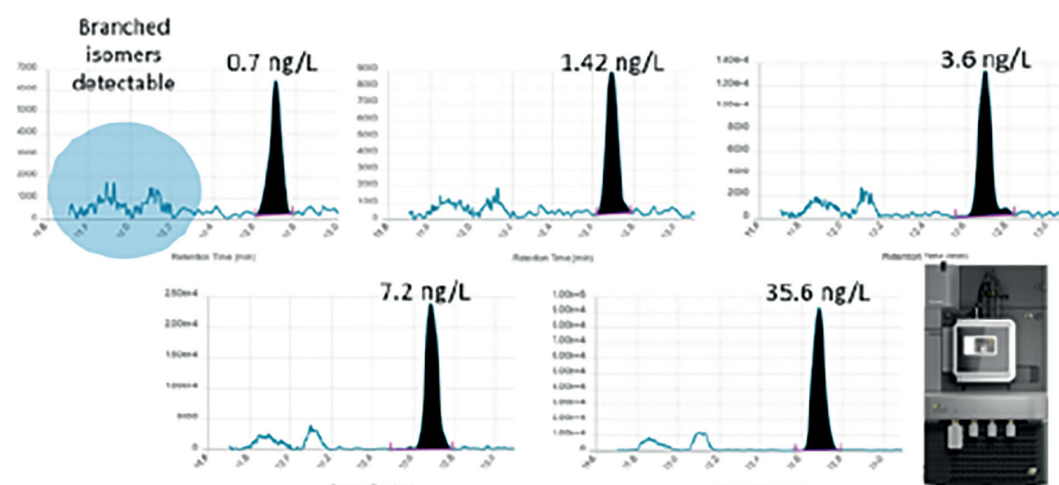


Figure 2: PFOS in wastewater influent at various spiked concentrations

sampling and analytical equipment and can easily contaminate solvents and reagents. Hence, laboratory contamination is common and near impossible to eliminate. Background issues with perfluorobutane sulfonic acid and its potassium salt (PFBS) are extremely common. Such contamination can lead to reporting of false positives and/or higher reporting limits due to elevated background. It is essential to take steps to try to mitigate this contamination:

- Avoid all products likely to contain fluoropolymers – eg vials with Teflon seals
- Minimise risks from contaminated dust and air

- Screen all analytical consumables, solvents and reagents including water purifying systems
- Carry out extensive use of procedural blanks from sample storage all the way through the LC-MS/MS step
- Implement traceability systems for the consumables used in the laboratory

To exclude contaminations from the LC system, it can be modified with a PFAS Installation Kit. This establishes a complete flow path for analysis of PFAS-containing samples while minimizing interference from background contamination. It involves removing and replacing components such as some

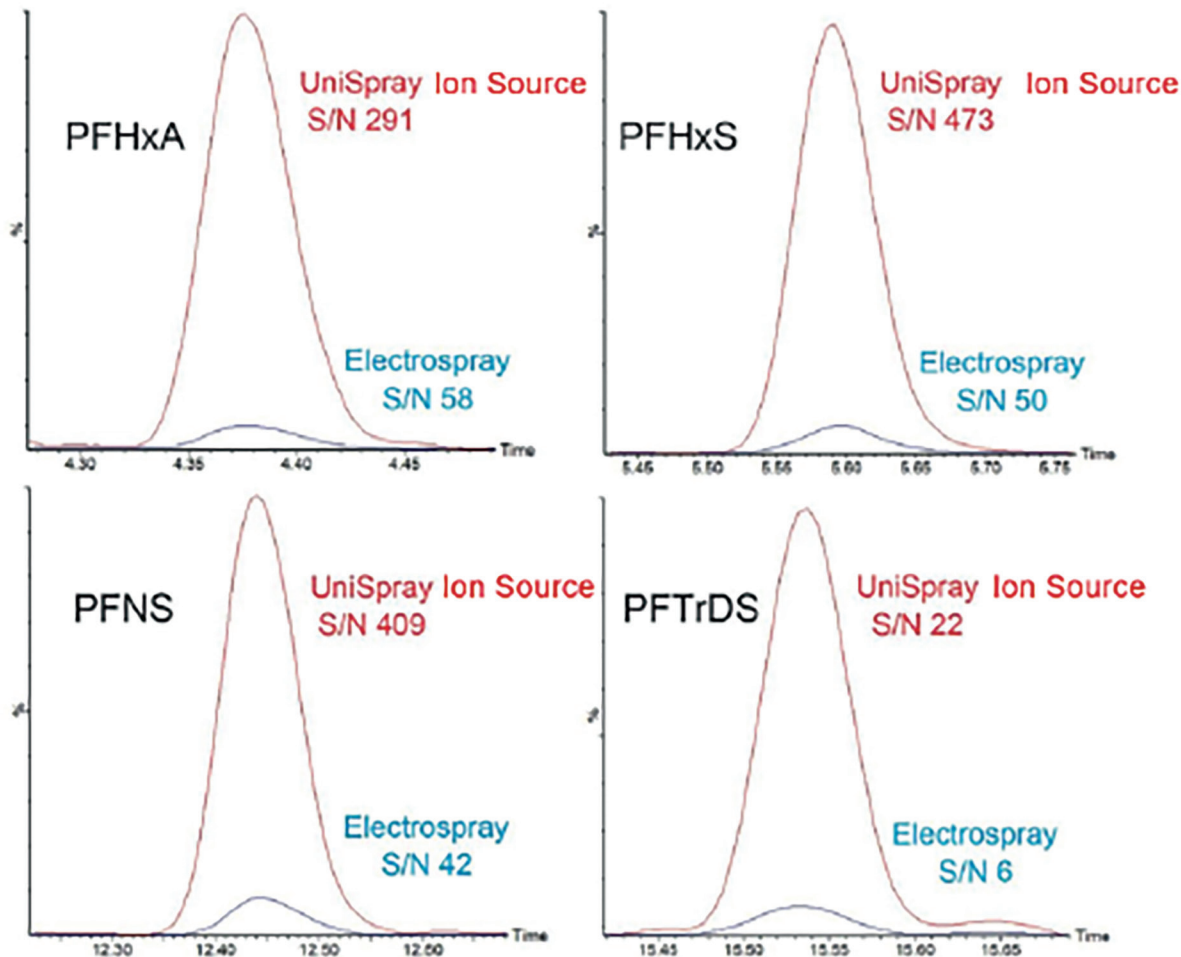


Figure 3. Signal to noise and peak response comparison between UniSpray Ion Source (red) and Electrospray (blue) ionization techniques demonstrated at 2 ng/L in hard water (average S/N).

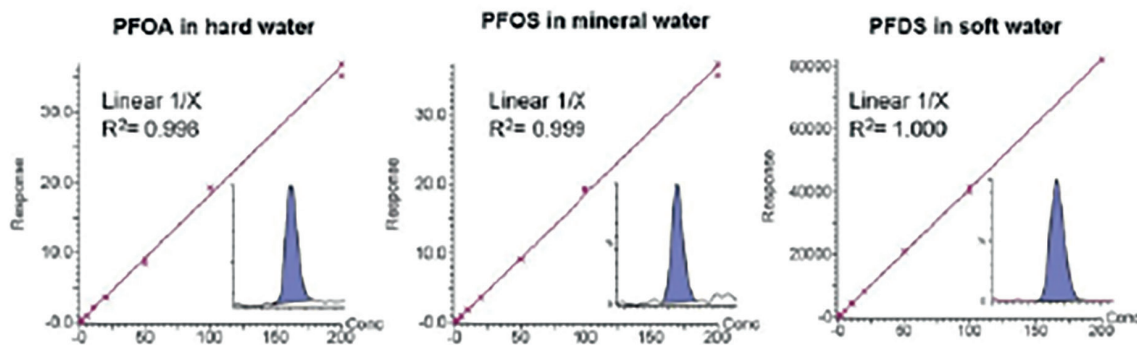


Figure 4. Bracketed matrix-matched calibration curves for a selection of PFAS at 1 ng/L to 200 ng/L (0.6 ng/L to 120 ng/L in vial concentration), including chromatograms for the quantitative transitions at 1 ng/L. All residuals are within 20% of nominal values.

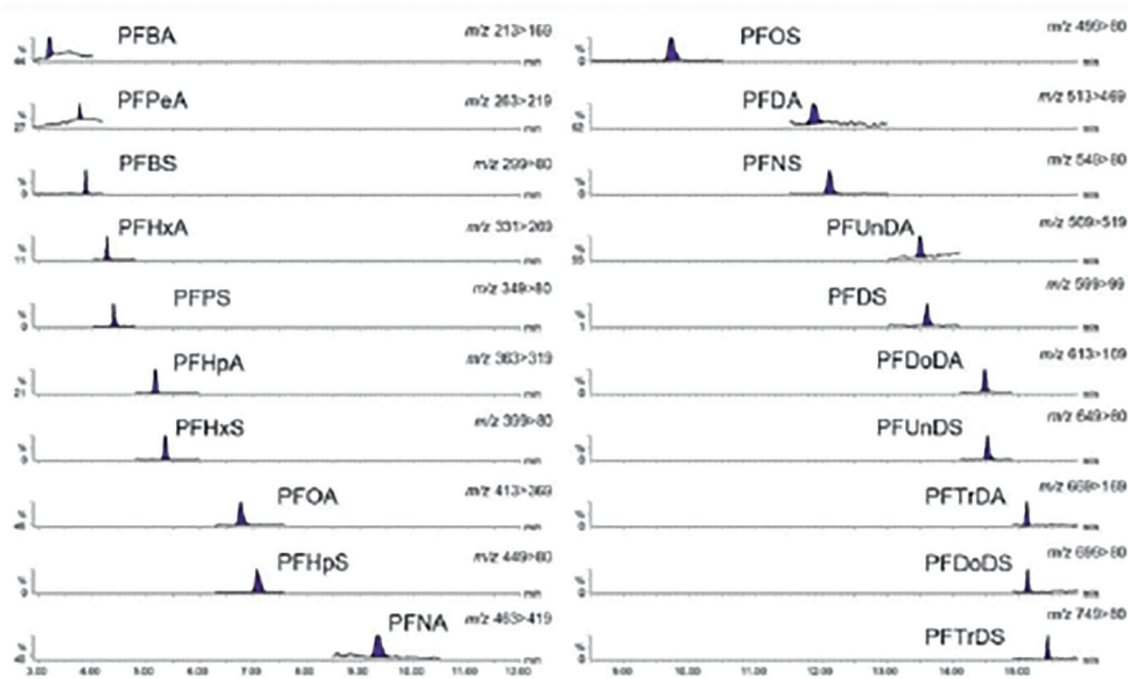


Figure 5. Typical chromatograms for the 20 PFAS listed in EU 2020/2184 Part B of Annex III at 1 ng/L in water.

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tubing assemblies that contain known PFAS and separating any unavoidable interference from sources such as mobile phase by delaying their signal from the sample using an isolator column.

Improve detection and sensitivity with the Xevo TQ Absolute or switching to the UniSpray™ Ion Source

The direct injection approach for PFAS analysis requires a highly sensitive mass spectrometer to reach necessary performance criteria. The enhanced negative ion sensitivity of the Xevo TQ Absolute tandem quadrupole mass spectrometer allows for utilization of the direct injection method for PFAS analysis with a reduced sample injection volume of 10 µL without compromise to method performance. Figure 2 shows some chromatograms to illustrate the detection of PFOS and its branched isomers in wastewater at 0.7 ng/L.

An alternative option is to switch from electrospray to the novel UniSpray source. UniSpray or impactor ionization is a novel atmospheric ionization technique that makes use of a high-velocity spray, created from a grounded nebulizer impacting on a high-voltage target (stainless steel rod), to ionize analytes in a similar fashion to electrospray but promotes extra droplet break-up and desolvation via additional Coanda and vortex effects. A direct comparison was carried out to evaluate the relative sensitivity of each ionization source for PFAS analysis. The UniSpray ion source displayed consistent gains in sensitivity for all compounds, measured by comparing peak area, peak height, and signal to noise (see Figure 3). Although PFAS respond well using electrospray ionization in negative ion mode, UniSpray was shown to exhibit consistent gains in sensitivity for all twenty PFAS and offers a practical alternative to check compliance with water regulations for PFAS.

Method performance

We have previously reported the development of a direct injection method for PFAS suitable for checking compliance with the 2020 EU Drinking Water Directive.⁴ A limit of quantitation (LOQ) of 0.001 µg/L was achieved for each individual PFAS to be confident of implementing the 0.1 µg/L sum of the twenty PFAS limit, without the need for any pre-concentration steps. The method used an ACQUITY Premier BEH™ Shield RP18 Column on an ACQUITY™ UPLC I-Class PLUS System with Xevo TQ-XS Tandem Quadrupole Mass Spectrometer and the unique UniSpray ion source. In addition, the novel MaxPeak™ High Performance Surfaces (HPS) technology of the ACQUITY Premier UPLC Column provided an increase in sensitivity for the longer-chain PFAS. Subsequently, we reported the results of an interlaboratory study to assess the ease of implementation of the method and to further evaluate the performance of the method.⁵ Each laboratory successfully implemented the method, including installation of the ACQUITY UPLC PFAS Kit, using the start-up guide, and demonstrated stable chromatography and satisfactory sensitivity. Participants demonstrated good accuracy for the quantification of the PFAS except PFBA in a water. Trueness was shown to be between 96 and 100%, and values for repeatability within each laboratory and reproducibility between laboratories were all <20%. All but three laboratories experienced issues relating to contamination with PFBA. This study confirms that this direct injection UPLC-MS/MS method can be implemented in multiple laboratories and is suitable for checking drinking water supplies for compliance with various regulatory and advisory limits globally. Figure 4 also shows typical calibration graphs and Figure 5 chromatograms for compounds injected at 1 ng/L concentration in water.

Conclusions

Detection requirements for per- and polyfluorinated alkyl substances (PFAS) have been getting more challenging as regulations to protect consumers and preserve the environment continue to be created and updated. The demand for sensitive solutions for direct injection to determine PFAS has also increased, since time-consuming sample preparation with SPE and the risk of contamination can be avoided. Using ACQUITY UPLC fitted with the PFAS Installation Kit and the novel UniSpray ion source or the performance of the new Xevo TQ Absolute, it is possible to obtain sufficient performance using direct injection of water samples to check compliance with regulations for PFAS in water.

References,

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