Critical Insights in the detection of PFAS in our environment: A deeper look at various methods in water samples

1 Introduction

Per- and polyfluoroalkyl substances (PFAS) represent a diverse group of synthetic fluorinated organic compounds that have been produced and widely used in industrial applications and consumer products since the 1930s. Common applications where PFAS are used include surfactants, fire-fighting foams, nonstick cookware coatings, lubricants, and coatings for food packaging. Because of their wide use, testing of various sources including drinking water is of great importance to mitigate potential risks to our health and the environment.

The work presented will demonstrate a PFAS method capable of accommodating the different global regulations while at the same time offering high-performance solutions to optimize your laboratory workflows, e.g., direct injection or even sample preparation. Global regulations and sometimes their standardized methods require various sample preparation steps to reach the required detection limits. In the work presented we will focus on the new European Union Water Framework Directive 2020/2184, but the method can also be adapted for various regulation (EPA, ISO and EU). The method described here is a comprehensive solution including all details related to the LC and MS methods. Moreover, it provides details on the necessary steps to prevent any possible contamination arising, by using PerkinElmer's PTFE-free injection kit. The data presented here is a method validation over three separate days showing recoveries within 70-130 % for spiked drinking water and bottled mineral water samples at 2 ng/L, 10 ng/L and 100 ng/L. Moreover, a linear range for most PFAS was achieved from 0.5-100 ng/L demonstrating the sensitivity of the method and giving a sum of all 20 LOQs to be 24.5 ng/L, which is 4x lower than the 100 ng/L parametric value set by the 2020/2184 directive.

Key Points

- Complete LC/MS/MS solution covering PFAS analysis in drinking water
- Full LC and MS method details included
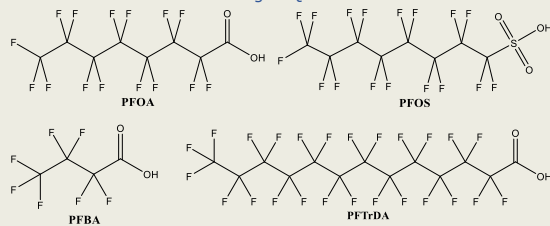- Overview of results including LOQs and recoveries

Figure 1: Examples of the various PFAS covered in the different regulations.

2 Materials and Methods

Hardware and Software

The chromatographic separation and subsequent detection were carried out using the LX50 ultra high-performance liquid chromatograph (UHPLC) and the QSight® 420 series triple quadrupole tandem mass spectrometer, respectively. The LX50 Autosampler was modified by replacing all polytetrafluoroethylene (PTFE) based tubing with polyether ether ketone (PEEK) tubing to reduce or eliminate any contamination from PFAS compounds introduced from the PTFE tubing (Figure 2).
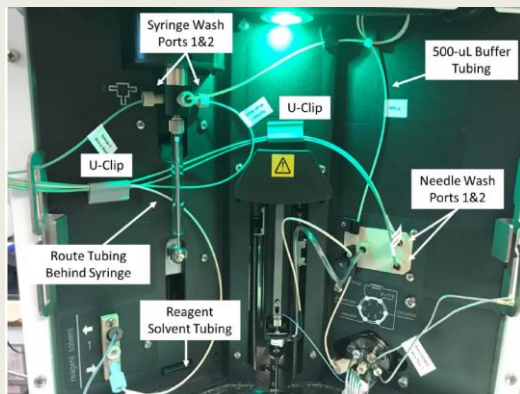

Figure 2: QSIGHT™ LX50 PTFE Free Injection Kit showing the various lines that are exchanged on the autosampler

Table 1: UPHLC parameters

UHPLC conditions	
LC Column	Brownlee SPP C18 100x4.6 mm, 2.7 μm (N9308416)
Delay Column	Brownlee SPP C18 50x3 mm, 2.7 μm (PN: N9308408)
Solvent A	10 mM Ammonium acetate in Water
Solvent B	Methanol
Flowrate	0.8 mL/min
Column oven temp.	40°C
Injection volume	100 uL

Method Parameters

The LC method is shown in Table 1. MS source parameters are presented in Table 2. Drying and nebulizer gas flow and temperature settings were optimized by flow injection analysis (FIA) for the MS source conditions.

Table 2: MS parameters

MS Source parameters	
ESI negative voltage	-4000 V
Drying gas	80
Nebulizing gas	400
Source temp.	400°C
HSID Temp.	275°C
Detection mode	MRM

3 Results and Discussion

To evaluate the performance of the method, calibration curves were generated for the 20 different PFAS compounds on three separate days. Example chromatograms, from day one, are shown in Figure 2. The calibration standards range from 0.5-100 ng/L and each of the 20 PFAS demonstrated excellent linearity with regression coefficients (R2) of $\geq$ 0.99, which is also shown in Table 3. Moreover, to show the separation and peak shape for all 20 PFAS, Figure 3 represents a sample chromatogram at 25 ng/L.
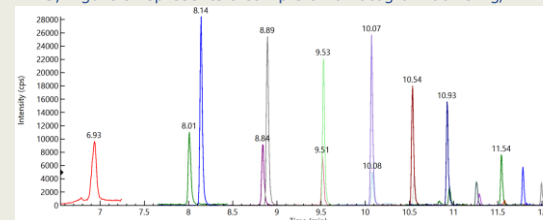

Figure 3: Overlay of the 20 PFAS quantifier fragments at 25 ng/L.

Figure 4 shows chromatograms at the LOQ. Over 60% of the 20 PFAS have a LOQ of 0.5 ng/L, easily achieving the new limits put for by the EU Drinking Water Directive 2020/2184. Table 4 further details the entire dataset for the method, first displaying the LOQs for each compound with a total of 24.5 ng/L putting it 4x lower than the parametric value of 100 ng/L. Moreover, recovery experiments were also conducted on three different days with freshly prepared calibration standards and spiked water samples each injected five times. Table 4 shows all recoveries are within the acceptable limits (70-130%).
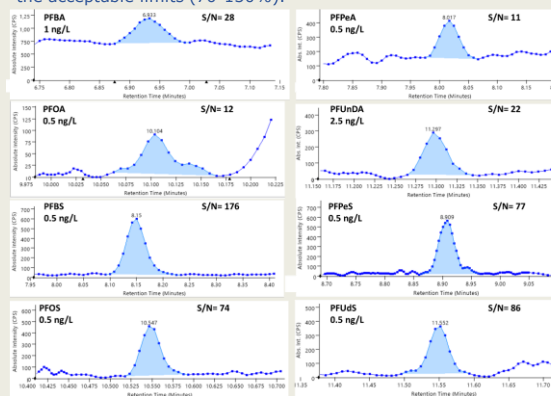

Figure 4: Example chromatograms at the LOQ for various PFAS along with the calculated S/N.

Table 3. Details the entire results pertaining to the calibration-curve, LOQ and recoveries in both drinking water and mineral water. The recovery experiments were done on three separate days with 5 injections of each spiked level per day, giving an n=15.

Analyte	Calibration Curve			Drinking Water			Mineral Water		
	LOQ	Linear Range	Linearity	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)
	(ng/L)	(ng/L)	(R²)	Spiked 2 ng/L	Spiked 10 ng/L	Spiked 100 ng/L	Spiked 2 ng/L	Spiked 10 ng/L	Spiked 100 ng/L
PFBA	1	1 - 100	0.9923	107	117	106	118	113	106
PFPeA	0.5	0.5 - 100	0.9933	114	110	110	114	113	107
PFBS	0.5	0.5 - 100	0.9929	118	113	109	109	115	106
PFHxA	0.5	0.5 - 100	0.9915	106	109	107	112	114	107
PFPeS	0.5	0.5 - 100	0.992	111	110	106	105	112	104
PFHpA	0.5	0.5 - 100	0.9946	113	110	108	117	112	107
PFHxS	0.5	0.5 - 100	0.994	122	114	110	104	116	108
PFOA	0.5	0.5 - 100	0.9963	119	110	108	120	115	108
PFHpS	0.5	0.5 - 100	0.998	115	115	113	114	117	110
PFNA	1	1 - 100	0.9981	103	107	111	104	111	111
PFOS	0.5	0.5 - 100	0.9927	110	111	109	113	114	108
PFDA	2.5	2.5 - 100	0.9979	-	117	113	-	112	113
PFNS	0.5	0.5 - 100	0.996	117	125	124	118	119	116
PFUnDA	2.5	2.5 - 100	0.9918	-	105	107	-	103	100
PFDS	1	1 - 100	0.9946	107	126	130	102	110	117
PFDoDA	5	5 - 100	0.9967	-	93.6	108	-	91	96
PFUdS	0.5	0.5 - 100	0.9972	120	114	125	120	109	106
PFDoS	0.5	0.5 - 100	0.9905	107	113	125	102	106	101
PFTrDA	5	5 - 100	0.997	-	102	120	-	100	107
PFTrDS	0.5	0.5 - 100	0.998	94	114	129	91	90	90
QSight LOQ	24.5								

Conclusion

A large volume direct injection method covering the 20 newly listed PFAS, according to the EU Drinking Water Directive 2020/2184, was successfully established and showcased. The method sensitivity and robustness were demonstrated in the three-day experimental setup showing excellent recoveries, linearities and extremely low LOQs for each compound. This clearly shows that the PerkinElmer QSight LC/MS/MS system is fit for purpose when it comes to PFAS analysis. One reason for the excellent sensitivity is the low background noise observed for each these compounds along with minimal contamination. The lack of contamination can be attributed to the PTFE-Free injection kit, where the autosampler is refitted with PEEK lines and a delay column separates any possible contamination. Moreover, the extremely low background can simply be linked to the design of the QSight as it is a flow-based mass spectrometer which not only allows for maximum ion formation, but also reducing any potential chemical noise. Overall, the QSight's combination of sensitivity, versatility, and reliability make it an excellent choice for PFAS analysis in EU drinking laboratories.

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