



Quantitation of PFAS in Water by LC-HR-QTOF MS/MS

Abstract

This study demonstrates the utility of high-resolution mass spectrometry for the direct analysis and quantitation of numerous PFAS in water samples collected within Northern Europe using the Bruker Elute UHPLC

coupled to the Bruker impact II VIP QTOF system. Concentrations above current EU regulatory limits and proposed US EPA limits were identified in two samples.

Keywords:

PFAS; water; impact II VIP QTOF; VIP-HESI; Elute UHPLC; TASQ

Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a diverse group of extensively used industrial chemicals. They are classified as persistent pollutants, with known environmental accumulation and global circulation. Due to their suspected toxicity, they are a growing threat to both humans and wildlife, and thus their analysis is an increasingly important task for analytical chemists. Global regulations for PFAS in food and drinking water differ widely and are constantly evolving. The EU Directive 2020/2184 for drinking water, e.g., requires a limit of 500 ng/L for the total amount of all PFAS in a sample and 100 ng/L for the sum of twenty specific PFAS of highest health risk. Currently proposed US EPA regulations would limit PFOA and PFOS to a Maximum Contaminant Level (MCL) of 4 ng/L. HFPO-DA, PFBS, PFNA, and PFHxS are proposed to be quantitated together according to a Hazard Index, with "health-based value" thresholds of 10, 2000, 10, and 9 ng/L, respectively.

In many laboratories, PFAS are quantitated via liquid chromatography coupled to triple

quadrupole (TQ) mass spectrometers. Here, we present a method to quantify PFAS in water using a time-of-flight (QTOF) mass spectrometer. In addition to the rapid, automated, and confident detection of expected and targeted PFAS compounds, analysis via this high resolution QTOF system offers the unique potential to detect unexpected or novel PFAS via retrospective reviewing of data sets. An unlimited number of compounds may be targeted in each run, and processing methods may be easily extended to include new PFAS compounds, providing flexibility for current and future regulatory criteria.

This work describes the direct analysis of fourteen common household and environmental water samples using a Bruker Elute UHPLC, with specific components modified to avoid potential system-related PFAS contamination, coupled to a Bruker impact II VIP QTOF MS. With no sample concentration or pretreatment, seven PFAS compounds were quantified in eight of the water samples, with two samples containing hazardous levels of specific PFAS.

Rafaela Martin and Andrea Kiehne, ; Bruker Daltonics GmbH & Co. KG, Bremen, Germany

Experimental

The system configuration and instrumental parameters are shown in Table 1.

For accurate sample analysis, it is essential to use a Teflon-free system to avoid PFAS contamination originating from the instrumentation. The UHPLC used for this study was equipped with an Elute PFAS kit (Bruker part # 1894795). The kit includes a delay column, which was installed between the pump and the autosampler to retain system-related PFAS, as well as PEEK equivalents of all possible PTFE system components.

For the preparation of the calibration solutions, PFAS standards (EPA 533 PAR, Wellington Laboratories, Ontario, Canada) were diluted in bottled LC-MS grade water. For the determination of method reproducibility, five technical replicates of medium (4 ng/L) and high (40 ng/L) concentrations of PFAS spiked into LC-MS grade water were measured.

Fourteen varied water samples (tap waters, bottled mineral water, ground waters, and surface waters from the Baltic Sea, North Sea, rivers and harbours) were collected for analysis (Figure 1). Samples were collected and stored in 50 mL polypropylene tubes. Samples were centrifuged (10 minutes at 1400 rpm) prior to transfer to polypropylene UHPLC vials, from which 200 μ L were injected via autosampler.

Data processing and reviewing was performed with Bruker's cross-platform TASQ® software. Compound identification was based on retention time, exact mass, diagnostic fragmentation ions, and the isotope pattern fit, with color coding of screening results and flagging based on customizable evaluation rules (Figure 2).

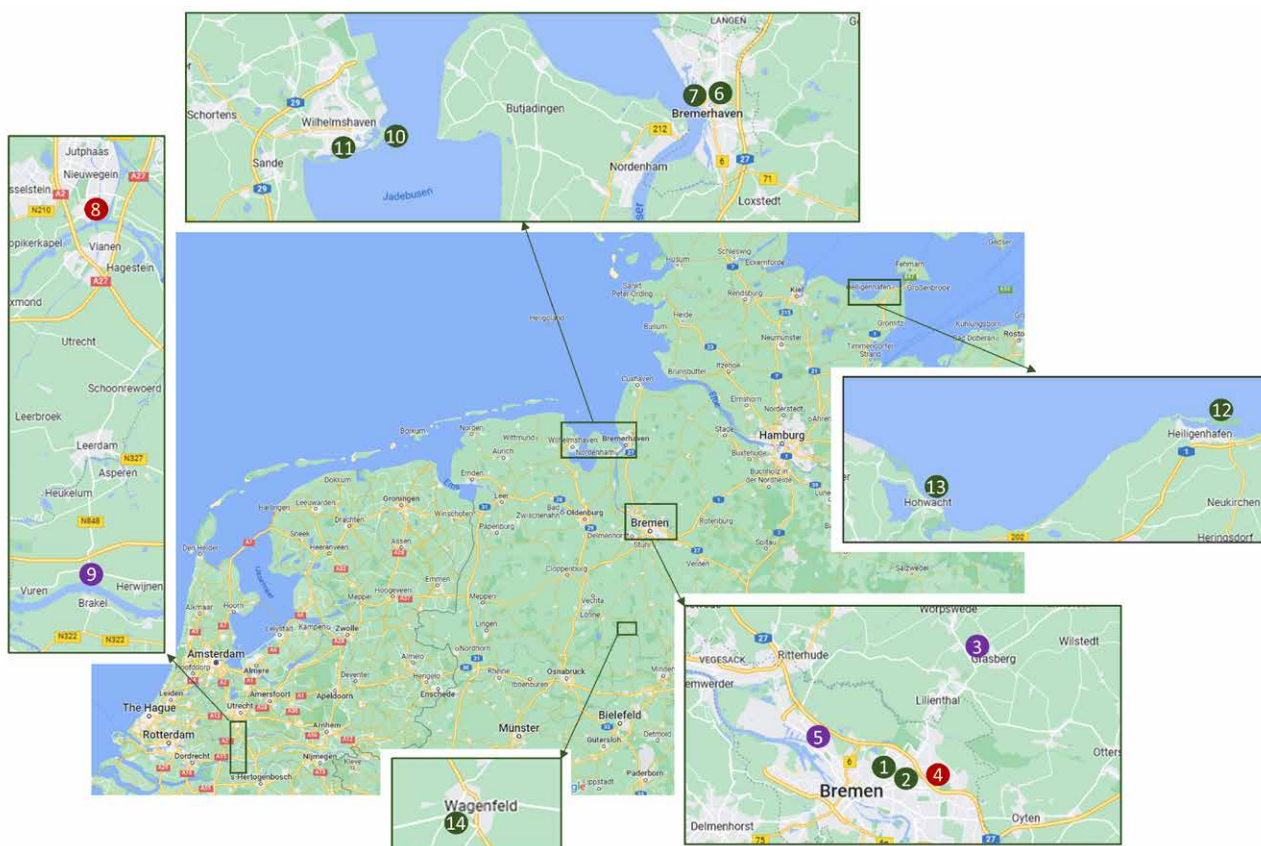


Figure 1.

Water sampling locations. Samples containing PFAS above current EU regulatory limits are shown in red.

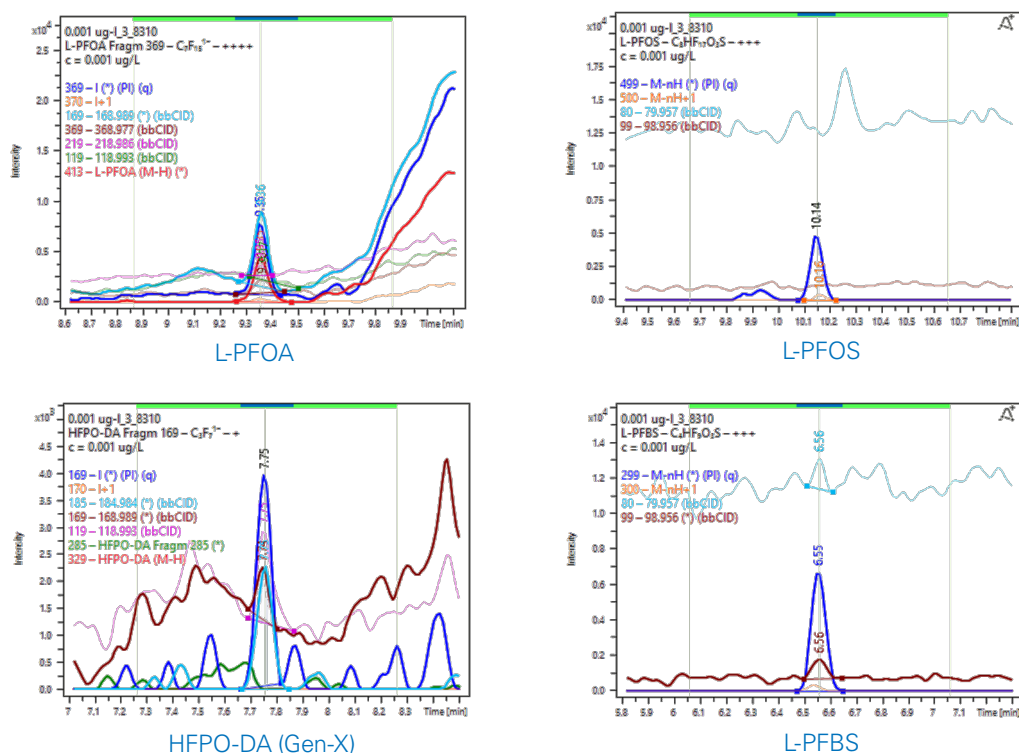
Samples containing PFAS at levels of concern are shown in purple (see Table 3). [Google Maps (2023), maps.google.com]



Table 2. Calibration data and results of reproducibility measurements. Specific PFAS target detection meets current EU regulatory requirements according to EU Directive 2020/2184.

Analyte	RT [min]	R ²	LOD [ng/L]	LOQ [ng/L]	calibration range [ng/L]	RSD @ 4 ng/L [%]	RSD @ 40 ng/L [%]
3,6-OPFHpA	7.48	0.9962	<0.5	1.0	1 - 500	2.1	5.4
4:2 FTS	7.56	0.9992	0.5	1.0	1 - 1000	1.5	1.7
6:2 FTS	9.52	0.9973	2.5	2.5	2.5 - 500	7.0	2.9
8:2 FTS	11.08	0.9951	10.0	10	10 - 1000	12.4	8.7
9Cl-PF3ONS	10.73	0.9992	1.0	2.5	2.5 - 500	7.6	8.8
ADONA	8.76	0.9992	<0.5	0.5	0.5 - 500	1.8	1.6
HFPO-DA	7.97	0.9933	1.0	1.0	1 - 500	1.7	4.4
L-PFBS	6.73	0.9911	0.5	0.5	0.5 - 500	2.1	3.0
L-PFHpS	9.57	0.9994	0.5	0.5	0.5 - 500	15.3	4.8
L-PFOA	9.58	0.9994	1.0	1.0	1 - 500	5.0	2.8
L-PFOS	10.35	0.9967	1.0	1.0	1 - 500	13.0	6.3
L-PFPeS	7.74	0.9994	0.5	0.5	0.5 - 500	1.7	0.3
PF4OPeA	5.91	0.9949	0.5	0.5	0.5 - 500	2.8	1.8
PF5OHxA	6.92	0.9988	0.5	1.0	1 - 500	2.4	1.4
PFBA	5.52	0.9961	1.0	2.5	2.5 - 500	1.0	1.8
PFDA	11.08	0.9990	1.0	2.5	2.5 - 500	8.6	7.1
PFEESA	7.16	0.9913	<0.5	1.0	1 - 500	1.9	0.8
PFHpA	8.67	0.9911	0.5	5.0	5 - 500	1.6	1.5
PFHxA	7.67	0.9952	0.5	0.5	0.5 - 500	1.2	3.6
PFHxS	8.70	0.9998	1.0	1.0	1 - 500	3.2	1.4
PFNA	10.38	0.9991	0.5	1.0	1 - 500	16.2	4.8
PFPeA	6.60	0.9903	0.5	1.0	1 - 500	1.9	3.0

Figure 3. Chromatograms of example PFAS at 1 ng/L, exceeding current EU and proposed US sensitivity requirements for PFAS of highest risk to human health.



Tools you can trust for PFAS analysis

- Accuracy in PFAS quantitation begins with an awareness of their current ubiquity within common laboratory equipment. As such, the analysis of these water samples was made with a specially equipped Bruker Elute UHPLC to avoid potential system-related PFAS contamination.
- The Bruker **impact II VIP QTOF** system with VIP-HESI source provides class-leading sensitivity for the detection of PFAS in the analysis of water samples. Without pretreatment or concentration and a direct injection volume of 200 µL, the average PFAS LOD (excluding two compounds at 2.5 and 10 ng/L) was 1 ng/L, well below any current regulatory requirements.
- Visual scoring cues within the user-friendly TASQ software support confident identification, with seamless incorporation of multiple layers of data for each target, including precise retention times, high-accuracy MS and MS/MS fragments, and True Isotopic Pattern (TIPTM) comparisons.
- Data analysis via TASQ, which can be used for the processing of triple quadrupole MRM data as well, readily facilitates the use of the same data set for broad screening and for specific multi-target quantitation according to regulatory requirements.
- Where no PFAS standards are available, the high resolution, high mass accuracy data can be used for suspect screening based on elemental composition and isotopic patterns. Surrogate semi-quantitation is also possible via TASQ.
- This PFAS detection method further benefits from data-independent acquisition, with full scan high speed MS and MS/MS data collection via broadband CID (bbCID)(Table 1), providing a unique depth of data for the analysis of unknowns or retrospective analysis. With no additional data collection required, analyses for other environmental hazards, including pesticides or other endocrine disruptors, can be quickly made with the addition of alternate databases within Bruker's TargetScreener portfolio.

Sample #	Water type	Source Location	L-PFBS	L-PFOA	PFBA	PFHpA	PFHxA	PFHxS	PFPeA	Sum of Detected PFAS
1	Tap water	Bremen, DE	-	-	-	-	-	<1	-	<1
2	Tap water	Bremen, DE	-	-	-	-	-	<1	-	<1
3	Groundwater	Grasberg, DE	-	1.0	1.4	-	2.9	-	1.2	6.5
4	Groundwater	Bremen, DE	0.9	143.0	9.9	97.2	43.2	-	24.4	318.6
5	Surface water - River Weser	Bremen, DE (Harbour)	-	-	2.3	<5	5.3	-	4.0	11.6
6	Surface water - River Weser	Bremerhaven, DE (Harbour)	-	-	-	-	-	-	-	-
7	Surface water - River Weser	Bremerhaven, DE	-	-	-	-	-	-	-	-
8	Surface water - River Lek	Nieuwegein, NL	7.0	2.0	115.5	<5	2.9	1.0	2.6	131
9	Surface water - River Waal	Brakel, NL	3.7	5.0	24.1	<5	4.2	1.0	3.7	41.7
10	Surface water - North Sea	Wilhelmshaven, DE	-	-	-	-	-	-	-	-
11	Surface water - North Sea	Wilhelmshaven, DE (Harbour)	-	-	-	-	-	-	-	-
12	Surface water - Baltic Sea	Heiligenhafen, Graswarder, DE	-	-	-	-	-	-	-	-
13	Surface water - Baltic Sea	Hohwacht, DE (Harbour)	-	-	1.3	-	1.7	-	-	3
14	Bottled mineral water	Wagenfeld, DE	-	-	-	-	-	-	-	-

Table 3. Concentrations [ng/L] of PFAS found in analyzed water samples.

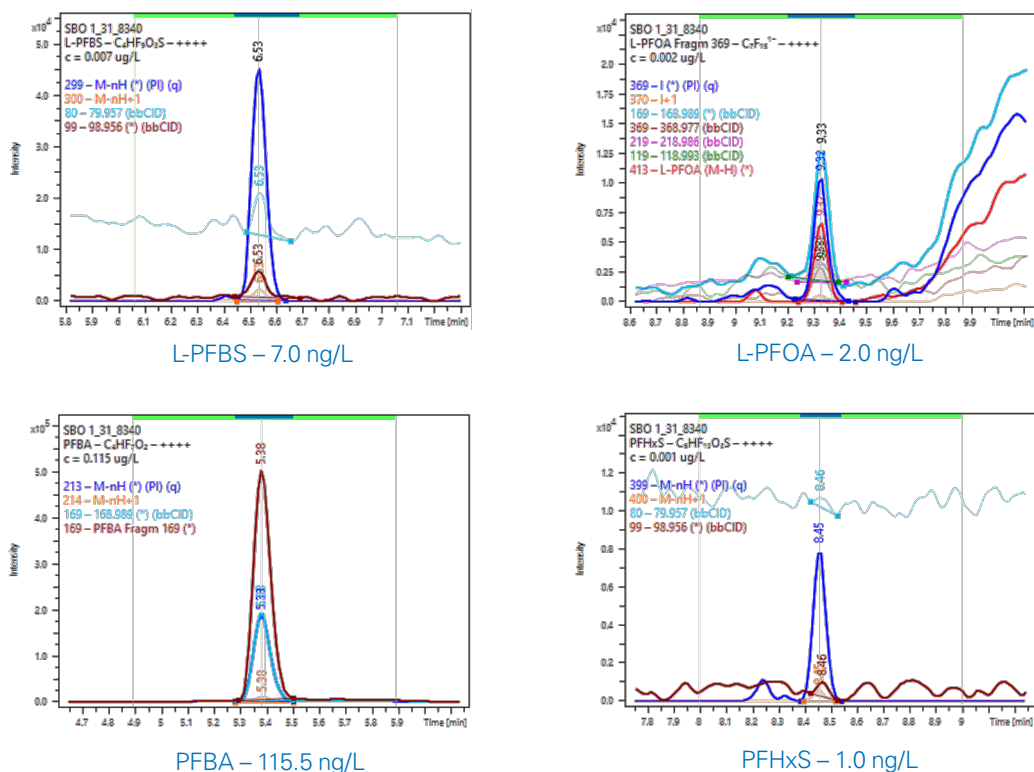


Figure 4. Example PFAS detected in surface water collected from the River Lek (Nieuwegein, NL).

Conclusion

This application note demonstrates the use of Bruker's impact II VIP QTOF MS system, equipped with VIP-HESI source, for confident identification and accurate quantitation of PFAS in various authentic water samples, with no sample pretreatment required. Beyond its utility to meet current EU and proposed US EPA regulatory requirements, this complete analytical system offers unique flexibility to

rapidly review data for broad screening or specific target quantitation via TASQ. The use of broadband collision-induced dissociation, with alternating MS and data-independent (bbCID) MS/MS collection, permits retrospective data analysis of additional unexpected or newly regulated PFAS compounds, supporting both "snapshot" and time-lapse views of PFAS contamination.

For Research Use Only. Not for use in clinical diagnostic procedures.

Bruker Switzerland AG

Fällanden · Switzerland
Phone +41 44 825 91 11

Bruker Scientific LLC

Billerica, MA · USA
Phone +1 (978) 663-3660

