Fast and ultra-sensitive screening of PFAS in surface waters using a novel TIMS-QTOF MS and large volume injection

Birgit Schneider[1], Carsten Baessmann[1]; Ilona Nordhorn[1]; Karin Wendt[1]; Sam Putnam[2], Artem Filipenko[2], Yann Hebert[3]

1: Bruker Daltonics GmbH & Co. KG, Bremen, Germany [2]Bruker Scientific LLC, Billerica, MA, USA;; [2]Bruker France SAS, Wissembourg, France

Introduction

Per- and polyfluoroalkyl substances (PFAS) are widespread environmental contaminants that pose risks to human health and ecosystems. Their analysis in environmental samples is challenging due to their structural diversity, low concentrations, and matrix interferences. While LC-triple quadrupole (LC-TQ) methods are commonly used for routine targeted analysis, comprehensive characterization requires advanced non-targeted approaches.

In this study, a novel small-molecule TIMS-QTOF platform (timsMetabo™, Bruker) was evaluated for screening of PFAS in surface water.

Methods

To determine the limits of detection (LOD) and quantification (LOQ), a mixture of 40 regulated PFAS (Wellington EPA-1633STK) was spiked in a dilution series in surface water at concentrations ranging from 0.1 to 100 ng/L.

Bruker Elute® SL with PFAS kit and large volume injection of 100 µL

Column	Phenomenex Gemini C18, 3 µm, 50 x 2.0 mm
Delay column	Restek Delay Column, 5 µm, 50 x 2.1 mm
Eluent A	2 mM NH_4 acetate in H_2O
Eluent B	2 mM NH_4 acetate in MeOH
Gradient	

	Time (min)	Flow (mL/min)	%A	%B
1	0.00	0.300	95.0	5.0
2	0.40	0.300	95.0	5.0
3	0.50	0.300	85.0	15.0
4	7.00	0.300	0.0	100.0
5	9.50	0.300	0.0	100.0
6	9.60	0.300	95.0	5.0
7	12.00	0.300	95.0	5.0

Column oven 40°C

MS-System: Bruker timsMetabo™

Ion source VIP-HESI source, negative mode

Scan mode: TIMS-bbCID and PASEF/TIMS-DDA-MoRE

Scan range *m/z* 30-1,000

The samples were analyzed using a large-volume injection of 100 µL on a Bruker Elute® SL UHPLC system with a fast, 9.6-minute gradient on a Phenomenex Gemini 3 µm C18 column (50 × 2 mm). The limit of detection (LOD) was determined using the TIMS-bbCID acquisition mode. We investigated the impact of key hardware and acquisition innovations on sensitivity and mass/mobility range coverage.

These innovations include the Mobility Range Enhancement (MoRE) mode, a brighter ion beam, collision energy sweeping from 10-30 eV and 3-70 eV, and the Athena Ion Processor (AIP) system. For non-targeted workflows, the samples were analyzed with TIMS-DDA-MoRE and processed with MetaboScape®.

Results

These limits of detection (LODs) reached as low as 0.1 ng/L for 23 PFAS, including PFNA. For 33 compounds, LODs were ≤0.3 ng/L, and for 37 PFAS, ≤1 ng/L. Limits of quantification (LOQs) and LODs were determined in blank surface water samples or pure water. Application of a collision energy (CE) sweep from 10 to 70 eV resulted in substantially richer MS/MS spectra compared to the conventional CE stepping approach, enabling more confident and reliable compound annotation.

- Calibration data and sensitivity for **PFNA** in surface water
- Linearity 0.1–100 ng/L
- R^2 = 0.9983
- LOD 0.1 ng/L
- LOQ 0.3 ng/L

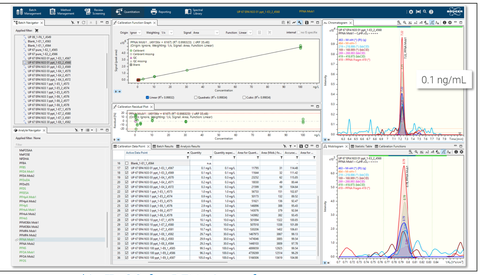


Fig. 1: Calibration curve processed in TASQ for PFNA in surface water

Calibration range 0.1-100 ppt (triplicate injections)

PFAS	Linearity [ng/L]	R^2	Accuracy [%]	LOD [ng/L]	LOQ [ng/L]
11Cl-PF3OUdS	0.1 - 100	0.9997	91-117	0.1	0.3
3:3 FTCA	3 - 100	0.9947	86-114	3.0	10
4:2 FTS	0.3 - 100	0.9999	93-117	0.1	0.3
5:3 FTCA	1 - 100	0.9990	86-120	0.3	1.0
6:2 FTS*	0.3 - 100	0.9967	85-123	0.1	0.3
7:3 FTCA	1 - 100	0.9988	93-119	0.3	1.0
8:2 FTS	1 - 100	0.9974	90-114	0.3	1.0
9Cl-PF3ONS	0.3 - 30	0.9969	89-104	0.1	0.3
ADONA	0.1 - 100	0.9975	86-105	0.1	0.3
EtFOSA	1 - 100	0.9986	92-104	1.0	1.0
EtFOSAA	0.3 - 100	0.9990	92-109	0.3	1.0
EtFOSE	1 - 100	0.9974	89-117	1.0**	1.0**
HFPO-DA	0.3 - 100	0.9998	83-108	1.0	1.0
MeFOSA	0.3 - 100	0.9976	81-106	0.3	1.0
MeFOSAA	0.3 - 100	0.9973	85-111	0.3	0.3
MeFOSE	10 - 100	0.9978	94-105	10**	10**
NFDHA	0.3 - 100	0.9993	86-113	0.1	0.3
PFBA*	1 - 100	0.9987		1.0***	
PFBS*	0.1 - 30	0.9994	93-110	0.1	0.1
PFDA*	0.3 - 100	0.9988	93-118	0.1	0.3

PFAS	Linearity [ng/L]	R^2	Accuracy [%]	LOD [ng/L]	LOQ [ng/L]
PFDoDA	0.1 - 100	0.9985	86-111	0.1	0.1
PFDoDS	0.3 - 100	0.9990	82-113	0.1	0.3
PFDS	0.1 - 100	0.9992	86-120	0.1	0.1
PFEESA	0.1 - 30	0.9993	89-118	0.1	0.1
PFHpA*	0.3 - 100	0.9995	80-114	0.1	0.3
PFHpS	0.1 - 30	0.9971	82-120	0.1	0.1
PFHxA*	0.3 - 100	0.9997	82-117	0.1	0.3
PFHxS*	0.1 - 100	0.9961	80-110	0.1	0.3
PFMOBA	0.3 - 100	0.9994	78-116	0.3	1.0
PFMPA	3 - 100	0.9996	92-107	3.0	10
PFNA*	0.1 - 100	0.9983	90-116	0.1	0.3
PFNS	0.3 - 30	0.9990	83-119	0.1	0.3
PFOA*	0.3 - 100	0.9985	90-120	0.3	0.3
PFOS*	0.3 - 100	0.9956	87-117	0.1	0.3
PFOSA	0.3 - 100	0.9966	80-108	0.1	1.0
PFPeA*	0.3 - 100	0.9996	80-117	0.3	0.3
PFPeS*	0.1 - 30	0.9944	83-106	0.1	0.3
PFTeDA	0.3 - 100	0.9953	82-119	0.3	1.0
PFTrDA	0.3 - 100	0.9995	80-121	0.1	1.0
PFUnDA	0.1 - 100	0.9997	81-120	0.1	0.1

Fig. 2: LODs, LOQs, and linearity determined for 40 regulated EPA 1633 PFAS in surface water and pure water.

*The compound was detected in surface water which is why the LOD and LOQ were determined in pure water. Peak areas in surface water were similar to or lower than those measured at 0.1 ppt, suggesting that the LOD and LOQ are effectively equivalent.
** Fragment ions were detected only at noise levels.
*** The chromatographic peak shape was insufficient, preventing a reliable determination of the LOQ.

Sweeping: Ramp1 10-30 eV; Ramp 2 30-60 eV

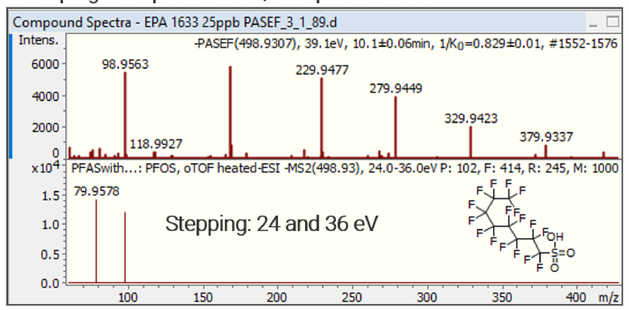
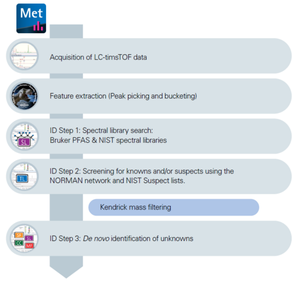


Fig. 3: Collision energy sweeping results in much richer MS/MS spectra.



MetaboScape software supports the ID Steps 2 and 3 by the following tools:

- **SmartFormula** generates a list of potential elemental compositions
- **CompoundCrawler** searches for corresponding structures in databases and suspect lists
- **MetFrag** applies comprehensive in-silico fragmentation
- **CCS-Predict** Pro verifies the structure by comparing experimental CCS values and those predicted based on the structural information

Fig. 4: Workflow of the data acquisition, post-processing and identification of potential PFAS.

Fig. 4 illustrates the non-targeted workflow using PASEF or TIMS-DDA-MoRE on the timsTOF Pro 2 or timsMetabo, with data processing performed in MetaboScape. This workflow enables high-confidence annotation of regulated PFAS via spectral library matching, followed by suspect screening and de novo identification.

In a recently published study on comprehensive PFAS screening of Dutch surface waters from 18 sites (Liwara et al., https://doi.org/10.1016/j.envpol.2026.127846), we demonstrated the advantages of integrating target, suspect, and non-targeted approaches using a timsTOF Pro 2. PFAS identified through library matching were consistent with those obtained via the targeted approach, while the non-targeted workflow provided additional annotation depth. Fig. 5 shows the additional findings using non-target workflows.

A total of 137 features in the surface water samples were annotated as PFAS. The number of detected PFAS varied across the 18 sampling sites, reflecting differences in local conditions and infrastructure (Fig 5). Higher PFAS diversity was observed at sites 1, 13, and 17, whereas lower contamination levels were evident at sites 4 and 15.

Notably, several PFAS precursors and degradation products were identified that are not currently included in regulatory screening lists and would likely be overlooked in a purely targeted approach.

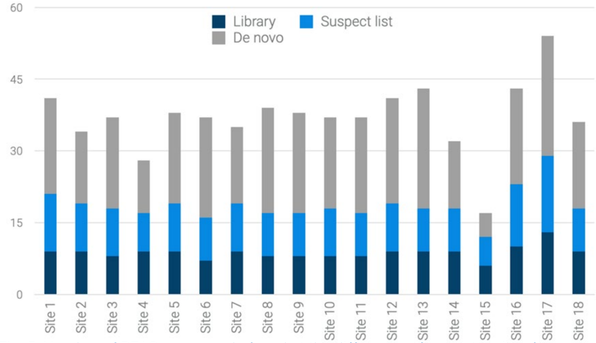


Fig. 5: Number of PFAS compounds found at the different surface water sites from a recently published study using timsTOF Pro 2 and PASEF.

Conclusions

- The timsMetabo platform introduces MoRE and AIP technologies for enhanced sensitivity and broader mass range.
- In surface water LODs and LOQs down to 0.1 or 0.3 ng/L can be achieved for most of the regulated PFAS
- Collision energy sweeping generates rich MS/MS spectra, supporting PFAS with diverse fragmentation behavior.
- The workflow allows fast and ultrasensitive identification of PFAS without the need of performing time consuming SPE and can be a good alternative for relatively simple matrices like surface or drinking water.

timsMetabo / PFAS