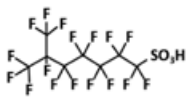
FlashNote

Environmental screening via timsTOF MS: A new dimension for discrimination and improved sensitivity in the detection of PFOS pollutants

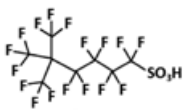
Environmental water screenings are regularly challenged by the number and diversity of chemical and biological targets in a given sample. In addition to appropriate means for collection and concentration to obtain a reliable representation of the monitored source, robust and reproducible means of analytical separation are necessary to detect compounds of interest. Samples may contain potentially hundreds of targets, and traditional chromatographic separation can be insufficient to discriminate between closely related compounds or meet established detection limits.

Among the thousands of known environmental pollutants, PFOS (perfluorooctanesulfonic acid) compounds are considered priority hazardous substances within the PFAS (per-polyfluoroalkyl substances) pollutant family due to their significant and long-lasting adverse effects on human and animal health [1, 2]. Contaminated water is most frequently the source of exposure, and as such water sources are subject to increasingly close monitoring and developing regulations within the EU and the US [3-5].

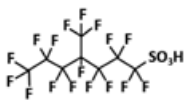
Perfluorooctane sulfonic acid (linear)



Perfluoro-6-methylheptane sulfonic acid (6)



Perfluoro-5,5-dimethylhexane sulfonic acid (5,5)



Perfluoro-4-methylheptane sulfonic acid (4)

Figure 1: Studied PFOS isomers. Bioaccumulation patterns and health effects in exposed organisms have been shown to vary with isomer form.

Differentiation between various PFOS compounds, including isomers (e.g., Figure 1), is often necessary to determine the pollutant source or meet specific detection limits based on their varying toxicities. Although their separation is incomplete via LC alone (Figure 2, inset), the combination of the Bruker TargetScreener LC method with trapped ion mobility spectrometry via the Bruker timsTOF Pro system enables rapid discrimination of these PFOS isomers, with significantly improved target detection sensitivity.

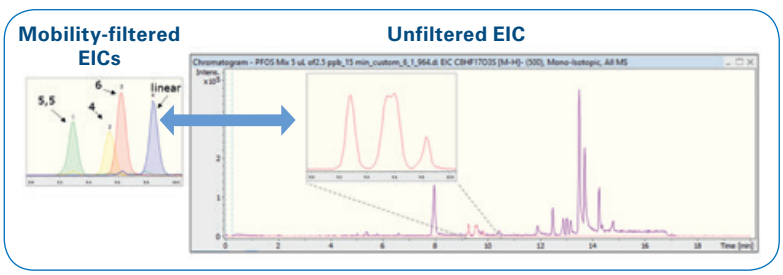


Figure 2: Extracted Ion Chromatogram (m/z 498.9302 ± 0.005 Da) for a 5 µL injection of a sample containing a 2.5 ng/mL (2.5 ppb) mix of four isomeric PFOS compounds. All analyses were made in negative ion mode. Using the BrukerTargetScreener LC method, the targeted compounds elute between 9 and 10 minutes, with coelution of perfluoro-4-methylheptane sulfonic acid (4) and perfluoro-6-methylheptane sulfonic acid (6). Left: Overlaid extracted ion chromatograms for the same elution range, using unique and specific ion mobility filtering to separate each PFOS isomer.

Authors: Silke Bodendiek, Karin Wendt, Andrea Kiehne; Bruker Daltonik GmbH, Bremen, Germany

The extra dimension of trapped ion mobility separation

Co-elution of target compounds – whether due to similar chemical nature or identical mass - can lead to missed detections or inaccurate peak assignments. Bruker's timsTOF Pro combines high ion mobility resolution with ultra-high resolution QTOF technology to enable clear and confident differentiation of low levels of these monitored pollutants.

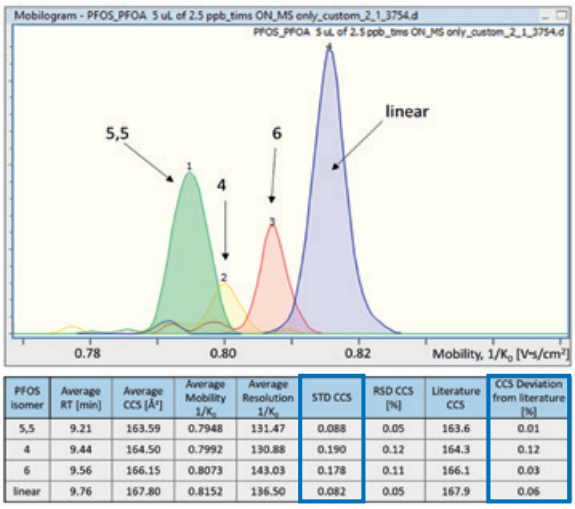
Separating via ion mobility based on the three-dimensional structure of each compound, the resulting collisional cross sections (CCS) add a unique and critical differentiation factor for target screening (Figure 3, top).

The CCS values measured for each PFOS isomer using the timsTOF Pro show excellent reproducibility and high accuracy to the literature values [6] (Figure 3, bottom).

Discrimination with high mass accuracy and isotopic fidelity

Using trapped ion mobility in combination with the Bruker TargetScreener LC method, the targeted PFOS isomers are definitively separated from other sample components, with mass accuracies between 0.1 – 2 ppm (0.1-1 mDa). Likewise, their isotopic pattern fit is excellent, as indicated by very low mSigma* values (Figures 4 and 5).

In targeted detection workflows, these analytical features support high confidence compound identification. In discovery workflows, this combination of mass accuracy and high resolution isotopic pattern assessment enables the determination of the elemental composition of unknown or unanticipated sample components.



PFOS isomer	Average RT [min]	Average CCS [Å²]	Average Mobility 1/K0	Average Resolution 1/K0	STD CCS	RSD CCS [%]	Literature CCS	CCS Deviation from literature [%]
5,5	9.21	163.59	0.7948	131.47	0.088	0.05	163.6	0.01
4	9.44	164.50	0.7992	130.88	0.190	0.12	164.3	0.12
6	9.56	166.15	0.8073	143.03	0.178	0.11	166.1	0.03
linear	9.76	167.80	0.8152	136.50	0.082	0.05	167.9	0.06

Figure 3: Extracted Ion Mobilograms and CCS characteristics for the studied mix of PFOS isomers. Perfluoro-5,5-dimethylhexane sulfonic acid (5,5) and perfluoro-4-methylhexane sulfonic acid (4) have similar CCS values but are well separated using the TargetScreener LC method applied (see Figure 2). Tabulated CCS values shown are averages from ten injections (5 µL, 2.5 ppb standard mix).

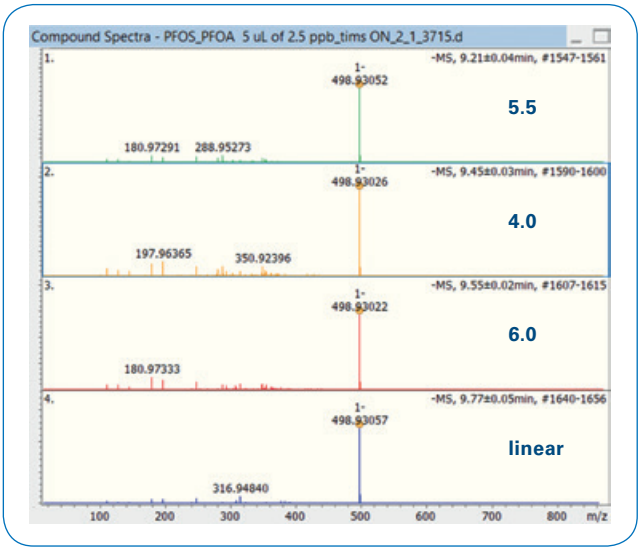


Figure 4: Mobility filtered mass spectra of each PFOS isomer within the studied sample. A 1:1 mixture of 10 mM sodium clusters and an Aglient tune mix solution was used for (external) mass and mobility calibration.

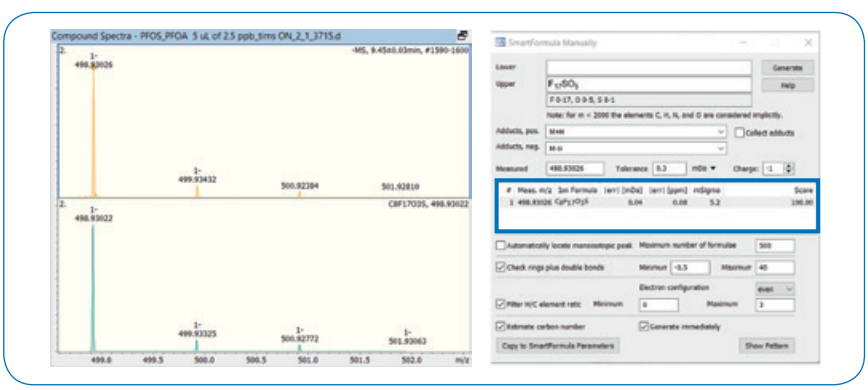


Figure 5: Mobility filtered mass spectra (target m/z range) for the perfluoro-4-methylheptane sulfonic acid (4), compared to theoretical (calculated) molecular weight and isotopic distribution of $C_8HF_{17}O_3S$. The mSigma value of 5.2 indicates a near-perfect fit. In this experiment, all mSigma values were <12.

* mSigma values range from 0-1000 and quantitate the goodness of fit between measured and theoretical isotopic patterns. Lower mSigma values indicate a better fit.

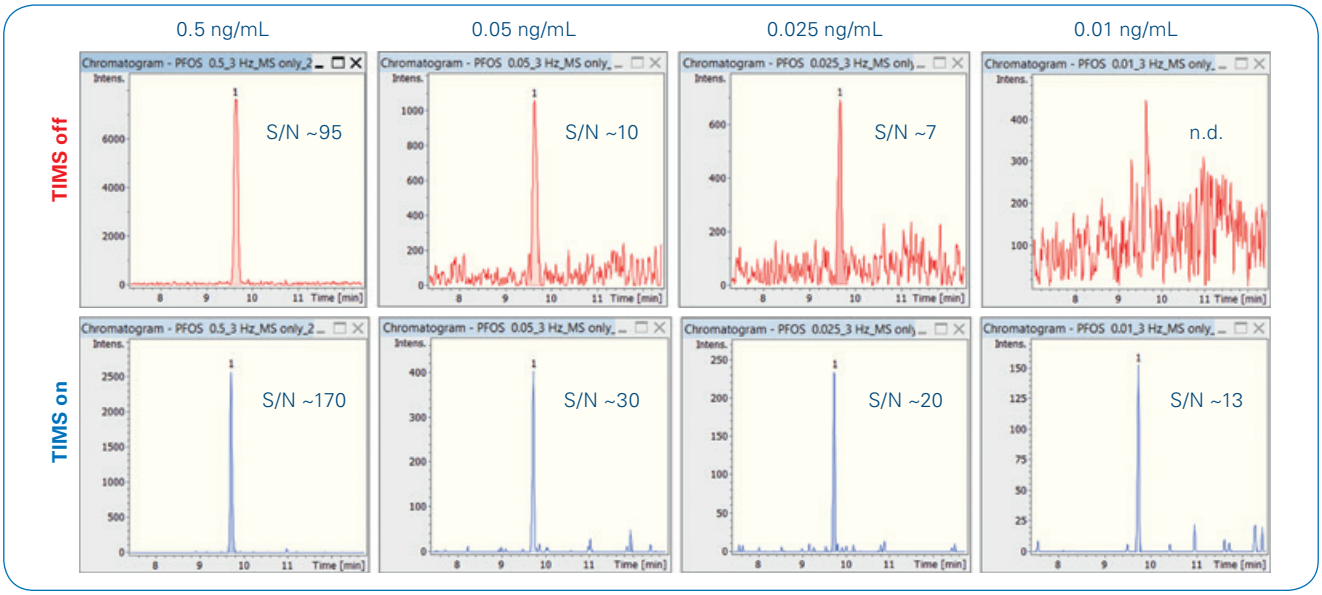


Figure 6: Extracted ion chromatograms (m/z 498.9302 ± 0.005 Da) for a serial dilution of (linear) perfluorooctane sulfonic acid without ion mobility filtration (TIMS off, upper spectra) and with ion mobility filtration (TIMS on, lower spectra). 5 µL injection of a 2.5 ng/mL standard. Trace width 0.01 Da, Gaussian smoothing (1 point, 3 cycles). As different digitizers are used in these two modes, relative peak intensity values can only be compared within a single mode.

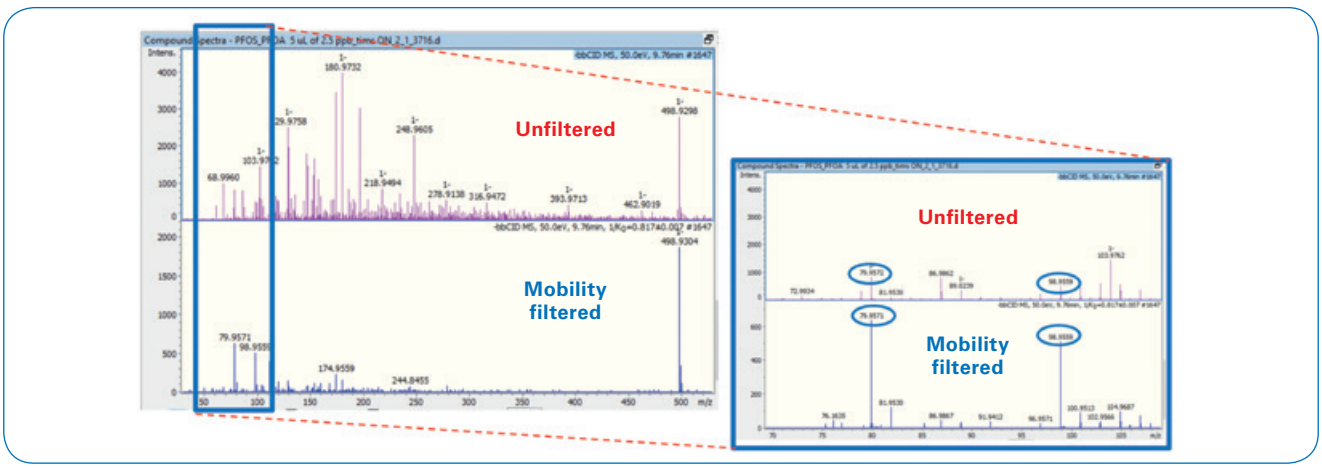


Figure 7: Linear perfluorooctane sulfonic acid analyzed in bbCID mode. Applying ion mobility filtering to the collected spectra (lower spectra set), diagnostic target fragments are easily visualized. 5 µL injection of 2.5 ng/mL sample.

Increased sensitivity in MS mode with trapped ion mobility separation

A serial dilution of the linear PFOS was analyzed in MS mode, without (Figure 6, top) or with (Figure 6, bottom) the inclusion of trapped ion mobility separation. The target detection limit and S/N values were significantly improved with TIMS.

Filtering by ion mobility in bbCID mode increases detection confidence and identification ease

Standard screening timsTOF Pro workflows use alternating MS and bbCID data collection, adding another layer of identification confidence in targeted pollutant monitoring. Along with the enhanced discriminatory capacities for the detection of multiple compounds, even within complex samples, visualization of lower molecular weight diagnostic fragments is enhanced by data filtering using the unique ion mobility for a given target (Figure 7, lower spectra). The benefits of the unbiased collection of "all of the data, all of the time" established in Bruker's TargetScreener workflows are expanded with the separatory dimension of TIMS, adding detection depth, clarity, and sensitivity for new target discovery and retrospective analyses.

Think in a new dimension for superior pollutant detection with the timsTOF Pro system

- Enables unmatched separatory power for compound discrimination via the combination of trapped ion mobility separation with high resolution QTOF technology
- Increases identification confidence and ease through the addition of compound-specific CCS values and improved detection of diagnostic fragment ions
- Expands detection scope in complex samples, facilitating both targeted and discovery workflows
- Supports environmental monitoring requirements today and offers unique capabilities to adapt to changing regulations and emerging threats tomorrow

References

[1] United States Environmental Protection Agency (May 2016). *Health Effects Support Document for Perfluorooctane Sulfonate (PFOS),* (EPA 822-R-16-002).

[2] Lau C. (2015). *Perfluorinated Compounds: An Overview. In Toxicological Effects of Perfluoroalkyl and Polyfluoroalkyl Substances.* Molecular and Integrative Toxicology; DeWitt J., (Ed); Humana Press, Cham, 2015; pp.1-21. https://doi.org/10.1007/978-3-319-15518-0_1

[3] European Union (2019). *Regulation (EU) 2019/1021 of the European Parliament and of the Council of 20 June 2019 on persistent organic pollutants* (Text with EEA relevance.) (OJ L).

[4] European Commission (2017). *Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on the quality of water intended for human consumption* (recast), COD No 0332.

[5] United States Environmental Protection Agency (February 2019). *EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan* (EPA 823R18004). https://www.epa.gov/pfas

[6] Dodds J.N. et al. (2020). *Rapid Characterization of Per- and Polyfluoroalkyl Substances (PFAS) by Ion Mobility Spectrometry–Mass Spectrometry (IMS-MS),* Anal Chem **92**:4427-4435. doi: 10.1021/acs.analchem.9b05364

Bruker Daltonik GmbH

Bremen · Germany
Phone +49 (0)421-2205-0

Bruker Scientific LLC

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

ms.sales.bdal@bruker.com – www.bruker.com

timsTOF Pro

Target-Screener

You are looking for further Information? Check out the Link or scan the QR Codes.

www.bruker.com/timstofpro

For Research Use Only. Not for Use in Clinical Diagnostic Procedures.