Identification of Novel Per-and-Polyfluoroalkyl Substance (PFAS) Isoform in Textile Using a Multi-Reflecting Time-of-Flight Mass Spectrometer Technology

Hania Hollins[1], Sara Beverley[1], Martin Palmer[1], Jayne Kirk[1], Richard Lock[1], Sean Wu[2]

, [1]Waters Corporation Wilmslow, Cheshire, UK, [2]Waters Corporation, Milford, MA, USA

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❶ Introduction

As awareness of the health risks associated with per- and polyfluoroalkyl substances (PFAS) grows, there is an increasing demand to determine total PFAS content to help reduce human exposure. Traditional targeted methods provide only a narrow insight of the PFAS content, making non-targeted screening with high-resolution mass spectrometry an effective approach to bridge quantitative analyses and discovery workflows.

In this study, high-resolution mass spectrometry (HRMS) combined with a non-targeted screening (NTS) workflow was applied to characterize PFAS profiles in textiles. Textile reference material (LCG) was analyzed using data dependent acquisition mode (DDA) and processed with waters_connect^{TM} Software Platform. Different PFAS isoforms and halogenated contaminants were identified with high confidence levels based on accurate mass measurement of the precursor and product ions.

❷ Experimental

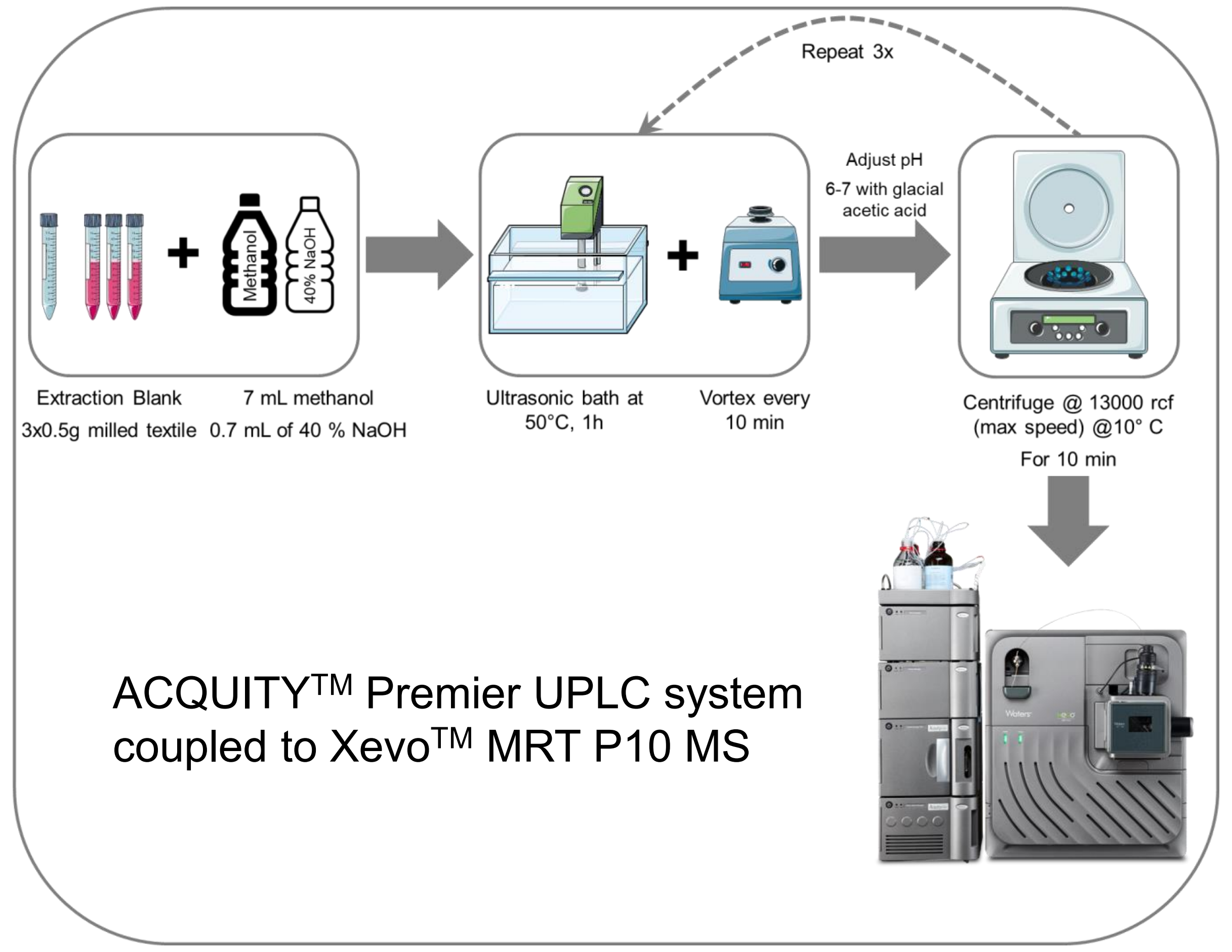


Figure 1. Illustration of PFAS extraction from textile reference material (TRM). Briefly, PFAS were exacted from milled textile material derived from outdoor clothing using 3x0.5 g of TRM according to EN 17681-1:2025[1].

❸ LC-MS conditions

Chromatographic conditions:

- **UPLC™ system:** Waters ACQUITY Premier modified with PFAS solution installation kit (p/n: 176004548).
- **Column:** ACQUITY Premier BEH^{TM} C18, 1.7 µm, 2.1 x 50 mm, 90 Å (p/n:186009452)
- **Column temp.:** 40℃
- **Sample temp.:** 10℃
- **Injection volume:** 5 µL

- **Mobile phase A:** 95:5 water:methanol + 2 mM ammonium acetate
- **Mobile phase B:** 100% methanol + 2 mM ammonium acetate

Chromatographic gradient

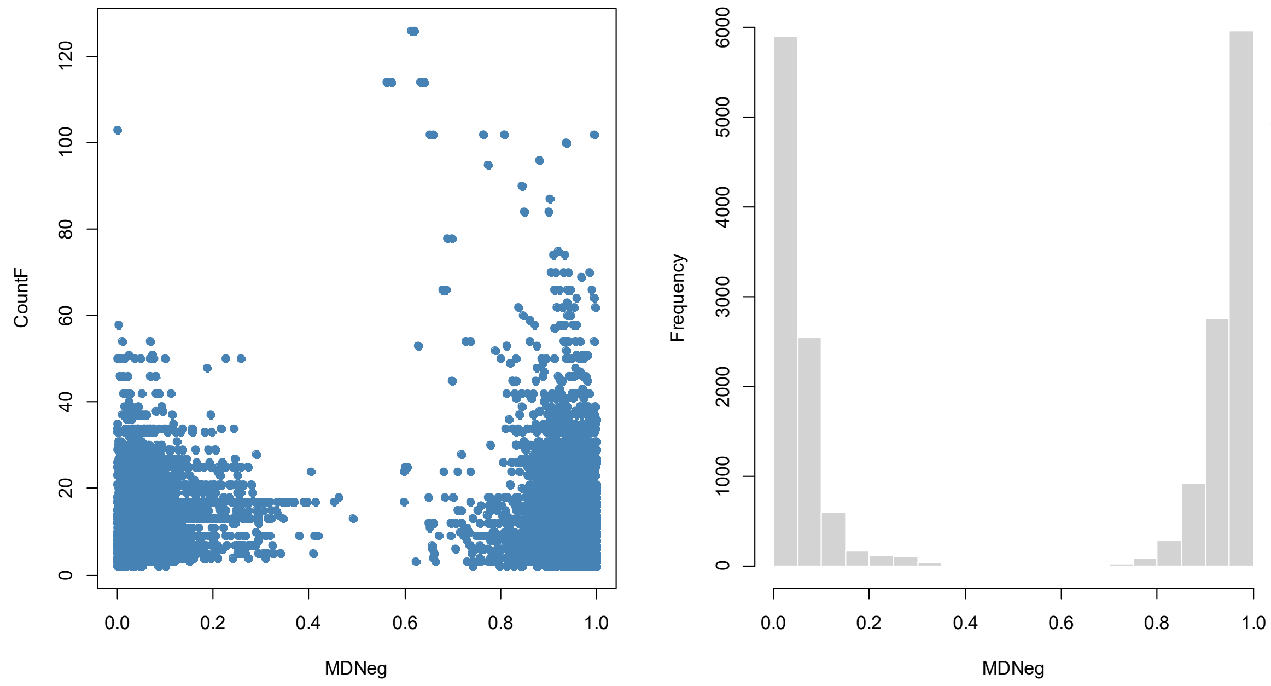
Time (min)	Flow rate (mL/min)	%A	%B	Curve
0	0.5	100	0	Initial
0.5	0.5	80	20	6
3.0	0.5	55	45	6
6.5	0.5	20	80	6
7.0	0.5	5	95	6
8.5	0.5	5	95	6
9.0	0.5	100	0	1
11.0	0.5	100	0	1

MS acquisition parameters

	Parameters	Value
Source	Capillary voltage	0.5 kV
	Cone voltage	10 V
	Source temp.	100°C
	Desolvation temp.	250°C
	Cone gas	100 L/h
	Desolvation gas	600 L/h
Transmission Settings	StepWave RF	100 V
	Body gradient	5 V
Acquisition mode	Data depended (DDA)	Top 5
Collision energy	Low mass ramp	20 - 40 V
	High mass ramp	35 - 75 V

❹ Rational

A merged database composed from CompTox[2] (14735 compounds) and EPA[3] (4969 compounds) was created. Common compounds were removed. To all unique 19610 compounds, the number of "F" atoms and the mass defect were calculated.



The majority of PFAS (and PCBs) have MD between 0.90 to 0.05, with "F" count between 3-35.

Figure 2 left is a plot of the Mass defect as function of the number of "F" atoms. Right is the frequency of mass defect in the created library.

❺ Results

Using Mass defect directed DDA reduced the number of MS/MS spectra by ~ 25 %

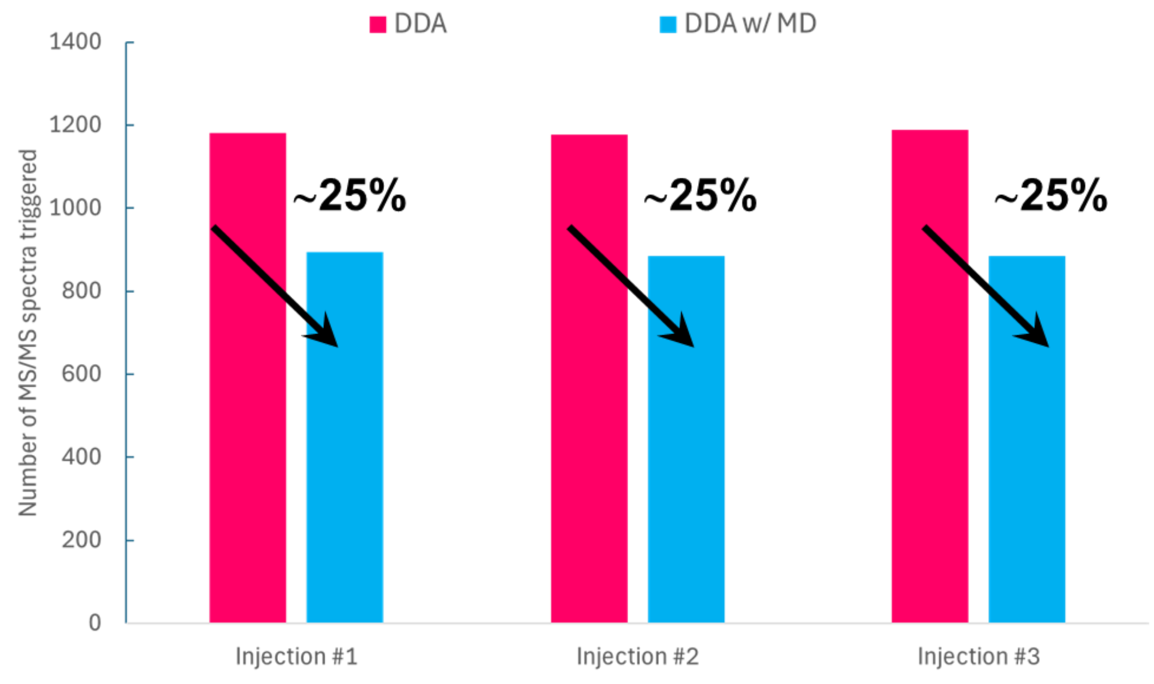


Figure 3. Number of MS/MS spectra triggered without (pink) and with (blue) mass defect in three consecutive injections of a standard mix at 5 ng/mL. The number of DDA triggered was reduced by ~25% in each of the individual injections.

❻ Results

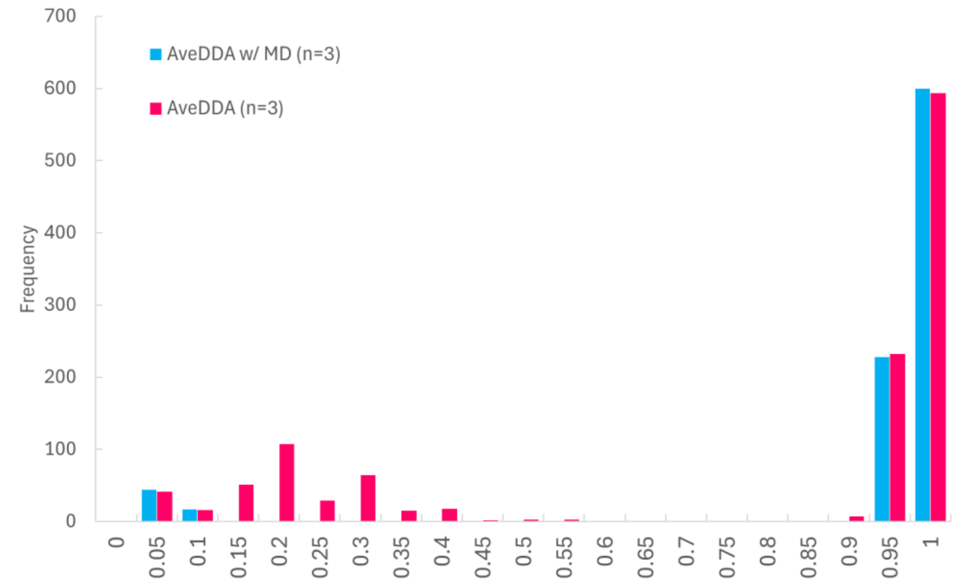


Figure 4. The frequency of triggered MS/MS using a DDA method without (pink) and with Mass Defect Derived DDA.

The frequency of DDA triggered on PFAS-like compounds was improved. Figure 4 demonstrated that without MD derived DDA (pink), compounds with Mass defects between 0.15-0.85 were selected from the survey scan and fragmented

➔ MD derived DDA improved the number of PFAS-like compounds selected for MS/MS

❼ Identification of PFAS in Textile Reference Material

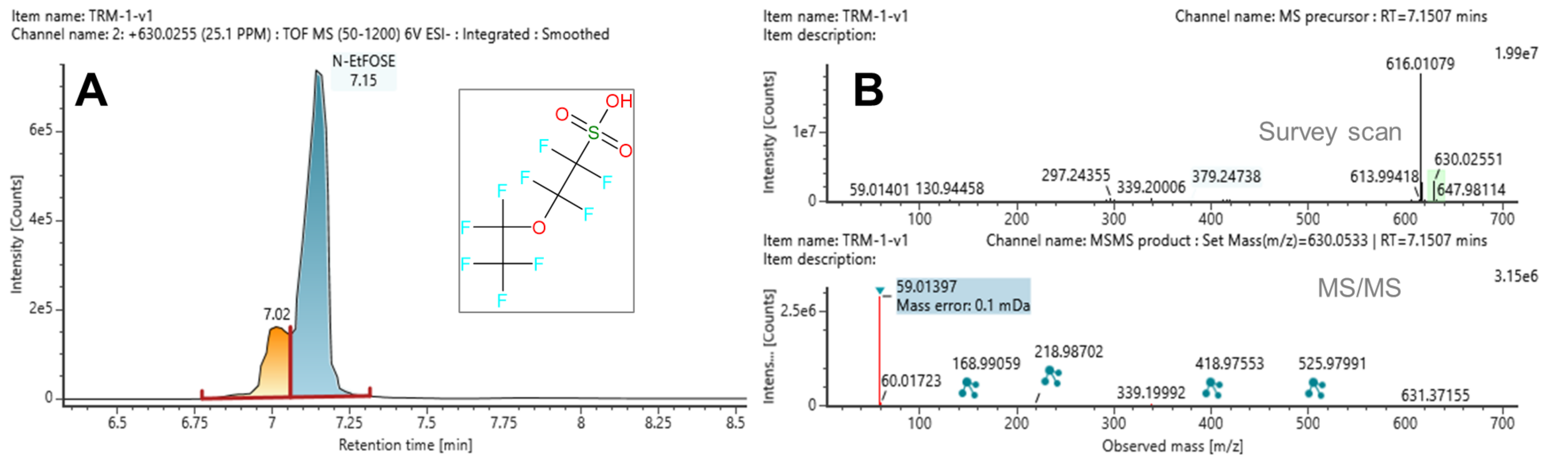


Figure 5. A: Extracted ion chromatogram of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) *in textile extract. B (Top) Survey scan and B (bottom) MS/MS spectra of N-EtFOSE. N-EtFOSE is identified at m/z 630.02551 with mass measurement accuracy 1.1 ppm.*

Conclusions

- Mass defect driven data dependant acquisition reduced the number of unspecific MS/MS spectra.
- Improved the number of identified PFAS and PFAS-like compound.
- DDA driven by mass defect can be used for other types of persistent contaminants such as polychlorinated and polybrominated biphenyls.

References

1. EN 17681-1-2025 Textiles and Textile products – Per and polyfluoroalkyl substances (PFAS) – Part 1: Analysis of an alkaline extract using liquid chromatography and tandem mass spectrometry
2. U.S. Environmental Protection Agency. CompTox Chemicals Dashboard. <https://comptox.epa.gov/dashboard/chemical-lists/pfasmaster> accessed November 2023.
3. Suspect List of Possible Per- and Polyfluoroalkyl Substances (PFAS). <https://data.nist.gov/od/id/mds2-2387> Accessed March 2023