

ABSTRACT

Mounting concern over per- and polyfluoroalkyl substances (PFAS) resistance to breaking down in the environment and toxicity at relatively low concentrations has created a need for developing various methods for their detection. Volatile PFAS can be carried long distances through the air, which may lead to contamination of soils and groundwater far from the PFAS source. Therefore, it has become critical to develop alternative analytical techniques to fully analyze and understand nearly 15,000 PFAS compounds. This research study aims to understand the feasibility of analyzing volatile PFAS in water by Purge and Trap (P&T) with detection by Chromatography/Mass Spectrometry (GC/MS) and highlight advantages and insights gained while developing this working application.



Lumin Purge & Trap Concentrator

INTRODUCTION

PFAS are a large group of human-made substances that were created in the 1930s and used in surface coating and protectant formulations due to their resistance to heat, water, and oil. PFAS are toxic at relatively low concentrations and can accumulate in the human body over time, causing adverse health effects. PFAS can be introduced into the body by eating or drinking contaminated food or water and breathing in or touching products treated with PFAS. If PFAS are spilled onto the ground or into lakes and rivers, they can get into the groundwater and are easily transported large distances and contaminate drinking water.

In mid-2025, the United States Environmental Protection Agency (EPA) announced that it will keep the current National Primary Drinking Water Regulations (NPDWR) for two types of PFAS, Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS) at a final Maximum Contaminate Levels (MCL) of 4.0 parts per trillion (ppt or ng/L).

Current EPA methods to analyze PFAS include Solid Phase Extraction (SPE) and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) or Isotope Dilution Anion Exchange SPE and LC/MS/MS. Combined, these methods analyze 29 PFAS compounds. Therefore, research is needed to develop alternative analytical techniques to fully analyze the expansive and varied range of PFAS compounds.

Creating a method and analyzing volatile PFAS by P&T-GC/MS could lead to a more automated, efficient, sensitive, and solvent extraction free analysis. This research study has provided the foundation to optimize method parameters for low-level volatile PFAS analysis by P&T-GC/MS in drinking water samples. When performing low-level drinking water analysis, excess water vapor in the system can be a major concern. The water peak will minimize the sensitivity of the analysis, cause compounds to co-elute, shift in retention time, and cause poor peak shape. The Teledyne Tekmar Lumin P&T has an innovative moisture control system (MCS) that improves water vapor removal, thereby reducing peak interference and increasing GC column lifespan. Calibration data, Method Detection Limit (MDL), and mid-point calibration check data will be presented.

SAMPLE PREPARATION

A 5 parts per million (ppm) working calibration standard was prepared in methanol from volatile PFAS standards from Millipore Sigma, AccuStandard, and TCI America. A six-point external calibration curve was prepared from 1 to 50 ppb with regression value (r^2) ≥ 0.995 or $\leq 20\%$ RSD.

Seven 2 ppb standards were prepared to calculate the MDL, and five 20 ppb calibration check standards were prepared for the accuracy and precision calculations. All calibration, MDL, and mid-point calibration standards were analyzed with the Tekmar Lumin P&T conditions in Table I. GC-MS conditions are shown in Table II.

EXPERIMENTAL INSTRUMENT CONDITIONS

Table I: Tekmar Lumin P&T Water Method Conditions			
Standby	Variable	Purge	Variable
Valve Oven Temp	150 °C	Preheat Time	1.00 min
Transfer Line Temp	150 °C	Sample Heater Enable	On
Sample Mount Temp	90 °C	Desorb	Variable
Standby Flow	10 mL/min	Desorb Preheat Temp	220 °C
Purge Ready Temp	35 °C	Desorb Temp	225 °C
MCS Purge Temp	20 °C	Desorb Time	2.00 min
Purge	Variable	Drain Flow	300 mL/min
Purge Temp	20 °C	GC Start Signal	Begin Desorb
Purge Time	11.00 min	Bake	Variable
Purge Flow	80 mL/min	Bake Time	5.00 min
Dry Purge Temp	20 °C	Bake Temp	230 °C
Dry Purge Time	0.00 min	MCS Bake Temp	180 °C
Dry Purge Flow	0 mL/min	Bake Flow	200 mL/min
Sample Temp	40 °C		
Pre-Purge Time	0.00 min	Trap	2 Trap (Tenax/Silica Gel)
Pre-Purge Flow	40 mL/min	Purge Gas	Helium

Table II: Agilent 8890 GC and 5977C MS System Conditions	
Agilent 8890 GC Conditions	
Column	DB-624 UI, 30 m x 0.25 mm, 1.4 μ m Film, Column Flow – 1.2 mL/min
Oven Profile	40 °C, 7 min, 5 °C/min to 188 °C, 40 °C/min to 250, 5 min, Run time 43.15 min
Inlet	240 °C, 10:1 Split, Septum Purge Flow 0.5 mL/min, 9.59 psi, Carrier Gas - Helium
Agilent 5977C MS Conditions	
Temp	Transfer Line 250 °C; Source 230 °C; Quad 150 °C
SIM	Dwell times, quantitation ions, confirmation ions, and retention time windows presented in Table III, Solvent Delay 6.00 min
Current	Gain Factor 20, Auto Tune

RESULTS

The external calibration curve, MDL, and mid-point calibration check data are shown in Table IV. In addition, the calibration curve was validated with the lowest level standard within $\pm 50\%$ of the true value and all other calibration standards within $\pm 30\%$ of the true value with data shown in Table V. Figure 1 displays an overlay of the calibration curve. Figure 2 displays an overlay of $n=7$, 2 ppb water standards of 8:2 FTAC, in SIM mode with a precision of 5.1% RSD. Figure 3 overlay of $n=5$, 20 ppb water standards of 8:2 FTMAC in SIM mode with quantitation ion ($m/z=532$) and two confirming ions ($m/z=86$, $m/z=113$) and a precision of 12.4% RSD and accuracy of 105% recovery.

Table III: Dwell times, Quantitation Ions, Confirmation Ions, and Retention Time Windows						
Group	Compound	RT, min	RT Window, min	Quant Ion, m/z	Quant Ion Dwell, ms	Confirmation Ions Confirmation Ions Dwell, ms
1	Perfluorohexyl iodide (PFHxl)	7.52	6.0 to 8.0 min	319	100	69,231 100
2	Perfluorooctyl iodide (PFOI)	13.13	8.0 to 14.0 min	169	100	419,119 100 (m/z 119, 50)
3	4:2 Fluorotelomer iodide (4:2 FTI)	15.56	14.0 to 17.0 min	374	100	227,69 100
4	6:2 Fluorotelomer iodide (6:2 FTI)	20.13	17.0 to 21.0 min	474	100	141,327 100
5	8:2 Fluorotelomer alcohol (8:2 FTOH)	22.79	21.0 to 23.0 min	127	100	131,119 100
6	6:2 Fluorotelomer acrylates (6:2 FTAC)	23.50	23.0 to 24.5 min	418	100	327 100
6	8:2 Fluorotelomer iodide (8:2 FTI)	23.97	23.0 to 24.5 min	574	100	119,427 100
7	10:2 Fluorotelomer alcohol (10:2 FTOH)	25.97	24.5 to 26.3 min	505	100	563 100
7	6:2 Fluorotelomer methacrylate (6:2 FTMAC)	26.00	24.5 to 26.3 min	432	100	113,367 100
8	8:2 Fluorotelomer acrylates (8:2 FTAC)	26.77	26.3 to 28.0 min	518	100	169,456 100
9	8:2 Fluorotelomer methacrylate (8:2 FTMAC)	29.04	28.0 to 32.0 min	532	100	86,113 100
10	N-Methyl perfluorooctane sulfonamide (MeFOSA)	33.66	32.0 to 33.9 min	131	100	94,119 100
11	N-Ethyl perfluorooctane sulfonamide (EtFOSA)	34.23	33.9 to END	448	100	80,108 100

Table IV: Volatile PFAS Calibration, MDL, and Mid-Point Calibration Check Data						
Compound	Calibration (1-50 ppb)		Method Detection Limits (n=7, 2 ppb)		Initial Demonstration of Capability (n=5, 20 ppb)	
	Average RRF	Linearity ($r^2 \geq 0.995$; $\leq 20\%$ RSD)	MDL (ppb)	Precision ($\leq 20\%$)	Average (ppb)	Precision ($\leq 20\%$) Accuracy ($\pm 20\%$)
PFHxl	0.939	0.999; 8.1	0.27	7.4	18.6	9.7 93
PFOI	7.35	0.998; 15.9	0.28	8.6	19.3	8.3 96
4:2 FTI	0.989	0.999; 8.5	0.26	7.0	18.3	12.4 92
6:2 FTI	3.73	0.996; 18.9	0.43	7.4	33.5	11.9 167
8:2 FTOH	2.97	0.999; 6.4	9.54	5.2	845.1	11.9 4226
6:2 FTAC	1.22	0.999; 10.1	0.18	4.9	19.8	13.8 99
8:2 FTI	1.52	0.996; 10.2	0.21	5.9	20.8	11.2 104
10:2 FTOH	3.84	87.9	1.78	40.1	6.9	51.8 34
6:2 FTMAC	3.82	0.995; 11.5	0.18	4.8	18.8	13.3 94
8:2 FTAC	0.886	0.999; 18.0	0.20	5.1	22.8	15.4 114
8:2 FTMAC	1.64	0.995	0.29	7.8	21.1	12.4 105
MeFOSA	1.00	57.6	35.73	51.2	82.7	21.4 413
EtFOSA	0.625	93.4	3.42	50.9	7.7	14.0 38

Table V: Validation of the Calibration Curve						
Compound	1 ppb ($\pm 50\%$)	2 ppb ($\pm 30\%$)	5 ppb ($\pm 30\%$)	10 ppb ($\pm 30\%$)	20 ppb ($\pm 30\%$)	50 ppb ($\pm 30\%$)
PFHxl	0.98 ppb (2.0%)	1.86 ppb (7.0%)	4.76 ppb (4.8%)	10.1 ppb (1.1%)	22.9 ppb (14.7%)	54.3 ppb (8.7%)
PFOI	0.81 (19.0%)	1.65 ppb (17.5%)	5.24 ppb (4.8%)	10.0 ppb (0.0%)	24.1 ppb (20.6%)	56.1 ppb (12.2%)
4:2 FTI	0.95 ppb (5.0%)	1.86 ppb (7.0%)	5.12 ppb (2.4%)	10.4 ppb (3.7%)	22.8 ppb (13.9%)	45.9 ppb (8.3%)
6:2 FTI	1.41 ppb (41.0%)	2.88 ppb (44.0%)	8.81 ppb (76.2%)	17.3 ppb (72.6%)	40.6 ppb (102.9%)	91.1 ppb (82.2%)
8:2 FTOH	41.6 ppb (4063.0%)	95.1 ppb (4655.0%)	322.2 ppb (6344.6%)	467.7 ppb (4577.0%)	945.7 ppb (4628.7%)	2190.9 ppb (4281.7%)
6:2 FTAC	0.84 ppb (16.0%)	1.85 ppb (7.5%)	5.56 ppb (11.2%)	10.5 ppb (5.2%)	21.4 ppb (6.8%)	50.2 ppb (0.4%)
8:2 FTI	0.86 ppb (14.0%)	1.87 ppb (6.5%)	5.51 ppb (10.2%)	9.75 ppb (2.5%)	22.7 ppb (13.4%)	49.4 ppb (1.2%)
10:2 FTOH	0.88 ppb (12.0%)	5.13 ppb (156.5%)	7.10 ppb (42.0%)	3.39 ppb (66.1%)	5.65 ppb (71.8%)	24.9 ppb (50.2%)
6:2 FTMAC	0.88 ppb (12.0%)	1.99 ppb (0.5%)	5.88 ppb (17.6%)	10.6 ppb (5.8%)	20.4 ppb (2.0%)	43.7 ppb (12.6%)
8:2 FTAC	0.86 ppb (14.0%)	2.00ppb (0.0%)	6.30 ppb (26.0%)	10.7 ppb (7.3%)	21.3 ppb (6.3%)	37.3 ppb (25.3%)
8:2 FTMAC	0.81 ppb (19.0%)	1.93 ppb (3.5%)	6.45 ppb (29.0%)	10.9 ppb (9.1%)	23.9 ppb (19.4%)	32.5 ppb (35.1%)
MeFOSA	27.8 ppb (2681.0%)	39.2 ppb (1859.5%)	51.5 ppb (926.6%)	43.7 ppb (336.8%)	50.6 ppb (152.8%)	141.4 ppb (182.7%)
EtFOSA	2.44 ppb (144.0%)	3.67 ppb (83.5%)	4.28 ppb (14.4%)	3.66 ppb (63.4%)	4.55 ppb (77.3%)	13.1 ppb (73.7%)

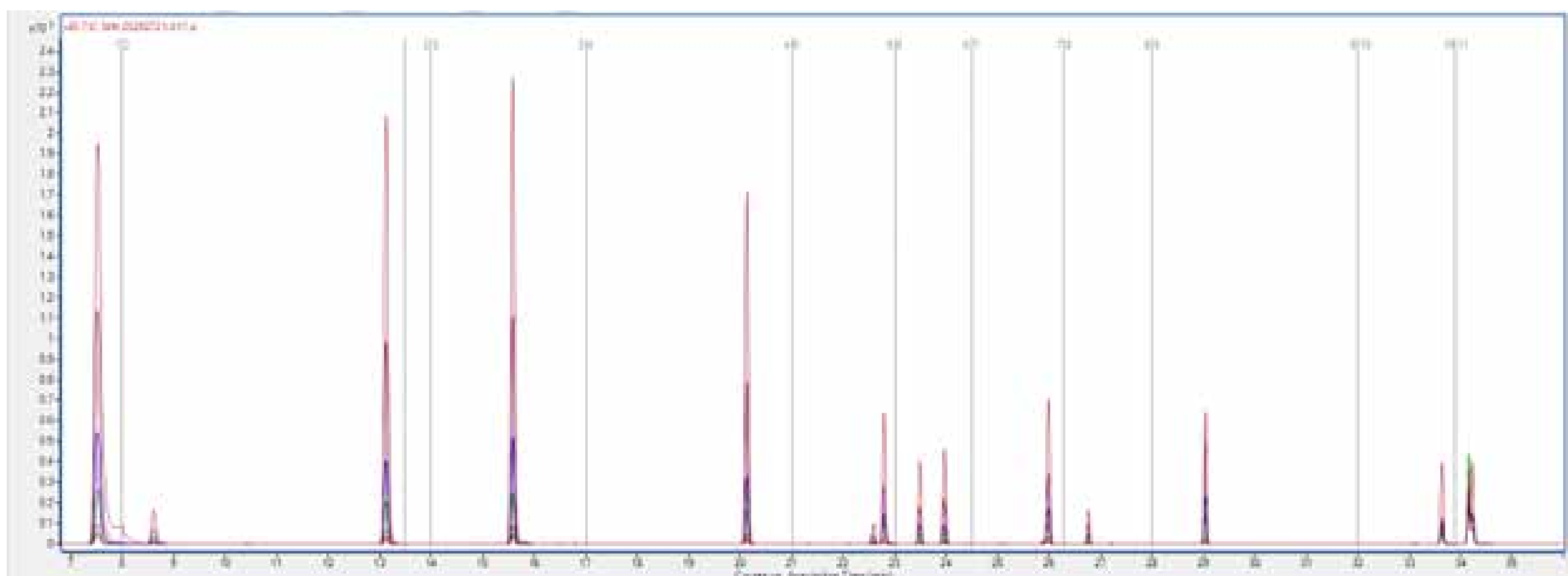


Figure 1: Extracted ion chromatogram of the calibration curve (1-50 ppb) in SIM mode.

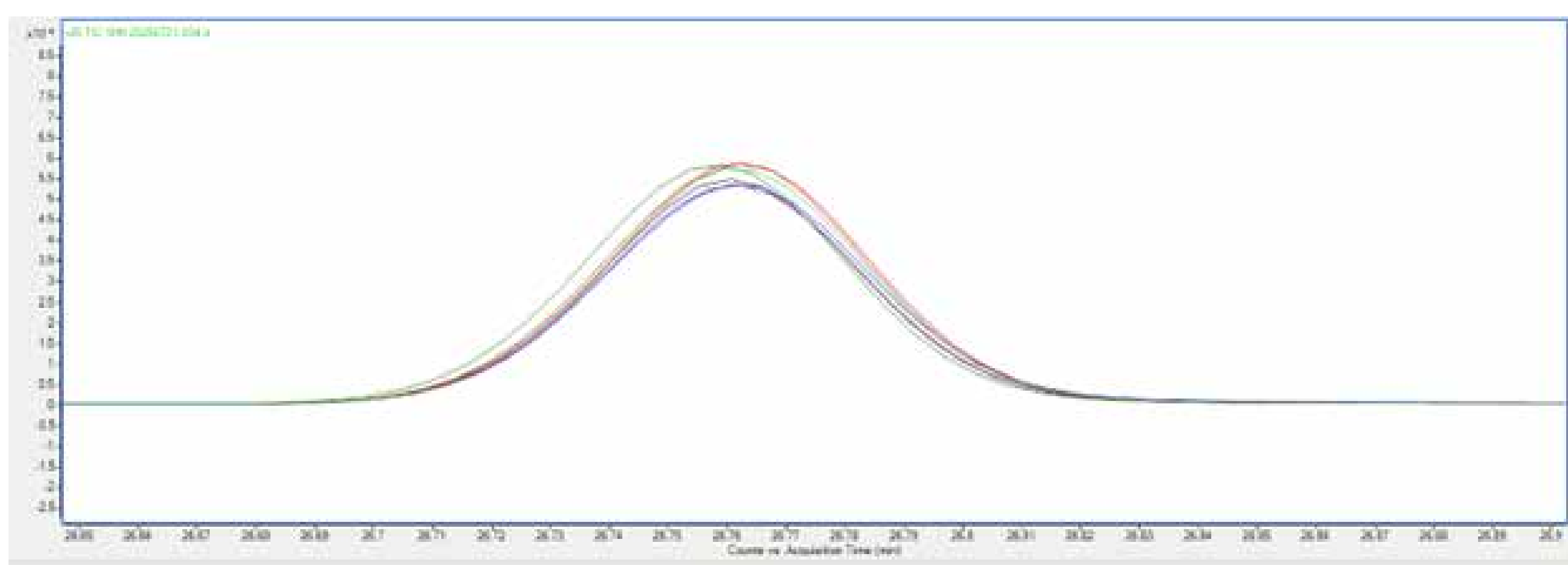


Figure 2: Extracted ion chromatogram overlay of $n=7$, 2 ppb water standard for 8:2 FTAC with a precision of 5.1% RSD.

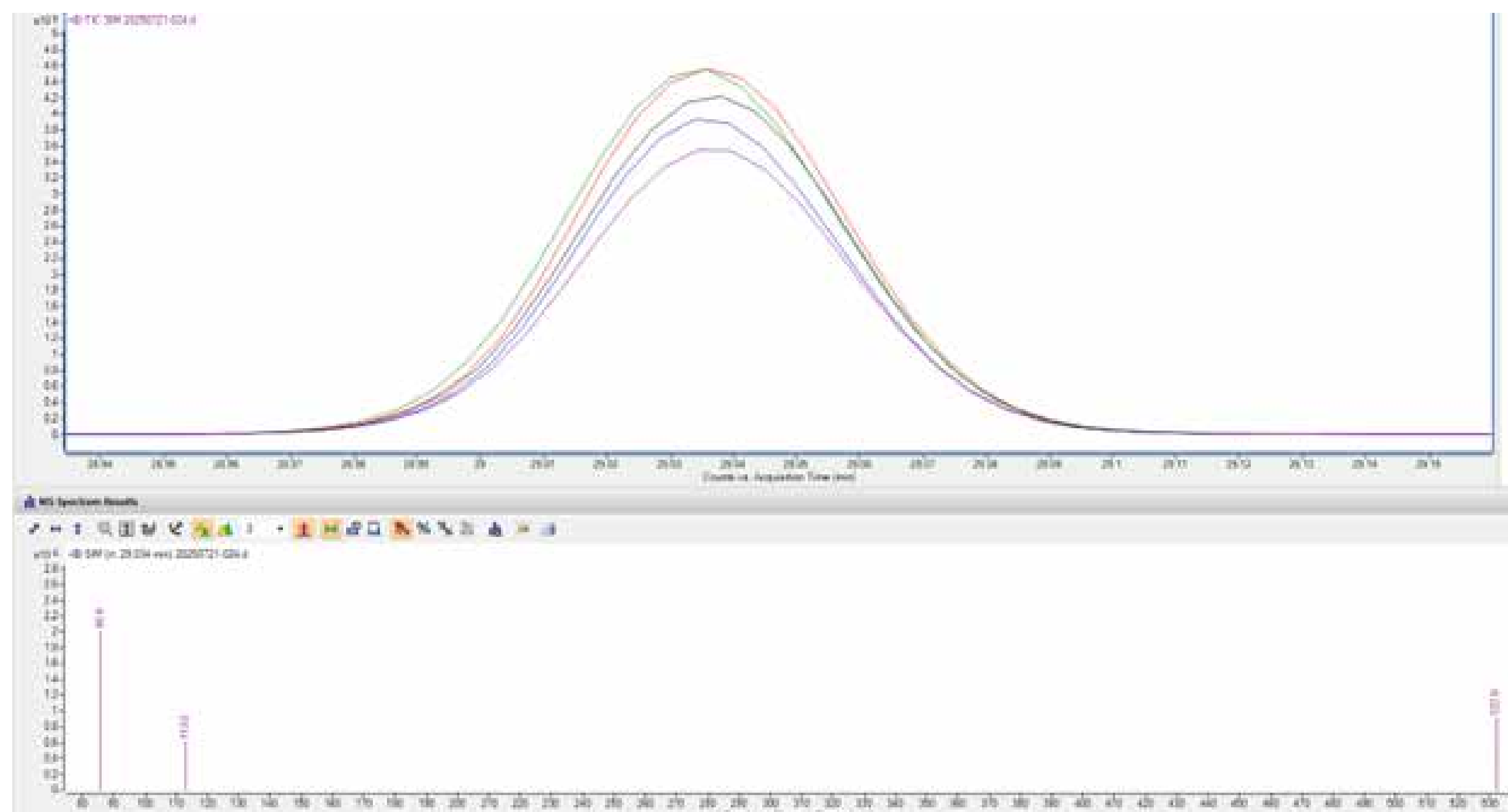


Figure 3: Extracted ion chromatograms overlay of $n=5$, 20 ppb water standard of 8:2 FTMAC with quantitation ion ($m/z=532$) and two confirming ions ($m/z=86$, $m/z=113$).

CONCLUSIONS

The data presented in this study shows promising preliminary results for most compounds under investigation. Two of Fluorotelomers, 6:2 FTI and 8:2 FTOH as well as the two Sulfonamides MeFOSA and EtFOSA struggled under the conditions and require further performance enhancements to optimize their recoveries. Since the study was done in parts per billion for the compounds of interest to show viability as a technique, future work will be performed to improve the overall sensitivity. Additional research into the trapping agents, gaseous and aqueous surface chemistry, purging options and use of autosampler configurations will also be performed. Finally, once optimization has been achieved overall robustness in the parts per trillion concentrations will be validated.

REFERENCES

- California Water Boards. "Frequently Asked Questions (FAQs) PFAS General." March 4, 2019. [Fact sheet] https://www.waterboards.ca.gov/pfas/docs/pfas_general_faq.pdf. (accessed July 24, 2025).
- United States Environmental Protection Agency. "EPA PFAS Drinking Water Laboratory Methods." April 24, 2025. <https://www.epa.gov/pfas/epa-pfas-drinking-water-laboratory-methods>. (accessed July 24, 2025).
- United States Environmental Protection Agency. "Per- and Polyfluoroalkyl Substances (PFAS) Final PFAS National Primary Drinking Water Regulation." May 21, 2025. <https://www.epa.gov/sdwa/and-polyfluoroalkyl-substances-pfas>. (accessed July 24, 2025).