Application Note

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Instrument: Pegasus® BT 4D

Determination of PFAS in Environmental Waters Using DHS-GCxGC-TOFMS

LECO Corporation; St. Joseph, Michigan USA

Key Words: Dynamic Headspace Sampling, Thermal Desorption Tubes, Per- and Polyfluoroalkyl Substances, Solid-Phase Extraction, Comprehensive Two-Dimensional Gas Chromatography, Time-of-Flight Mass Spectrometry, Persistent Organic Pollutants, Water Samples Analysis

Introduction

Per- and polyfluoroalkyl substances (PFAS) represent a vast group of synthetic organic compounds, with over 15,000 known variants. Their structure, characterized by strong carbon-fluorine bonds and amphipathic properties, makes them highly resistant to chemical and biological degradation.[1] These unique features led to extensive industrial and domestic applications, including coatings, textiles, firefighting foams, packaging, and cosmetics.[1] However, their persistence and mobility in the environment, along with their bioaccumulative nature, have raised serious health and ecological concerns. PFAS have been detected in human blood, breast milk, and umbilical cords, and studies since the 2000s have linked them to cancer, immune dysfunction, and endocrine disruption.[2]

Their recognition as persistent organic pollutants (POPs) under the Stockholm Convention in 2001 has prompted global efforts to limit their release.[3] Yet treating PFAS-contaminated water remains challenging, particularly for short-chain congeners that are not included in conventional removal methods. Monitoring is further complicated by their low concentrations and the interference of complex sample matrices. In addition, traditional sample preparation techniques like liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are laborious, solvent intensive, and prone to contamination.[4,5] In this context, the use of thermal desorption tubes (TDTs) is well suited for trace-level compounds. They enable effective preconcentration while minimizing solvent use and sample handling, reducing the risk of contamination.[6]

This research aimed to leverage dynamic headspace extraction (DHS) combined with thermal desorption as an alternative for the extraction of volatile and semi-volatile PFAS in water samples. Advanced analytical techniques such as gas chromatography coupled to time-of-flight mass spectrometry (GC-TOFMS) and comprehensive two-dimensional gas chromatography (GCxGC)-TOFMS were used to enhance resolution, sensitivity, and selectivity.

Experimental

Certified standards of nine target PFAS, including fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAcs), perfluorooctane sulfonamides (FOSAs), and perfluorooctane sulfonamidoethanols (FOSEs), were used for calibration (Table 2). An external calibration method was developed and validated for each compound. Stock solutions (1000 mg L^{-1}) of individual analytes were prepared in MS-grade methanol and stored at −20 °C in the dark.

For PFAS extraction, three types of thermal desorption tubes (Tenax-TA, Carbotrap 202, and Carbotrap T420) were evaluated, with Tenax-TA providing the best overall performance. Extraction volumes of 1, 2, and 5 L were tested to assess compound recovery, with 1 L selected as the best compromise between recovery and reproducibility.

For the calibration curves, standard solutions (5, 10, 20, 30, and 40 μg L^{-1}) were prepared by spiking ultrapure water with 1-octanol added as the internal standard, as this compound has a similar amphiphilic molecular structure to the targets. The curves were constructed by plotting each target peak area against concentration.

A real water sample from an industrial site was also analyzed by GCxGC-TOFMS. Analyte concentrations were determined by interpolation from the calibration curves. Additional environmentally relevant compounds were identified, including halogenated compounds, monoaromatics, and polycyclic aromatic hydrocarbons (PAHs).

Both GC-TOFMS and GCxGC-TOFMS analyses were performed on a *Pegasus* BT 4D GCxGC-TOFMS system (LECO Corporation, MI, USA) equipped with an Agilent 8890 GC and an RTC-PAL autosampler capable of automated handling of desorption tubes by employing a Capping/Decapping tool from GL Sciences (Eindhoven, The Netherlands). Sample injections were carried out using an Optic-4 multimode inlet (GL Science, Eindhoven, The Netherlands) with Peltier cooler and a liner exchanger (i.e., LINEX). The GC system was also equipped with a cryogenic trap, used for the secondary trapping/release stage. The instrument parameters are summarized in Table 1. Data were acquired and processed using ChromaTOF® software.[7]

Table 1: Instrumental parameters for GC(xGC)-TOFMS analysis.

GC(xGC) Parameters	LECO GC(xGC) with QuadJet™ Thermal Modulator
Carrier Gas	Helium 1.5 mL/min
Columns	^{1}D: Rxi-5SilMS (30 m x 0.25 mm ID x 0.25 μm *f.t.*) ^{2}D: Rxi-17SilMS (1.3 m x 0.25 mm ID x 0.25 μm *f.t.*)
Oven Program	40 °C (1 min), ramp 5 °C/min to 175 °C, ramp 30 °C to 300 °C (1 min)
Secondary Oven Temp	+5 °C (relative to the GC oven temperature)
Modulator Temp	+15 °C (relative to the secondary oven temperature)
Modulation Period	3 s
Transfer Line Temperature	280 °C
TOFMS	**LECO *Pegasus* BT 4D**
Ion Source Temperature	250 °C
Mass Range (*m/z*)	29–600
Acquisition Rate	10 Hz (150 Hz in GCxGC mode)

Results and Discussion

The performance of the GC-TOFMS analytical method was evaluated by assessing linearity, limits of detection (LOD), limits of quantification (LOQ), accuracy, and precision (Table 2). The method demonstrated linearity across the tested concentration range, with correlation coefficients above 0.98, further supported by Mandel's fitting test. LOD ranged from 2.17 ng L^{-1} for 4:2 FTOH up to 194.12 ng L^{-1} for N-EtFOSE, while LOQ extended from 6.57 to 588.24 ng L^{-1}. To confirm that a signal is near the calculated LODs, a blank water sample was spiked at 5 ng L^{-1}, resulting in successful detection of the target analytes.

Table 2. Quantification parameters of the nine target compounds determined by 1D GC-TOFMS.

Target	CAS	Quantifier Ion (m/z)	r^2	LOD (ng L^{-1})	LOQ (ng L^{-1})	Accuracy (%)[a]	Precision (%)[b]
4:2 FTOH	2043-47-2	31	0.9936	2.17	6.57	1.26	1.4
6:2 FTOH	647-42-7	31	0.9933	2.59	7.85	6.15	8.1
8:2 FTOH	678-39-7	31	0.9853	5.43	16.45	6.90	2.9
10:2 FTOH	865-86-1	31	0.9901	15.23	46.14	−4.23	9.0
8:2 FTAc	27905-45-9	77	0.9946	6.85	20.75	2.66	2.3
N-MeFOSA	31506-32-8	131	0.9851	9.25	28.03	4.45	7.9
N-EtFOSA	4151-50-2	131	0.9817	15.20	46.05	−5.38	6.7
N-MeFOSE	24448-09-7	131	0.9963	124.69	377.83	−1.57	3.4
N-EtFOSE	1691-99-2	131	0.9911	194.12	588.24	−1.53	7.0

[a]25 µg L-1, n = 3

[b]5 µg L-1, n = 3

The validated method was further applied to analyze a real water sample. However, the separation capacity of a 1D GC-system might be challenged by the complexity of a real water sample. Thus, applying GCxGC and taking advantage of the increased resolving power enhances the possibility for a non-targeted screening approach. The 2D chromatographic contour plot generated by the LECO *Pegasus* BT 4D system (Figure 1) illustrates the chemical complexity inherent to environmental samples. The separation power of GCxGC enabled the detection and effective resolution of some of the studied target analytes from numerous co-extracted matrix interferences, and the detection of 54 additional environmental contaminants, including aromatic compounds, halogenated compounds, and polycyclic aromatic hydrocarbons (Table 3).

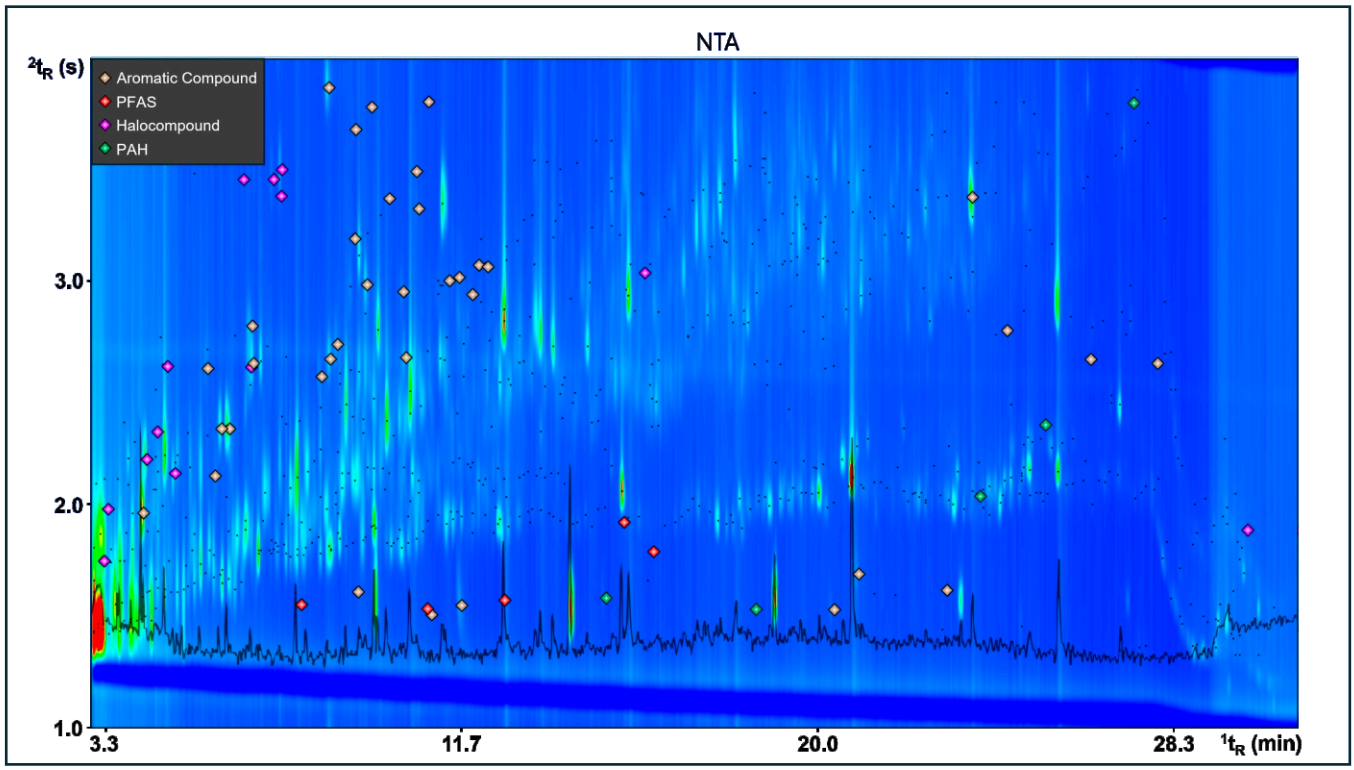

Figure 1: GCxGC-TOFMS contour plot and 1D chromatogram of a real-world water sample.

Table 3: Analytes from Figure 1 validated with reference standards (Validated ID) and putatively identified combining a spectral similarity higher than 850/1000, 1D retention index within ±20 units from reference values, and consistent positioning on the 2D plane. Class labels: (A) aromatic compounds; (H) halogen-containing compounds; (P) polycyclic aromatic compounds; (F) PFAS.

Compound	Class	Similarity (‰)	Characteristic *m/z*	^1t_R (min)	^2t_R (s)	RI_{Exp}	RI_{Lib}
1,2-Dichloropropane	H	931	63	3.20	1.87	696	701
Trichloroethylene	H	929	95	3.25	1.75	699	700
Bromodichloromethane	H	879	83	3.35	1.99	706	706
Toluene	A	852	91	4.15	1.98	762	763
1,1,2-Trichloroethane	H	966	97	4.25	2.22	769	768
1,3-Dichloropropane	H	866	76	4.45	2.34	783	780
Dibromochloromethane	H	898	129	4.65	2.63	797	800
Tetrachloroethylene	H	949	166	4.90	2.14	810	815
Chlorobenzene	A	960	112	5.65	2.62	844	849
p-Chlorobenzotrifluoride	A	881	180	5.85	2.14	853	868
Ethylbenzene	A	928	91	6.00	2.36	860	855
p-Xylene	A	949	91	6.15	2.35	867	865
Tribromomethane	H	941	173	6.50	3.46	883	892
Styrene	A	937	104	6.70	2.80	892	893
o-Xylene	A	914	91	6.75	2.64	894	888
1,1,2,2-Tetrachloroethane	H	939	83	7.20	3.47	912	916
Anisole	A	890	108	7.35	3.40	918	921
1,2,3-Trichloropropane	H	946	75	7.40	3.51	920	938
8:2 FTOH*	F	-	31	7.85	1.56	936	-
Propylbenzene	A	882	91	8.30	2.58	953	953
Benzaldehyde	A	940	77	8.50	3.87	960	962
p-Ethyltoluene	A	905	105	8.55	2.66	962	954
Mesitylene	A	910	105	8.70	2.73	968	972
α-Methylstyrene	A	919	118	9.10	3.20	982	986
Phenol	A	942	94	9.10	3.69	982	981
Benzonitrile	A	885	103	9.20	1.61	986	984
1,2,4-Trimethylbenzene	A	897	105	9.40	3.00	994	990
Benzofuran	A	921	118	9.50	3.79	997	1000
1,4-Dichlorobenzene	A	916	146	9.90	3.38	1011	1021
1,2,3-Trimethylbenzene	A	905	105	10.25	2.96	1023	1013
o-Cymene	A	904	119	10.30	2.67	1025	1022
1,2-Dichlorobenzene	A	888	146	10.55	3.49	1034	1043
Indane	A	897	117	10.60	3.33	1035	1029
10:2 FTOH*	F	-	31	10.80	1.53	1042	-
Indene	A	910	116	10.85	3.80	1044	1041
Benzeneacetaldehyde	A	858	91	10.90	1.52	1046	1045
Bis(2-chloroisopropyl) ether	H	865	45	11.20	3.35	1056	1061
1-Ethyl-3,5-dimethyl-benzene	A	850	105	11.30	3.01	1060	1059
o-Propyltoluene	A	877	105	11.55	3.02	1068	1051
Acetophenone	A	878	105	11.60	1.56	1070	1066
2-Ethyl-1,4-dimethyl-benzene	A	870	119	11.85	2.95	1079	1076
3-(1-methylethenyl)-Toluene	A	902	132	12.00	3.08	1084	1082
p-Cymenene	A	901	117	12.20	3.08	1091	1090
8:2 FTAc*	F	-	77	12.60	1.59	1105	-
Naphthalene	P	958	128	14.95	1.60	1186	1182
N-MeFOSA*	F	-	131	15.40	1.93	1202	-
Hexachloro-1,3-butadiene	H	952	225	15.90	3.05	1220	1231
N-EtFOSA*	F	-	131	16.10	1.80	1227	-
α-Methylnaphthalene	P	904	142	18.50	1.54	1315	1307
Biphenyl	A	951	154	20.30	1.53	1384	1381
Diphenyl ether	A	907	170	20.90	1.70	1408	1405
p-Methylbiphenyl	A	885	168	22.95	1.62	1491	1494
2,4-Di-tert-butylphenol	A	903	191	23.55	3.38	1516	1514
Dibenzofuran	P	855	168	23.70	2.05	1522	1515
(1-propylheptyl)-benzene	A	866	91	24.35	2.79	1550	1546
Benzophenone	A	914	105	26.35	2.66	1637	1635
1,3-Di-iso-propylnaphthalene	P	858	197	27.35	3.81	1682	1662
(1-Methyldecyl)-benzene	A	909	105	27.90	2.65	1707	1708
2,4',6-Trichloro-1,1'-biphenyl	A	874	119	30.00	1.88	1807	1808

**Identified with reference standards*

Even though the 1D GC-TOFMS LOD and LOQ were already low, a comparison between the 1D and 2D techniques at the lowest point was performed. Figure 2 shows the S/N ratio comparison for each of the perfluorinated target analytes between GC-TOFMS and GCxGC-TOFMS analysis. An average 11-fold higher S/N was observed thanks to the focusing effect of cryogenic modulation in GCxGC mode, ranging from 1.4 for 4:2FTOH to 24.5 for the N-EtFOSA. These results clearly show the higher sensitivity achieved using cryogenically modulated GCxGC, which is particularly valuable for trace analysis.

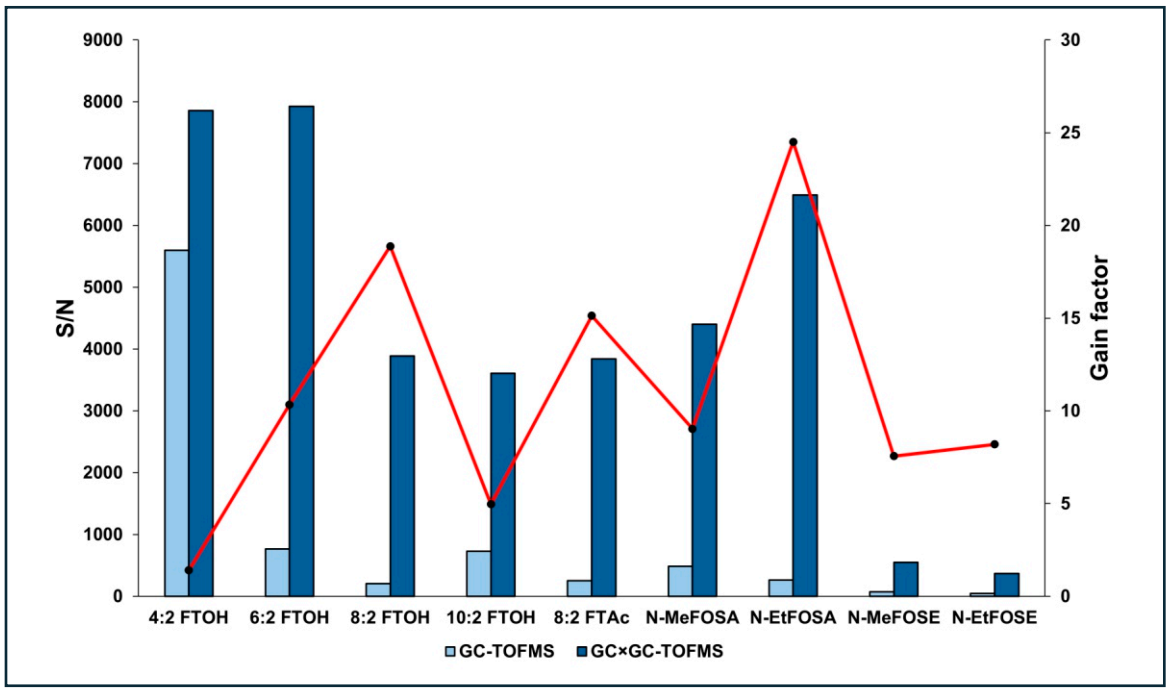

Figure 2: S/N ratio comparison of GC-TOFMS vs GCxGC-TOFMS at the lowest point of the calibration curve (5 µg L⁻¹).

Additionally, the gains of the GCxGC-TOFMS approach for resolving matrix interferences were demonstrated for a couple of different classes of PFAS. Figure 3 and Figure 4 illustrate the ability of the second chromatographic dimension to effectively resolve the target 8:2 FTAc and N-MeFOSA from co-extracted matrix interferents with overlapping isobaric MS signals, showcasing the importance of multidimensional separation for accurate quantification. These examples highlight the resolving capability of the LECO *Pegasus* BT 4D system, which increases confidence in analyte identification and quantification, even in challenging analytical scenarios.

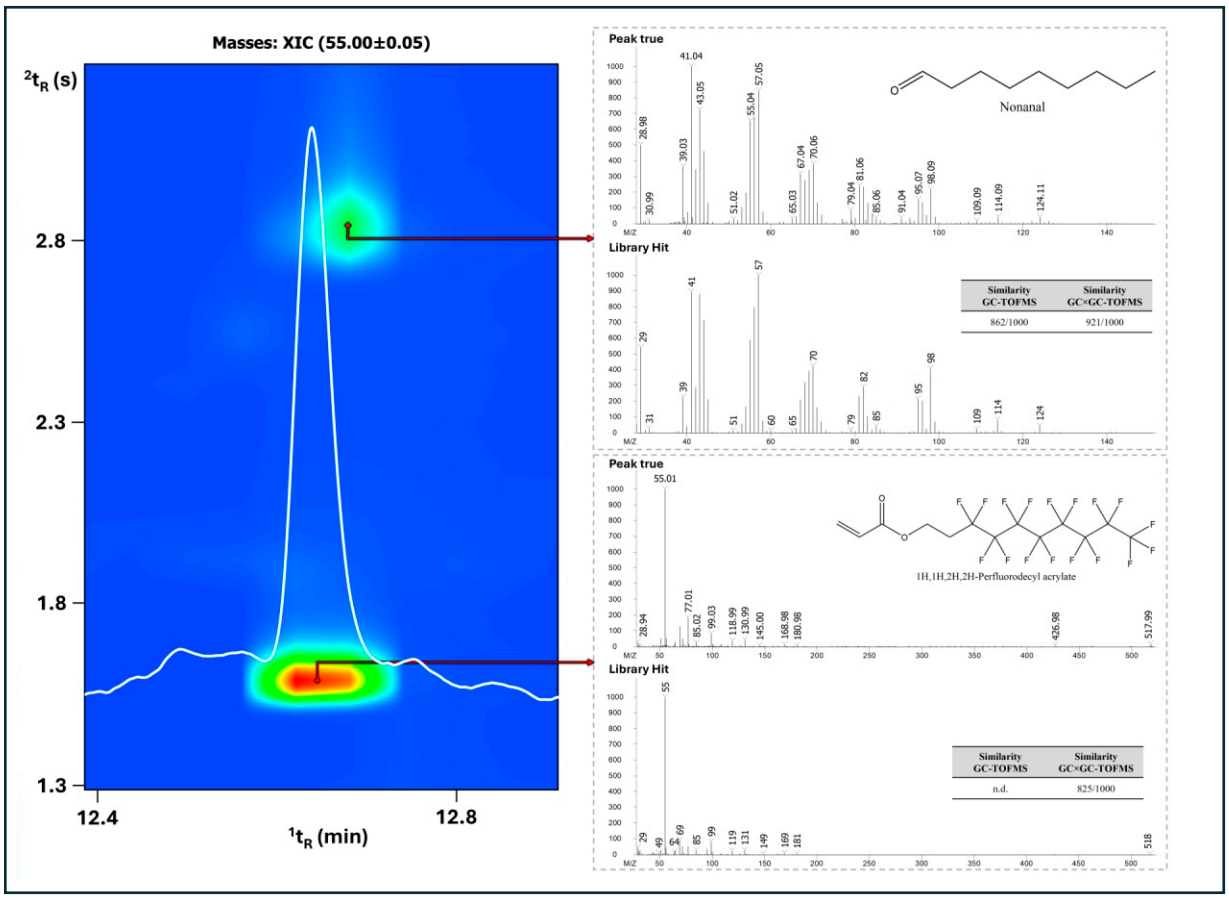

Figure 3: Section of a GC×GC-TOFMS extracted ion chromatogram (XIC) showing the 2D separation of 8:2 FTAc from an isobaric matrix interferent.

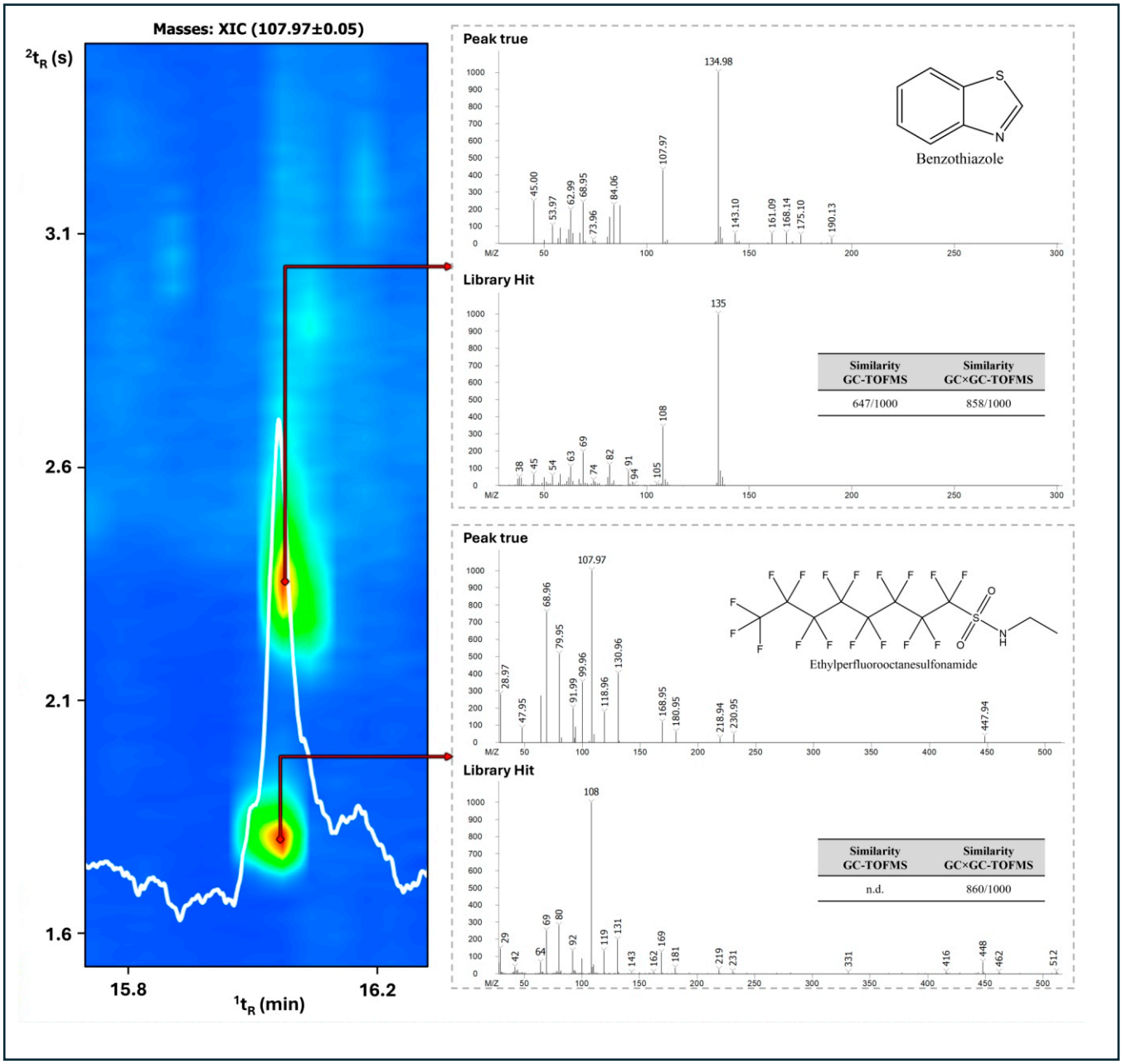

Figure 4: Expanded GCxGC-TOFMS chromatogram (XIC) illustrating the 2D separation of N-EtFOSA from an isobaric matrix interferent.

Conclusions

The use of dynamic head-space extraction and thermal-desorption GC(xGC)-TOFMS using the LECO *Pegasus* BT 4D enabled the determination of nine volatile PFAS targets, including fluorotelomer alcohols, acrylates, and alkyl sulfonamides. The method achieved sensitive and precise quantification, with LOQs down to 6.6 ng L^{-1} and repeatability between 1.4-7.9% RSD. When compared with 1D GC, the enhanced sensitivity of GCxGC allowed reliable detection of PFAS even at much lower concentrations. Moreover, the superior separation power of GCxGC supported effective non-target screening, enabling the identification of additional environmentally relevant compounds in an industrial water case study.

The combination of DHS-TD with GC-TOFMS, and particularly with GCxGC, provides a versatile platform that ensures robust quantification, high sensitivity, and expanded capabilities for both targeted PFAS analysis and non-targeted screening, supporting its application in environmental monitoring. Given the presence of hundreds of molecules, many of which are still poorly known and characterized, future studies will extend the workflow by including GC(xGC)-HRMS, which represents an important step toward a more comprehensive characterization of this emerging class of (semi-)volatile contaminants and will support the discovery of unknown congeners.

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Acknowledgment

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