Application note | 003507

Environmental

Quantitation of volatile PFAS in environmental samples using SPME Arrow and Orbitrap Exploris GC

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Keywords

SPME Arrow, PFAS, surface water, complex matrices, spectral deconvolution, GC Orbitrap, HRAM spectral library, unknown screening, gas chromatography, Orbitrap mass spectrometer

Application benefits

- A simple and robust sample preparation for volatile PFAS based on SPME Arrow for reducing manual handling and potential contamination issues.
- Sensitive and quantitative analysis of volatile PFAS in complex environmental samples using high resolution accurate mass (HRAM) that meets challenging reporting limits.
- Flexible data processing using full scan HRAM to include additional points of confirmation and quickly increase scope of analysis without reanalysis.

Goal

The aim of this application note is to demonstrate a sensitive and quantitative method for the simultaneous analysis of volatile per- and polyfluoroalkyl substances (PFAS) in environmental matrices using solid phase micro extraction (SPME) Arrow with a high-resolution accurate mass (HRAM) Thermo Scientific™ Orbitrap™ Exploris™ GC mass spectrometer.

Introduction

Per- and polyfluoroalkyl substances (PFAS) contain one or more alkyl radicals with all the hydrogens replaced by fluorine atoms. Traditionally, two groups of PFAS have been of the most concern and subject to control and monitoring. The first group includes ionic (or acidic) PFAS—the perfluorocarboxylic acids (perfluorooctanoic acid (PFOA)) and perfluoroalkylsulfonates (perfluorooctanesulfonic acid (PFOS))—where LC-MS-MS is the most common analytical technique. The second group includes neutral (or volatile) PFAS—the fluorotelomer alcohols[1] (FTOHs) and N-substituted fluoroalkylsulfonamides (FOSAs). For this group, due to the volatility, GC-MS is the analytical method of choice and is the focus of this study.

FTOHs are used in the synthesis of various surfactants and as intermediates in the manufacture of a variety of products with a wide range of applications, including textiles, polymers, paints, adhesives, waxes, and cleaning agents. FTOHs act as surfactants, lubricants, and intermediate products in manufacturing processes and can be emitted into the atmosphere during the production of fluoropolymers.

There is increasing commercial demand for the analysis of 6:2 and 8:2 FTOH due to the widespread use of fluorotelomer-based commercial products that has resulted in the extensive occurrence of FTOHs in the environment. Recent studies have focused on FTOH sources, fate, transport, and distribution in environmental media, along with human health risks and exposure. FTOHs have been found in various types of water sources including drinking water,[1,2] wastewaters,[4,6] industrial wastewater influents and effluents,[1,3,6] surface water,[2,7] and rainwater. New European regulations are currently pending for 6:2 and 8:2 FTOH, which are proposed for inclusion within a regulated sum of 24 per- and polyfluorinated alkyl substances (PFAS) of primary concern. Incorporation of these substances into the regulatory regimes of other regions may follow.

The accurate analysis of PFAS by testing laboratories requires robust and streamlined analytical workflows. These methods must overcome the challenges of an ever-growing list of PFAS compounds, diversity of sample matrices, and demanding analytical performance requirements. Typically, a gas chromatography instrument coupled to low-resolution, nominal mass triple quadruple mass spectrometer (GC-MS/MS) has been the system of choice for the sensitive and selective detection of a wide range of target PFAS compounds. However, the development of high-resolution accurate mass (HRAM) Orbitrap mass spectrometry coupled to GC has proved to be a valuable alternative to triple quadrupole GC-MS. With HRAM mass spectrometry, the default acquisition mode is untargeted (full-scan) meaning that all the ions are acquired with high selectivity at the same time across a specified mass range, making the method setup and data acquisition simple to manage and giving the analyst the flexibility to decide on which compounds to focus. This can extend into retrospective analysis of data to evaluate for the presence/absence of other contaminants not necessarily of interest at the time of acquisition. For example, this could allow the search for other PFAS compounds beyond the target list.

In this study, the performance of the Orbitrap Exploris GC high-resolution accurate mass (HRAM) spectrometer together with the headspace solid phase micro extraction (SPME) Arrow for the quantitative analysis of volatile PFAS including FTOH, fluorotelomer acrylates (FTACs), fluorotelomer methacrylates (FTMACs), fluorotelomer iodides (FTIs), Me/Et-FOSAs, and Me/Et-FOSEs is demonstrated.

Experimental

Sample and standard preparation

A total of 16 samples were analyzed including river water, groundwater, landfill leachate, trade effluent, and crude sewage. For sample and standard preparation, 10 mL sample/standard, 25 µL of internal standard working solution mix, and 0.5 mL methanol were dispensed to a 20 mL headspace vial. Blank samples (10 mL ultra-pure water) were prepared in addition to assess background contamination and determine the limit of detection and quantification. Commercial standard mix Fluorotelomer Mix 3 (PFAS Mix 07, Fluorotelomer Mix 03), fluorotelomer PT Mixture and individual N-MeFOSA 50 ppm and N-EtFOSA 50 ppm (Wellington) were diluted in methanol to provide a mixed intermediate standard of 0.5 ppm. Serial dilution of the intermediate standard mix was performed over the range from 5 to 125 ng/L. Internal standards were prepared from intermediate mix of Wellington Mix Cat containing D3-N-MeFOSA (0.5 ppm), D5-N-EtFOSA (0.5 ppm), D7-N-MeFOSE (5 ppm), D9-N-EtFOSE (5 ppm), and FTOH Internal Standard (IS) Solution containing 6:2 FTOH-13C2D2 and 18:2 FTOH-13C2D2 at 0.1 ppm. A working solution mix was prepared from 200 µL of the Wellington mix and 800 µL of the FTOH IS working solution.

Instrument and method setup

Headspace extraction and injection of samples were performed using the Thermo Scientific™ TriPlus™ RSH SMART autosampler equipped with the Thermo Scientific™ SMART SPME Arrow 1.1 mm PDMS 100 µm fiber (P/N 36SA10P1-SM). Incubation and extraction were performed online followed by sample injection/desorption. After sample injection, the SPME Arrow fiber was re-conditioned at high temperature under a nitrogen flow using an SPME conditioning station to avoid sample carryover between injections. Further details surrounding the SPME Arrow operating parameters can be found in Table 1.

Table 1. TriPlus RSH SMART autosampler and GC conditions

TriPlus RSH SMART SPME Arrow parameters	
Incubation temperature (°C)	70 °C
Incubation time (min)	5
Agitation speed (rpm)	1,200
Extraction time (min)	8
Needle depth in vial (mm)	30
Needle speed in vial (mm·s^{-1})	20
Fiber injection	
Injection liner depth (mm)	70
Penetration speed (mm·s^{-1})	40
Injection desorption time (min)	3
SPME fiber conditioning	
Conditioning temperature (°C)	290
Conditioning time (min)	10
TRACE 1610 GC system parameters	
Injector	Thermo Scientific™ iConnect™ SSL
Liner	Thermo Scientific™ SPME Arrow liner ID 1.7 mm (P/N 453A0415-UI)
Injection mode	Splitless
Split flow (mL·min^{-1})	60
Injector temperature (°C)	250
Carrier gas, (mL·min^{-1})	1.2
Oven temperature program	
Initial temperature (°C)	40
Hold time (min)	0.5
Rate 1 (°C·min^{-1})	20
Temperature 1 (°C)	150
Rate 2 (°C·min^{-1})	40
Temperature 2 (°C)	280
Final hold time (min)	2
Total analysis time (min)	11.25

A Thermo Scientific™ TRACE™ 1610 GC equipped with a Thermo Scientific™ TraceGOLD™ TG-5SilMS (30 m × 0.25 mm I.D. × 0.25 µm film) capillary column (P/N 26096-1420) was used to perform the chromatographic separation. Oven program conditions can be found in Table 1. Data acquisition was carried out in full scan analysis using an Orbitrap Exploris GC mass spectrometer. Additional MS method parameters are summarized in Table 2. External mass calibration was performed prior to analysis, while characteristic ions representing column bleed were used as lock masses when scanning in EI to perform internal mass calibration. Sample acquisition and qualitative processing was performed using the Thermo Scientific™ Chromeleon™ version 7.3.2 Chromatography Data System (CDS) software. Additional screening data processing was done using Thermo Scientific™ Compound Discoverer™ software with the Thermo Scientific™ Orbitrap GC-MS HRAM Contaminants Library.

Table 2. EI source and mass spectrometer conditions

Orbitrap Exploris GC MS parameters	
Transfer line (°C)	280
Thermo Scientific™ ExtractaBrite™ ion source temperature (°C)	250
Electron energy (eV)	70
Acquisition mode and scan range (*m/z*)	Full scan, 50–750
Resolving power (at 200 *m/z*)	30,000
Emission current (µA)	50
Mass accuracy on lock mass	5 ppm
Internal lock mass calibration (column bleed, *m/z*)	207.02235, 281.05114, 355.06993

Results and discussion

The objective of the study was to develop a robust method for the analysis of volatile PFAS compounds in environmental samples using GC-HRAM. The primary focus was on FTOH, but other species including fluorotelomer acrylates (FTACs), fluorotelomer methacrylates (FTMACs), fluorotelomer iodides (FTIs), Me/Et-FOSAs, and Me/Et-FOSEs were included as well. The sample preparation needed to be minimal to allow for fast analysis, reduce analyte loss, and potentially screen for other compounds beyond the target list. The method also needed to meet challenging reporting limits of low ng/L levels and be robust for high throughput of complex sample matrices.

The target list of sixteen compounds and six internal standards is shown in Table 3 alongside the retention times and accurate mass ions used for identification and confirmation. Analytical standards were used to build this database of retention times and accurate mass ions. The excellent and consistent mass accuracy on an Orbitrap Exploris GC allows for narrow mass extraction windows of ±5 ppm. This provides high selectivity in complex matrices to enable low-level compound detection with low background chemical noise. This is demonstrated in Figure 1, which shows extracted ion chromatograms in Chromeleon software for selected compounds including 6:2 and 8:2 FTOH at 1 ng/L in river water.

Sensitivity of target compounds

Compound sensitivity was evaluated by replicate analysis (n=12) of a 1 ng/L standard to determine the limit of detection (LOD at 3 x standard deviation) and the limit of quantification (LOQ at 10 x standard deviation). The results are summarized in Table 4, which shows the LOD ranged from 0.1 to 1.4 ng/L, well below the target 5 ng/L level. The LOQ ranged from 0.35 to 4.5 ng/L.

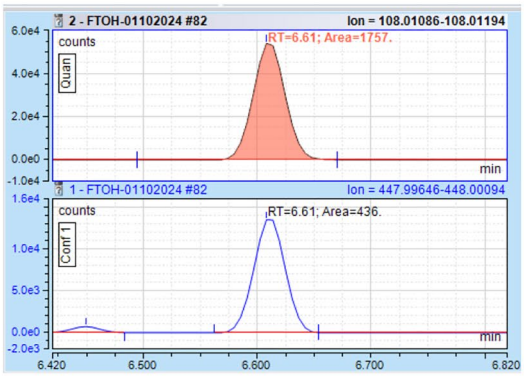
Table 3. Volatile PFAS included in the targeted method with their retention time and identifier ions with up to two qualifier accurate mass ions

Compound name	CAS number	Target or internal std	Retention time (min)	Quantification ion	Qualifier ion 1	Qualifier ion 2
4:2 FTI	2043-55-2	Target	3.42	373.9208	227.0102	-
6:2 FTOH	647-42-7	Target	3.54	127.0165	95.0103	294.9975
6:2 FTOH-13C2	647-42-7	Internal Std	3.54	129.0261	96.0136	314.9991
6:2 FTI	2043-57-4	Target	4.23	473.9145	327.0038	-
8:2 FTOH	678-39-7	Target	4.35	127.0165	95.0103	404.9955
8:2 FTOH-13C2	678-39-7	Internal Std	4.35	129.0261	96.0136	414.9930
6:2 FTAC	17527-29-6	Target	4.89	55.0178	77.0197	418.0233
8:2 FTI	2043-53-0	Target	5.12	573.9081	426.9974	-
10:2 FTOH	865-86-1	Target	5.17	127.0165	95.0103	504.9891
6:2 FTMAC	2144-53-8	Target	5.53	432.0389	77.0197	-
8:2 FTAC	27905-45-9	Target	5.7	55.0178	77.0197	518.0169
8:2 FTMAC	1996-88-9	Target	6.29	532.0326	77.0197	-
10:2 FTAC	17741-60-5	Target	6.43	55.0178	77.0197	618.0095
d3-N-MeFOSA	936109-37-4	Internal Std	6.43	97.0145	433.0271	-
N-MeFOSA	31506-32-8	Target	6.45	93.9957	430.0083	-
d5-N-EtFOSA-d	936109-40-9	Internal Std	6.59	113.0427	450.0113	-
N-EtFOSA	4251-50-2	Target	6.62	108.0114	447.9989	-
10:2 FTMAC	2144-54-9	Target	6.91	632.0262	77.0197	-
d7-N-MeFOSE	1265205-95-5	Internal Std	7.74	531.0074	467.0455	-
N-MeFOSE	24448-09-7	Target	7.77	525.9764	462.0145	-
d9-N-EtFOSE	1265205-96-6	Internal Std	7.97	547.0358	451.0177	-
N-EtFOSE	1691-99-2	Target	7.99	539.9921	447.9989	-

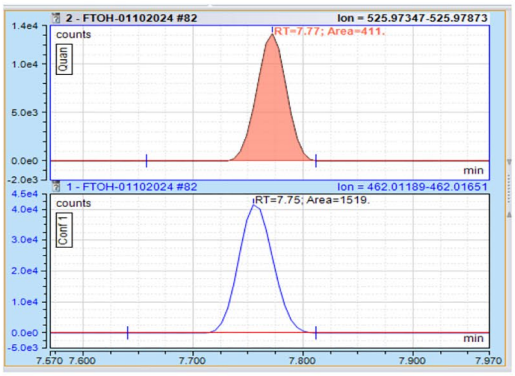
Table 4. Limit of detection (LOD) and limit of quantification of sixteen target PFAS compounds

Compound	LOD (ng/L)	LOQ (ng/L)
4:2 FTI	0.25	0.83
6:2 FTI	0.63	2.09
8:2 FTI	1.37	4.58
6:2 FTOH	0.15	0.49
8:2 FTOH	0.08	0.27
10:2 FTOH	0.33	1.10
6:2 FTAC	0.25	0.84
8:2 FTAC	0.80	2.65
10:2 FTAC	0.77	2.57
6:2 FTMAC	0.72	2.41
8:2 FTMAC	0.49	1.65
10:2 FTMAC	0.76	2.53
N-MeFOSA	0.13	0.43
N-EtFOSA	0.10	0.34
N-MeFOSE	0.87	2.91
N-EtFOSE	0.89	2.98

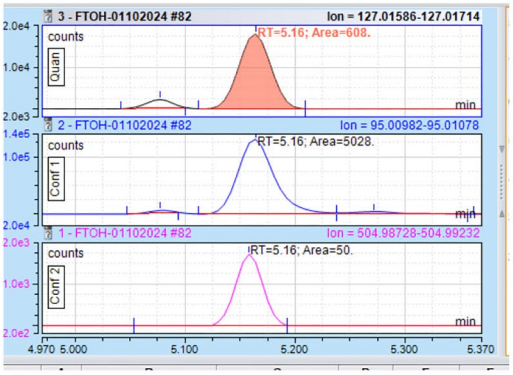
N-Et-FOSA



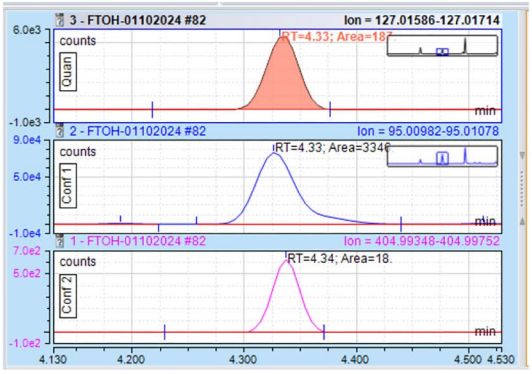
N-Me-FOSE



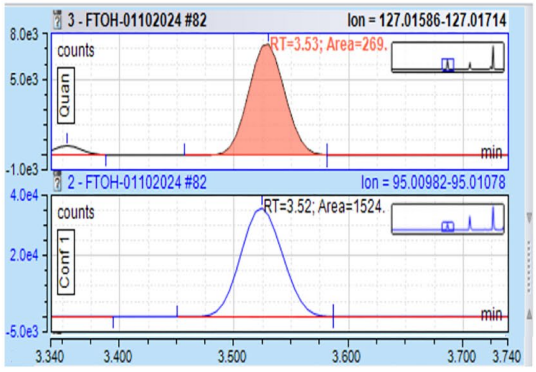
10:2 FTOH



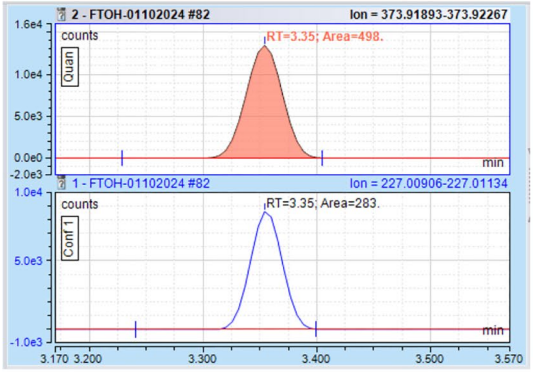
8:2 FTOH



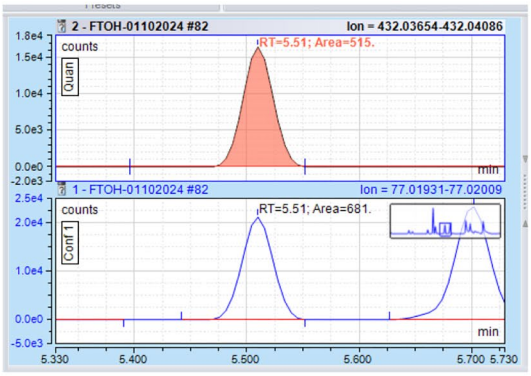
6:2 FTOH



4:2 FTI



6:2 FTMAC



8:2 FTAC

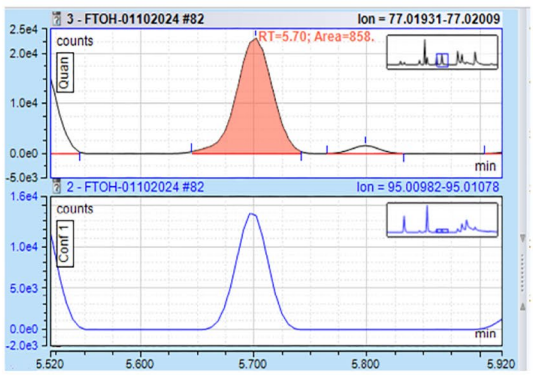


Figure 1. Extracted ion chromatograms for main quantifier and qualifier ions for selected PFAS compounds at 1 ng/L in river water

Linearity and recovery of target compounds

A calibration curve from 5 to 125 ng/L was prepared in river water to assess method linearity and recovery of target compounds from the SPME Arrow extraction protocol. Figure 2 shows the linearity is >0.99 for sixteen compounds. Internal standard correction was applied where appropriate for the target compound.

Compound	R^2
4:2 FTI	0.99934
6:2 FTI	0.97406
8:2 FTI	0.99823
6:2 FTOH	0.99564
8:2 FTOH	0.99996
10:2 FTOH	0.99932
6:2 FTAC	0.99892
8:2 FTAC	0.99803
10:2 FTAC	0.99879
6:2 FTMAC	0.99874
8:2 FTMAC	0.99282
10:2 FTMAC	0.99753
N-MeFOSA	0.99991
N-EtFOSA	0.99993
N-MeFOSE	1.00000
N-EtFOSE	0.99996

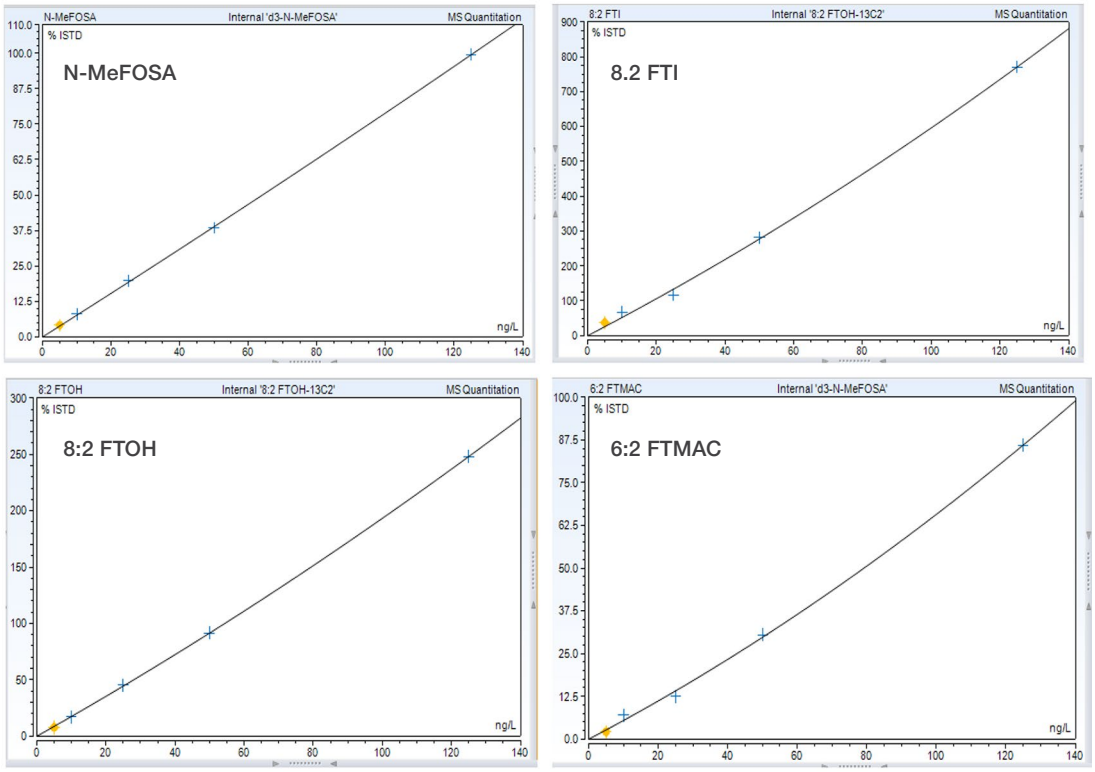


Figure 2. Linearity of the sixteen target compounds with R^2 shown and example calibration curves for N-MeFOSA, 8:2 FTI, 8:2 FTOH, and 6:2 FTMAC

Method recovery and repeatability were evaluated by spiking compounds at concentrations of 25 and 125 ng/L in river water. Six replicate samples were analyzed at both concentration levels. Acceptable recovery was observed across all target compounds and results are shown in Table 5. The repeatability could be improved for FTAC and FTMAC by using suitable labeled isotope compounds for these classes.

Table 5. Summary of volatile PFAS compounds recovery at 25 and 125 ng/L spike in river water. Six replicate analyses were conducted.

Compound	25 ng/L spike		125 ng/L spike	
	Recovery (%)	RSD %	Recovery (%)	RSD (%)
6:2 FTOH	102.8	4.0	105.1	7.4
8:2 FTOH	103.1	1.4	114.5	1.7
10:2 FTOH	84.5	7.4	87.9	5.0
6:2 FTAC	99.7	6.1	98.8	7.9
8:2 FTAC	87.3	21.8	71.1	15.8
10:2 FTAC	76.1	10.3	83.1	15.0
6:2 FTMAC	90.5	4.8	84.3	6.5
8:2 FTMAC	82.0	9.8	64.9	7.7
10:2 FTMAC	78.4	8.5	72.7	6.6
N-Me-FOSA	98.7	2.3	99.6	1.1
N-Et-FOSA	97.6	1.4	102.4	1.8
N-Me-FOSE	96.0	3.8	100.4	2.3
N-Et-FOSE	92.6	2.3	95.6	5.5

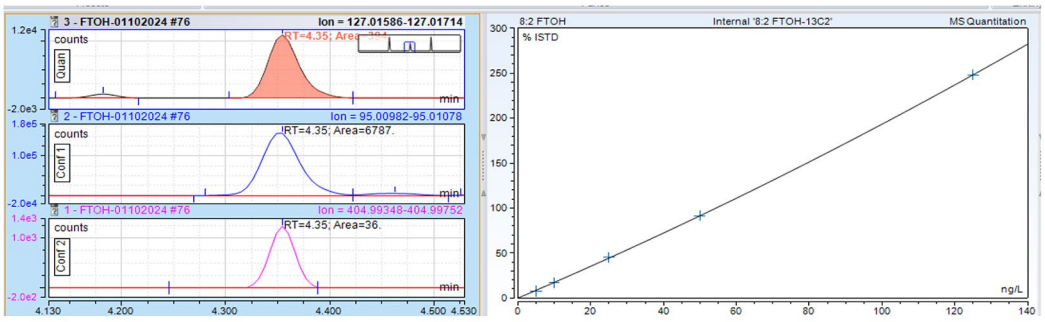
Analysis of real environmental samples

To test the method in complex matrices, a range of sixteen samples were analyzed for the list of target compounds. These included landfill leachate, trade effluent, crude sewage, and groundwaters. The results are summarized in Table 6 and show that all samples contained at least two target PFAS compounds. FTAC, FTMAC, and FTI compounds were not detected in any samples, while FTOH and FOSE were detected in at least one of the samples. One crude sewage sample (sample 11) contained 1,050 ng/L of 6:2 FTOH. This concentration is approximately ten times higher than the highest standard of 125 ng/L. Such elevated concentrations underscore the critical importance of monitoring volatile PFAS compounds in the environment. The sensitivity and linearity of the system is demonstrated in Figure 3, which shows positive detections in samples 6 and 1 at low concentrations of 0.46 8:2 FTOH and 2.19 ng/L N-Et-FOSE, respectively.

Table 6. Summary of volatile PFAS compounds detected in sixteen samples ranging in complexity. Concentrations reported in ng/L.

		Concentration ng/L						
Sample	Matrix	6:2 FTOH	8:2 FTOH	10:2 FTOH	N-MeFOSA	N-EtFOSA	N-MeFOSE	N-Et-FOSE
Sample 1	Landfill leachate	0.74	0.17	0.93	n.d	n.d	3.62	2.19
Sample 2	Landfill leachate	2.8	5.2	2.3	n.d	n.d	43.4	23.2
Sample 3	Landfill leachate	3.02	23.2	5.91	n.d	n.d	96.5	98.3
Sample 4	Trade effluent	7.2	90.2	95.4	n.d	n.d	68	39.2
Sample 5	Trade effluent	0.14	0.17	0.73	n.d	n.d	n.d	n.d
Sample 6	Landfill leachate	0.94	0.46	0.41	0.28	n.d	6.49	5.09
Sample 7	Landfill leachate	5.97	39.7	7.75	n.d	n.d	82.2	27.3
Sample 8	Landfill leachate	11.5	137	118	1.08	n.d	79.4	28.4
Sample 9	Landfill leachate	3.46	4.14	4.24	n.d	n.d	29.7	118
Sample 10	Trade effluent	6.14	35.7	87.2	n.d	n.d	187	123
Sample 11	Crude sewage	1050	7.35	0.33	n.d	n.d	n.d	n.d
Sample 12	Crude sewage	28.1	1.76	n.d	n.d	n.d	n.d	n.d
Sample 13	Crude sewage	4.67	0.13	n.d	n.d	n.d	n.d	n.d
Sample 14	Trade effluent	0.74	0.17	0.08	n.d	n.d	n.d	n.d
Sample 15	Groundwater	n.d	n.d	n.d	0.49	0.55	1.08	0.99
Sample 16	Groundwater	n.d	n.d	n.d	0.46	0.57	1.04	0.76

Sample 6
8:2 FTOH at 0.46 ng/L



Sample 1
N-EtFOSE at 2.19 ng/L

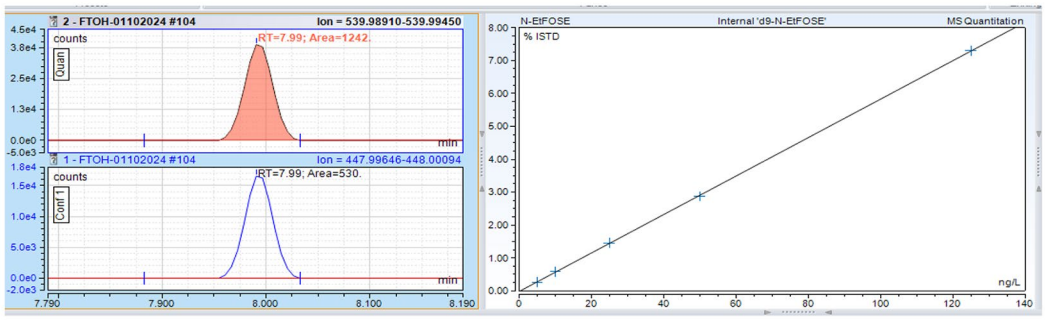
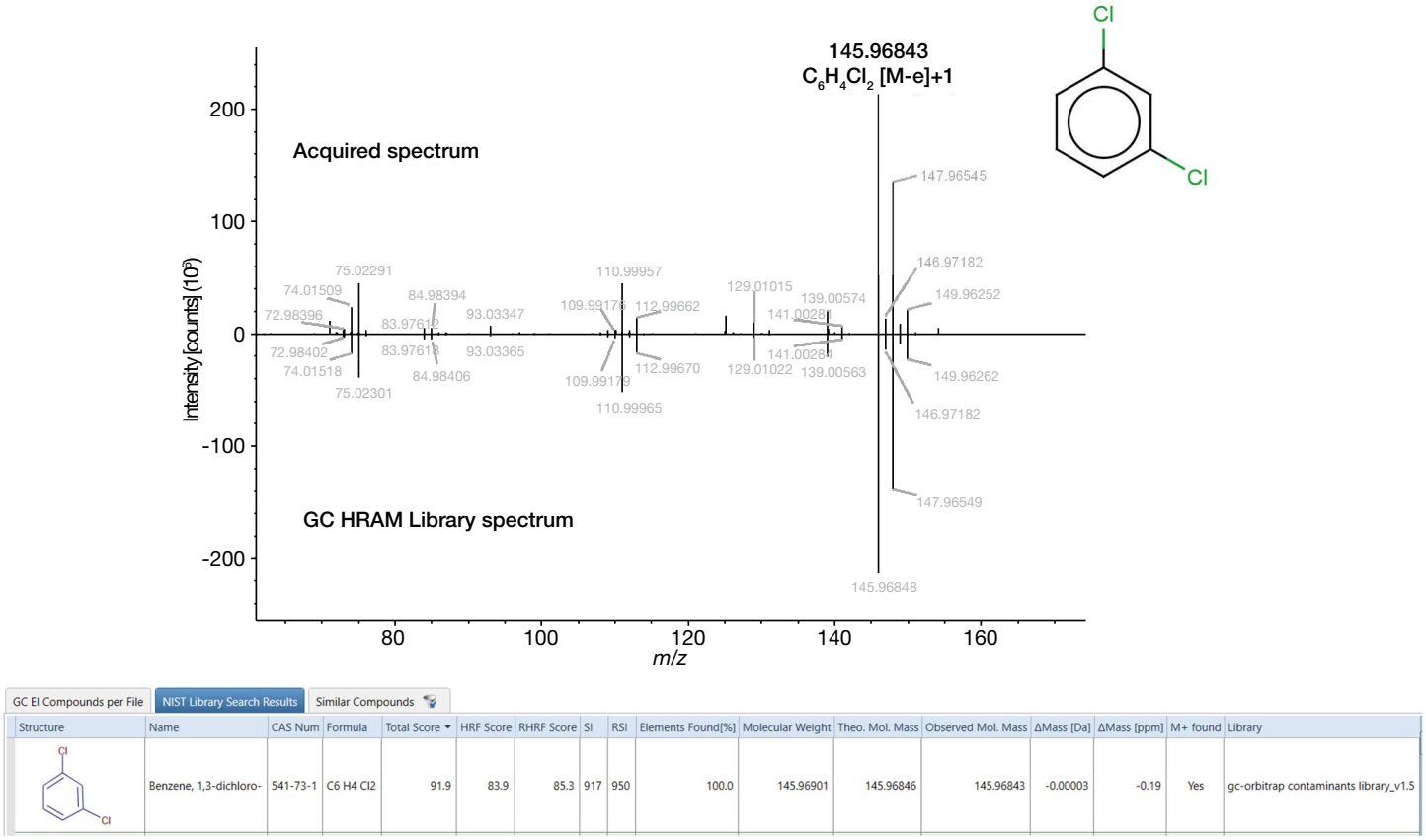


Figure 3. Target compound detections in landfill leachate sample numbers 6 and 1. The main quantification ion and qualifier ions are clearly detected at low concentrations. Calibration curves are linear (>0.99) to support accurate quantitation.

Screening beyond the target compound list

An additional benefit to using GC-HRAM in full scan is that it opens up the possibility to screen samples for compounds beyond the target list by using spectral libraries. As an example, the landfill leachate sample 7 was additionally processed in Compound Discoverer software to first deconvolute the data to clean the spectra and then search against the Thermo Scientific Orbitrap GC-MS HRAM Contaminants Library. Figure 4 shows an example match for dichlorobenzene with a search index score of 917. The molecular ion is present in this EI spectrum with the mass accuracy of *m/z* 145.96846 at 0.2 ppm adding confidence to the identification.



GC EI Compounds per File | NIST Library Search Results | Similar Compounds

Structure	Name	CAS Num	Formula	Total Score	HRF Score	RHRF Score	SI	RSI	Elements Found[%]	Molecular Weight	Theo. Mol. Mass	Observed Mol. Mass	ΔMass [Da]	ΔMass [ppm]	M+ found	Library
	Benzene, 1,3-dichloro-	541-73-1	C6 H4 Cl2	91.9	83.9	85.3	917	950	100.0	145.96901	145.96846	145.96843	-0.00003	-0.19	Yes	gc-orbitrap contaminants library_v1.5

Figure 4. Sample mass spectrum (upper) and matching HRAM spectrum (lower) with the Orbitrap GC-MS Contaminants Library hit of dichlorobenzene including search results table. SI score of 917 indicates a strong match. Molecular ion *m/z* 145.96846 mass accuracy is 0.2 ppm.

Conclusion

Volatile perfluoroalkyl substances (PFAS) have become a significant focus in environmental analysis due to their potential health and environmental risks. The inherent complexity of environmental samples and the need for minimal sample handing of volatile PFAS is critical in accurate quantitation and detection. The method presented utilizes a combination of HS-SPME Arrow with an Orbitrap Exploris GC to provide an efficient workflow for the analysis of PFAS compounds giving analytical advantages including:

- Minimal sample preparation and online extraction using the TriPlus RSH SMART robotic autosampler increase the sample throughput and minimize the risk of contamination. Using SPME Arrow extraction technique, good recovery of all target volatile PFAS compounds was demonstrated.
- Full scan acquisition at high mass resolution provides targeted quantitative analysis together with non-target analysis to quickly increase the scope of analysis and screen for other compounds outside the target list.
- Full scan acquisition facilitates versatile data processing and allows for the incorporation of additional confirmation points, including supplementary confirmation ions, spectral matching, and isotope pattern.
- Limits of detection ranging from 0.1 to 1.4 ng/L are well below the target 5 ng/L level of PFAS compounds in complex environmental matrices.
- Application of the method to real samples showed PFAS compounds present in all samples with some very high concentrations in crude sewage and landfill leachate.

References

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