

Analysis of Neutral PFAS in Ambient Air Using Thermal Desorption GC-MS

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User Benefits

- ◆ A thermal desorption GC-MS system can accurately measure quantities of volatile and semivolatile per- and polyfluoroalkyl substances (PFAS) in ambient air.
- ◆ The TD-30R thermal desorption system can perform high-throughput analysis as it does not require solvent extraction.

Introduction

Because of the excellent heat-resistance and water-repelling properties of per- and polyfluoroalkyl substances (PFAS), they are used in many consumable products and industrial applications. However, their resistance to degradation and concerns over their persistence in the environment and toxicity to organisms mean they are increasingly regulated throughout the world. As one of the pollution routes of PFAS, the atmospheric dispersion of PFAS exhaust gas emitted from factories using PFAS is a concern. Therefore, monitoring studies have been conducted considering the risk of long-term exposure of PFAS to the respiratory system and the spread of PFAS pollution from atmospheric dispersion of PFAS.

Because of the tightening of PFAS regulations, analytical methods are being developed for a variety of matrices, including water, soil, and food. While most of these methods target non-volatile (ionic) PFAS and use a liquid chromatograph-mass spectrometer (LC-MS/MS), volatile or semivolatile neutral PFAS are not easily measured by these methods, so a gas chromatograph-mass spectrometer (GC-MS) is suitable for those compounds.

In this Application News, the TD-30R thermal desorption system coupled to a GC-MS system (Fig. 1) measured the quantities of nine volatile and semivolatile neutral PFAS (Table 1) in ambient air.

Table 1 Compounds Targeted for Measurement

Acronym	Compounds	Formula
Fluorotelomer alcohols (FTOHs)		
4:2 FTOH	2-Perfluorobutyl ethanol	C ₆ H ₅ F ₉ O
6:2 FTOH	2-Perfluorohexyl ethanol	C ₈ H ₅ F ₁₃ O
8:2 FTOH	2-Perfluorooctyl ethanol	C ₁₀ H ₅ F ₁₇ O
10:2 FTOH	2-Perfluorodecyl ethanol	C ₁₂ H ₅ F ₂₁ O
Fluorotelomer acrylates (FTACr)		
6:2 FTACr	1H,1H,2H,2H-Perfluorooctyl acrylate	C ₁₃ H ₁₁ F ₁₃ O ₂
8:2 FTACr	1H,1H,2H,2H-Perfluorodecyl acrylate	C ₁₅ H ₁₁ F ₁₇ O ₂
10:2 FTACr	1H,1H,2H,2H-Perfluorododecyl acrylate	C ₁₇ H ₁₁ F ₂₁ O ₂
Perfluoroalkyl sulfonamides (FOSA)		
N-MeFOSA	N-methylperfluoro-1-octanesulfonamide	C ₈ H ₄ F ₁₇ NO ₂ S
N-EtFOSA	N-ethylperfluoro-1-octanesulfonamide	C ₁₀ H ₆ F ₁₇ NO ₂ S



Fig. 1 TD-30R and GCMS-QP2020 NX

Analytical Conditions

Detailed analytical conditions are shown in Table 2. Dual-layered thermal desorption tubes (Tenax TA and Carboxen 1000) were used to capture highly volatile compounds. Analysis was performed using the Fast Automated Scan/SIM Mode (FASST), which offers high-speed switching between scan mode and SIM mode in a single measurement. The data acquired by SIM mode was used to determine the quantities of the targeted PFAS. FASST offers the ability to perform a SIM mode-based quantitative analysis of target compounds and a scan mode-based qualitative analysis of other compounds in a single measurement.

Table 2 Analytical Conditions

Model:	GCMS-QP2020 NX
Autosampler:	TD-30R
[TD-30R]	
Sample Tube:	Tenax TA/Carboxen 1000 (P/N: 223-52884-91)
Trap Tube:	Tenax TA
Tube Desorb Temp.:	280 °C
Tube Desorb Flow:	100 mL/min (10 min)
Trap Cooling Temp.:	-20 °C
Trap Desorb Temp.:	280 °C (10 min)
Joint Temp.:	250 °C
Valve Temp.:	250 °C
Transfer Line Temp.:	250 °C
[GC]	
Injection Mode:	Split
Split Ratio:	15
Carrier Gas:	He
Carrier Gas Control:	Linear velocity 45 cm/sec
Column:	SH-200 (60 m × 0.32 mm I.D., 1.0 μm) (P/N: 227-36186-02)
Column Temp.:	50 °C (1 min) – 15 °C/min – 280 °C (5 min)
[MS]	
Ion source Temp.:	200 °C
Interface Temp.:	250 °C
Ionization Method:	EI
Measurement Mode:	Scan/SIM (FASST mode)
Scan Range:	<i>m/z</i> 40 - 650
SIM Ions:	See Table 3
Event Time:	Scan 0.2 sec, SIM 0.3 sec

Table 3 MS Table

Compound	Retention Time (min)	Quantifier Ion	Qualifier Ion
4:2 FTOH	5.388	95	69
6:2 FTOH	6.925		
8:2 FTOH	8.363		
10:2 FTOH	9.663		
6:2 FTACr	9.240	55	95, 69
8:2 FTACr	10.446		
10:2 FTACr	11.546		
N-MeFOSA	12.179	94	69
N-EtFOSA	12.499	108	69

■ Preparation of Standards

Four FTOHs and two FOSAs were diluted with methanol to prepare a 6-component mixed calibration curve standard solution (solution A) at 0.025, 0.05, 0.1, 0.25, 0.5, 1, 2.5, 5, and 6.25 ng/μL. Three FTACs were diluted in isooctane to prepare a 3-component mixed calibration curve standard solution (solution B) at 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, and 12.5 ng/μL.

Standards containing 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, and 12.5 ng of each of the 9 compounds were prepared by adding 2 μL of the solution A and 1 μL of the solution B to a sample tube and purging with nitrogen gas (50 mL/min) for 3 minutes.

■ Measuring Standards

Calibration curves (0.05 to 12.5 ng) and SIM chromatograms (0.2 ng) for the 9 PFAS are shown in Fig. 2, and the correlation coefficient R of each calibration curve and repeatability at 0.2 ng (n = 3) are shown in Table 4.

The results confirm that the analysis method can detect all compounds from a minimum amount of 0.05 ng. The correlation coefficient R was greater than 0.998 in the range of 0.05 to 12.5 ng for all calibration curves, showing good linearity. All the area and concentration %RSD (n = 3) results at 0.2 ng were below 6, so again showing good repeatability.

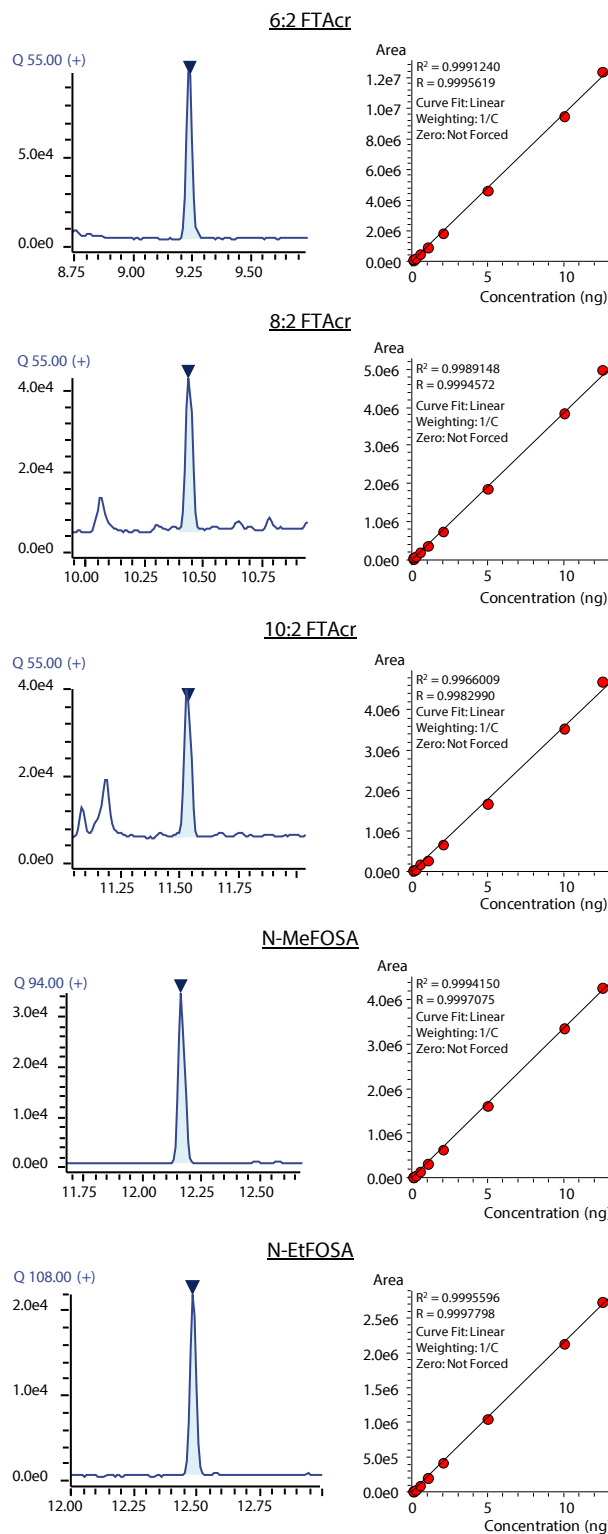
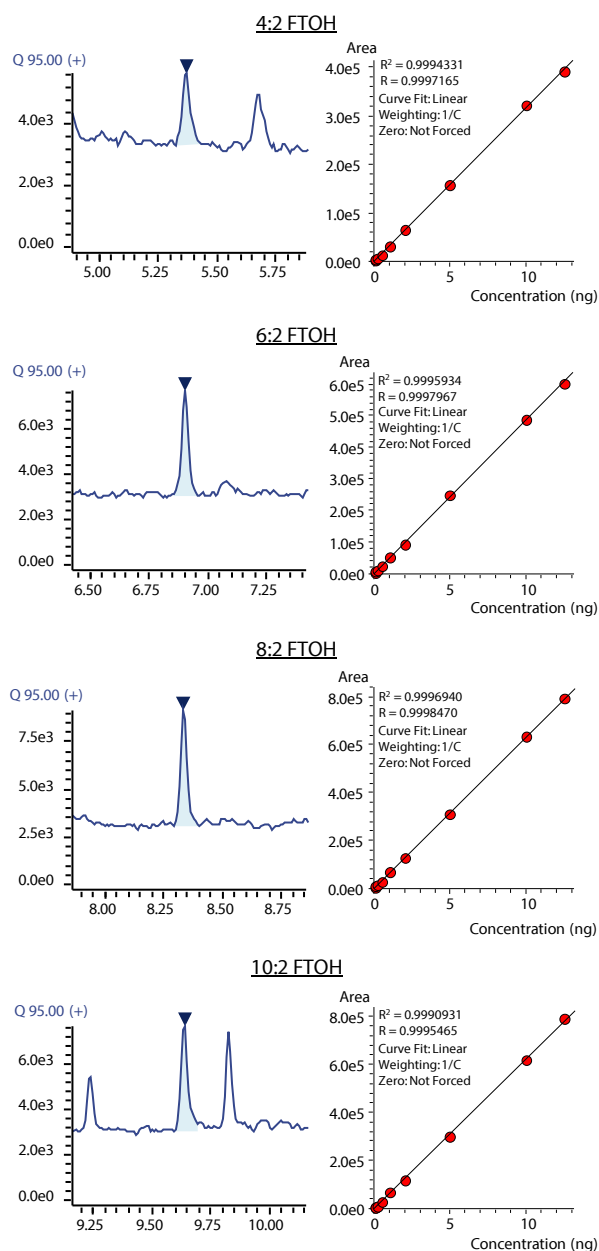


Fig. 2 SIM Chromatograms (0.2 ng) and Calibration Curves

Table 4 Calibration Curve Correlation Coefficients and Repeatability

Compound	Correlation Coefficient R	0.2 ng (n=3)	
		Area %RSD	Conc. %RSD
4:2 FTOH	0.9997	3.6	3.8
6:2 FTOH	0.9998	4.2	4.6
8:2 FTOH	0.9998	4.7	5.1
10:2 FTOH	0.9995	3.6	3.5
6:2 FTACr	0.9996	2.3	2.3
8:2 FTACr	0.9995	5.4	5.5
10:2 FTACr	0.9984	3.5	3.2
N-MeFOSA	0.9997	0.6	0.6
N-EtFOSA	0.9998	0.5	0.5

■ Spike-and-Recovery Test with Ambient Air

Standard solutions were prepared containing 10 ng of four FTOHs and 1 ng of three FTACs and two FOSAs and these standard solutions were added to the Tenax TA/Carboxen 1000 sample tubes. 20 L of ambient air was also collected at 100 mL/min. Spike-and-recovery test and repeatability results are shown in Table 5 and SIM chromatograms are shown in Fig. 3.

The recovery rates were between 77 and 106 % and all concentration %RSD (n = 3) were below 8, showing generally good performance.

Table 5 Spike-and-Recovery Test Results with Ambient Air

	Spike Concentration (ng)	Mean Recovery (% , n = 3)	Conc. %RSD (n=3)
4:2 FTOH	10	77	3.0
6:2 FTOH	10	97	4.8
8:2 FTOH	10	98	1.0
10:2 FTOH	10	98	5.0
6:2 FTACr	1	93	4.8
8:2 FTACr	1	99	7.9
10:2 FTACr	1	99	7.2
N-MeFOSA	1	99	4.3
N-EtFOSA	1	106	3.5

■ Conclusion

The TD-30R and GCMS-QP2020 NX were used to measure quantities of nine neutral PFAS in ambient air.

The measurements of standards demonstrated favorable results for sensitivity, calibration curve linearity, and repeatability for all the targeted compounds. A spike-and-recovery test with ambient air also demonstrated favorable results for recovery and repeatability.

Using the TD-30R during sample pretreatment allows the sampling tube to be analyzed directly without a solvent extraction, enabling high-throughput analysis.

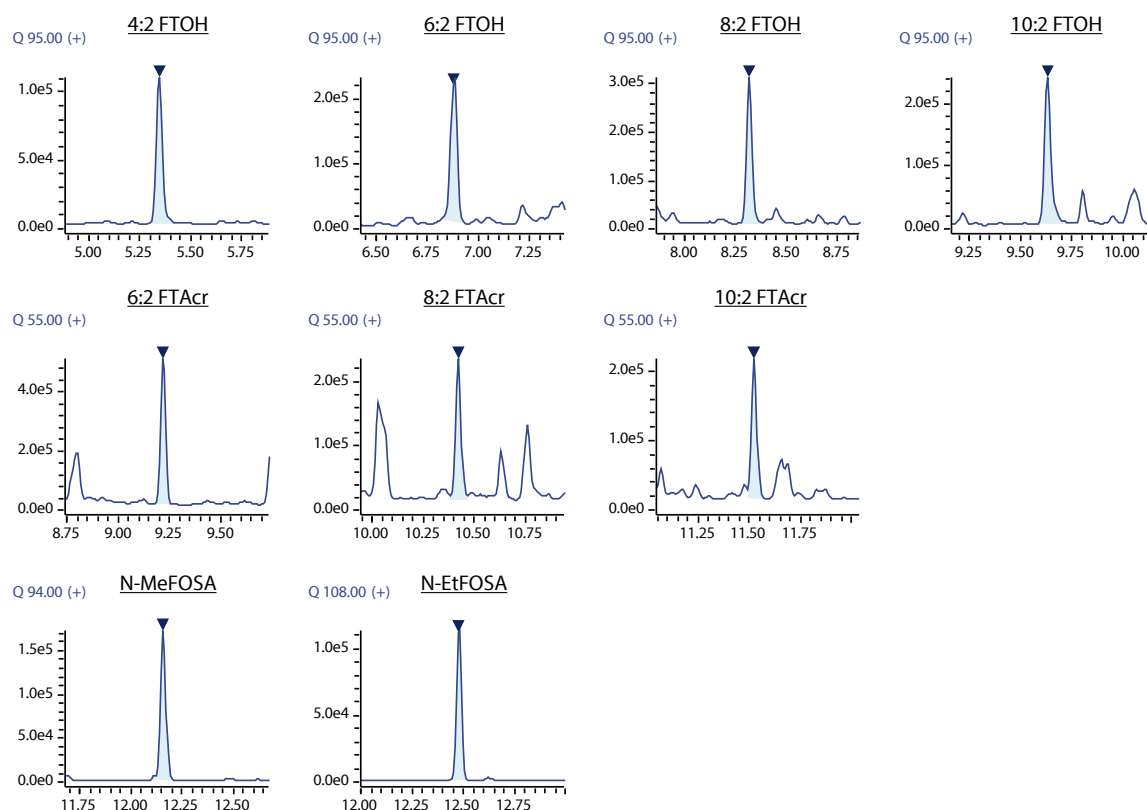


Fig. 3 SIM Chromatograms from Spike Recovery Test (FTOHs: 10 ng, FTACs and FOSAs: 1 ng) Using Ambient Air