

Indoor Air Analysis of Fluorotelomer Alcohols and Per- and Polyfluoroalkyl Substances

Using cryogen-free thermal desorption GC/TQ

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Abstract

An Agilent 8890 GC with an Agilent 7000E GC/TQ is used for the analysis of fluorotelomer alcohols (FTOH) in indoor air samples. A GERSTEL TD Core System enables thermal desorption (TD) sampling of ambient air, while the GC/TQ system provides high selectivity for these complex samples. Four target FTOH compounds demonstrated good recovery, ranging from 87.5 to 115.4%, with reproducibility between 4.20 and 10.2% relative standard deviation (RSD). Indoor air samples were collected from various locations. At least one FTOH compound was detected in each sample. This prevalence highlights the need for an analytical method such as this to address the potential public health concern of long-term exposure to low concentrations of FTOH indoors.

Introduction

FTOHs are a subcategory of per- and polyfluoroalkyl substances (PFAS). FTOH compounds are primarily used as precursors for PFAS compounds, such as perfluorinated carboxylic acids (PFCA), including perfluorooctanoic acid (PFOA) and perfluorohexanoic acid (PFHxA). FTOH compounds are also used as raw materials in various industrial applications due to their water- and oil-repellent characteristics.

The presence of PFAS in air is an emerging concern, prompting the growth of air quality monitoring for PFAS in analytical chemistry. Existing methods like the United States Environmental Protection Agency (EPA) Other Test Method 50 (OTM-50) are used to detect volatile fluorinated compounds and short-chain PFAS compounds in air emissions from stationary sources.¹ It is suspected that indoor air monitoring for PFAS will be a future focus area due to the use of PFAS in several household and consumer products.

Volatile PFAS concentrations in ambient and indoor air can be low, requiring large volumes of air to be sampled. Thermal desorption, where air is drawn onto sorbent-filled tubes and later analyzed using GC/MS, is an ideal technique for large-volume sampling. However, large amounts of the matrix are also drawn into the tubes and can present issues with both carryover and interference with analyte signals. GC/TQ largely eliminates these interferences and background noise while adding more specificity to detection. The elimination of noise also lowers detection limits, which is critical when determining low levels of PFAS in air.

This application note introduces a thermal desorption GC/TQ method for determining FTOH in indoor air samples. The effectiveness of the analytical method is demonstrated through the successful analysis of several real-world indoor air samples.

Experimental

Instrumentation

The analysis of FTOH in indoor air was performed on an Agilent 8890 GC with an Agilent 7000E GC/TQ. The system was equipped with a GERSTEL TD Core System for TD sampling, which is optimized for ambient air analyses. GC and MS method parameters are detailed in Tables 1 to 3.

Table 1. Agilent 8890 GC method parameters for the analysis of FTOH in indoor air.

Parameter	Value
Analytical Column	Agilent J&W CP-Select 624 CB GC column, 60 m × 0.25 mm, 1.40 μm (p/n CP7413) Note: An Agilent J&W DB-624 GC column works equivalently for separation of these analytes.
CIS Inlet Mode	Solvent vent (50 mL/min), split 20:1
CIS Temperature	10 °C (0.2 min), 12 °C/s, 280 °C (3 min)
Oven Temperature	50 °C (1 min), 15 °C/min, 280 °C (2 min)
Carrier Gas	Helium, constant flow at 1 mL/min
MS Transfer Line Temperature	280 °C
Run Time	18 minutes

Table 2. Agilent 7000E GC/TQ source method parameters for the analysis of FTOH in indoor air.

Parameter	Value
Ion Source Temperature	280 °C
Quadrupole Temperature	150 °C
Ionization	Electron ionization (EI) mode
EMV Mode	Gain factor
Gain Factor	10
Solvent Delay	1 min
Scan Type	MRM
Data Rate	3 cycles/s

Table 3. Agilent 7000E GC/TQ multiple reaction monitoring (MRM) acquisition method parameters for the analysis of FTOH in indoor air.

Compound	Time Segment (min)	Dwell Time (ms)	Quantifier Ion		Qualifier Ion 1		Qualifier Ion 2	
			(m/z)	CE (eV)	(m/z)	CE (eV)	(m/z)	CE (eV)
4:2 FTOH	3.0	50	244 → 127	10	95 → 69	15	127 → 77	15
6:2 FTOH	10.5	50	344 → 127	10	95 → 69	15	127 → 77	15
8:2 FTOH	11.6	25	444 → 127	10	95 → 69	15	127 → 77	15
10:2 FTOH	12.5	25	544 → 127	10	95 → 69	15	127 → 77	15
10:2 FTOH [M + 4]	12.5	25	129 → 79	20	515 → 96	15	548 → 129	5

Standards

4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were obtained from AccuStandard (New Haven, CT). 10:2 FTOH [M + 4] was purchased from Wellington Laboratories (Guelph, ON, Canada).

TD tube standard preparation

Three μL of calibration and internal standard were spiked with a 10 μL syringe onto conditioned TD tubes. Dry nitrogen was passed through the tubes at a flow rate of 40 mL/min for 3 minutes.

Sample preparation

Three μL of internal standard was spiked with a 10 μL syringe onto conditioned TD tubes. Conditioned PFAS-specific TD 3.5+ tubes were connected to a triple adjustable low-flow tube holder attached to an SKC Pocket Pump TOUCH sampling pump. The samples were collected on the TD 3.5+ tubes at a flow rate of 40 mL/min for 24 hours.

Sample introduction

Samples were desorbed in splitless mode with 50 mL/min helium flow at 300 °C for 3 minutes. Analytes were trapped in a GERSTEL Cooled Injection System CIS 4 inlet at 10 °C on a Tenax TA-filled liner. When desorption was complete, analytes were transferred to the column in split (10:1) mode by heating the inlet rapidly to 280 °C for 3 minutes.

Results and discussion

FTOH standards were used to generate calibration data for the four target compounds. Analytes were evaluated at concentrations between 0.075 and 15 ng/tube. For simplicity, instrument detection limits were approximated as being 10-fold lower than the lowest calibration concentration. Calibration results are shown in Table 4.

Table 4. Calibration curve statistics for four target FTOH compounds (n = 7; N = 21; range = 0.075 to 15 ng/tube).

Compound	Calibration		Instrument Detection Limit (ng/tube)
	Relative Response Factor	Relative Standard Deviation	
4:2 FTOH	0.0497	8.40	0.02
6:2 FTOH	0.0057	7.18	0.02
8:2 FTOH	0.0731	10.1	0.01
10:2 FTOH	0.0698	9.06	0.02

Recovery was also evaluated for the four target FTOH compounds. Recovery was assessed at three different spike levels (0.075, 0.75, and 7.5 ng/tube). Average recoveries ranged from 87.5 to 115.4%, with RSDs from 4.20 to 10.2%. Details are listed in Table 5.

Table 5. Recovery statistics of four target FTOH compounds (n = 3 at each spike level).

ng/tube	Recovery							
	4:2		6:2		8:2		10:2	
	Average	RSD	Average	RSD	Average	RSD	Average	RSD
0.075	87.5	7.92	101.6	4.20	101.5	6.81	95.3	6.69
0.75	102.1	6.48	108.1	8.24	99.9	5.04	98.9	7.73
7.5	104.9	5.91	115.4	10.2	93.8	9.44	100.3	8.91

To demonstrate the real-world applicability of this analysis, indoor air samples were taken in several locations in both a commercial office building and a private residence. Example chromatograms are shown in Figure 1, and all results are listed in Table 6.

Table 6. Airborne FTOH compounds and their respective vapor concentration.

Location	6:2		10:2	
	ng/m ³	RSD	ng/m ³	RSD
Family Room	16.1	8.5	3.06	11.4
Dining Room	12.0	14.7	7.34	16.7
Main Lab	16.5	1.62	3.19	4.20
Old Office	9.42	8.69	9.57	3.58
Warehouse	4.56	12.2	Not detected	Not detected
Training Room	3.47	9.71	Not detected	Not detected

The top chromatogram shows a total ion chromatogram with many peaks and no clear FTOH peaks as this is data collected in scan mode. Analyzing the same sample using multiple reaction monitoring (MRM) mode demonstrates the power of GC/TQ for this analysis. Using MRM mode, the targeted FTOH peaks are clearly visible and easily quantifiable (middle and lower chromatograms) with orders of magnitude more sensitivity due to the elimination of background noise. Complex chromatograms often result from analyses where large volumes of air are sampled, even in a relatively clean, indoor environment, such as the air samples tested in this work. GC/TQ greatly improves analytical sensitivity and reproducibility due to the high selectivity of MRM acquisition mode.

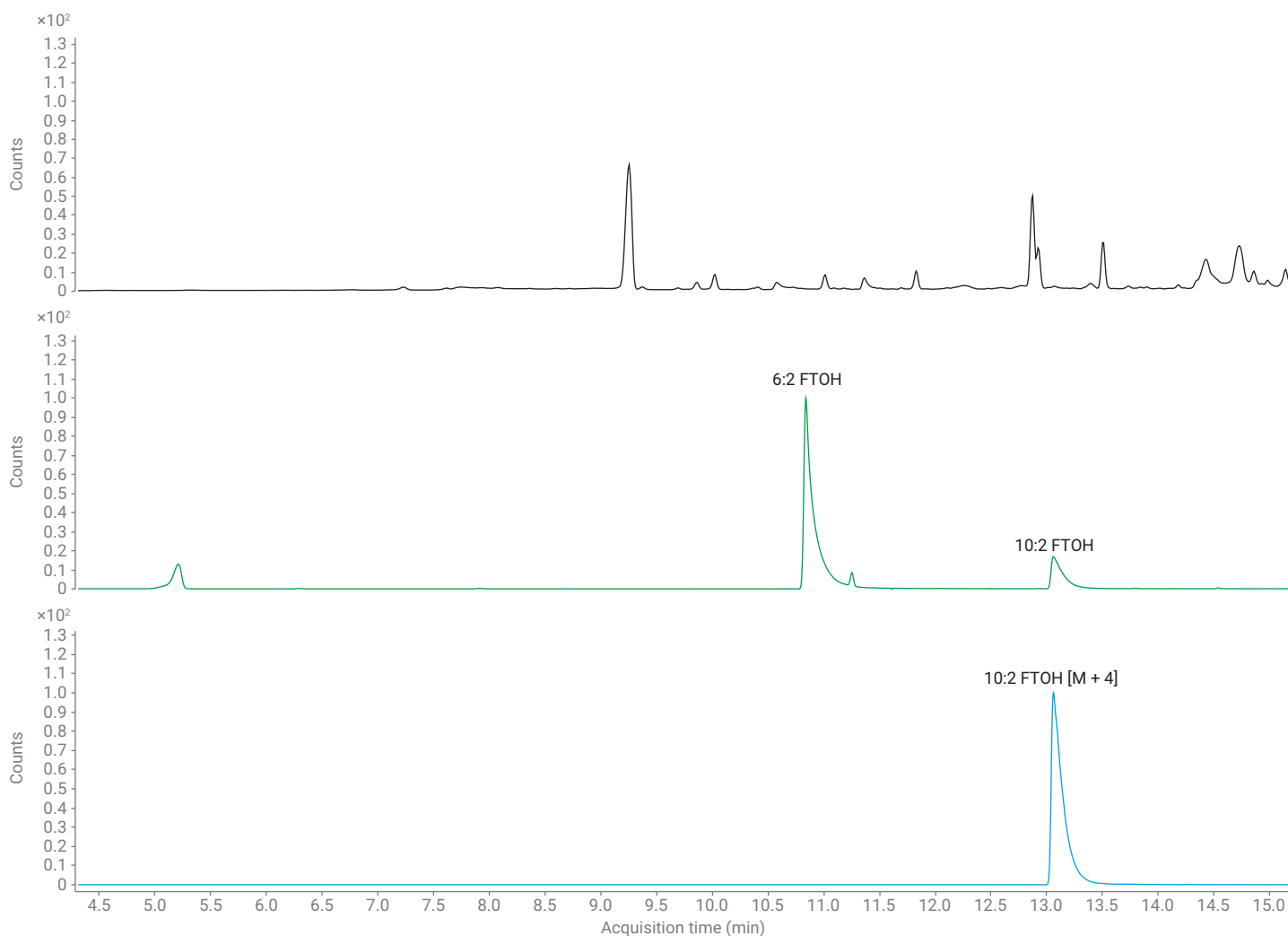


Figure 1. Example chromatogram from the old office air sample.

At least one FTOH target compound was detected in each sample. FTOH 6:2 was detected in all locations sampled. The vapor concentration ranged from 3.47 to 16.5 ng/m³. Additionally, FTOH 10:2 was detected in four of the six locations. It was not detected in the warehouse or training room. The vapor concentration ranged from 3.58 to 16.7 ng/m³.

Although low in concentration, the presence of FTOH compounds in every sample shows both the concern from a public health perspective and issues from an analytical chemistry perspective. Exposure to low concentrations over long periods of time indoors could pose health concerns. Also, sources and sinks of PFAS-related analytes must be accounted for in the analytical process and removed, as mentioned in EPA OTM-50, to ensure accurate quantitation.¹

Conclusion

This study demonstrates the utility of an Agilent 8890 GC with an Agilent 7000E GC/TQ for the analysis of FTOH compounds in indoor air samples. The GC/TQ system was equipped with a GERSTEL TD Core System, which enabled thermal desorption sampling of ambient air. This selective GC/TQ analytical method provided good reproducibility, recovery, and sensitivity. Real-world indoor air samples proved the necessity of methods like the one described in this work, as FTOH compounds were present in all samples.

Reference

1. Other Test Method 50 (OTM-50) Sampling and Analysis of Volatile Fluorinated Compounds from Stationary Sources Using Passivated Stainless-Steel Canisters. United States Environmental Protection Agency. https://www.epa.gov/system/files/documents/2024-01/otm-50-release-1_0.pdf (accessed 2024-07-16).