

## GERSTEL AppNote 262

# Determination of Fluorotelomer Alcohols in Indoor Air using Cryogen-free Thermal Desorption GC-MS/MS

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## Keywords

PFAS, Air Sampling, Fluorotelomer Alcohols, Gas Chromatography, Tandem Mass Spectrometry

## Abstract

Measurements for per- and polyfluoroalkyl substances (PFAS) in air have expanded. There are few analytical methods available which measure PFAS in air. Thermal desorption, gas chromatography, and tandem mass spectrometry (TD-GC-MS/MS) is being successfully used for this purpose by the US EPA for the evaluation of indoor air and indoor materials using a simple, valve-free thermal desorber architecture.

Once the analytes are trapped on a thermal desorption tube, the tubes are desorbed and the analytes are refocused onto a concentrator trap. In the past, low temperatures were used ( $< -40$  °C) to non-selectively trap and refocus PFAS analytes. This approach was particularly suited for the determination of unknown compounds (non-targeted analysis) since it removes the possibility of analyte interaction with the sorbent in the concentrator trap. Also, the use of low temperatures provided a drastic reduction in method development time since only one temperature and one type of trap is needed for all analyses.

A complete cryogen-free, valve-free method for determining FTOHs in indoor air has now been developed [4] and evaluated using samples taken from both commercial and residential locations. The method called "dynamic focussing" has excellent figures of merit and results in data that is reliable and simple to review. Small but measurable amounts of FTOHs in air were found at every location tested.

## Introduction

The fate of PFAS in air, both in outdoor and indoor environments, is relatively unknown and is now becoming a new area of concern. GERSTEL, in partnership with Agilent Technologies and CAMSCO, have described the use of thermal desorption, gas chromatography, and tandem mass spectrometry (TD-GC-MS/MS) as means to perform demanding PFAS in air work where the matrix is challenging due to high volume sampling, or due to issues with a complex environmental matrix, such as those often seen in soil vapor intrusion work. The work has been successful, with many academic presentations at conferences, commercial sampling and analysis of PFAS now underway, and the contribution of this work to PFAS standards at ASTM, ISO, and other standards organizations [2,3].

Volatile PFAS concentrations in air, like their water counterparts, can be in the low ppb to ppt (V/V) range. To enable detection at these low levels, large volumes of air need to be sampled (50+ Liters). Alternately, for time-weighted average sampling, long sampling times are advantageous, but this also leads to large amounts of air sampled. Possible sources of unwanted gain or loss of PFAS species at these low levels must also be anticipated and removed (removal of PTFE and related materials from the sampling train, instrumentation, etc.).

Thermal Desorption, where air is drawn onto sorbent-filled tubes and later analyzed using gas chromatography-mass spectrometry (GC-MS), is an ideal technique for large-volume sampling and works well in either case above. However, large amounts of the matrix are also drawn into the tubes and can present issues with

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both carryover and interference with analyte signals. Gas chromatography-tandem mass spectrometry (GC-MS/MS) largely eliminates these interferences as well as chemical noise in general. The elimination of this noise also lowers detection limits, which is critical when determining PFAS in air.

As time has progressed, some targeted volatile PFAS species, such as FTOHs, have been identified as targets of particular concern by the US EPA [1], allowing for a new focus on targeted, high throughput analyses. The change from non-targeted to targeted approaches allows for a change in preconcentration strategy. We will now discuss sorbent/substrate choices for PFAS preconcentration as well as recent breakthroughs in preconcentration techniques and technology, and how these make reliable and durable determination of PFAS in challenging matrices possible.

### Experimental

#### 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).

#### Instrumentation

GERSTEL TD Core System on Agilent 8890 GC and 7000E GC/TQ



#### Analysis Conditions TD Core System

TD 3.5 <sup>+</sup>	splitless 40 °C (1 min); 400 °C/min; 300 °C (3 min)
CIS 4	Tenax TA filled liner solvent vent (50 mL/min) split 10:1 10 °C (0.2 min); 12 °C/sec; 280 °C (3 min)

#### Analysis Conditions Agilent 8890 GC

Column	60 m CP-Select 624 CB (Agilent) $d_i=0.25$ mm, $d_f=1.4$ $\mu$ m
Pneumatics	He, $P_i = 17.5$ psi constant flow 1 mL/min
Oven	50 °C (1 min); 15 °C/min; 280 °C (2 min)

#### TD Tube Standard Preparation

3  $\mu$ L of calibration and internal standard were spiked with a 10  $\mu$ L 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

3  $\mu$ L of internal standard was spiked with a 10  $\mu$ L syringe onto conditioned TD tubes. Conditioned PFAS-specific TD 3.5<sup>+</sup> tubes were connected to a triple adjustable low-flow tube holder attached to an SKC Pocket Pump Touch sampling pump. An example of this setup is shown in Figure 1. The samples were collected on the TD 3.5<sup>+</sup> tubes at a flow rate of 40 mL/min for 24 hrs.



**Figure 1:** Low-flow tube holder attached to an SKC pocket pump touch sampling pump.

#### Sample Introduction

Samples were desorbed in splitless mode with 50 mL/min helium flow at 300 °C for 3 minutes. Analytes were trapped in the 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.

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### Results and Discussion

**Table 1** lists the MRM parameters used for the determination of FTOHs by TD-GC-MS/MS.

Compound	TS	Dwell	Quantifier		Qualifier 1		Qualifier 2	
	[min]	[ms]	[m/z]	[eV]	[m/z]	[eV]	[m/z]	[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

TS=time segment=time segment for MRM scan; min=minutes; ms=milliseconds; m/z=mass-to-charge ratio; eV=collision energy electron volts.

**Table 2:** Calibration curve statistics for TD-GC-MS/MS analysis of four target FTOHs (n=7; N=21; range=0.075-15 ng/tube).

Compound	Calibration		IDL
	RRF	%RSD	ng/tube
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

**Table 3:** Recovery statistics of four target FTOHs. (n=3 at each level spiked onto tube; recovery range=87.5-115.4; RSD range= 4.20-10.2).

ng/tube	Recovery							
	4:2		6:2		8:2		10:2	
	Avg	%RSD	Avg	%RSD	Avg	%RSD	Avg	%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

**Table 4:** Airborne FTOH compounds and their respective vapor concentrations.

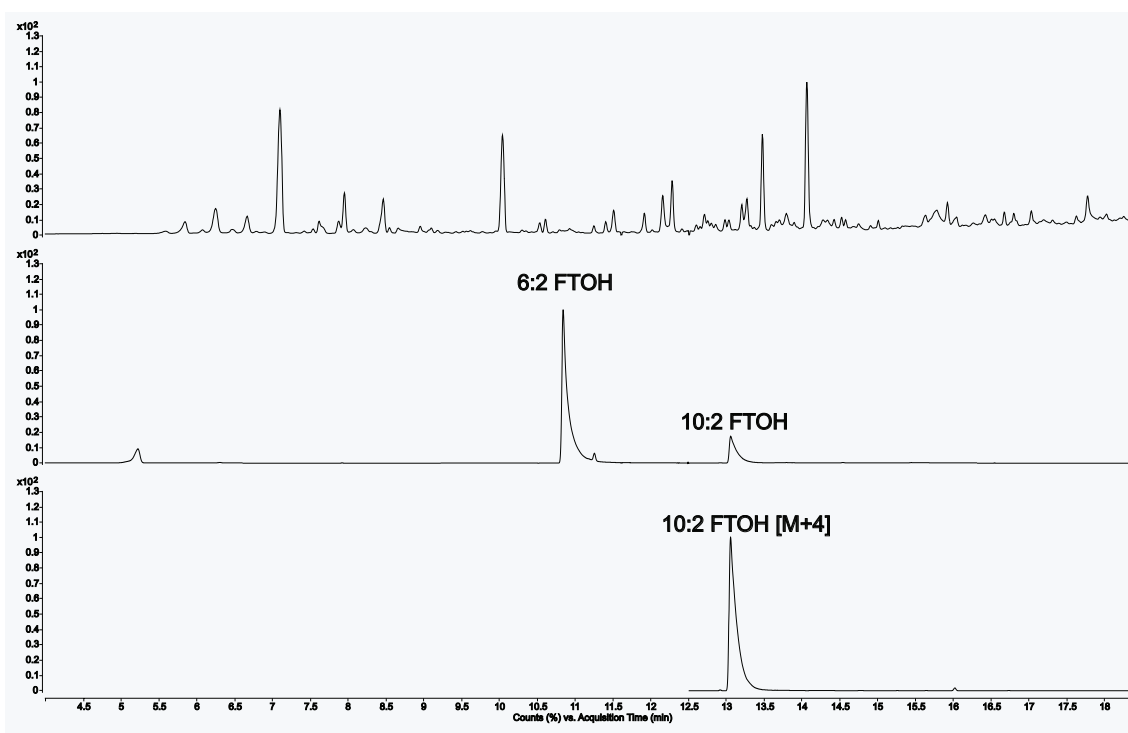
Location	6:2		10:2	
	ng/m <sup>3</sup>	%RSD	ng/m <sup>3</sup>	%RSD
Family room	16.1	8.5	3.06	11.4
Dining room	12.0	14.7	7.34	16.7
Main lab	16.5	1.62	3.19	4.20
Old office	9.42	8.69	9.57	3.58
Warehouse	4.56	12.2	-	-
Training room	3.47	9.71	-	-

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For simplicity, IDLs were approximated as being at least 10x lower than the lowest concentration calibration point (while still being significantly above blank values).

Samples were taken in several locations in both a commercial office building and a private residence. An example chromatogram

of one such sample is in Figure 2. The top, total ion chromatogram (TIC) shows a large number of peaks, and no FTOH peaks are clearly visible. When an identical sample was run using the multiple reaction monitoring (MRM) mode of the triple quadrupole, only the targeted FTOHs were present.



**Figure 2:** Office air sample.

The reason GC-MS/MS works so well for FTOH determinations is that the high volumes of air sampled, even in a 'clean' indoor environment, result in relatively complex chromatograms. Using MRM mode with a GC-MS/MS removes this complexity, making evaluation of the data simpler and dramatically reducing false positives. Ironically, the signal in MRM mode is lower than in TIC mode, but the noise is even lower (less than 10 counts/second), and detectability and detection limits are better. MRM mode was used for all further measurements.

FTOH 6:2 was detected in all locations sampled. The vapor concentration ranged from 3.47-16.5 ng/m<sup>3</sup>. FTOH 10:2 was detected

in four of six locations. It was not detected in the warehouse or training room. The vapor concentration ranged from 3.58-16.7 ng/m<sup>3</sup>.

Although low in concentration, the presence of at least one FTOH in every sample shows both the concern from a public health perspective (exposure to low concentrations over long periods of time indoors) and issues from an analytical chemistry perspective (sources and sinks of PFAS-related analytes must be accounted for in the analytical process and removed, as mentioned in US EPA's OTM-50 method).

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### Conclusions

This study demonstrated the TD-GC-MS/MS method developed is suitable for the quantification of FTOHs in air.

### References

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