

Analysis of Trace Perfluorinated and Polyfluorinated Organic Vapors in Air

Using cryogen-free thermal desorption and GC/MS

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Abstract

This application note describes the sampling and analysis of a challenging range of trace-level volatile and semivolatile vapors of perfluorinated and polyfluorinated alkyl substances (PFAS) in air. The analytical system used combines the Agilent 8890 gas chromatography (GC) system with the Agilent 5977B Series gas chromatograph/mass selective detector (GC/MSD), and the TD100-xr automated thermal desorption (TD) system from Markes International, which operates without a liquid cryogen coolant and complies fully with relevant international standard methods.¹⁻⁵ Excellent method performance (linearity, repeatability, and storage stability) was demonstrated across the range of compounds tested, including low- or sub-parts per trillion (ppt) detection limits for all compounds.

The study also demonstrates the benefits of using quantitative TD sample re-collection for validation of analyte recovery through the entire analytical TD process. Quantitative TD sample re-collection is a relatively recent TD innovation. It overcomes the one-shot limitation of traditional TD technology, and allows samples or standards to be rerun for data confirmation and/or repeat analysis using different conditions, such as split flows, GC columns, detectors, and so on. The study analyzed 18 representative PFAS spanning several classes, and method performance was evaluated, including blanks, linearity, limits of detection (LODs), and precision. Finally, real ambient air samples were also analyzed.

Introduction

PFAS are a class of persistent organic pollutants, which enter our environment from multiple industrial and everyday sources, including water-resistant coatings, fire-fighting equipment, and nonstick cookware. They include a wide range of chemicals covering different volatilities, polarities, and functional groups, with recent reports citing over 6,000 compounds of potential interest.⁶

The current challenges for PFAS monitoring include:

- The sheer number of potential compounds of interest (no single analytical method can be used for them all)
- Low concentrations (typically low and sub-ppt)
- The identity and levels of PFAS compounds present in real environments is not yet known

PFAS are currently a global focus of regulatory overview in many matrices, including drinking water, wastewater, soils, textiles, personal-care products, and others. Many nonvolatile PFAS are analyzed by LC/MS. Agilent has complete workflows for the analysis of PFAS, complying with regulatory methods such as USEPA 533, USEPA 537.1, and ASTM 7979 in water and soil, while also providing end-to-end solutions for the analysis of >70 legacy and emerging PFAS using LC/MS/MS. Importantly, volatile PFAS are also thought to be an important factor in covering the entire mass balance, and the need for GC/MS is critical in this case. Air is a known sink of PFAS and carries them large distances. For air analysis of PFAS, a TD is required for suitable trapping, while GC/MS is ideal for analysis.

The types of PFAS compounds compatible with analysis by TD–GC/MS fall into two groups:

- Very volatile perfluorinated hydrocarbons (C₁ to C₃), also known as potent greenhouse gases and ozone-depleting substances, typically requiring whole-air sampling (canisters, online monitoring, or sampling bags).
- Volatile or semivolatile PFAS species, such as perfluoroalkyl carboxylic acids (C₄ to C₁₄), fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAcrs) and fluorotelomer sulfonamides (FOSAs), which are compatible with pumped sampling onto sorbent tubes

While trace PFAS in air are of concern from an environmental perspective, the analytical technology required by air-monitoring scientists to address this area is already available; modern analytical TD–GC/MS systems were

designed specifically for monitoring trace-level organic vapors, and recent developments in automated TD technology have meant these methods can be applied to more challenging compounds. The aim of this study was to evaluate the performance of the latest off-the-shelf sorbent tube sampling and automated TD–GC/MS analytical technology for analyzing volatile and semivolatile PFAS.

Experimental

Standards

This study analyzed 18 standard PFAS compounds, spanning different subclasses, to validate the method; 11 perfluorinated carboxylic acids (PFCAs), four fluorotelomer alcohols, perfluoroalkane sulfonamide, sulfonamide alcohol, and the semivolatile 8:2 FTAc were included. A full list of compounds used in the standard is presented in Table 1.

Table 1. PFAS compounds tested.

Compound		Concentration of Standard
Perfluoroalkylcarboxylic Acids		
Perfluorobutyric acid	PFBA	2 ng/μL
Perfluoropentanoic acid	PFPeA	
Perfluorohexanoic acid	PFHxA	
Perfluoroheptanoic acid	PFHpA	
Perfluorooctanoic acid	PFOA	
Perfluorononanoic acid	PFNA	
Perfluorodecanoic acid	PFDA	
Perfluoroundecanoic acid	PFUDA	
Perfluorododecanoic acid	PFDoA	
Perfluorotridecanoic acid	PFTrDA	
Perfluorotetradecanoic acid	PFTeDA	
Fluorotelomer Alcohols		
2-Perfluorobutyl ethanol	4:2 FTOH	50 ng/μL
2-Perfluorohexyl ethanol	6:2 FTOH	
2-Perfluorooctyl ethanol	8:2 FTOH	
2-Perfluorodecyl ethanol	10:2 FTOH	
Fluorotelomer Acrylates		
1H,1H,2H,2H-Perfluorodecyl acrylate	FTAc	50 ng/μL
Perfluorooctanesulfonamide and Perfluorooctanesulfonamidoethanol		
N-Methylperfluoro-1-octane sulfonamide	N-MeFOSA	50 ng/μL

GC column selection

The sheer number of PFAS compounds makes GC column selection difficult. However, after extensive tests, an Agilent J&W VF-200ms GC column was selected, as it had the best combination of resolution and peak shape for the extensive compound range (Figure 1).

Gas chromatograph/mass selective detector (GC/MSD) instrumentation and setup

The GC/MSD used for this analysis was a 8890 GC system coupled with a 5977B GC/MSD. The 8890 GC was operated in Constant Flow mode, and chromatographic separation of the PFAS was achieved with an Agilent J&W VF-200ms GC column (30 m × 0.25 mm, 1 µm). The 5977B GC/MSD was operated with a conventional 70 eV electron ionization (EI) source and in single ion monitoring (SIM) mode. The detailed TD-, GC-, and MS-optimized parameters are highlighted in Table 2.

Table 2. Optimized TD, GC, and MSD parameters.

Sampling Conditions (Standard)	
Model	Calibration Standard Loading Rig (Markes International, p/n C-CSLR)
Injection Amount	1 µL
Gas	N ₂
Flow	100 mL/min
Purge Time (CSLR)	From 10 to 20 min
Sampling Tube	Material Emissions (Markes International, p/n C-TBME10)
Sampling Volume	500 L max
TD Method	
Model	TD100-xr (Markes International, p/n G8128A)
Cold Trap	Material Emissions trap (Markes International, p/n MKI-U-T12ME-2S)
Flow Path Temperature	200 °C
Dry Purge: Purge Flow	2 min × 50 mL/min
Desorption Temperature and Time	300 °C × 12 min
Trap in Line (Flow)	50 mL/min
Trap Purge	1 min × 50 mL/min at 25 °C
Trap Low Temperature	-30 °C
Trap Heating Rate	Max
Trap High Temperature	300 °C
Trap Desorption Time	4 min
Outlet Split	6:1
GC Parameters	
Model	Agilent 8890 GC system
Column	Agilent J&W VF-200ms, 30m × 0.25 mm, 1.0 µm (p/n CP8860)
Column Pneumatics	Constant flow
Flow Rate	1.2 mL/min
Oven Temperature Program	35 °C for 2 min, 15 °C/min to 280 °C, hold 5 min
MS Parameters	
Model	Agilent 5977B GC/MSD
Source	Extractor
Ionization Mode	EI, 70 eV
Acquisition Mode	SIM/scan
GC Transfer Line Temperature	280 °C
Ion Source Temperature	250 °C
Quadrupole Temperature	150 °C
Scan Range	40 to 650 amu
SIM Ions	45, 55, 69, 93, 95, 119, 131, 181 (two groups)
	95 m/z FTOH quantifier ion
	131 m/z PFCAs quantifier ion
	Qualifiers 55 m/z FTAc/93 m/z MeFOA

Results and discussion

Determining breakthrough volumes

A routinely used Agilent stainless steel material emissions tube for indoor air monitoring (part number C-TBME10) was selected for this study due to its versatile nontargeted sampling range for compounds ranging from 1,3-butadiene to *n*-C₃₀. This tube's combination of hydrophobic sorbents minimizes concerns with respect to water retention when sampling humid atmospheres.

Half of the conditioned tubes were left blank for use as backup tubes, while half were spiked with 1 μ L of mixed standards (2 ng of PFCAs, 12.5 ng of FTOHs, and 16.6 ng of each of the other PFAS compounds) in methanol, except for the 8:2 FTAc, which was diluted in *iso*-octane. The spiked tubes were prepared following recommendations in standard methods¹⁻⁵ using a Calibration Solution Loading Rig (CSLR; Markes International, part number C-CSLR) and a 100 mL/min flow of N₂ for 10 minutes.

Pairs of identically conditioned tubes were connected in series for these experiments, with the sampling end of the blank tube attached to the exhaust of the front spiked tube using the recommended inert unions (part number C-UNS10).

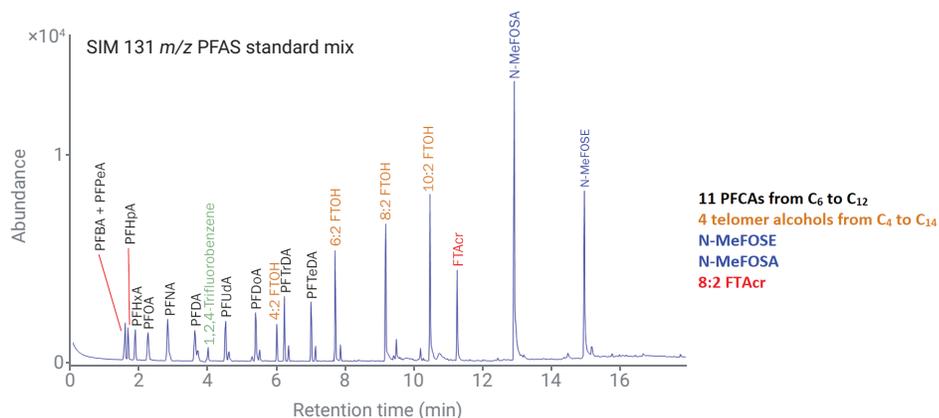


Figure 1. Chromatogram of 18 representative PFAS separated with the Agilent J&W VF-200ms GC column.

Different volumes of N₂ gas were then purged through each tube pair at 100 mL/min. According to standard methods, breakthrough is said to have occurred when the level of analyte found on the backup tube is 5% or more of the level measured on the front tube.

The different PFAS compound types were tested separately with all measurements collected in duplicate (Table 3). No breakthrough of any PFAS compound was detected up to a volume of 500 L.

Sampling volumes of 500 L give analysts the flexibility to sample for multiple days and detecting pg/m³ levels of PFAS.

Table 3. Mean breakthrough of compounds (%) for a 500 L sample.

Compound	Mean Breakthrough (%)
Perfluoroalkylcarboxylic Acids (PFCA)	
PFBA	1.72
PFPeA	1.26
PFHxA	0.00
PFHpA	0.26
PFOA	0.21
PFNA	0.11
PFDA	0.09
PFUdA	0.14
PFDoA	0.13
PFTTrDA	0.10
PFTTeDA	0.22
Fluorotelomer Acrylates (FTAc)	
8:2 FTAc	1.73
Fluorotelomer Alcohols (FTOH)	
4:2 FTOH	0.29
6:2 FTOH	1.80
8:2 FTOH	1.89
10:2 FTOH	3.08
Perfluorooctanesulfonamides (FOSE)	
Me-FOSE	0.15
Et-FOSE	0.19

Storage stability

Two material emissions tubes were spiked with 1 µL of mixed PFAS standard (2 ng/µL for PFCAs, 12.5 ng/µL for FTOH, and 16.6 ng/µL for the other compounds) using a CSLR, as described earlier. They were then sealed using the long-term storage caps (recommended in standard methods) and stored; some were stored at room temperature, and others under refrigerated conditions. Tubes were removed from storage and analyzed in triplicate after different periods of time (Figures 2 and 3).

These excellent results for 7- and 15-day storage of challenging PFAS compounds under ambient and refrigerated conditions, respectively, indicate that material emissions tubes offer practical stability for sample transport and storage, giving busy laboratories a useful level of flexibility.

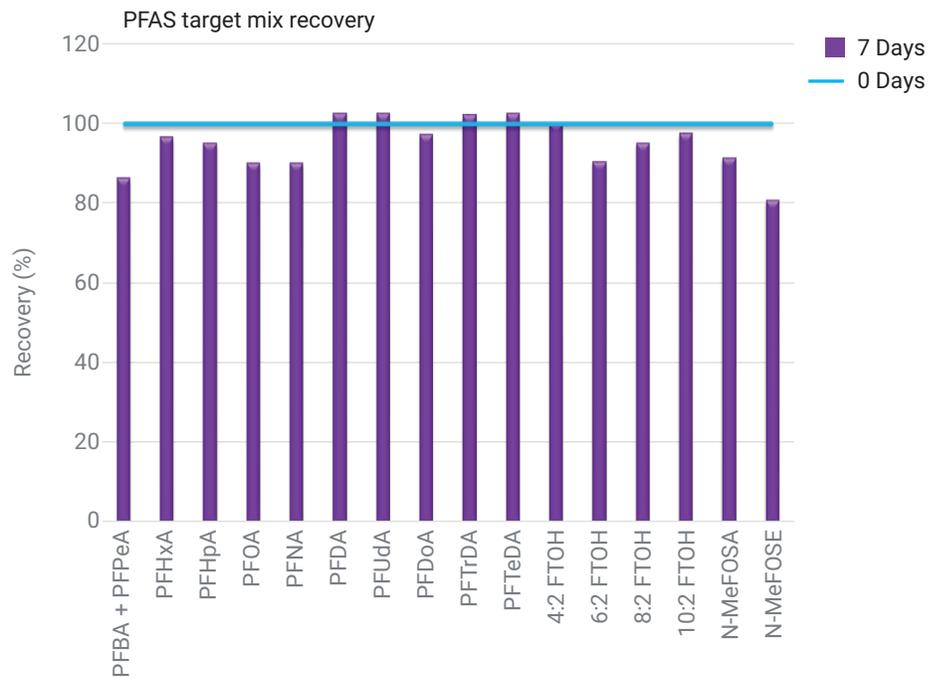


Figure 2. Recovery from sorbent tubes spiked with PFAS standard mixture and stored for 7 days at ambient temperature.

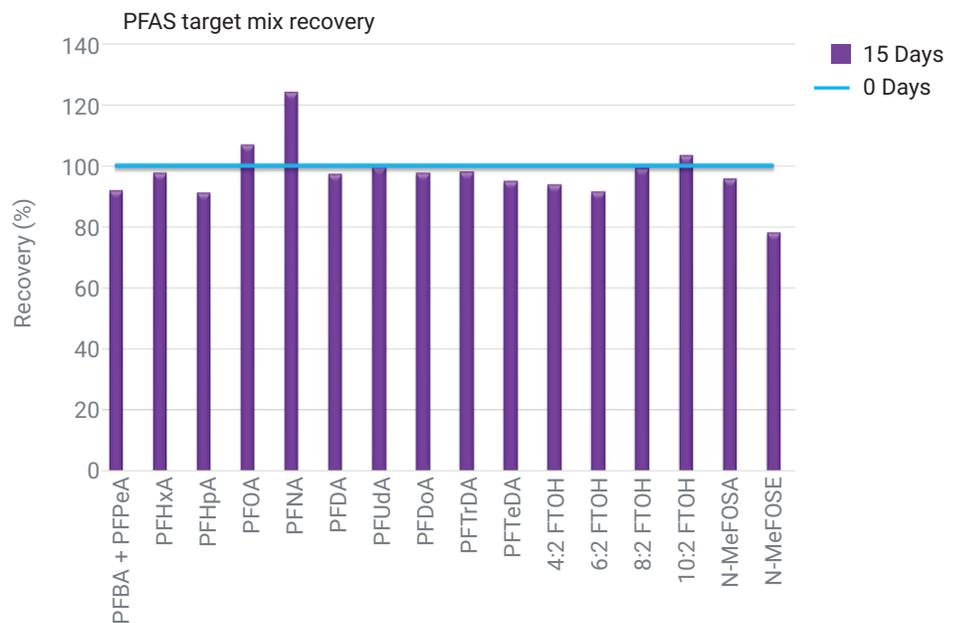


Figure 3. Recovery of sorbent tubes spiked with a PFAS standard mixture and stored for 15 days at 5 °C.

System and sampling tube blanks

A series of blanks was run using the mass spectrometer in SIM/scan mode to check the levels of system and sampling tube contributions to the analytical background. The results are shown in Figures 4 and 5. These data show no measurable concentration of any of the target PFAS compounds.

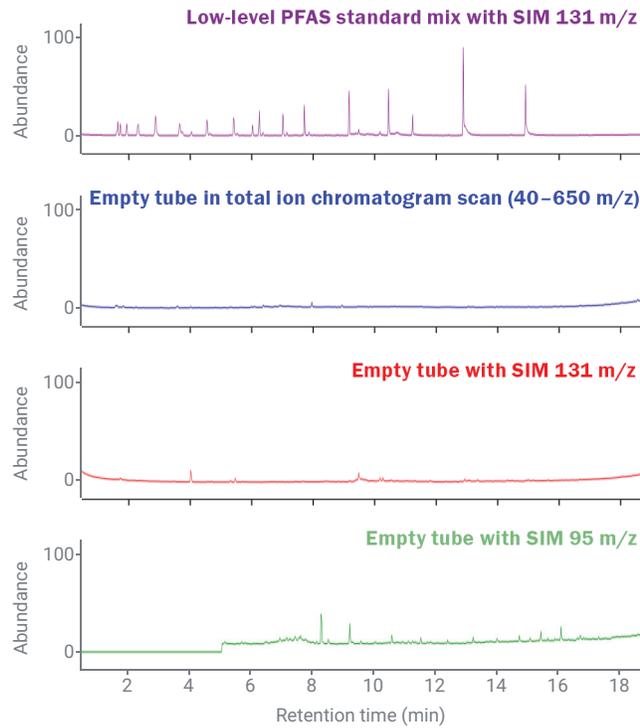


Figure 4. Background of an empty tube under analytical conditions.

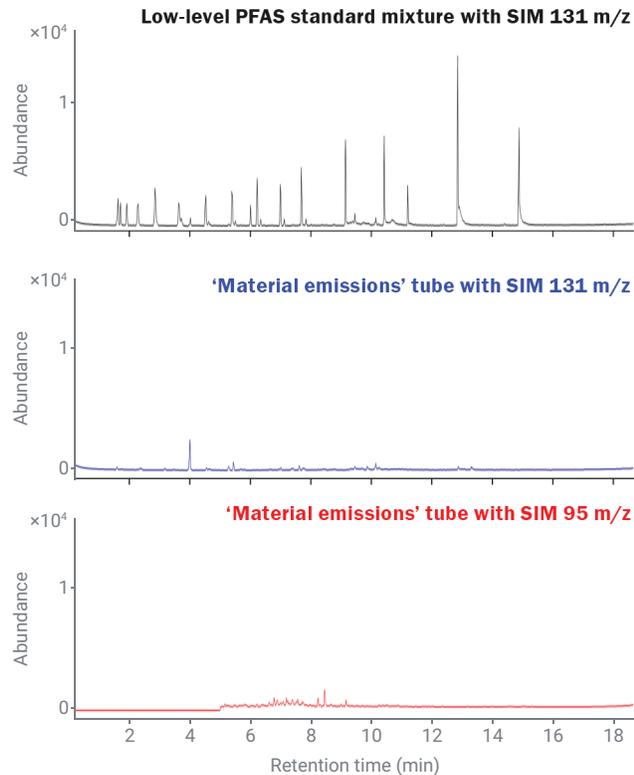


Figure 5. Background of a conditioned material emissions tube under analytical conditions.

Using quantitative re-collection to validate analyte recovery

Three tubes spiked with 2 ng of PFCAs, 12.5 ng of FTOHs, and 16.6 ng of N-MeFOSA, N-MeFOSE, and FTAc were desorbed under standard analytical conditions and run through a series of four desorption and re-collection experiments. During this automatic process, target compounds pass through the entire TD flow path as usual, through

both stages of desorption, before the split effluent is quantitatively re-collected (Figure 9).

The mass of each compound that should reach the re-collection tube from the original spiked tubes and from all subsequent desorptions can therefore be calculated from the split ratio, allowing ready identification of any compounds that are being selectively lost or generated. It is also a further

stringent test of system background because artefacts, if any, are continually accumulated throughout the series of re-collections. The results from these experiments are shown in Figure 6 and demonstrate good recovery across the range. Further, no generation of target or other PFAS compounds was observed, even in the fourth and last analysis (third re-collection).

SIM 131 m/z PFAS standard mix

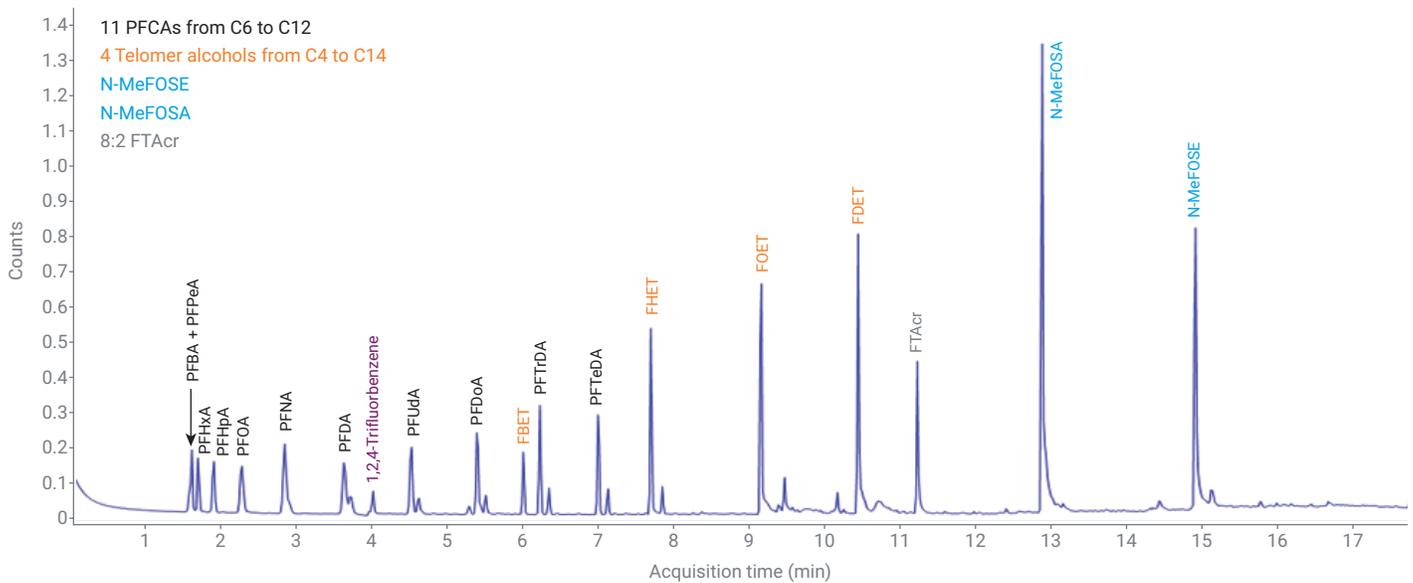


Figure 6. SIM 131 m/z from 1 μL of a PFAS standard mixture with the following levels: 0.3 $\text{ng}/\mu\text{L}$ of each PFAC, 10 $\text{ng}/\mu\text{L}$ of FBET, 30 $\text{ng}/\mu\text{L}$ of FHET, FOET, and FDEET, 4 $\text{ng}/\mu\text{L}$ of FTAc, 7 $\text{ng}/\mu\text{L}$ N-MeFOSA, and 5.5 $\text{ng}/\mu\text{L}$ of N-MeFOSE.

Linearity and limits of detection (LODs)

Conditioned sorbent tubes were spiked with a PFAS standard mixture at different concentrations covering nearly two orders of magnitude and analyzed under the analytical conditions specified earlier. Each data point was collected in duplicate. LODs were calculated from the lowest-level standards. The results (Table 4) show the exceptional sensitivity and stability of the method, ideal for both routine and research PFAS applications.

Repeatability

Repeatability was investigated using five replicates of relatively low-level standards: 2 ng of PFCAs, 12.5 ng of FTOHs, and 16.6 ng of N-MeFOSE/N-MeFOSA/FTAc. The results are shown in Table 5. RSDs are on the order of 5% or less for all target analytes tested.

Real air sample

To complete this evaluation, three conditioned sorbent tubes were spiked with low levels of PFAS standards (Table 5) before 20 L of air was pumped through two of them at a multistorey car park. Ambient conditions during the monitoring exercise were 27 °C and 52% relative humidity. The air samples were collected at 100 mL/min for 3 hours 20 minutes.

Table 4. LOD and linearity for PFAS tested.

Compound	LODs (pg/m ³)	LODs (ppq)	Calibration Range (ng)	R ²
Perfluoroalkylcarboxylic Acids (PFCA)				
PFBA	<25	2.86	0.05 to 2 ng	0.9987
PFPeA		2.31		0.9987
PFHxA		1.95		0.9993
PFHpA		1.68		0.9992
PFOA		1.48		0.9989
PFNA		1.32		0.9991
PFDA		1.19		0.9997
PFUdA		1.08		0.9991
PFDoA		1.00		0.9997
PFTTrDA		0.92		0.9983
PFTeDA		0.86		0.9975
Fluorotelomer Acrylates (FTAc)				
8:2 FTAc	<25	1.18	0.05 to 12 ng	0.9998
Fluorotelomer Alcohols (FTOH)				
4:2 FTOH	<50	4.63	0.1 to 12 ng	0.9926
6:2 FTOH		3.36		0.9981
8:2 FTOH		2.63		0.9968
10:2 FTOH		2.17		0.9976
Perfluorooctanesulfonamides (FOSA)				
N-MeFOSA	<25	1.19	0.05 to 16.6 ng	0.9992
N-EtFOSA		1.16		0.9982

Table 5. Repeatability of target compounds at varying concentrations (n = 5).

Compound	Mass in Tube	m/z	%RSD (n = 5)
Perfluoroalkylcarboxylic Acids			
PFBA and PFPeA	2 ng/μL	131	4.13
PFHxA			4.19
PFHpA			4.14
PFOA			3.12
PFNA			3.70
PFDA			3.23
PFUdA			4.35
PFDoA			3.55
PFTTrDA			3.45
PFTeDA			3.73
Fluorotelomer Alcohols			
4:2 FTOH	12.5 ng/μL	95	1.79
6:2 FTOH			2.29
8:2 FTOH			2.45
10:2 FTOH			3.45
Fluorotelomer acrylates			
8:2 FTAc	16.6 ng/μL	131	2.45
Perfluorooctanesulfonamide and Perfluorooctanesulfonamidoethanol			
N-MeFOSA	16.6 ng/μL	131	1.37
N-MeFOSE			5.80

The two samples were collected sequentially, so it is likely that the composition of the car park air differed slightly between the two samples; however, these differences are not expected to be great. Results (Table 6) show recoveries of 80% or more for all analytes tested.

Table 6. Average recovery data of two spiked tubes, sampled with 20 L of air from a car parking facility.

Compound	Average	% RSD
Perfluoroalkylcarboxylic Acids		
PFBA + PFPeA	81.73	2.98
PFHxA	134.16	3.78
PFHpA	109.76	6.53
PFOA	151.53	5.43
PFNA	144.02	1.26
PFDA	102.97	3.09
PFUdA	86.31	4.99
PFDoA	99.03	1.38
PFTTrDA	123.45	11.04
PFTeDA	125.14	1.34
Fluorotelomer Alcohols		
4:2 FTOH	79.25	4.44
6:2 FTOH	97.59	12.32
8:2 FTOH	111.76	5.36
10:2 FTOH	117.84	1.02
Fluorotelomer Acrylates		
8:2 FTAc	146.20	4.80
Perfluorooctanesulfonamide and Perfluorooctanesulfonamidoethanol		
N-MeFOSA	73.94	12.90
N-MeFOSE	120.60	8.51

The results achieved in this study, using off-the-shelf sorbent sampling tubes with the latest cryogen-free TD and quadrupole GC/MS technology, demonstrate the applicability of this general approach to trace PFAS air measurements. However, the broader robustness of TD–GC/MS methods for such challenging applications depends on many factors, not just analytical performance. There are other instrument considerations that are fundamentally important to the reliability and quality of the analytical data generated. Many of these TD system functions and features are already cited in relevant standard methods and they include the following (listed in order of operation, not importance):

- Leak-tightness of sorbent tubes on the TD autosampler (both before and after analysis)
- Predesorption leak testing of all tubes at ambient temperature and without gas flow
- Automated dry purging in the sampling direction (optional)
- Automated internal standard addition onto the sampling end of sorbent tubes
- Prepurge of air to vent
- Isolation of the tube from the sample flow path, post tube desorption, to prevent interference
- Backflush desorption of the focusing trap
- Cryogen-free operation and water management
- Proper installation and maintenance of the GC column
- Routine maintenance and cleaning of the GC/MSD

The reliability of the analytical method

The results achieved in this study, using off-the-shelf sorbent sampling tubes with the latest cryogen-free TD and quadrupole GC–MS technology, demonstrate the applicability of this general approach to trace PFAS air measurements and the exceptional analytical performance of the Markes International TD100-xr. However, the broader robustness of TD–GC/MS methods for such challenging applications depends on many factors, not just analytical performance. There are other instrument considerations that are fundamentally important to the reliability and quality of the analytical data generated.

Conclusion

This study demonstrates that cryogen-free TD technology coupled to the Agilent 8890 GC and 5977B GC/MSD can be applied to PFAS monitoring at the low- and sub-ppt levels required, with very little adaptation or optimization. This study obtained excellent linearity, sensitivity, robustness, and reliability for the analysis of 18 PFAS spanning multiple subclasses for analysis in indoor air samples. Having demonstrated the capability of routine TD–GC/MS methods and systems for PFAS monitoring at trace levels, future development work will focus on configuring the TD with advanced GC/MS technology (triple quadrupole, time-of-flight, and so on) to enhance detection and compound identification.

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