

Application Note 158

Analysis of trace per- and polyfluorinated organic vapours in air using cryogen-free thermal desorption and gas chromatography–mass spectrometry

Summary

This application note describes the sampling and analysis of a challenging range of trace-level volatile and semi-volatile vapours of per- and polyfluorinated alkyl substances (PFAS) in air. The analytical system used combines modern single-quadrupole gas chromatography–mass spectrometry (GC–MS) technology and a 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, storage stability, etc.) was demonstrated across the range of compounds tested, including low or sub-ppt detection limits for all compounds.



The study also demonstrates the benefit 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 pioneered in commercial form by Markes International and is now available across all Markes' TD platforms. It overcomes the one-shot limitation of traditional TD technology and allows samples or standards to be re-run for data confirmation and/or repeat analysis using different conditions – split flows, GC columns, detectors, etc. It also allows critical samples to be retained or archived if required. This functionality is especially important for challenging new applications such as PFAS, where samples from complex uncharacterised atmospheres (i.e., indoor/in-vehicle air, landfill gas and industrial air) may need to be screened for thousands of targeted and non-targeted analytes at ultra-low levels.

Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a class of persistent organic pollutants that enter our environment from multiple industrial and everyday sources including water-resistant coatings, fire-fighting equipment and non-stick cookware. They include a wide range of chemicals covering different volatilities, polarities and functional groups with recent reports citing over 6000 compounds of potential interest.⁶

The current challenges for PFAS monitoring include:

- The sheer numbers 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.

Importantly, this last point means that unknown (non-target) PFAS are often just as important to regulators and researchers as known target compounds such as perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), which are already listed within the Stockholm convention.⁷

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

- Very volatile perfluorinated hydrocarbons (C_1 to C_3), also known as potent greenhouse gases and ozone depleting substances, typically require whole-air sampling (canisters, online monitoring or sampling bags).
- Volatile or semi-volatile PFAS species, such as perfluoroalkyl carboxylic acids (C_4 to C_{14}), fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAcRs) and fluorotelomer sulfonamides (FOSAs), are compatible with pumped sampling onto sorbent tubes.

While trace PFAS in air is clearly of concern from a human health and 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 vapours and recent developments in automated TD technology have meant these methods can be applied to more and 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 analysing volatile and semi-volatile PFAS.

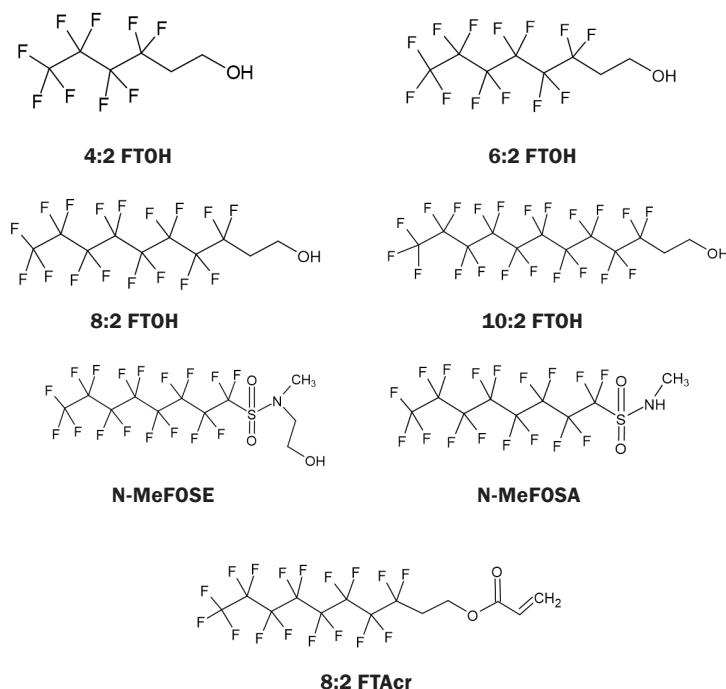


Figure 1: Molecular structures of the fluorotelomer alcohols, acrylate and sulfonamides in the standard.

Experimental

Standards

For this study, we chose 18 standard compounds to validate the method. These analytes cover a range of different chemical groups, all of which are compatible with GC–MS analysis. Eleven perfluorinated carboxylic acids (PFCAs), four fluorotelomer alcohols, perfluoroalkane sulfonamide and sulfonamide alcohol and the semi-volatile 8:2 fluorotelomer acrylate (FTAc) were included. It is worth noting that analytical systems implemented in characterising PFAS from water struggle to identify some species such as fluorotelomer alcohols (the volatile precursors to PFCAs) and compounds with chain lengths below C₈. A full list of compounds used in the standard is presented in Table 1 and example structures are shown in Figure 1.

(a) Determining breakthrough volumes

A routinely used indoor air monitoring tube was selected for this study (stainless steel ‘Material emissions’ tube, part no. C3-AAXX-5304), due to its versatile non-targeted sampling range for compounds ranging from 1,3-butadiene to n-C₃₀. This combination of hydrophobic sorbents (Tenax® TA backed up by a strong graphitised carbon black) minimises 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 µL of mixed standards (2 ng PFCAs, 12.5 ng FTOHs and 16.6 ng of each of the other PFAS compounds) in methanol, with the exception of the 8:2 FTAc, which was diluted in iso-octane. The spiked tubes were prepared following recommendations in standard methods^{1–5} using a Calibration Solution Loading Rig™ (Markes International, part no. C-CSLR) and a 100 mL/min flow of N₂ for 10 minutes.

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	PFTTrDA	
Perfluorotetradecanoic acid	PFTTeDA	
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
2-(N-Methylperfluoro-octanesulfonamido) ethanol	N-MeFOSE	

Table 1: PFAS compounds tested.

Pairs of identical 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 no. C-UNS10) (Figure 2).



Figure 2: A pair of identical conditioned tubes connected in series for the breakthrough experiment.

Various volumes of N_2 gas were then purged through each tube pair at 50 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 2). No breakthrough of any perfluoro carboxylic acid, including the C_4 , was detected up to 50 L and no breakthrough of any of the PFAS standards was detected up to 20 L.

It was therefore decided to standardise on 20 L purge volumes for subsequent experiments and to calculate detection limits on this basis. 20 L air volumes would allow 14 mL/min air sampling for 24 hours, 28 mL/min for 12 hours or 42 mL/min for eight hours.

Compound	Air volume	Mean breakthrough (%)
Perfluoroalkylcarboxylic acids		
PFBA + PFPeA	50 L	2.5
PFHxA		0.0
PFHpA		2.8
PFOA		2.4
PFNA		4.9
PFDA		3.9
PFUdA		2.1
PFDoA		2.2
PFTTrDA		2.3
PFTeDA		1.5
Fluorotelomer alcohols		
4:2 FTOH	20 L	0.0
6:2 FTOH		2.0
8:2 FTOH		2.9
10:2 FTOH		2.1
Fluorotelomer acrylate		
8:2 FTAcr	20 L	0.0
Perfluorooctanesulfonamide and perfluorooctanesulfonamidoethanol		
N-MeFOSA	20 L	0.9
N-MeFOSE		5.8

Table 2: Breakthrough experiments with data recovery in % for the second tube compared to the first tube.

Storage stability

Two 'Material emissions' tubes were spiked with 1 μ L of mixed PFAS standard (2 ng/ μ L for PFCAs, 12.5 ng/ μ L for FTOH and 16.6 ng/ μ L for the other compounds) using Markes' Calibration Solution Loading Rig as described earlier. They were then sealed using the long-term storage caps recommended in standard methods (Figure 3) and stored, some at room temperature and others under refrigerated conditions.



Figure 3: Conditioned sorbent tube capped at each end with the long-term storage caps recommended in international standard methods.

Tubes were removed from storage and analysed in triplicate after various periods of time (Figures 4 and 5).

These excellent results for seven- 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.

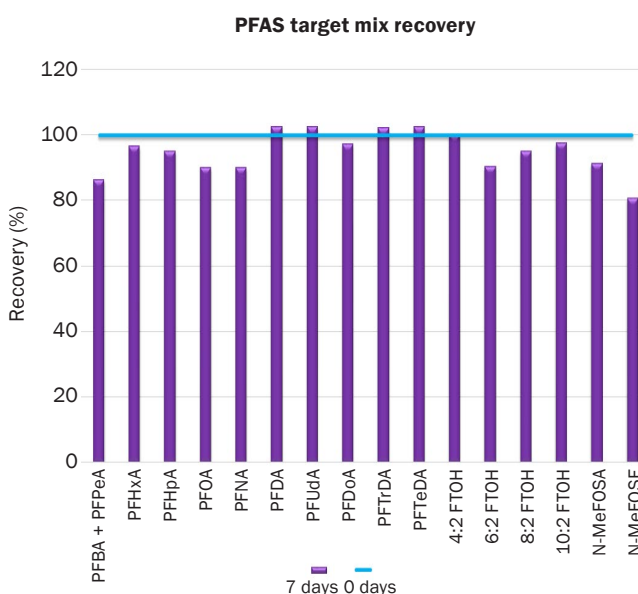


Figure 4: Recovery from sorbent tubes spiked with a PFAS standard mixture and stored for seven days at ambient temperature.

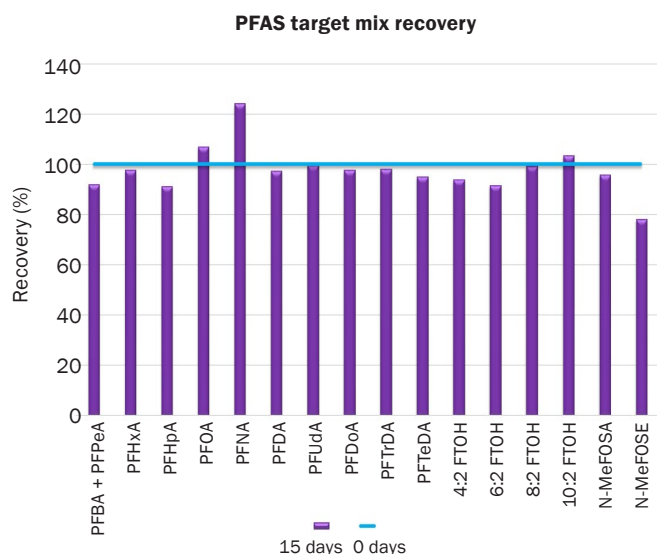


Figure 5: Recovery of sorbent tubes spiked with a PFAS standard mixture and stored for 15 days at 5°C.

GC column selection

The sheer number of PFAS compounds makes GC column selection difficult; however, after extensive tests, a VF-200 MS column was selected due to the best combination of resolution and peak shape for the extensive compound range (Figure 6).

Analytical conditions

Tubes:	Standard 89 mm (3.5-inch) x 6.4 mm O.D. stainless steel 'Material emissions' tubes containing Tenax TA backed up by a strong carbon black sorbent (C3-AAXX-5304)
Flow path:	150°C
Automatic dry purge:	2 min at 50 mL/min (dry gas flowing in sampling direction)
Tube desorption:	300°C for 12 min with 50 mL/min
Trap purge:	1 min x 50 mL/min (carrier gas flowing in the focusing direction)
Focusing trap:	'Material emissions' focusing trap (U-T12ME-2S)
Focusing trap low:	-30°C to 25°C
Focusing trap high:	300°C (4 min)
Trap heat rate:	MAX
Outlet split:	6:1

GC

Column:	VF-200ms 30 m x 0.25 mm x 1.0 µm
Carrier gas:	Helium
Column flow:	1.2 mL/min, constant flow
GC oven:	35°C for 2 min, 15°C/min to 325°C. Hold for 5 min

MS

Source:	250°C
Transfer line:	325°C
Scan range :	m/z 40–650
Selected ions (SIM mode):	Quantifier ions – 95 (FTOH), 131 (PFCAs, FTAcr, N-MeFOSA)

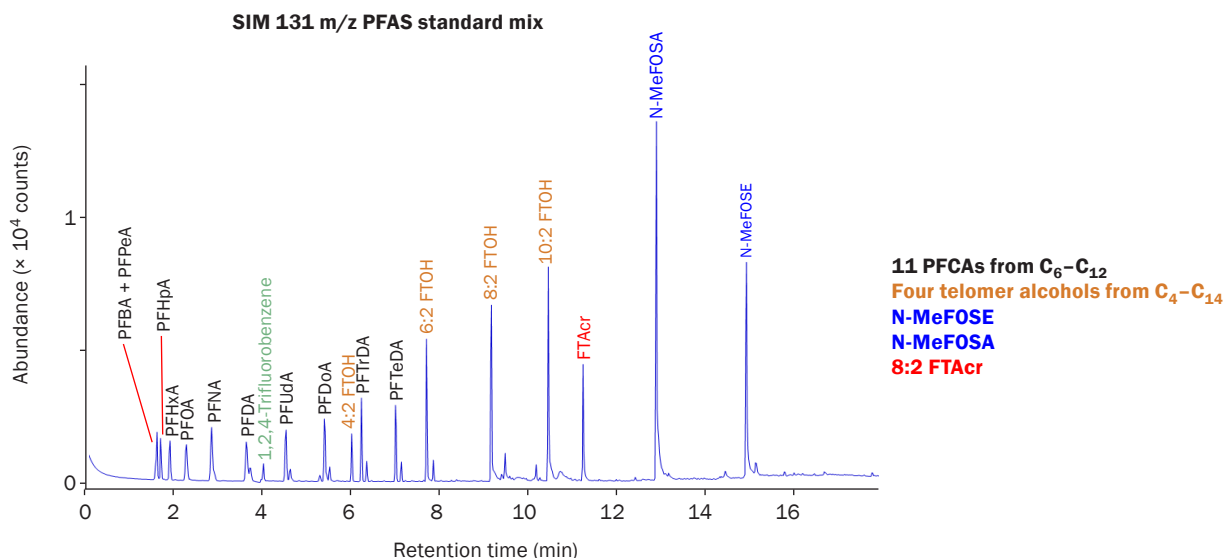


Figure 6: SIM 131 m/z from 1 µL of a PFAS standard mixture with the following levels: 0.3 ng/µL of each PFAC, 10 ng/µL of 4:2 FTOH, 30 ng/µL of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH, 4 ng/µL of FTAcr, 7 ng/µL of N-MeFOSA and 5.5 ng/µL of N-MeFOSE.

Results

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 7 and 8.

This data shows no measurable concentration of any of the target PFAS compounds.

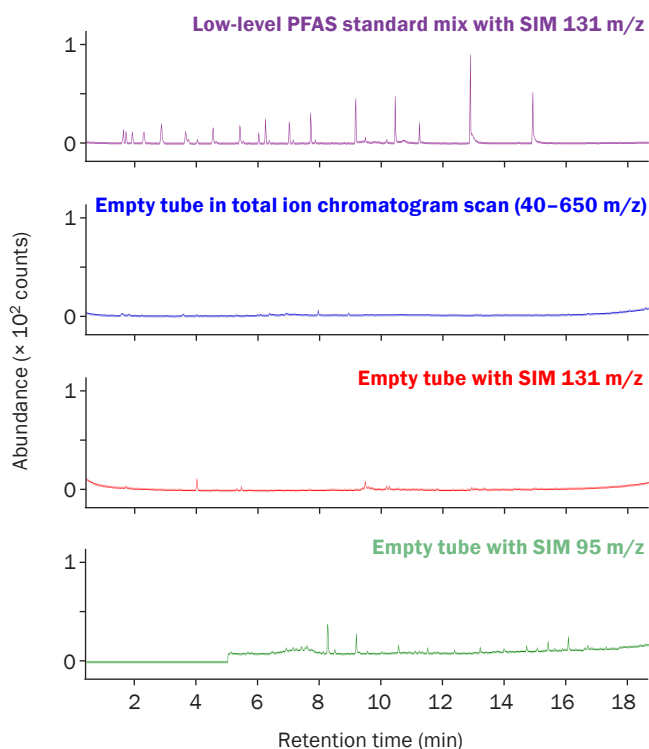


Figure 7: Background of an empty tube under analytical conditions.

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 10 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).

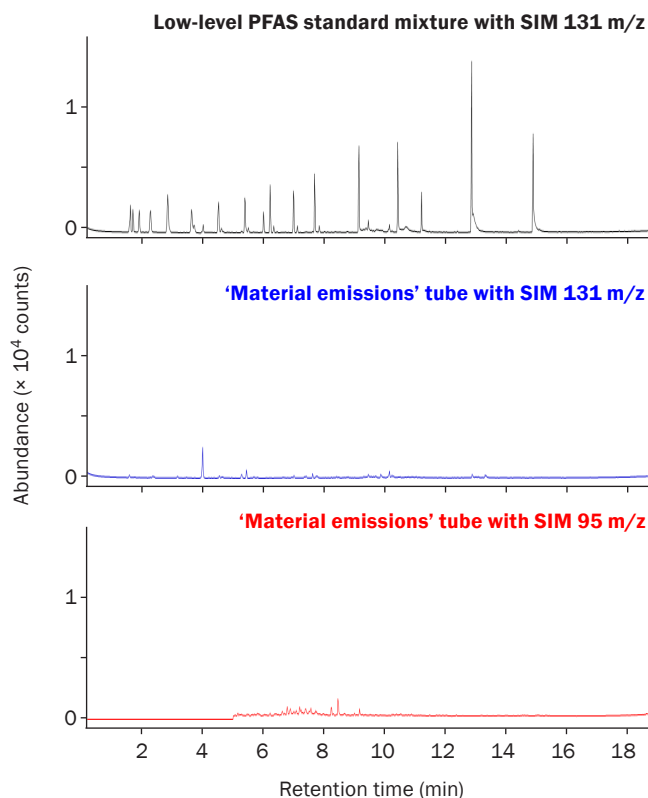


Figure 8: Background of a conditioned 'Material emissions' tube under analytical conditions.

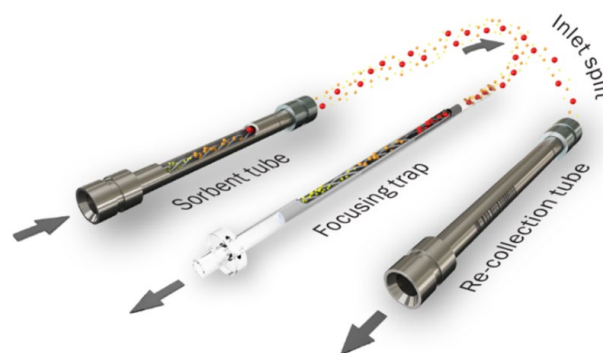


Figure 9: Operation of two-stage thermal desorption.

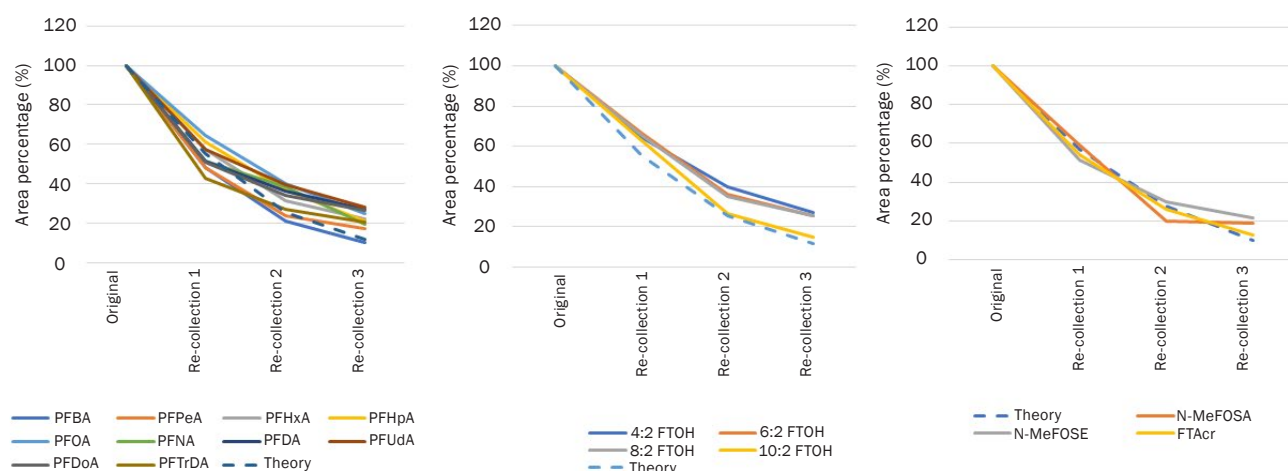


Figure 10: Re-collection of specified PFAS compounds where the dashed line indicates the theoretical reduction in response. The profiles of each target compound follow the same profile demonstrating no losses of any of the compounds of interest and highlighting a PFAS-free flow path.

Linearity and limits of detection

Conditioned sorbent tubes were spiked with a PFAS standard mixture at various concentrations covering nearly two orders of magnitude and analysed under the analytical conditions specified earlier. Each data point was collected in duplicate. Limits of detection (LODs) were calculated from the lowest-level standards. The results (Table 3) show the exceptional sensitivity and stability of the method – ideal for both routine and research PFAS applications.

Compound	LODs (ng/m ³)	LODs (ppt)	Calibrated concentration range	r ²
Perfluoroalkylcarboxylic acids				
PFBA + PFPeA	<5	<0.25	0.05–2 ng	0.9987
PFHxA				0.9993
PFHpA				0.9992
PFOA				0.9989
PFNA				0.9991
PFDA				0.9997
PFUdA				0.9991
PFDaA				0.9997
PFTTrDA				0.9983
PFTeDA				0.9975
Fluorotelomer alcohols				
4:2 FTOH	<50	<3	0.1–12 ng	0.9926
6:2 FTOH				0.9981
8:2 FTOH				0.9968
10:2 FTOH				0.9976
Fluorotelomer acrylates				
8:2 FTAc	<8	<0.35	0.05–16.6 ng	0.9998
Perfluorooctanesulfonamide and perfluorooctanesulfonamidoethanol				
N-MeFOSA	<14	<0.6	0.05–16.6 ng	0.9992
N-MeFOSE	<26	1.5		0.9982

Table 3: The TD–GC–MS method's LODs and linearity.

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 4. RSDs are in the order of 5% or less for all target analytes tested.

Compound	Mass in tube	m/z	%RSD (n = 5)
Perfluoroalkylcarboxylic acids			
PFBA + 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
PFTeDA			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

Table 4: Repeatability of target compounds at varying concentrations (n = 5).

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 multi-storey car park. Ambient conditions during the monitoring exercise were 27°C and 52% RH. The air samples were collected at 100 mL/min for 3 hours and 20 minutes.

Compound	Mass spiked on tube (ng)	ppt
Perfluoroalkylcarboxylic acids		
PFBA	0.3	1.43
PFHxA		0.97
PFHpA		0.84
PFOA		0.74
PFNA		0.66
PFDA		0.60
PFUdA		0.54
PFDaA		0.50
PFTTrDA		0.46
PFTeDA		0.43
Fluorotelomer alcohols		
4:2 FTOH	10	38.61
6:2 FTOH	30	84.01
8:2 FTOH	30	65.90
10:2 FTOH	20	36.15
Fluorotelomer acrylates		
8:2 FTAcr	3.5	6.89
Perfluorooctanesulfonamide and perfluorooctanesulfonamidoethanol		
N-MeFOSA	7	12.81
N-MeFOSE	5.5	10.93

Table 5: Spiked tube level for air sampling information.

The two samples were collected sequentially so it is quite 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 (Figure 11 and Table 6) show recoveries of 80% or more for all analytes tested.

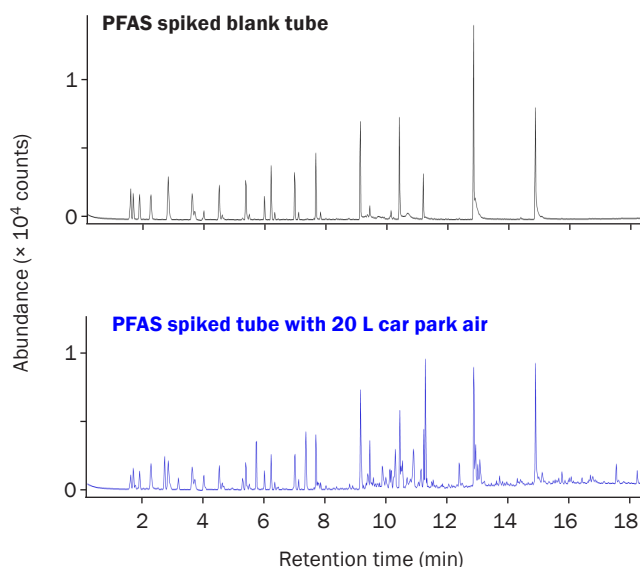


Figure 11: Spiked unsampled tube vs. one example of the two spiked tubes used to sample a 20-L volume of car park air.

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 FTAcr	146.20	4.80
Perfluorooctanesulfonamide and perfluorooctanesulfonamidoethanol		
N-MeFOSA	73.94	12.90
N-MeFOSE	120.60	8.51

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

Discussion

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 Markes' 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. 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). Note that a very similar list is given in US EPA Method TO-17:

(1) Leak-tightness of sorbent tubes on the TD autosampler (both before and after analysis)

Both sampled tubes (awaiting desorption) and desorbed tubes (awaiting the end of an automated sequence) must be stringently protected from analyte loss and ingress of lab air contaminants while they are on the system to protect their integrity. The analytical DiffLok™ caps used on Markes' TD100-xr and ULTRA-xr™ autosamplers have been shown to maintain the integrity of blank and sampled tubes for over a week and remain in place on the tubes throughout the sequence. In contrast, the PTFE-coated o-rings used on some other TD systems to facilitate uncapping or tube removal have been reported to leak rapidly, for example up to 25% loss of benzene after 14 hours.⁸

(2) Pre-desorption leak testing of all tubes at ambient temperature and without gas flow

During an automated TD sequence, a section of the carrier gas flow path is effectively changed every time a new sample is loaded and sealed into position and leaks are theoretically possible whenever this happens. An automatic ambient temperature leak test is therefore required after each tube is loaded and before it is analysed and has been specified by regulators and in standard methods since the earliest days of automated TD. The reason for this is obvious. Without a stringent leak test, ideally under stop-flow conditions, the analysis of leaking samples will proceed, causing samples to be lost and calling the reliability of all results into question. Without a leak test, no one knows which, if any, tubes leaked and which didn't.

(3) Automated dry purging in the sampling direction (optional)

Humid air/gas sampled on tubes packed with non-hydrophobic sorbents will contain water, which must be selectively eliminated from the system and prevented from reaching the GC column and detector to minimise analytical interference and extend the lifetimes of instruments and consumables. Humid tubes can be dry-purged off-line prior to analysis, but it can be more convenient to include a dry-purge step in the automated analytical sequence. Note that the use of sorbent focusing traps and moderate cooling temperatures

also allows water to be selectively purged through the trap and out of the system during primary desorption (see points 7 and 8).

(4) Automated internal standard addition onto the sampling end of sorbent tubes

Gas-phase internal standards are widely recommended for TD-GC-MS methods to improve analytical quality control and data confidence and are referenced in most standard methods. Analytical internal standards are automatically introduced to the sampling end of sampled and standard tubes after the leak test and before desorption, allowing users to distinguish between detector drift and any analyte losses from standards or samples over the duration of the sequence. Note that internal standards (or surrogates) can also be introduced to conditioned tubes before sampling as a check on the entire monitoring procedure, including sample transportation and storage. When this is done, a different compound is used for the analytical internal standard.

(5) Pre-purge of air to vent

Residual air from the sampling process must be purged from the tubes prior to analysis to prevent sorbent and/or analyte oxidation. The purged air must be sent to vent and prevented from reaching the GC column or mass spectrometer to minimise system background and degradation.

(6) Isolation of the tube from the sample flow path, post tube desorption, to prevent interference

At the end of primary (tube) desorption, it is important to isolate the hot sample tube from the carrier gas flow path to stop 'ghosting' from any residual high-boiling components or artefacts eluting late from the sample tube and interfering with the GC analysis.

(7) Backflush desorption of the focusing trap

Reversing the direction of gas flow through the focusing trap during secondary desorption (Figure 9) is important because it allows focusing traps to be packed with a series of sorbents of increasing strength, which in turn extends the range of analyte volatilities that can be analysed simultaneously. Volatiles are retained by the stronger sorbents at the rear of the trap while higher boiling semi-volatile compounds are trapped and released by the weaker sorbents at the front of the trap without ever coming into contact with stronger sorbents. This arrangement even allows very volatile compounds such as C₂ hydrocarbons to be quantitatively retained without liquid cryogen cooling (see point 8).

(8) Cryogen-free operation and water management

The big benefit of operating automated TD systems without liquid cryogen is clear in any busy laboratory and it is made possible by the use of small sorbent-packed focusing traps that desorb in backflush mode as explained earlier and in Figure 9. Other important benefits of this type of TD configuration are that electrically-cooled sorbent traps aren't prone to plugging with ice during the desorption of humid samples and they can be automatically dry-purged in the focusing direction prior to analysis as part of the water management strategy for humid samples.

It is also important to note that almost all of these essential functions (and other important features such as quantitative TD sample re-collection for repeat analysis) are made possible by using a suitable inert heated valve in the TD sample flow path. While the valve mustn't compromise system performance in any way (no sample losses, artefacts, band-broadening, etc.), it is a critical component of reliable automated TD operation. Without it, essential functions such as leak testing, purging, backflushing and tube isolating cannot be done properly.

The proprietary heated valve incorporated into TD100-xr and used on all Markes TD platforms was designed specifically for analytical TD and has proven its exceptional reliability and performance in thousands of TD installations, including the most challenging applications.

Conclusions

This study demonstrates that fully automated cryogen-free TD technology, as would be used for routine air applications of many kinds, can be applied to PFAS monitoring at the low and sub-ppt levels required, without any adaptation or optimisation.

It has further shown how quantitative re-collection and repeat analysis is invaluable for validating analyte recovery through the two-stage TD process – allowing users to scrutinise data from a sequence of runs and check for any contribution from the system to PFAS levels (background or chemical reaction) and for any indication of compound losses.

Having demonstrated the capability of routine TD–GC–MS methods and systems for PFAS monitoring at trace levels, future development work will focus on two key approaches to method improvements:

- Optimising sorbent selection to allow the collection of larger air sample volumes.
- Configuring the thermal desorber with advanced GC–MS technology (triple quad, time-of-flight, etc.) to enhance detection and compound identification.

References

1. [EN ISO 16017: Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 1: Pumped sampling.](#)
2. [US EPA TO-17: The determination of volatile organic compounds \(VOCs\) in air collected in SUMMA canisters and analysed by gas chromatography/mass spectrometry.](#)
3. [ISO 16000-6: Indoor air – Part 6: Determination of organic compounds \(VVOC, VOC, SVOC\) in indoor and test chamber air by active sampling on sorbent tubes, thermal desorption and gas chromatography using MS or MS FID.](#)
4. [ASTM D6196: Standard practice for choosing sorbents, sampling parameters and thermal desorption analytical conditions for monitoring volatile organic chemicals in air.](#)
5. [HJ 759: Ambient air. Determination of volatile organic compounds. Collected by specially-prepared canisters and](#)

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7. S. Nakayama et al., Worldwide trends in tracing poly- and perfluoroalkyl substances (PFAS) in the environment, *Trends in Analytical Chemistry*, 2019, 121: 115410, <https://www.sciencedirect.com/science/article/pii/S0165993618306605?via%3Dihub>.

8. P.P. Ballesta, Losses from ATD-400, *The Diffusive Monitor*, issue 9, November 1997.

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