MARKES international

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Application Note 166

Measuring PFAS pollution in ambient air using TD–GC–MS/MS

Summary

Markes International's TD100-xr™ thermal desorption instrument coupled to a gas chromatograph and a triple quadrupole mass spectrometer enables measurement of per- and polyfluoroalkyl substances (PFAS) in air at concentrations as low as 2 pg/m^3.

Introduction

Concerns over the environmental effects of PFAS compounds have risen dramatically, and as a result, strategies are being developed by environment agencies to manage their levels in ambient air. PFAS are aliphatic compounds containing one or more carbon atoms on which all the hydrogens have been replaced by fluorine atoms. To date, the total number of PFAS compounds exceeds 6000.

As the PFAS group is so large, for convenience, it is split into families of compounds, one of which is a non-polymers group. The non-polymers are of most concern with respect to human health and the environment. Of these, the perfluoroalkyl carboxylic acids/carboxylates (PFCAs) are considered the most dangerous; therefore, they are the most widely researched. Next are the neutral PFAS (n-PFAS), examples of which include fluorotelomer alcohols (FTOHs), fluorotelomer carboxylic acids (FTCAs) and perfluorooctanesulfonamides (FOSAs). In the environment, some n-PFAS (*e.g.*, FTOHs) have been shown to undergo atmospheric oxidation and transform into PFCAs,[1] making them equally important to understand and monitor. These facts have determined the compound classes targeted in this study.

PFAS sources and how they are spread

Detecting airborne PFAS is important for measuring emissions, investigating how they spread and understanding human exposure. Unlike water and soil, there are very few constraints on how far and wide PFAS can spread when released into ambient air. Once compounds have been released into the environment, they can travel through the air for thousands of kilometres. Emission sources include chemical manufacturing sites, thermal waste treatment facilities and the commercial applications of PFAS.[2]

Airborne PFAS can also be deposited in water and soil. This mechanism for spreading PFAS contamination to various media is of concern because of the distances airborne PFAS can travel. As little as 5% of PFAS emitted from a source may be deposited within 150 km of the site, with 95% travelling further afield.[3] Data from polar and background monitoring sites, which are in remote locations, confirm that PFAS are being spread by long-range atmospheric transport.

Using thermal desorption with gas chromatography and triple quadrupole mass spectrometry to monitor PFAS

With thermal desorption (TD), sorbents are used as sampling media to preconcentrate samples from hundreds of litres of air. This inherent preconcentration effect with no requirement for any dilution prior to analysis means that single-digit pg/m^3 concentrations can be measured from <500 L of ambient air when combined with triple quadrupole mass spectrometry for detection.

The non-selective nature of the sorbents means that a targeted analysis method can easily be adapted to give information on untargeted species that have also been captured during sampling. This option is enhanced further when using Markes' patented re-collection feature during analysis (see below for details on re-collection). This approach can be applied to non-target PFAS species as well as other VOCs.

To date, liquid chromatography–mass spectrometry (LC–MS) has been the most commonly-used technique to measure PFAS in air. However, more volatile PFAS, such as fluorotelomer alcohols, can be a challenge for LC. Equally, sorbent sampling media, such as PUF and XAD, which have been used for sampling gases, also struggle to capture more volatile species. In this respect, the move to TD–GC–MS/MS makes sense as the technique is already used to monitor organic compounds in air, including ultra-volatile species.

Markes' TD100-xr (Figure 1) is an automated TD unit for GC and GC–MS/MS and a high-performance, high-throughput platform for the analysis of sub-ppt to percent levels of volatile and semi-volatile organic compounds in air. TD100-xr combines versatility, productivity and reliability through its

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ability to handle a wide range of analytes (ranging in volatility from C_3 to n-C_{44} plus reactive compounds), its 100-tube autosampler and ease of use. It also includes advanced features for peace of mind and workflow flexibility such as automated sample re-collection and internal standard addition.

Figure 1: The TD100-xr – An automated, analytical thermal desorption system.

The process of re-collection is invaluable for method development/validation, troubleshooting and sample archiving. It also allows users to re-run samples using different MS methods or using a completely different detector, which is of great use when trying to identify unknowns in a sample. More information on re-collection can be found in Application Note 027: A review of sorbent-based sampling methods for volatile and semi-volatile organic compounds in air.

Another invaluable feature when looking at broad compound lists (which are often encountered in PFAS analysis) is the ability to backflush the focusing trap at the heart of the TD100-xr. Backflushing allows multiple sorbents to be used for trapping and negates the need for cryogenic cooling – a method used in early TD systems when the technique was being developed in the 1970s. Backflushed focusing traps also enable the analyst to purge excess water from the sample during the analysis process, a critical feature when sampling large volumes of air, and one that is required to reach pg/m^3 levels of detection. Cryogenic cooling of the trap does not enable water to be managed in the same way and a common problem is ice formation, which can cause blockages and subsequent loss of important samples.

Experimental

Our aim was to develop and validate a method for sampling and analysing 19 target PFAS compounds across four different functional groups – perfluoroalkyl carboxylic acids/carboxylates (PFCAs), fluorotelomer alcohols (FTOHs), fluorotelomer carboxylic acids (FTCAs) and perfluorooctane sulfonamides (FOSAs) – from ambient air.

Standards

Individual component standards were purchased from Wellington Laboratories Inc, Canada, at a concentration of 50 ng/µL, except the PFCAs, which were available in a mixture at 2 ng/µL and used as a stock standard. The individual component standards were combined and diluted to create 5 ng/µL stock standards. Serial dilution of the stock standards produced the range used in calibration and further tests.

To spike sorbent tubes with standards, 1 µL of each standard was injected using a Calibration Solution Loading Rig™ (CSLR™) onto the sorbent tube in a flow of nitrogen at 100 mL/min and purged for 60 minutes to remove methanol. Markes' TC-20™ unit was used to purge up to 20 tubes simultaneously, significantly speeding up the spiking process. The TC-20 was also used to re-condition the sorbent tubes in nitrogen prior to sampling, freeing up the analytical instrument and saving helium.

Sampling

Ambient air from three sites at a light industrial location were pumped onto a sorbent tube at a flow rate of 100 mL/min using an ACTI-VOC PLUS™ constant flow sampling pump for 50 hours until a volume of 300 L was reached. Flow rates for sampling onto TD tubes typically range from 10–500 mL/min. Sample flow rates can be optimised to enable sampling across the desired time window – though higher flow rates may affect breakthrough volumes. TD tubes can be used over 100 times in their lifetime as the sorbent is re-generated each time it is heated.

Analytical conditions

Tubes:	PFAS Extended volume tubes C3-AAXX-5426 (stainless steel, conditioned and capped; Markes International)
System:	TD100-xr Advanced (Markes International)
Flow path:	200°C
Automatic dry purge:	1 min at 50 mL/min
Tube desorption:	300°C for 10 min at 50 mL/min
Trap purge:	1 min at 50 mL/min
Focusing trap:	'PFAS' focusing trap (U-T24PFAS-2S, Markes International)
Focusing trap low:	-30°C
Elevated trap purge:	25°C
Focusing trap high:	300°C (4 min)
Trap heat rate:	MAX
Outlet split:	6:1

GC

Column:	TG-200MS 30 m × 0.25 mm × 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 280°C. Hold for 5 min

MS/MS

Source:	300°C
Transfer line:	280°C
Acquisition mode:	Timed single-reaction monitoring (SRM) and full scan
Scan range :	m/z 35–650
SRM:	SRM transitions (see Appendix for details).

Results and discussion

Chromatography

Figure 2 shows the chromatogram for a sorbent tube spiked with a PFAS mid-point concentration standard. The 19 target species are labelled. There is excellent separation of the compounds and sharp Gaussian peaks for each species. The wide range of chemistries present within the PFAS standard made column choice an essential factor during method development.

System and method blank

Analytical methods are expected to achieve lower and lower detection limits. Instrumentation is no longer the limiting factor; in most cases, it is the blank levels. Therefore, in 2017, the US Environmental Protection Agency (US EPA) moved from calculating the method detection limits for an analysis based solely on the limit of detection to include blank levels.

In this analysis, we are striving to reach method detection limits in the range of 5–50 pg/m^3, which translates to femtogram (fg) levels of individual compounds on-column. At these levels, we must be mindful of the fact that the sorbents used in the tubes to collect the samples are also materials with inherent artefacts. Whilst they are very clean, and for most applications can be considered to contribute nothing detectable to background levels, they should be treated in the same manner as column phases and expected to 'bleed' some low-level artefacts upon heating. These artefacts are focused into peaks by the GC column, so it is important that possible contributions are understood before embarking on sampling projects.

Characterisation process

To fully characterise the background, we split the assessment into three stages: (1) a trap and valve blank, (2) a system blank to ascertain the suitability of the analytical instrument and (3) a method blank, which introduces the sorbent sampling media. In each case, we focused on the target compounds and used SRM mode to ensure the best sensitivity.

The trap and valve blank step was conducted by desorbing the sorbent-packed, cryogen-free focusing trap of the TD100-xr under the optimised method conditions and running the full GC–MS method to measure any artefact contributions. The system blank was assessed by desorbing an empty stainless steel sorbent tube in the TD100-xr under the full TD–GC–MS method. The method blank was then conducted by repeating the process with seven replicates of the PFAS extended range sorbent tubes. Any positive results were then compared to the concentrations spiked for the individual compounds during the method detection limit (MDL) tests.

Results

No background was detected for the target species in the trap and valve blank.

In the system blank, while some peaks were discernible, only one was above the MDL spike level – perfluorotetradecanoic acid (PFTeDA), a PFCA that was detected at 9 pg *versus* the 5 pg spike level. For context, during the sampling study, the mass of PFTeDA collected (when present in the sample) was five to 10 times higher.

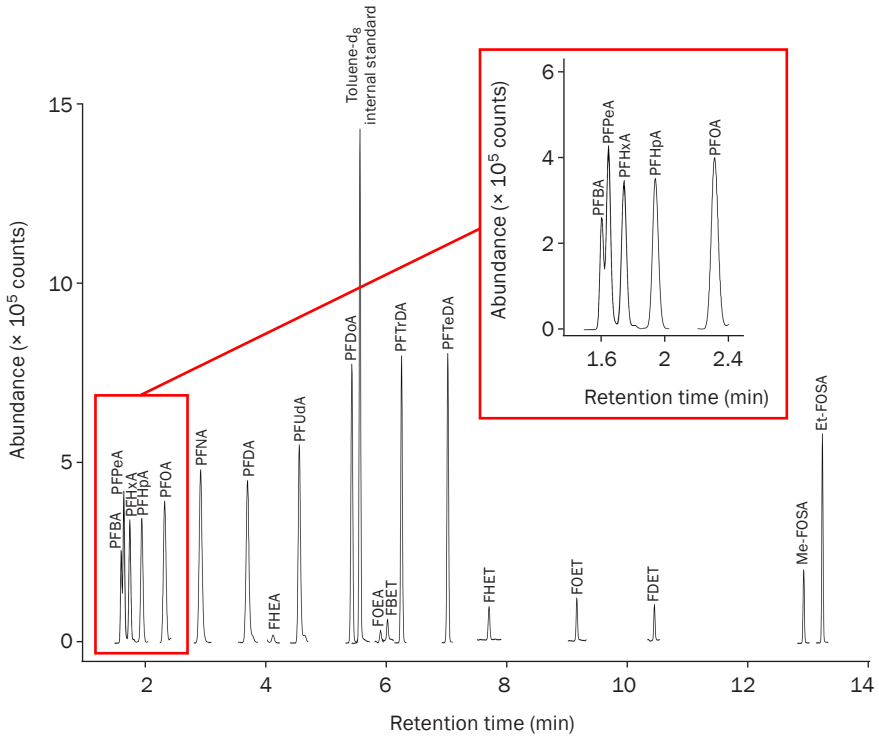

Figure 2: Mixed PFAS standard at 500 pg on-tube. The inset shows a close-up view of the chromatogram for the first five compounds, which are perfluoroalkylcarboxylic acids (PFCAs). Baseline separation was not possible for PFBA and PFPeA at the oven start temperature of 35°C but this chromatography could be further optimised.

For the method blank, five compounds were found to be above the spike level. One of these compounds was not present in all the tubes tested, indicating the importance of not just looking at the average blank value but also understanding variations with a view to choosing samplers for field sampling that do not show background for target compounds. In the results table (see the Appendix), the MDLs for these compounds reflect the level at which they were found in the method blank.

Discussion

The main challenge when monitoring PFAS compounds in air is their low concentration levels. To detect low levels of PFAS compounds, preconcentration of samples using a sorbent is required. However, samples can become contaminated, for example from any gases or solvents used, glassware, containers for transportation, sampling media and laboratory air. Some of these cannot be avoided entirely but the more steps involved in sample preparation, the higher the risk of contamination. With thermal desorption, there are no extra sample preparation steps before the sample is placed into the instrument, which helps to negate many of the risks.

To counter background, it is important that cleanliness is at the forefront of any standard operating procedure. Full characterisation of the sorbent medium is important and, as we have shown, blank values should always be considered when monitoring compounds at such low environmental levels.

Linearity

Due to the concentrations of the stock standards, different compound classes were calibrated over different ranges, but a minimum of six calibration points were used for each of the compounds (Table 1). All compounds were linear down to 10 pg except the FTCAs, including perfluorohexyl ethanoic acid (FHEA) and perfluorooctyl ethanoic acid (FOEA), which were linear to 100 pg on-tube. Linearity for all compounds was $R^2 > 0.99$. Please see the Appendix for individual values.

Compound class	Concentration range (pg/µL)	No. of calibration points
Perfluorocarboxylic acids (PFCAs)	10–2000	8
Fluorotelomer carboxylic acids (FTCAs)	100–5000	6
Fluorotelomer alcohols (FTOHs)	10–5000	9
Perfluorooctanesulfonamides (FOSAs)	10–5000	9

Table 1: Calibration ranges (due to the concentrations of the stock standards, different compound classes were calibrated over different ranges).

Method detection limits

The concentration of individual PFAS species in ambient air varies depending on location, *i.e.*, urban *versus* rural environments. Background monitoring sites, usually in remote locations such as mountains, heavy forests or the poles, typically report PFAS concentrations of <1–200 pg/m^3.[4] In urban environments, due to the presence of multiple PFAS sources, typical concentrations can be much higher (<1–800 pg/m^3), depending on the compound.[4]

The method detection limit for this study was calculated by comparing n = 7 method blanks with n = 7 sorbent tubes that were spiked with a standard at a 'challenge level' in accordance with US EPA guidance.[5] As described earlier, this process is designed to account for any background contaminants introduced during sample handling, preparation and analysis.

The average limit of detection was 9 pg. In our previous study (Application Note 158: Analysis of trace per- and polyfluorinated organic vapours in air using cryogen-free TD and gas chromatography–mass spectrometry), breakthrough volumes for the compounds targeted in this work were shown to be greater than 500 L of air. Using this volume, the average pg/m^3 method detection limit was 31.2 pg/m^3. These values match the lower concentration range for both background and urban monitoring sites. Please see the Appendix for individual compounds' values.

Ambient air samples

Ambient air from three sites (Sites 1, 2 and 3) at a light industrial location was pumped onto a sorbent tube to a volume of 300 L.

Each sample was analysed twice using the automated re-collection feature of the TD100-xr. In the first run, the targeted SRM method on the MS/MS was used to detect the 19 target PFAS compounds. In the second, the GC–MS was run in full scan mode to look for non-target species and other VOCs of interest. The full scan data will not be discussed further in this application note but could be used by analysts to investigate non-targets in the same sample.

Table 2 shows which PFAS compounds were detected and at what concentration (some compounds were detected at a lower concentration than the MDL and these have been indicated on the table). The results show that most of the compounds monitored were found at each site except six: PFHpA, PFUdA, FBET, PFTrDA, FDET and EtFOSA. The compounds with the highest concentrations were carboxylic acids – PFBA, PFHxA and PFOA. In many studies, PFOA is often the carboxylic acid with the highest concentration, so it is interesting that PFBA was detected at a higher level here. Figures 3 and 4 show the chromatogram from the SRM for Site 1 and the quantitation and qualification transitions for key compounds.

Compound	Abbreviation	RT	Concentration (pg/m^3)		
			Site 1	Site 2	Site 3
Perfluoro-n-butanoic acid	PFBA	1.59	2903	2097	4790
Perfluoro-n-pentanoic acid	PFPeA	1.63	ND	ND	ND
Perfluoro-n-hexanoic acid	PFHxA	1.73	850	750	1000
Perfluoro-n-heptanoic acid	PFHpA	1.93	ND	403	477
Perfluoro-n-octanoic acid	PFOA	2.33	1267	1433	3090
Perfluoro-n-nonanoic acid	PFNA	2.89	*60	217	520
Perfluoro-n-decanoic acid	PFDA	3.66	147	*17	103
2-Perfluorohexyl ethanoic acid (6:2)	FHEA	3.97	ND	ND	ND
Perfluoro-n-undecanoic acid	PFUdA	4.60	23	ND	ND
Perfluoro-n-dodecanoic acid	PFDoA	5.40	333	*33	287
2-Perfluorooctyl ethanoic acid (8:2)	FOEA	5.90	ND	ND	ND
2-Perfluorobutyl ethanol (4:2)	FBET	6.01	ND	ND	180
Perfluoro-n-tridecanoic acid	PFTrDA	6.22	27	ND	ND
Perfluoro-n-tetradecanoic acid	PFTeDA	6.96	170	ND	110
2-Perfluorohexyl ethanol (6:2)	FHET	7.67	ND	ND	ND
2-Perfluorooctyl ethanol (8:2)	FOET	9.13	ND	ND	*3
2-Perfluorodecyl ethanol (10:2)	FDET	10.41	137	ND	ND
N-Methylperfluoro-1-octanesulfonamide	Me-FOSA	12.88	130	107	113
N-Ethylperfluoro-1-octanesulfonamide	Et-FOSA	13.19	180	ND	ND

Table 2: Concentrations of each target PFAS compound found at each site in the light industrial area. *Compounds detected below the MDL.

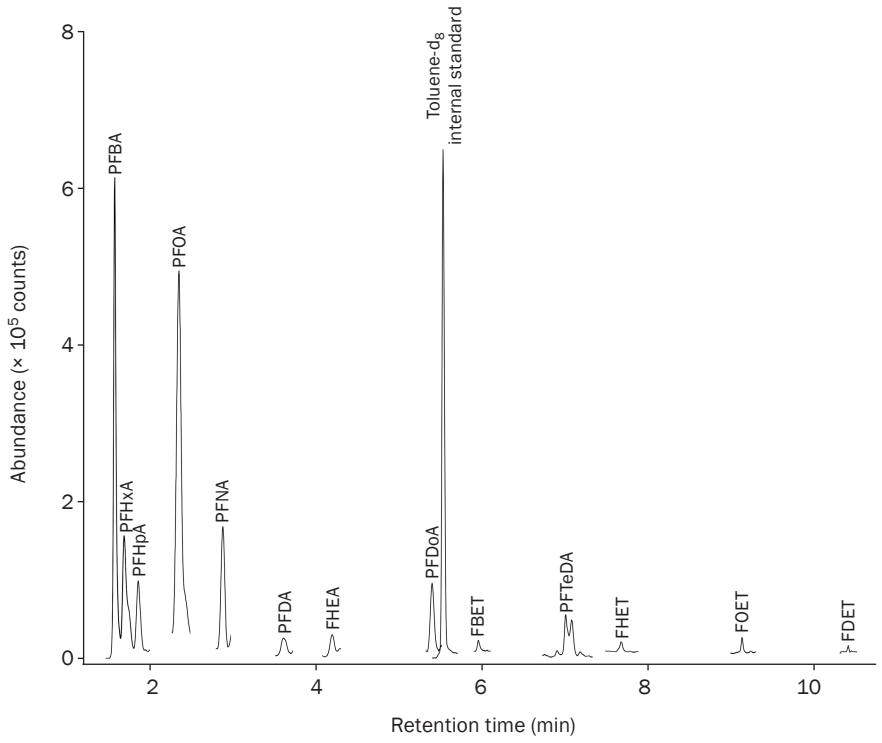

Figure 3: Chromatogram from the SRM trace of 300 L of ambient air sampled in a light industrial location. Compounds were identified from each of our target classes (PFCAs, FTOHs, FTCAs, FOSAs) but the PFCAs were the most abundant in the air sample.

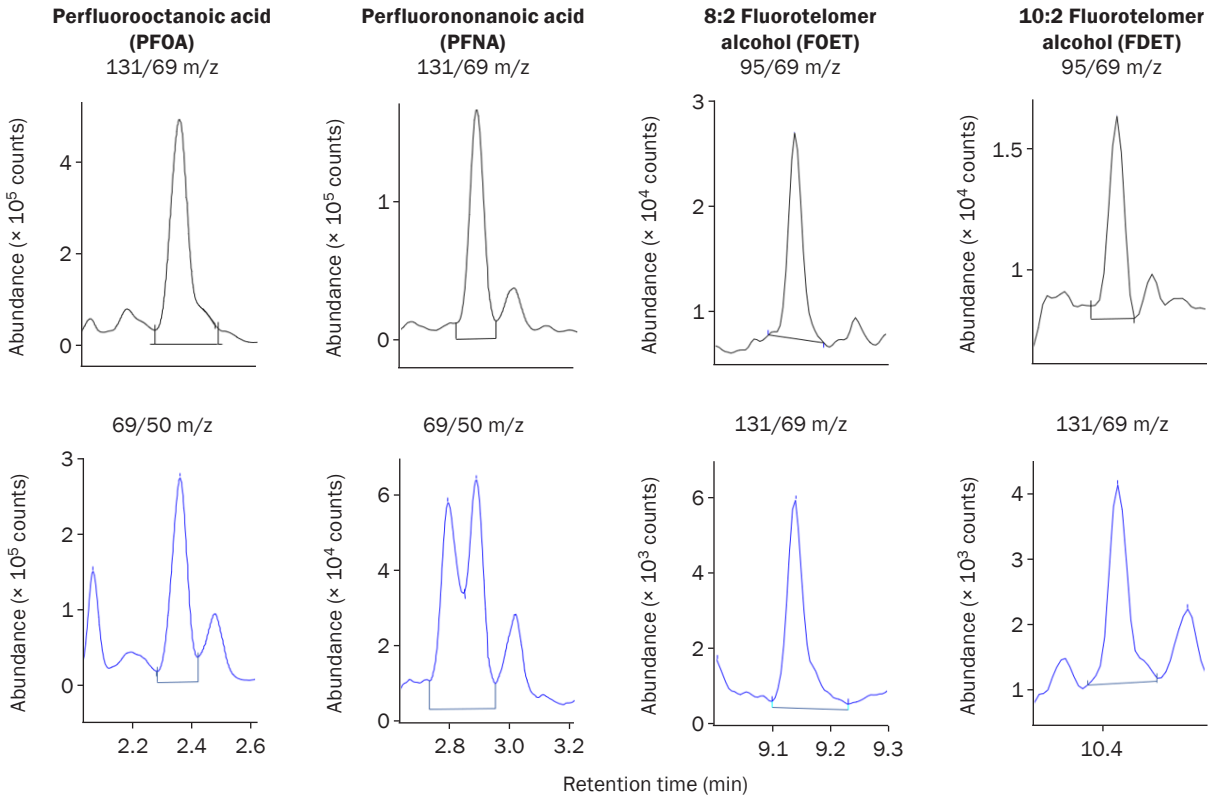

Figure 4: Peak shapes for four compounds when looking at two of the quantitation SRM transitions in the sample taken at Site 1.

The re-collection feature on the TD100-xr was used during method development to validate the water management steps. With sampling volumes of 300 L, a large amount of water vapour from the air becomes trapped on the sorbent tubes. The water must be removed prior to injecting the samples into the gas chromatograph. This is because water vapour affects the overall reproducibility of the analysis and can lead to the entire analytical system needing more frequent maintenance. The toluene-d_8 internal standard was also monitored throughout the process to ensure sample integrity.

Two automated water management steps were carried out by the TD100-xr prior to injection – a dry purge and an elevated temperature trap purge – to remove the greatest amount of water vapour possible from the sorbent tubes and focusing trap prior to injection whilst retaining 100% of the target analytes. The effectiveness of the two steps was then monitored through repeat injections of a sample under the same conditions. By monitoring the peak area of our target compounds, we can plot a decay curve that should match a theoretical curve calculated from the peak area of the first injection; in the case of retained excess water, significant deviations from the theoretical curve would be observed. More information on re-collection can be found in Instant Insight 006: How can I use re-collection to simplify method validation and development?

Conclusions

The TD–GC–MS/MS method developed for the 19 compounds targeted in this study delivered an average method detection limit of 31.2 pg/m^3. Each compound gave a linear calibration and the analysis itself was highly repeatable (see Appendix). The technique is stable and sensitive enough to analyse the more volatile neutral PFAS species and volatile PFCAs in a single run.

Features of Markes' TD100-xr, such as backflushing of the focusing trap, automated water removal steps during analysis and sample re-collection, make handling challenges associated with analysing large volumes of air manageable and provide checks that can easily be used to determine their effectiveness during method development.

As with any technique, one of the consistent challenges when monitoring at such low levels is background interferences. In this study, the importance of characterising the sampling media and including blank values in MDL calculations is shown.

Networks measuring PFAS compounds typically focus on target compounds consisting of the most widely researched and understood PFAS species. As our knowledge of the environmental and health effects of specific PFAS compounds increases, more compounds may need to be included in monitoring campaigns. The non-selective nature of the sorbents used for TD mean that targeting additional

compounds will often require very little change to the previously validated sampling and analysis method.

As they belong to such a wide class of compounds, not all PFAS compounds can be captured using sorbent tubes. Compounds such as Freons, which are also PFAS compounds, are known ozone-depleting substances but due to their high volatility, require sampling using whole air sampling methods. More information on this can be found in Application Note 087: Monitoring trace greenhouse gases in air using cryogen-free TD–GC–MS.

References

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Trademarks

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

Appendix

Compound	Abbreviation	RT	Quantitation SRM transition	R^2	% RSD	MDL (pg)	MDL (pg/m^3)
Perfluoroalkyl carboxylic acids (PFCAs)							
Perfluoro-n-butanoic acid	PFBA	1.593	131/69	0.9985	4.52	5	10
Perfluoro-n-pentanoic acid	PFPeA	1.638	131/69	0.9966	3.80	2	4
Perfluoro-n-hexanoic acid	PFHxA	1.728	131/69	0.9970	3.25	23	46
Perfluoro-n-heptanoic acid	PFHpA	1.933	131/69	0.9981	2.42	3	6
Perfluoro-n-octanoic acid	PFOA	2.311	131/69	0.9986	2.00	2	4
Perfluoro-n-nonanoic acid	PFNA	2.9	131/69	0.9983	1.48	46	92
Perfluoro-n-decanoic acid	PFDA	3.665	131/69	0.9978	2.48	27	54
Perfluoro-n-undecanoic acid	PFUdA	4.522	131/69	0.9974	3.67	4	8
Perfluoro-n-dodecanoic acid	PFDoA	5.392	131/69	0.9975	2.71	21	42
Perfluoro-n-tridecanoic acid	PFTrDA	6.216	131/69	0.9974	3.00	3	6
Perfluoro-n-tetradecanoic acid	PFTeDA	6.981	131/69	0.9975	3.01	2	4
Fluorotelomer carboxylic acids (FTCAs)							
2-Perfluorohexyl ethanoic acid (6:2)	FHEA	3.973	131/69	0.9953	5.75	64	128
2-Perfluorooctyl ethanoic acid (8:2)	FOEA	5.904	131/69	0.9983	2.65	52	104
Fluorotelomer alcohols (FTOHs)							
2-Perfluorobutyl ethanol (4:2)	FBET	6.01	95/69	0.9951	4.10	13	26
2-Perfluorohexyl ethanol (6:2)	FHET	7.669	95/69	0.9971	2.61	18	36
2-Perfluorooctyl ethanol (8:2)	FOET	9.122	95/69	0.9963	3.99	4	8
2-Perfluorodecyl ethanol (10:2)	FDET	10.41	95/69	0.9937	4.08	6	12
Perfluorooctanesulfonamides (FOSAs)							
N-Methylperfluoro-1-octanesulfonamide	Me-FOSA	12.87	94/30	0.9953	0.83	1	2
N-Ethylperfluoro-1-octanesulfonamide	Et-FOSA	13.18	108/80	0.9953	5.29	1	2

Table 1A: Full data table for individual PFAS species analysed during this study.