

Application Note 153

Untargeted screening of volatile per- and polyfluoroalkyl substances (PFAS) released during the application of aqueous film-forming foam (AFFF)

Summary

In this application note, we show how thermal desorption with gas chromatography–mass spectrometry (TD–GC–MS) can be used to monitor the release of per- and polyfluoroalkyl substances (PFAS) during the application of aqueous film-forming foam (AFFF). The results of the study show that TD–GC–MS can be used to analyse target compounds and screen for non-target compounds, enabling researchers to gain a greater understanding of AFFF emissions.



Introduction

PFAS are a large family of man-made chemicals with over 6000 registered species. They are typically defined as aliphatic compounds with one or more carbon atoms in which all the hydrogen atoms have been replaced by fluorine. Many PFAS species are resistant to grease, oil, water and heat, giving them many commercial and industrial uses.

However, as PFAS and their degradation products are persistent pollutants, difficult to remove from the environment and highly mobile once released,¹ they are now considered environmental 'chemicals of concern'. They are found in drinking water, ambient air, soil and food, so human exposure is inevitable and they can bio-accumulate within the body,² leading to concerns about potential health impacts. Studies on two specific PFAS species – perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) – link long-term exposure at environmental levels to diverse and serious conditions including decreased fertility, thyroid disease, low infant birth weights and, in the case of PFOA, cancer.³

At the time of writing, several thousand PFAS compounds are being used in a wide range of applications around the world, many of which are vital to society and for which there are few, if any, alternatives.⁴ The main sources of environmental PFAS contamination are industrial facilities, landfill, wastewater treatment effluent, land application of biosolids and AFFF.

Widely used in firefighting, AFFF is one of the most well-known PFAS-containing products. PFAS are released into the air, and thence to groundwater and soil, each time AFFF is used in training and emergency response situations.

Thermal desorption for sampling and analysis of volatile PFAS

For many years, PFAS analysis has typically focused on C_8 species and less volatile compounds, using HPLC as the main reference technique. However, shorter chain ($<C_8$), more volatile PFAS are becoming more common and these are ideally suited to sample collection using sorbent tubes and analysis by TD and gas chromatographic methods (TD–GC/ TD–GC–MS). Also, TD–GC–MS is more suitable than HPLC for the analysis of neutral telomer species, such as fluorotelomer alcohols.

TD is a solvent- and cryogen-free sample introduction technique for GC, combining selective preconcentration of trace target compounds with fast injection into the GC column. Preconcentration occurs in two stages with one or multiple litre volumes of air first being drawn through a tube packed with sorbents selected to quantitatively retain the compounds of interest while water, carbon dioxide and other permanent gases pass through to vent. Sampled tubes are then sealed and loaded onto the thermal desorber for extraction using heat and a flow of inert (carrier) gas. Released PFAS vapours are subsequently re-focused on a small electrically-cooled sorbent trap within the TD system before fast second-stage TD injects them into the GC capillary column (Figure 1).

TD offers many advantages for monitoring organic vapours in air. First and foremost, it enables the entire PFAS sample to be concentrated and transferred into the GC column without solvent dilution. This allows ppt detection limits from as little as 1 L air sample volumes, thus simplifying and speeding up sample collection. It also reliably delivers >98% analyte recovery versus the 75% routinely expected from solvent extraction methods and can be fully automated for up to 100 or even 200 sampled sorbent tubes.

1 Tube desorption and inlet split

The sample tube is heated in a flow of carrier gas and the analytes are swept onto an electrically-cooled focusing trap, typically held between -30°C and ambient temperature.

2 Trap desorption and outlet split

The focusing trap is heated rapidly (up to 100°C/s) in a reverse flow of carrier gas, to transfer/inject analytes into the GC column in a narrow band for optimum sensitivity.

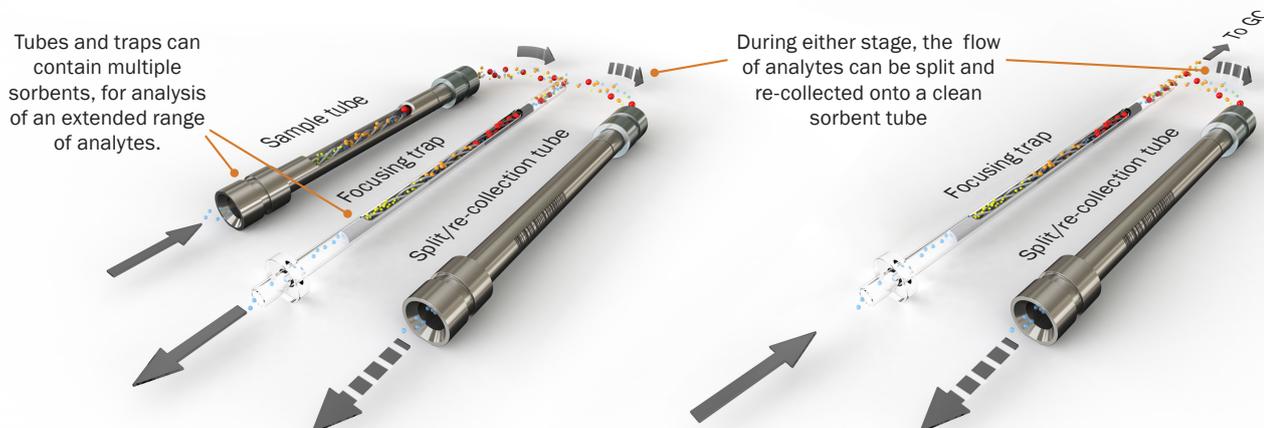


Figure 1: Operation of two-stage thermal desorption. Note that the flow of carrier gas through the focusing trap during stage 2 (trap desorption) is the reverse of that used during stage 1 (tube desorption and focusing.) This 'backflush' operation allows a series of sorbents of increasing sorbent strength to be used in the focusing trap and extends the volatility range of compounds that can be analysed at the same time.

TD sampling tubes are available in glass, stainless steel or inert-coated steel and are packed with a wide range of one, two or three sorbents. They are compatible with vapour-phase compounds ranging in volatility from propane to $n\text{-C}_{40}$ and are reusable indefinitely. TD is also used to automatically preconcentrate and analyse canister or other whole air samples if PFAS compounds such as ultra-volatile freons (e.g., CF_4) are of interest (see application note '[Monitoring trace greenhouse gases in air using cryogen-free TD-GC-MS](#)').⁵

In this study, TD-GC-MS was used first to measure the background level of PFAS in the air and then to analyse PFAS released into the air on application of AFFF.

Experimental

The experimental procedures are described briefly below. Full details can be found in the original study⁶ and its supporting material.

Sampling procedure

20 L chambers constructed of high-density polyethylene (HDPE) were designed to allow the vapours above an agitated sample of diluted AFFF to be pumped onto clean TD sorbent tubes. The AFFF was diluted by water in a 1:1 ratio.

A second identical chamber containing a sample of PFAS-free water was used as a check on PFAS background levels. The same conditions and sampling times were applied to each chamber and the volume of PFAS-free water used in the blank chamber matched the volume of diluted AFFF sample used in the other.

Conditioned sorbent tubes were connected to the sampling ports of each chamber and air was sampled at a rate of 200 mL/min for two minutes immediately after agitation of the samples. A total of 400 mL of air was sampled from each chamber.

TD:

Sorbent tubes:	Universal tubes (C3-AAXX-5266)
TD instrument:	TD100-xr™ (Markes International)
Flow path:	180°C
Tube desorption:	300°C (8 minutes) at 75 mL/min
Focusing trap:	'Air Toxics' (U-T15ATA-2S)
Trap low:	25°C
Trap desorption:	300°C (4 minutes)
Trap outlet split flow:	6 mL/min

GC:

Column:	DB-VRX (Agilent Technologies)
Column flow:	60 m x 0.25 mm x 1.4 μm
Oven:	1.2 mL/min, helium
	35°C (5 min), 10°C/min , 230°C (15 min)

Quadrupole MS:

Scan mode:	m/z 35–350
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PFAS	Molecular formula	Control/blank ($\mu\text{g}/\text{m}^3$)	Immediately after AFFF agitation ($\mu\text{g}/\text{m}^3$)
PFOA	$\text{C}_8\text{HF}_{15}\text{O}_2$	1.7	8121 ± 1262
PFHxA	$\text{C}_6\text{HF}_{11}\text{O}_2$	—	127.1 ± 38.6
4:2 FTOH	$\text{C}_6\text{H}_5\text{F}_9\text{O}$	4.8	36.3 ± 7.5
6:2 FTOH	$\text{C}_8\text{H}_5\text{F}_{13}\text{O}$	—	33.5 ± 0.4
PFDA	$\text{C}_{10}\text{HF}_{19}\text{O}_2$	0.1	27.0 ± 9.6
10:2 FTOH	$\text{C}_{12}\text{H}_5\text{F}_{21}\text{O}$	1.4	10.8 ± 1.5
7:2 sFTOH	$\text{C}_9\text{H}_5\text{F}_{15}\text{O}$	0.1	5.8 ± 1.7
PFHpA	$\text{C}_7\text{HF}_{13}\text{O}_2$	0.1	4.5 ± 1.8
PFTeDA	$\text{C}_{14}\text{HF}_{27}\text{O}_2$	—	2.8 ± 1.0
PFPeA	$\text{C}_5\text{HF}_9\text{O}_2$	—	1.5 ± 0.5
PFNA	$\text{C}_9\text{HF}_{17}\text{O}_2$	0.1	1.1 ± 0.6
PFDoA	$\text{C}_{12}\text{HF}_{23}\text{O}_2$	—	1.1 ± 0.5
PFHxDA	$\text{C}_{16}\text{HF}_{31}\text{O}_2$	—	0.8 ± 0.3
5:2 sFTOH	$\text{C}_7\text{H}_5\text{F}_{11}\text{O}$	—	0.5 ± 0.1
PFTrDA	$\text{C}_{13}\text{HF}_{25}\text{O}_2$	—	0.4 ± 0.1
PFUdA	$\text{C}_{11}\text{HF}_{21}\text{O}_2$	0.5	—
N-MeFOSA-M	$\text{C}_9\text{H}_4\text{F}_{17}\text{NO}_2\text{S}$	0.9	0.2 ± 0.1
N-EtFOSA-M	$\text{C}_{10}\text{H}_6\text{F}_{17}\text{NO}_2\text{S}$	2.9	0.2 ± 0.1
N-MeFOSE-M	$\text{C}_{11}\text{H}_8\text{F}_{17}\text{NO}_3\text{S}$	0.4	—
PFODA	$\text{C}_{18}\text{HF}_{35}\text{O}_2$	—	—
8:2 FTOH	$\text{C}_{10}\text{H}_5\text{F}_{17}\text{O}$	—	—

Table 1: Airborne PFAS compounds identified and their respective vapour concentrations. Data reproduced from J. Roth *et al.*⁶

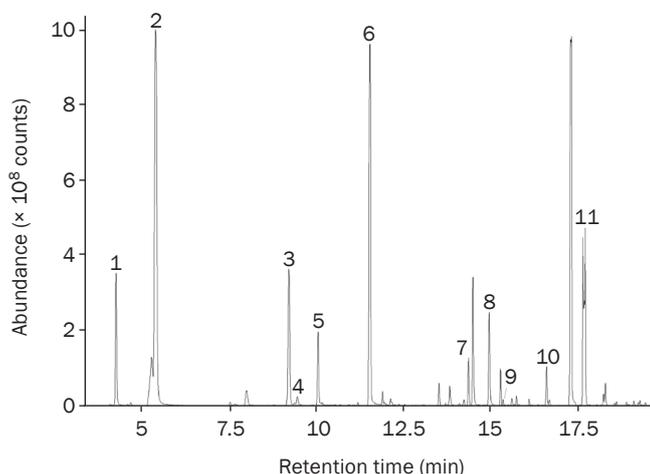


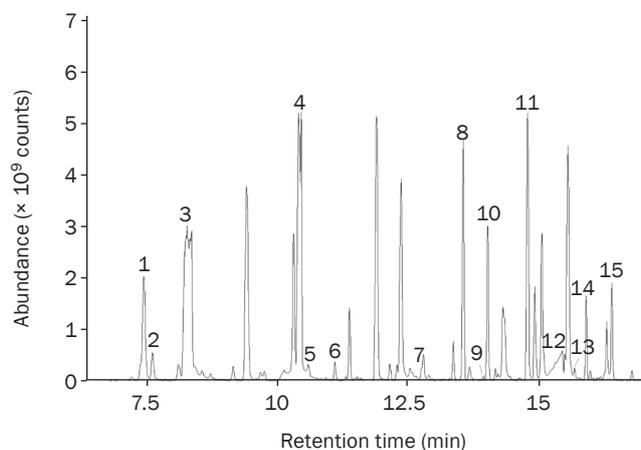
Figure 2: Extracted ion chromatogram (m/z 69) with suspected PFAS compounds numbered based on the fragmentation pattern. Table 2 details the tentative identifications based on spectral matching with the NIST database.

Peak no.	RT	Compound	Formula
1	4.11	Perfluorohexane	C_6F_{14}
2	5.33	1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluorohexane	C_6HF_{13}
3	9.43	1H,1H,2H-Perfluoro-1-octene	$\text{C}_8\text{H}_3\text{F}_{13}$
6	11.90	Perfluorohexyl iodide	$\text{C}_6\text{F}_{13}\text{I}$
10	17.30	3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodo-1-octene-1	$\text{C}_8\text{H}_2\text{F}_{13}\text{I}$
11	18.42	1H,1H,2H,2H-Perfluorooctyl iodide	$\text{C}_8\text{H}_4\text{F}_{13}\text{I}$

Table 2: Tentative identification and formulae of the suspected PFAS compounds highlighted in the extracted ion chromatogram where a spectral match was available.

Results and discussion

TD-GC-MS results from the chamber containing the diluted AFFF sample showed the detection of 15 target PFAS compounds. Five fluorotelomer alcohols (FTOHs) and 10 perfluoroalkylcarboxylic acids (PFCAs) were identified (Table 1). Identification of the 15 compounds was confirmed by comparing the spectra and retention times against those of authentic standards of each compound run on an identical analytical system.



- | | |
|-------------------------|--------------------------------|
| 1 Acetone | 9 n-Propyl acetate |
| 2 Furan | 10 2,4,4-Methyl-1-pentene |
| 3 2-Methyl-2-propanol | 11 Methyl isobutyl ketone |
| 4 Butanal | 12 Butanoic acid |
| 5 n-Hexane | 13 Toluene |
| 6 Trichloromethane | 14 1-Octene |
| 7 Benzene | 15 3,4-Dimethyltetrahydrofuran |
| 8 1-(Ethenyloxy)-butane | |

Figure 3: Total ion chromatogram for the AFFF sample with selected peaks showing other VOCs that were identified alongside the PFAS compounds.

An extracted ion chromatogram (EIC) of m/z 69 of the same data set was then examined to search for further trace PFAS compounds. The selected ion is associated with fragmentation of a terminal CF_3 group and is common in EI spectra for PFAS. 11 of the peaks seen in the EIC (Figure 2) were identified as likely fluorine-containing compounds from the mass spectra and six were tentatively identified (Table 2).

One of the objectives of the study was to determine whether PFAS and other volatile organic compounds (VOCs) produced during application of AFFF products would pass through filters within firefighters' masks, rendering them ineffective and allowing the wearer to be exposed to potentially harmful compounds during their work.

Figure 3 shows that other hazardous compounds were identified alongside the PFAS species during this study. Compounds such as benzene (peak 7), for example, are known carcinogens.

Conclusions

TD with GC-MS provides a robust and readily automated alternative procedure for monitoring many target and non-target PFAS vapours in air at trace levels. The flexibility of the sampling technique means that it can be applied to many air monitoring scenarios: indoors, outdoors and in the workplace, including monitoring of industrial gases as well as testing emissions from PFAS-containing materials. This is backed up by a range of national and international standards (see application note '[National and international standard methods relating to speciated monitoring of vapour-phase organic chemicals in air](#)').⁷

The solvent-free workflow described optimises sensitivity, simplifies sampling and reduces the risk of analytical error. It also has the added benefits of reducing costs and providing a 'greener' option.

The ability to collect and analyse samples over a wide volatility range is also valuable for PFAS monitoring, given the sheer numbers and range of compounds of interest.

Combining TD with the best modern GC-MS technology also facilitates detection of unknown, non-targeted compounds (PFAS and other) as well as target PFAS species.

References

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7. [Markes International Application Note 003, National and international standard methods relating to speciated monitoring of vapour-phase organic chemicals in air, 2017.](#)

Trademarks

TD100-xr™ is a trademark of Markes International.

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