

PFAS in Air: Sampling and analytical techniques for the identification of persistent contaminants and new method updates

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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 They are typically defined as aliphatic compounds with one or more carbon atoms in which all the hydrogen atoms have been replaced by fluorine.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

The primary source of PFAS is production of the chemicals themselves and from there they go on to be used in processes for chemical and product manufacturing, they are found within industrial products such as lubricants and fire fighting foams and are also key components in many consumer products. The list of industries that use them is extensive – anything which is stain or heat resistant is very likely to contain PFAS. This includes food packaging, non-stick cookware, paints, waterproof clothing and even some shampoos.

Thermal desorption for sampling and analysis of volatile PFAS

For many years, PFAS analysis has typically focused on C8 species and less volatile compounds, using HPLC as the main reference technique. However, shorter chain (<C8), more volatile PFAS are becoming more common and these are ideally suited to sample collection using sorbent tubes and analysis by thermal desorption and gas chromatographic methods (TD-GC/ TD-GC-MS). 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.

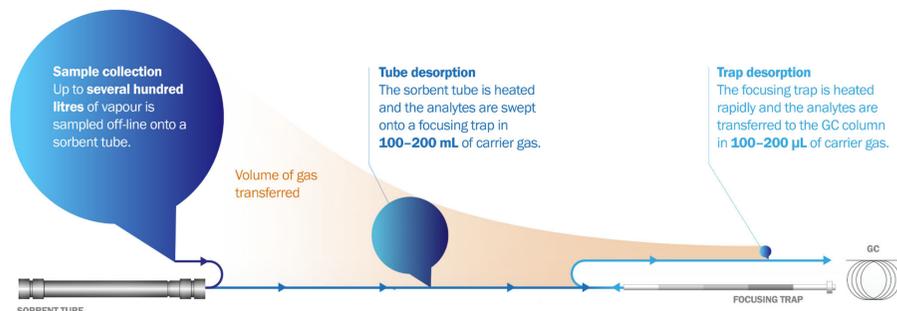


Figure 1: Preconcentration using sorbent tubes and Thermal Desorption

Preconcentration occurs in two stages a sample of air is first 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

Sampling aqueous film-forming foam (AFFF)

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

Results and discussion

| 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 | $\text{C}_8\text{H}_5\text{F}_9\text{O}$ | 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 | $\text{C}_8\text{H}_5\text{F}_{15}\text{O}$ | 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 | $\text{C}_9\text{HF}_{17}\text{O}_2$ | – | 1.5 ± 0.5 |
| PFNA | $\text{C}_8\text{HF}_{17}\text{O}_2$ | 0.1 | 1.1 ± 0.6 |
| PFDoA | $\text{C}_{12}\text{HF}_{23}\text{O}_2$ | – | 1.1 ± 0.5 |
| PFHxDA | $\text{C}_{10}\text{HF}_{19}\text{O}_2$ | – | 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-EiFOSA-M | $\text{C}_{10}\text{H}_6\text{F}_{17}\text{NO}_2\text{S}$ | 2.9 | 0.2 ± 0.1 |
| N-MeFOSE-M | $\text{C}_{11}\text{H}_8\text{F}_{17}\text{NO}_2\text{S}$ | 0.4 | – |
| PFODA | $\text{C}_{18}\text{HF}_{35}\text{O}_2$ | – | – |
| 8:2 FTOH | $\text{C}_{10}\text{H}_5\text{F}_{17}\text{O}$ | – | – |

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.

Table 1: Airborne PFAS compounds identified and their respective vapour concentrations. Data reproduced from J. Roth *et al.*⁵

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 3) were identified as likely fluorine-containing compounds from the mass spectra and six were tentatively identified (Table 2).

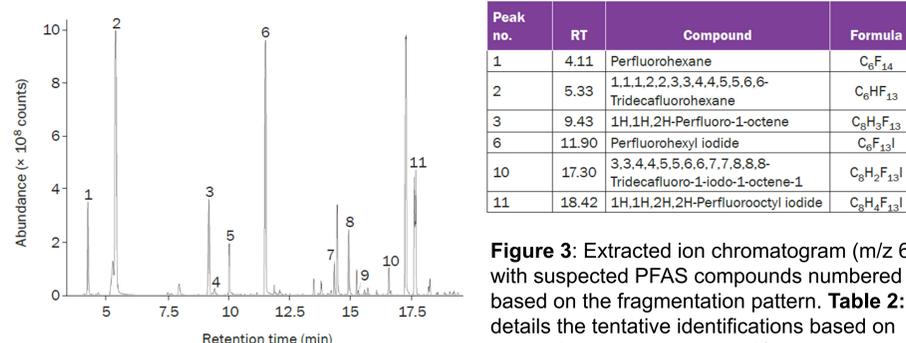


Figure 3: Extracted ion chromatogram (m/z 69) with suspected PFAS compounds numbered based on the fragmentation pattern. Table 2: details the tentative identifications based on spectral matching with the NIST database.

| 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 | $\text{C}_6\text{H}_2\text{F}_{13}$ |
| 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 | $\text{C}_8\text{H}_4\text{F}_{13}\text{I}$ |

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.

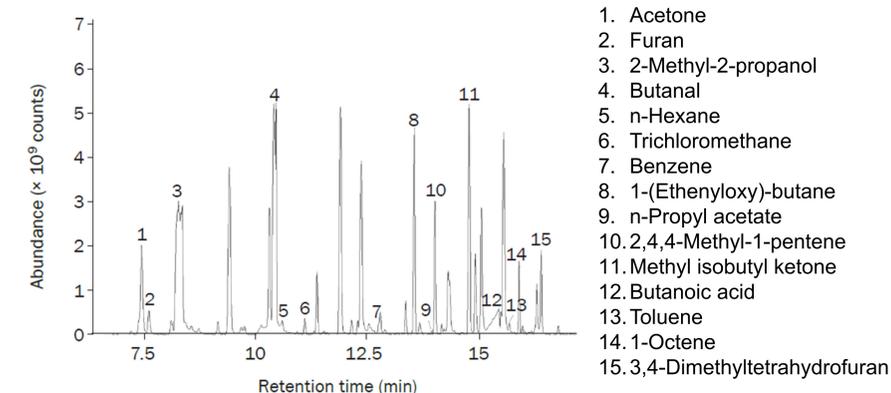


Figure 4: Total ion chromatogram for the AFFF sample with selected peaks showing other VOCs that were identified alongside the PFAS compounds.

Figure 4 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. 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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