

MONITORING GAS PHASE POLY AND PER FLUOROALKYL SUBSTANCES IN THE ENVIRONMENT AND FROM SOURCES

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INTRODUCTION

Poly And Per Fluoroalkyl Substances (PFAS) are everywhere. Whilst there has been a lot of focus internationally on PFAS in water, researchers and governments globally are turning their attention to volatile gas phase species in air.

Gaseous PFAS have many sources including PFAS production facilities, aqueous film forming foams (AFFF), soil gas, materials and remediation of PFAS impacted sites/materials. PFAS in the air can spread easily, transform into more toxic species¹ and impact other matrices, such as water and soil, through deposition. Understanding and monitoring PFAS in air is an important part of controlling the spread of PFAS and reducing exposure to humans.

Thermal desorption coupled to gas chromatography and mass spectrometry (TD-GC-MS) is commonly applied to monitoring of hazardous organic compounds in ambient air. The technique is being utilised successfully by environmental agencies and researchers globally to monitor gaseous PFAS².

In this study we will show how TD-GC-MS can offer a robust approach to target and non-target screening of PFAS in a variety of samples.

EXPERIMENTAL

As a class, PFAS number over 14,000 compounds³. Within that class there is a huge variety of chemistries and volatilities. Research related to monitoring PFAS in air can currently be split into two areas:

1. PFAS related to destruction/breakdown of larger PFAS compounds, typically referred to as Volatile fluorinated compounds (VFCs). US EPA Other Test Method 50 (OTM-50) was recently released to aid in monitoring PFAS destruction.
2. Volatile PFAS which can be found in the gas phase where these chemicals are being used or have been used on a large scale commercially.

These two separate areas of research also require two different approaches to sampling and analysis – both based around TD-GC-MS.

Volatile fluorinated compounds (VFCs)

Some PFAS removal technologies breakdown compounds into smaller components which are captured or neutralized e.g., hydrogen fluoride, carbon dioxide and water.

During this process products of incomplete destruction (PIDs) can easily be created. These are VFCs, the smallest being CF₄ which is incredibly volatile. Sampling and analysis must be carried out using silicon ceramic lined canisters which capture a whole air sample.

Analysis is carried out using the UNITY-CIA Advantage-xr coupled to an Agilent 8890 GC and 5977 with Extractor EI source.

Gas phase PFAS

There are many possible sources of PFAS which will remain in the gas phase. If we exclude VFCs, the most common species detected are fluorotelomer alcohols (FTOHs), fluorotelomer carboxylic acids (FTCAs) and perfluorooctane sulfonamides (FOSAs) regardless of the source. These key species can all be collected using a single sorbent tube.

Analysis is usually carried out using a TD100-xr coupled to a GC-Triple quadrupole MS.



Figure 1: Silicon ceramic lined canister for VFC analysis



Figure 2: ACTI-VOC™ Plus air sampling pump for gas phase PFAS analysis

RESULTS AND DISCUSSION – VFCs

Exceptional detection limits, reproducibility and linearity data were achieved for all species tested (see table 1), including the the most volatile, tetrafluoromethane (CF₄), which is most likely to be found when PFAS destruction is incomplete. Due to its high volatility, 20 mL samples were taken instead of 250 mL for the other species, but despite this smaller sample size, the performance data for CF₄ are still excellent.

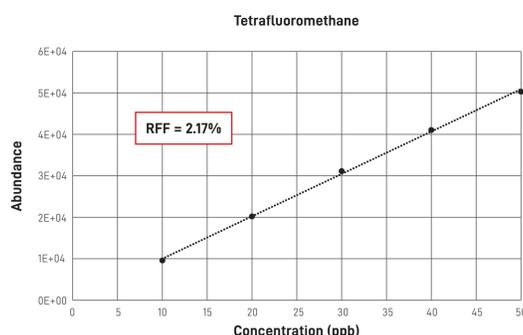


Figure 3 (above): Calibration for CF₄ performed by taking 20 mL from 5 individual canisters showing excellent linearity.

Compound	R2	RRF	Repeatability (5ppb) n = 10	MDL (0.5ppb)
Tetrafluoromethane	0.9990	2.17%	2.03%	30ppt
Compound	R2	RRF	Repeatability (5ppb) n = 10	MDL (0.25 ppb)
Hexafluoroethane	0.9999	1.86%	0.48%	6ppt
Chlorotrifluoromethane	0.9977	2.52%	0.44%	8ppt
Trifluoromethane	0.9977	5.12%	1.13%	10ppt
Difluoromethane	0.9993	3.11%	0.64%	11ppt
Octafluoropropane	0.9996	7.64%	0.38%	14ppt
1,1,1-Trifluoroethane	0.9988	5.33%	0.76%	13ppt
Octafluorocyclobutane	0.9998	7.14%	0.26%	11ppt
Perfluorobutane	0.9995	4.00%	0.29%	9ppt
Dodecafluoropentane	0.9989	7.65%	0.43%	9ppt
Average	0.9990	4.65%	0.60%	12ppt

Table 1 (left): Performance for a range of VFCs expected to be found if PFAS is not destroyed fully, with exceptional method detection limits, linearity and reproducibility.

RESULTS AND DISCUSSION – GAS PHASE PFAS

Gas phase PFAS method

PFAS are present in the air and dust in indoor environments⁴, the toxicology and bioaccumulation of these compounds means that understanding their presence and concentration in indoor air is important.

Using the Markes' TD100-xr™ high through-put automated thermal desorption (TD) instrument to preconcentrate the sample and maximise sensitivity, coupled to a gas chromatograph (GC) and a triple quadrupole mass spectrometer (MS/MS), enables measurement of PFAS in indoor air at a detection limit as low as 1 pg for Me-FOSA.

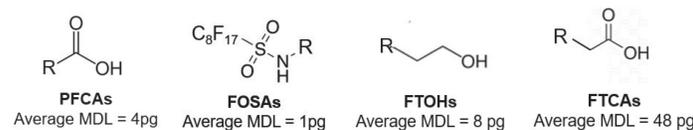


Figure 4: Average method detection limit for each of the compound classes. When applied to a 20L sample this made the average MDL ~780 pg/m³.

Indoor air samples

Samples of 20L were collected from four separate workplace environments and then transported to the lab in brass storage caps. A toluene-D8 internal standard (IS) was automatically added to each sample tube before analysis by the TD100-xr to ensure high data quality was maintained across all samples.

When comparing the four workplace environments (Figure 5), the location with the highest overall PFAS levels for the 19 species measured was the corridor (156.95 ng/m³) and the lowest was the storeroom containing painted materials (38.35 ng/m³). By comparison, ambient air outside the site contained on average 7.2 ng/m³.

Detected concentrations of target compounds

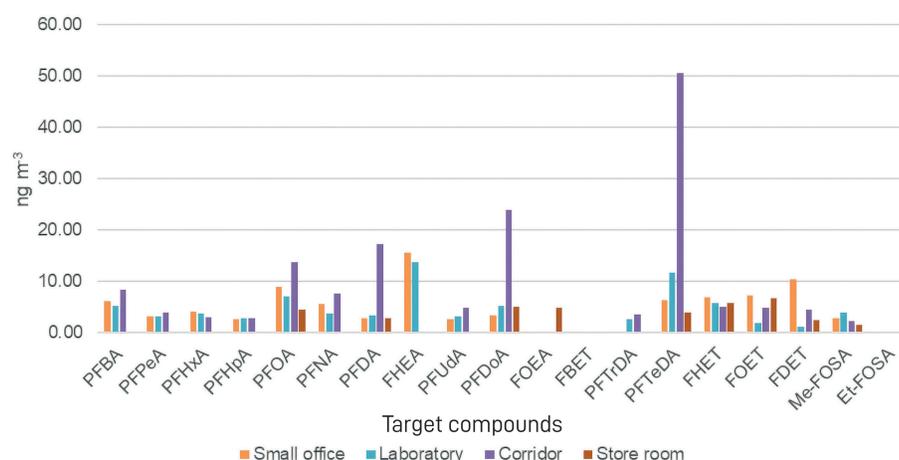


Figure 5: Total concentration of each of the target compounds detected in each individual workspace. The concentration of PFTeDA quantified in the air of the corridor (50 ng/m³) contributes greatly to the total concentration detected in that environment.

CONCLUSIONS

Two runs enable the analysis of the ultra-volatile CF₄ and the other VFCs/OTM-50 compounds without the need to change the hardware or consumables. It should be noted that 100% RH has been assessed in other studies of similar compounds without issue thanks to the Kori-xr module selectively removing water. The highlights for VFC analysis include the excellent:

- Method detection limits of 30ppt for CF₄ and <14ppt all other VFCs
- Reproducibility of <2.04% RSD 5ppb
- Linearity of >0.9976 R².

For gas phase PFAS, the TD-GC-MS/MS method developed for the 19 compounds targeted in this study delivered an average detection limit of 16 pg. The technique is stable and sensitive enough to analyse the more volatile neutral PFAS species and volatile PFCAs in a single run. The highlights for gas phase PFAS analysis include impressive:

- Method detection limits of <65pg (as low as 1 pg for Me-FOSA)
- Reproducibility of <5.76% RSD
- Linearity of >0.9936 R².

REFERENCES

- [1] <https://pubs.acs.org/doi/abs/10.1021/acs.estlett.4c00364>
- [2] https://www.epa.gov/system/files/documents/2024-01/otm-50-release-1_0.pdf
- [3] <https://comptox.epa.gov/dashboard/chemical-lists/PFASSTRUCT>
- [4] <https://doi.org/10.1021/acs.estlett.1c00481>



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