

Environmental

High-throughput analysis of both neutral and ionic PFAS in ambient air using thermal desorption coupled to gas chromatography – mass spectrometry (TD-GC-MS/MS)

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Goal

The aim of this application note is to demonstrate a high-throughput method for the simultaneous analysis of neutral (FTOH, FOSA) and ionic (PFCA, FTCA) per- and polyfluoroalkyl substances (PFAS) in air using thermal desorption coupled to gas chromatography mass spectrometry.

Introduction

Per- and polyfluoroalkyl substances (PFAS) contain one or more alkyl radicals with all the hydrogens replaced by fluorine atoms. Traditionally, two groups of PFAS have been of the most concern and subject for control and monitoring. The first group includes ionic (or acidic) PFAS—the perfluorocarboxylic acids (perfluorooctanoic acid (PFOA) being the most infamous one) and perfluoroalkylsulfonates (perfluorooctanesulfonic acid (PFOS), the most infamous), where LC-MS-MS is the most commonly chosen analytical technique. The second group includes neutral (or volatile) PFAS—the fluorotelomer alcohols¹ (FTOHs) and *N*-substituted fluoroalkylsulfonamides (FOSAs). For this group, GC-MS is the analytical method of choice. Detecting airborne concentrations of both ionic and neutral PFAS is critical for measuring atmospheric emission distribution and potential human exposure. Unlike water and soil matrices, there are fewer factors that slow the dispersal of PFAS after release into ambient air. These compounds can travel thousands of kilometers from the original point of emission, which could be chemical manufacturing sites, thermal waste treatment plants, or commercial applications of PFAS².

Thermal desorption (TD) represents a suitable technique for analysis of organic contaminants in air, including ultra-volatile species. Stainless-steel tubes packed with special sorbents are used as sampling media to preconcentrate samples from hundreds of liters of air. This inherent preconcentration effect with no requirement for any dilution prior to analysis means that single-digit pg/m³ concentrations can be measured from <500 L of ambient air when combined with triple quadrupole GC-MS/MS.

In this study, a single, fast, and high-throughput method for the analysis of 19 target PFAS across four functional groups including ionic perfluoroalkylcarboxylic acids (PFCAs) and fluorotelomer carboxylic acids (FTCAs) and neutral FTOHs and FOSAs is demonstrated for ambient air, using thermal desorption coupled to gas chromatography mass spectrometry.

Experimental

In the experiments described here, a Markes International™ TD100-xr™ Advanced thermal desorber with electronic flow control and equipped with the Internal Standard Addition / Dry Purge (ISDP) accessory for automated addition of gaseous internal standard was used. This sample introduction technique was coupled to a Thermo Scientific™ TRACE™ 1610 GC connected to a Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer, equipped with an Advanced Electron Ionization (AEI) ion source. Chromatographic separation was achieved on a Thermo Scientific™ TraceGOLD™ TG-200MS capillary column (30 m × 0.25 mm × 1.0 μm, P/N 26084-2960). The trifluoropropylmethyl polysiloxane stationary phase provides exceptional inertness for improved thermal stability, low column bleed, and reliable run-to-run and batch-to-batch reproducibility. The Markes International TD100-xr thermal desorption unit offers sequential and unattended analysis of up to 100 samples, eliminating the cost of liquid cryogen through the use of electrical trap cooling. Markes' systems also allow samples to be split and re-collected onto a clean sorbent tube at the sample desorption and/or trap desorption stages, providing "insurance" against failed runs and simplifying demonstration of complete analyte transfer and absence of analytical bias. TD100-xr and GC-MS/MS experimental conditions optimized in this study as well as a complete list of the target compounds are detailed in Table 1 and Table 2 (page 6), respectively.

Table 1. TD100-xr Advanced and GC-MS/MS experimental conditions for the analysis of PFAS in air

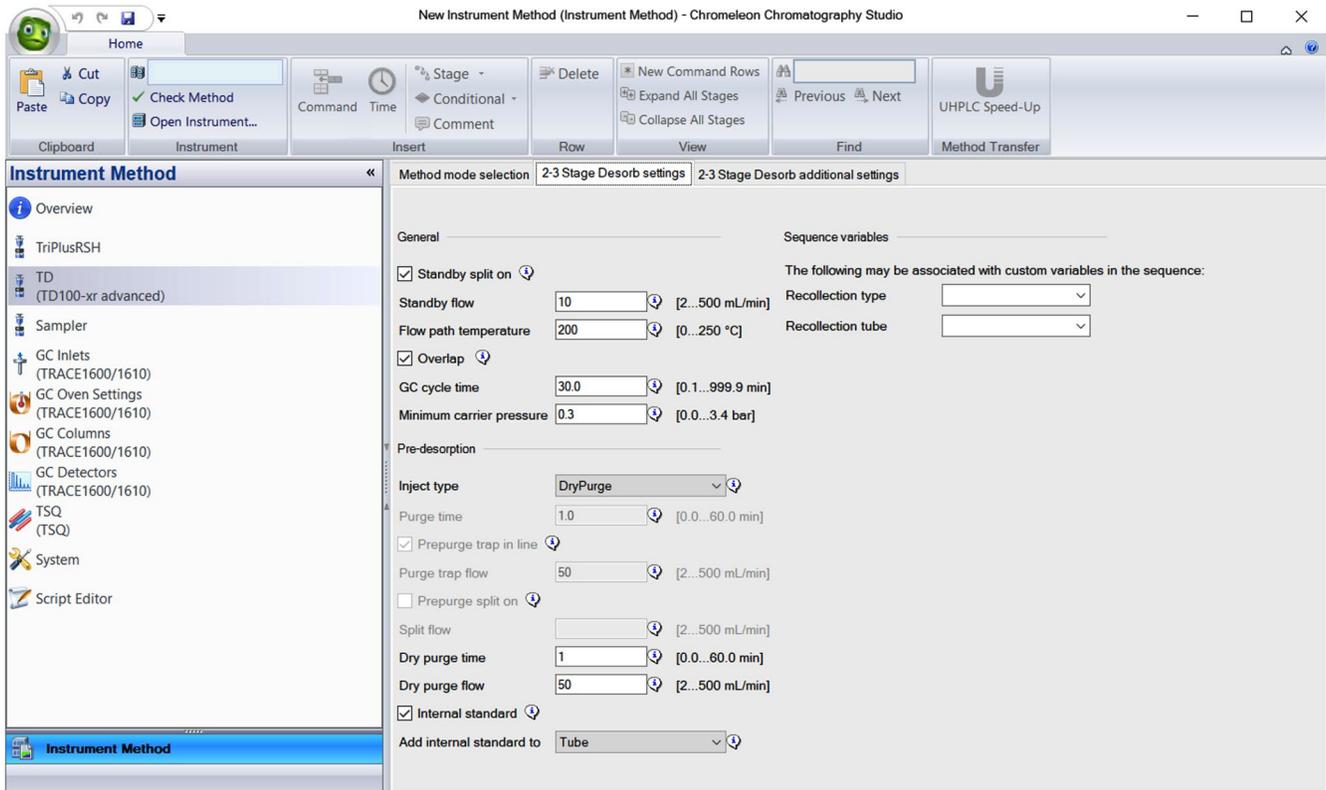
Markes International TD100-xr Advanced parameters	
Tube type	PFAS Extended volume tubes (P/N 76473-0942)
Flow path temperature (°C)	200
Automatic dry purge	1 min at 50 mL/min
Tube desorption	300 °C for 10 min at 50 mL/min
Trap purge	1 min at 50 mL/min
Focusing trap	PFAS focusing trap (P/N 76473-0940)
Focusing trap low temperature (°C)	-30
Elevated trap purge (°C)	25
Focusing trap high temperature (°C)	300 (4 min)
Trap heat rate	Max
Outlet split	6:1
TRACE 1610 GC parameters	
Oven temperature program	
Temperature (°C)	35
Hold time (min)	2
Rate (°C/min)	15
Temperature 2 (°C)	280
Hold time (min)	5
GC run time (min)	23.33
Carrier gas	He
Carrier flow (mL/min)	1.2
Column	
TraceGOLD TG-200MS	30 m, 0.25 mm, 1.0 μm (P/N 26084-2960)
TSQ 9610 mass spectrometer parameters	
Transfer line temperature (°C)	280
Ion source type and temperature (°C)	AEI, 300
Ionization type	EI
Emission current (μA)	50
Acquisition mode	timed-SRM
Tuning parameters	AEI Smart Tune
Collision gas and pressure (psi)	Argon at 70

Data acquisition, processing, and reporting

Data were acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. Integrated TD100-xr instrument control ensures full automation of the analytical workflow from tube desorption to data acquisition, combined with an intuitive user

interface for data analysis, processing, customizable reporting, and storage in compliance with the Federal Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11). Figure 1 shows the Chromeleon CDS method editor wizard for the TD100-xr thermal desorber.

A



B

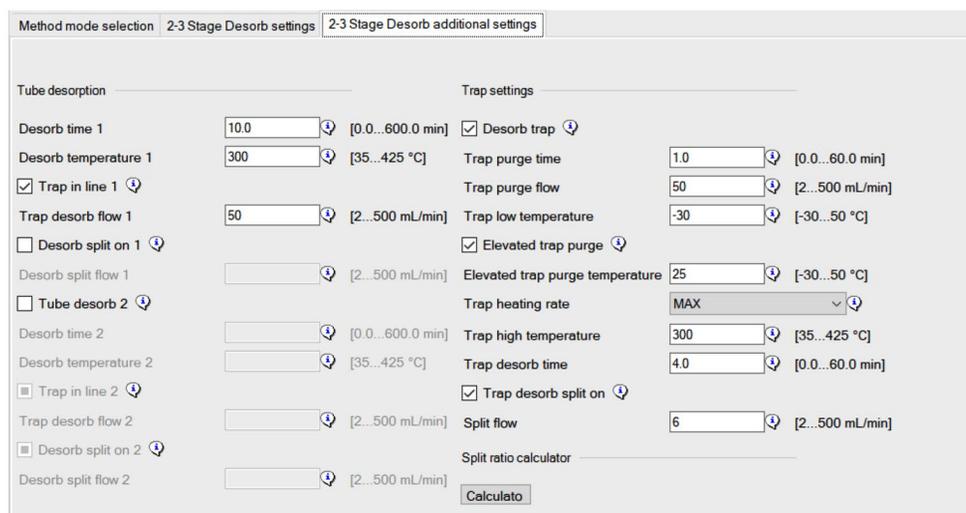


Figure 1. Chromeleon CDS browser showing the method editor wizard for the TD100-xr thermal desorption unit: (A) 2-3 Stage Desorb settings and (B) additional settings.

Standard and sample preparation

Standard preparation

Individual component standards were purchased from Wellington Laboratories Inc, Canada, at a concentration of 50 ng/μL, with exception for 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 obtain the working standards used to assess the method performance. A calibration curve was prepared by using a Markes International™ Calibration Solution Loading Rig (CSLR™) by spiking 1 μL of each standard onto the sorbent tubes in a flow of nitrogen at 100 mL/min and purged for 60 minutes to remove methanol. A Markes International™ 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.

Sample preparation

Ambient air from three sites at an industrial park were collected onto a sorbent tube at a flow rate of 100 mL/min using a Markes International™ 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 to 500 mL/min. Sample flow rates can be optimized 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. Toluene-d8 gaseous internal standard at 100 ppb in nitrogen was automatically added by using the ISDP accessory of the TD100-xr and used to monitor the process to ensure sample integrity. The IS (2 mL) was added to the sample tubes by using a 1 mL loop pressurized to 15 psi.

Results and discussion

Background assessment

One of the main challenges of PFAS analysis lies in the low detection limits that must be achieved as these compounds occur at trace concentrations in air. Dedicated PFAS tubes packed with sorbent material (P/N 76473-0942) have been designed to allow effective sample pre-concentration to detect such low levels of PFAS. It is therefore vital that sorbent tubes used for sampling are free from contamination. It is also important to highlight that artifacts from the sorbent materials may occur at very low levels upon heating, therefore the system background and possible artifacts need to be assessed before embarking on sampling projects. The artifacts contribution was evaluated by desorbing the dedicated PFAS focusing trap of the TD100-xr (P/N 76473-0940) under the optimized method conditions reported in Table 1. The instrument background was assessed by desorbing an empty stainless-steel sorbent tube applying the aforementioned optimized conditions. The method blank was then evaluated by desorbing at least n=7 PFAS extended range sorbent tubes and comparing the blank chromatograms with the ones obtained during the method detection limit (MDL) assessment.

No background was detected for the target species in the trap and valve blank. In the system blank, only perfluorotetradecanoic acid (PFTeDA) was detected at 9 pg versus the 5 pg spiked level used to assess the MDL. For context, during the sampling study, the mass of PFTeDA collected (when present in the sample) was five to 10 times higher. 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 tubes for field sampling that do not show background for target compounds. The calculated method detection limit (MDL) for these compounds reflects the level at which they were found in the method blank.

Chromatography

PFAS are a group of synthetic compounds with different chemical and physical properties, therefore the proper column choice is essential to get adequate resolution and sensitivity for both qualitative and quantitative analysis. The polar phase of the TraceGOLD TG-200MS column provided adequate chromatographic separation of the target compounds combined with Gaussian peak shapes as demonstrated in Figure 2.

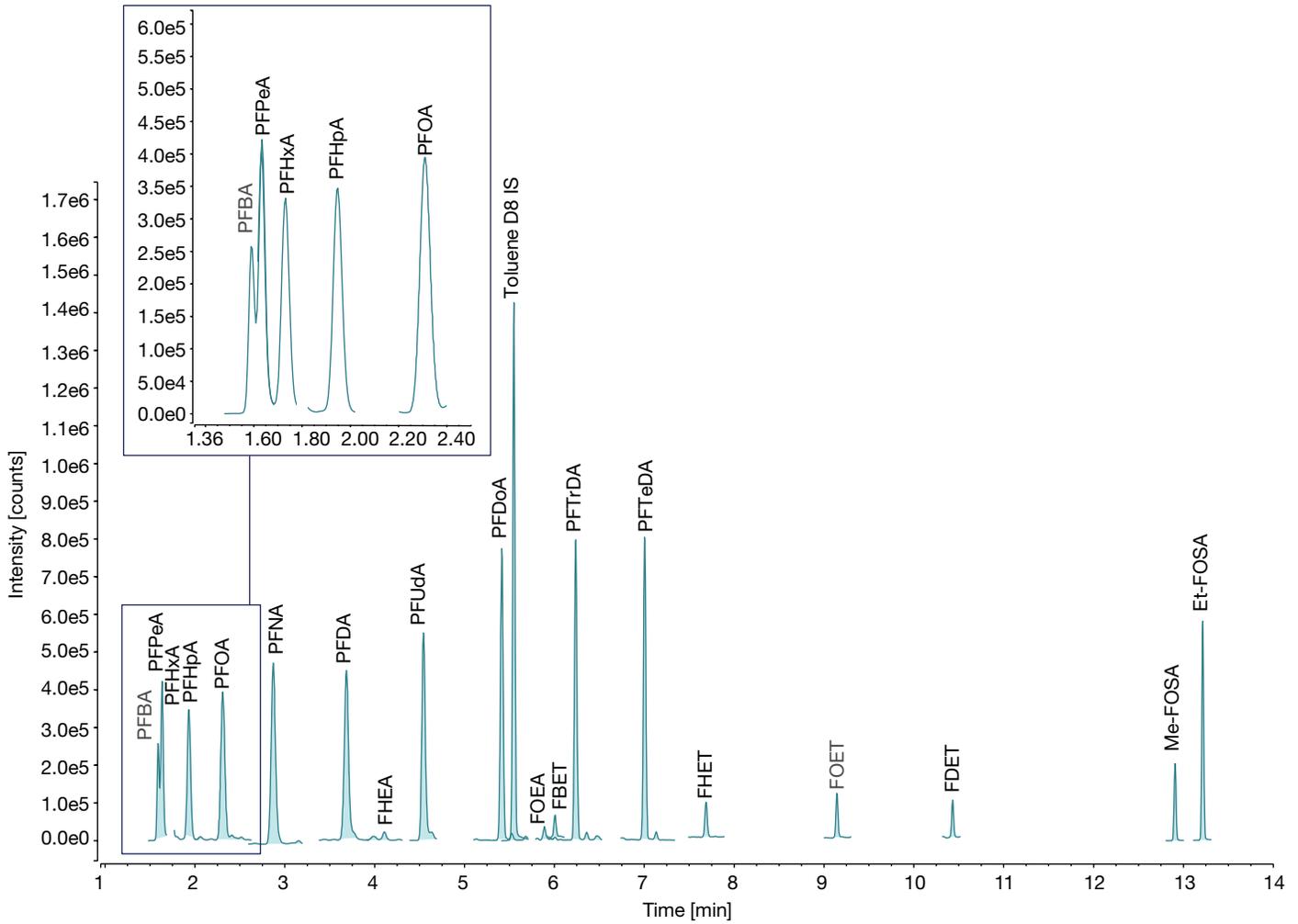


Figure 2. Mixed PFAS standard at 500 pg on-tube. The inset shows a close-up view of the chromatogram for the first five compounds, which are perfluoroalkylcarboxylic acids (PFCAs). Baseline separation was not possible for PFBA and PFPeA at the oven start temperature of 35 °C.

Linearity

Calibration curves were prepared by spiking 1 μL of the stock solution on the sorbent tubes. Due to the concentrations of the stock standards, different compound classes were calibrated over different ranges. All compounds showed a linear trend within the used calibration ranges with the coefficient of determination (R^2) > 0.990 as reported in Table 2.

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 Polar Regions, typically report PFAS concentrations of <1 and up to 200 pg/m^3 .⁴ In urban environments, due to the presence of multiple PFAS sources, typical concentrations can be much higher (up to 800 pg/m^3), depending on the compound.⁴

The MDL 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 U.S. EPA guidance.⁵ As described earlier, this process was designed to account for any

background contaminants introduced during sample handling, preparation, and analysis. The average limit of detection was 9 pg on tube corresponding to 31.2 pg/m^3 when considering the sampled air volume as reported in Table 2. These values match the lower concentration range for both background and urban monitoring sites.

Analysis of ambient air samples

Ambient air from three sites (Sites 1, 2, and 3) within the industrial park sampling site were collected at a volume of 300 L. When sampling such a large air volume, a significant amount of water vapor from the air is trapped on the sorbent tubes together with the analytes. Moisture must be removed prior to injecting the samples into the gas chromatograph as this can negatively affect the column performance, reducing reproducibility of the analysis. The TD100-xr offers an integrated water management system that combines a dry purge of the tubes before desorption with an elevated temperature trap purge. This allows for the removal of most of the water vapor from the sorbent tubes and the focusing trap prior to injection while retaining 100% of the target analytes. After sampling, the tubes were stored until analysis.

Table 2. List of target compounds as well as retention times (RT), quantitation ions, coefficient of determination (R^2), peak area %RSD ($n=7$) and calculated MDLs.

Compound	RT (min)	Quantitation ion (m/z)	Calibration range ($\text{pg}/\mu\text{L}$)	R^2	Peak area %RSD ($n=7$)	Calculated MDL (pg)	Calculated MDL (pg/m^3)
Perfluoroalkyl carboxylic acids (PFCAs)							
Perfluoro- <i>n</i> -butanoic acid (PFBA)	1.59	131/69	10-2000	0.9985	4.52	5	10
Perfluoro- <i>n</i> -pentanoic acid (PFPeA)	1.64	131/69	10-2000	0.9966	3.8	2	4
Perfluoro- <i>n</i> -hexanoic acid (PFHxA)	1.73	131/69	10-2000	0.9970	3.25	23	46
Perfluoro- <i>n</i> -heptanoic acid (PFHpA)	1.93	131/69	10-2000	0.9981	2.42	3	6
Perfluoro- <i>n</i> -octanoic acid (PFOA)	2.31	131/69	10-2000	0.9986	2	2	4
Perfluoro- <i>n</i> -nonanoic acid (PFNA)	2.9	131/69	10-2000	0.9983	1.48	46	95
Perfluoro- <i>n</i> -decanoic acid (PFDA)	3.67	131/69	10-2000	0.9978	2.48	27	54
Perfluoro- <i>n</i> -undecanoic acid (PFUDA)	4.52	131/69	10-2000	0.9974	3.67	4	8
Perfluoro- <i>n</i> -dodecanoic acid (PFDoA)	5.39	131/69	10-2000	0.9975	2.71	21	42
Perfluoro- <i>n</i> -tridecanoic acid (PFTTrDA)	6.22	131/69	10-2000	0.9974	3	3	6
Perfluoro- <i>n</i> -tetradecanoic acid (PFTeDA)	6.98	131/69	10-2000	0.9975	3.01	2	4
Fluorotelomer carboxylic acids (FTCAs)							
2-Perfluorohexyl ethanoic acid (6:2) (FHEA)	3.97	131/69	100-5000	0.9953	5.75	64	128
2-Perfluorooctyl ethanoic acid (8:2) (FOEA)	5.9	131/69	100-5000	0.9983	2.65	62	104
Fluorotelomer alcohols (FTOHs)							
2-Perfluorobutyl ethanol (4:2) (FBET)	6.01	95/69	10-5000	0.9951	4.1	13	26
2-Perfluorohexyl ethanol (6:2) (FHET)	7.67	95/69	10-5000	0.9971	2.61	18	36
2-Perfluorooctyl ethanol (8:2) (FOET)	9.12	95/69	10-5000	0.9963	3.99	4	8
2-Perfluorodecyl ethanol (10:2) (FDET)	10.41	95/69	10-5000	0.9937	4.08	6	12
Perfluorooctanesulfonamides (FOSAs)							
<i>N</i> -Methylperfluoro-1-octanesulfonamide Me-(FOSA)	12.87	94/30	10-5000	0.9953	0.83	1	2
<i>N</i> -Ethylperfluoro-1-octanesulfonamide Et-(FOSA)	13.18	108/80	10-5000	0.9953	5.29	1	2

Each sample tube was analyzed twice using the automated re-collection feature of the TD100-xr, offering the possibility of analyzing the samples for both targeted analysis by using an optimized SRM method and untargeted screening of other volatile compounds by using full-scan acquisition (m/z 35–650). Most of the compounds monitored were found at each site, with the exception of PFHpA, PFUdA, FBET, PFTrDA, FDET, and EtFOSA.

The compounds with the highest concentrations were carboxylic acids (PFBA, PFHxA, and PFOA) as reported in the Appendix. In many studies, PFOA is often the polyfluorinated carboxylic acid with the highest concentration, so it is interesting that PFBA was detected at a higher level here. An example of extracted ion chromatogram (XIC) for air samples in site 1 (A) as well as SRM transitions for some of the detected compounds (B) are shown in Figure 3.

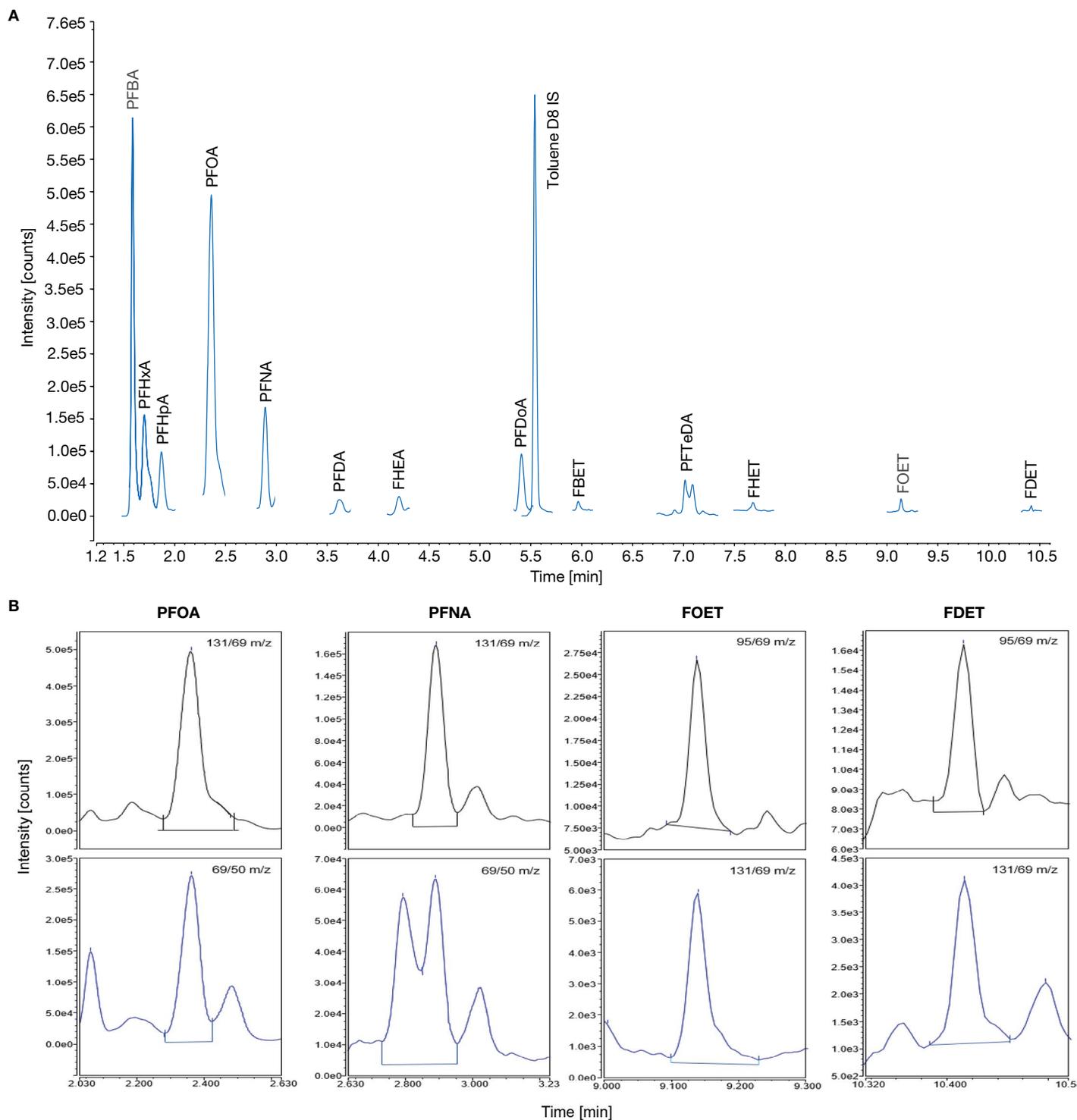


Figure 3. XIC ambient air sampled in a light industrial location (A) as well as SRM transitions for some of the detected compounds (B). Compounds were identified from each of our target classes (PFCAs, FTOHs, FTCAs, FOSAs) with PFCAs being the most abundant.

Conclusions

The results obtained in these experiments demonstrate that the TD100-xr Advanced coupled to the TRACE 1610 GC and TSQ 9610 mass spectrometer equipped with the AEI ion source delivers reliable analytical performance for analysis of PFAS in air, allowing for the analysis of the volatile neutral PFAS species and volatile ionic PFCAs in a single run.

- Adequate chromatographic separation was achieved for the investigated compounds in <14 minutes thanks to the high selectivity of the TraceGOLD TG-200MS column, allowing for high sample throughput analysis.
- Accurate quantitative performance for the investigated compounds was obtained with coefficient of determination of $R^2 > 0.990$ over a concentration range of 10 to 5,000 pg/ μ L (compound dependently).
- Low detection limits were achieved with average MDL of 31.2 pg/m³ calculated considering a sample volume of 300 L.
- Most of the investigated compounds were found in the analyzed air samples with carboxylic acids (PFBA, PFHxA, and PFOA) being present with the highest concentrations.
- Targeted analysis and untargeted screening of the same sample are possible thanks to the sample re-collection capability of the Markes' TD systems.

References

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Appendix

Table A1. Calculated amounts for the target PFAS compounds found at each site in the light industrial area

Compound	RT (min)	Amount (pg/m ³)		
		Site 1	Site 2	Site 3
Perfluoroalkyl carboxylic acids (PFCAs)				
Perfluoro- <i>n</i> -butanoic acid (PFBA)	1.59	2903	2097	4790
Perfluoro- <i>n</i> -pentanoic acid (PFPeA)	1.64	ND	ND	ND
Perfluoro- <i>n</i> -hexanoic acid (PFHxA)	1.73	850	750	1000
Perfluoro- <i>n</i> -heptanoic acid (PFHpA)	1.93	ND	403	477
Perfluoro- <i>n</i> -octanoic acid (PFOA)	2.31	1267	1433	3090
Perfluoro- <i>n</i> -nonanoic acid (PFNA)	2.9	*60	217	520
Perfluoro- <i>n</i> -decanoic acid (PFDA)	3.67	147	*17	103
Perfluoro- <i>n</i> -undecanoic acid (PFUdA)	4.52	23	ND	ND
Perfluoro- <i>n</i> -dodecanoic acid (PFDoA)	5.39	333	*33	287
Perfluoro- <i>n</i> -tridecanoic acid (PFTrDA)	6.22	27	ND	ND
Perfluoro- <i>n</i> -tetradecanoic acid (PFTeDA)	6.98	170	ND	ND
Fluorotelomer carboxylic acids (FTCAs)				
2-Perfluorohexyl ethanoic acid (6:2) (FHEA)	3.97	ND	ND	ND
2-Perfluorooctyl ethanoic acid (8:2) (FOEA)	5.9	ND	ND	ND
Fluorotelomer alcohols (FTOHs)				
2-Perfluorobutyl ethanol (4:2) (FBET)	6.01	ND	ND	ND
2-Perfluorohexyl ethanol (6:2) (FHET)	7.67	ND	ND	ND
2-Perfluorooctyl ethanol (8:2) (FOET)	9.12	ND	ND	*3
2-Perfluorodecyl ethanol (10:2) (FDET)	10.41	137	ND	ND
Perfluorooctanesulfonamides (FOSAs)				
<i>N</i> -Methylperfluoro-1-octanesulfonamide Me-(FOSA)	12.87	130	107	113
<i>N</i> -Ethylperfluoro-1-octanesulfonamide Et-(FOSA)	13.18	180	ND	ND

*Compounds detected below the MDL.

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