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Volatile PFAS in Air

Developing methods for targeted analysis and discovery of non-target volatile PFAS

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Why are we talking about PFAS?

- PFAS are persistent in the environment
  - Classed as Persistent Organic Pollutants (POPs)
  - Hyper mobile within the environment
- There is evidence that exposure to PFAS may lead to adverse human health effects, such as:
  - low infant birth weights
  - effects on the immune system, suppressing the ability to make antibodies
  - cancer (for PFOA), and thyroid hormone disruption (for PFOS)
- PFOS and PFOA
  - Most extensively produced
  - Listed within the Stockholm convention
- We'll show an optimised sampling and analysis TD-GCMS system for routine, automated analysis of volatiles PFAS in air down to ppq levels.

Why is monitoring air for PFAS important?

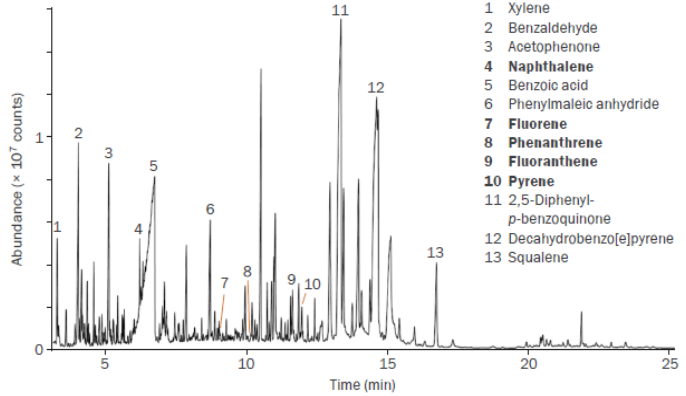
- Air is a significant source of PFAS. Contributors include:
  - Manufacturing
  - Product emissions
  - PFAS product incineration
  - Landfill gas

- Spreads PFAS over wide areas quickly
  - Including into residential areas
  - Rapid transcontinental transport

- Contribute to PFAS levels in water and soils…
- And levels in air are not yet regulated!!

What is thermal desorption (TD)?

A sample introduction technique for GC and GC–MS, thermal desorption enables the analysis of trace-level Volatile and Semi-Volatile Organic Compounds (VOC & SVOC) from a wide range of samples covering numerous application areas using extraction and pre-concentrations techniques.



Sampling air

1 Particulate sampling

A **Direct desorption of filters**

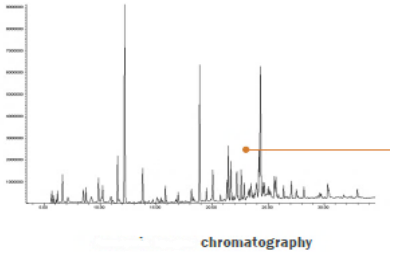
2 Gas phase sampling

A **Pumped sampling onto sorbent tubes**

B **Passive sampling onto sorbent tubes**

C **Canisters and bags**

D **On-line monitoring**



chromatography

The five main sampling approaches to monitoring VOCs and SVOCs in air from the environment are all compatible with TD

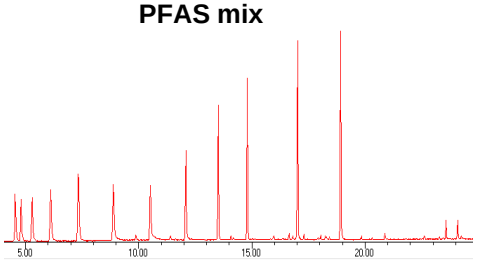
Multiple sample Introduction techniques on one system

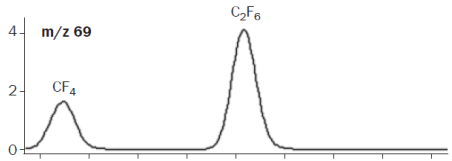
Tube methodology

- PFAS compounds from the source
- Other VOCs from the source

Online/Canister methodology

- Ultra-volatile PFAS species and products of incomplete combustion monitoring
  - CF_4 and other CFCs are already monitored using bags and canisters and on-line

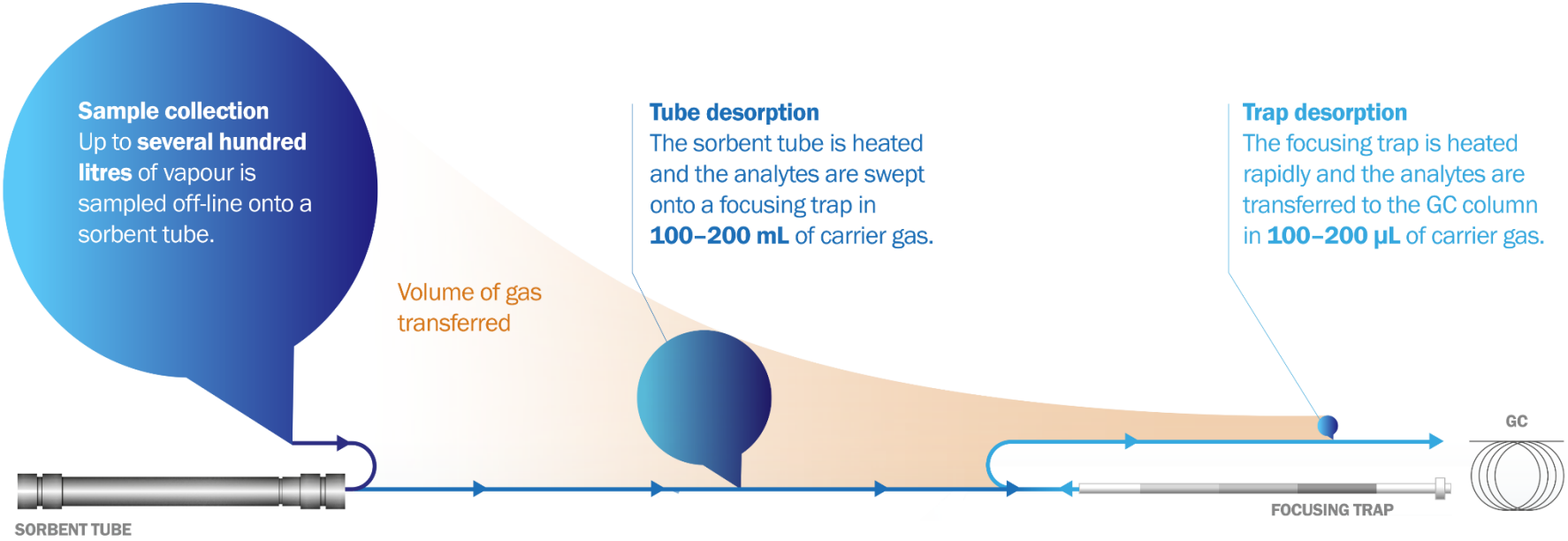




It is possible to carry out combined injection of canister and tube samples in a single GC–MS run, which is particularly useful if the samples have been co-located.

Pre-concentration: Sensitivity boost for trace-level analytes

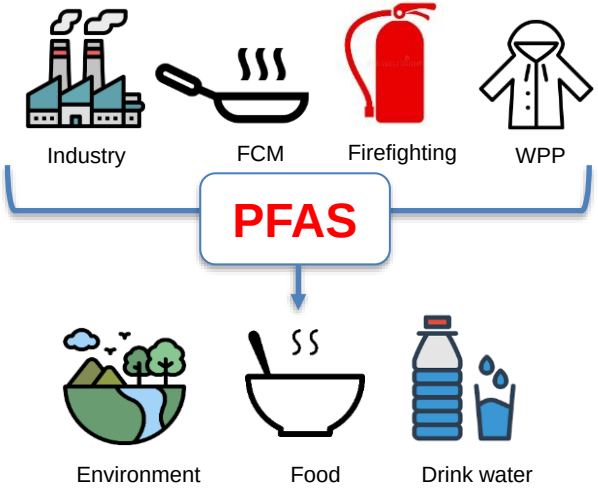
Sorbent tubes: best solution for low pg/m^3 monitoring



What are our target compounds?

Analytes

- PFAS compound classes compatible with TD & GCMS
- Target wide range of PFAS classes
  - PFCAs (Perfluoroalkyl carboxylic acids)
  - Non-ionic species – FTOHs, FOSAs, FOSEs, Acrylates
  - Most freons
  - Aliphatic fluorinated and mixed halogenated Hydrocarbons

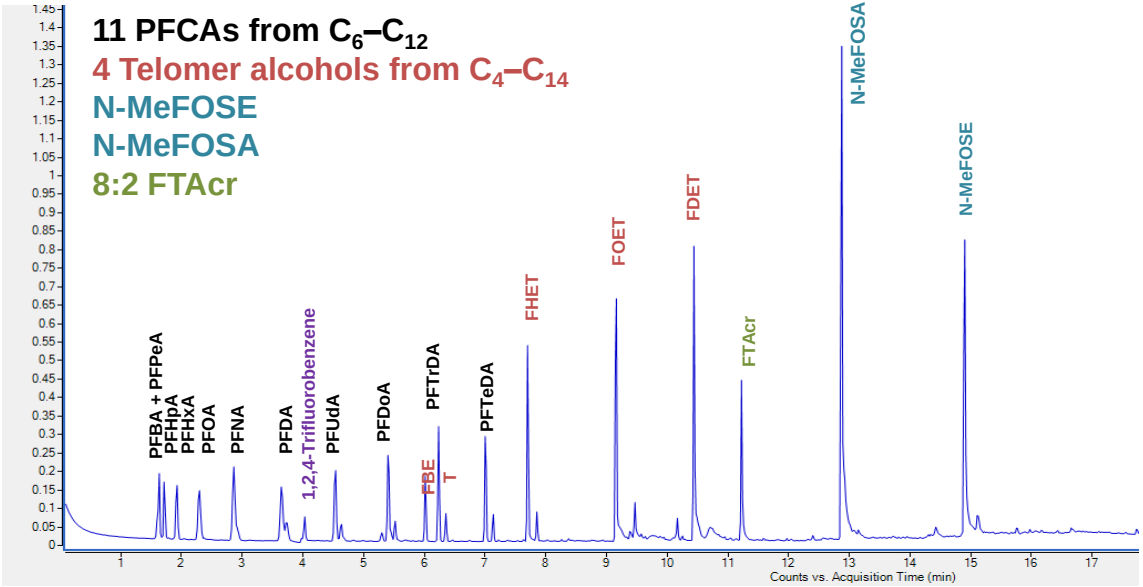


- Cannot do: Sulfonic acids/sulfonates

Wide range of analytes

Excellent separation and peak shape

SIM 131 m/z PFAS standard mix



Method conditions:

TD100-xr™ automated thermal desorber
Flow path: 150°C
Tube desorption: 300°C for 12 min, 50 mL/min
Focusing trap low: -30 low to +25°C
Focusing trap high: 300°C (4 min)

Column: VF-200 ms 30 m x 0.25 mm x 1.0 µm
Column flow: 1.2 mL/min, constant
GC oven: 35°C (2'), 15°C/min to 325°C (5')

Source: 250°C, Transfer line: 325°C
Scan range: m/z 40–650
Selected ions (SIM/SCAN mode): Quantifier ions – 95 (FTOH), 131 (PFCAs, FTAC, Me-FOSA)

How much air can we sample

New optimised PFAS sorbent tubes

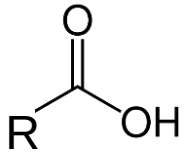
- Tubes connected in series
- Spiked with the target analytes
- Challenged with a volume of **500L** N_2

- No compound showed breakthrough at 500L.

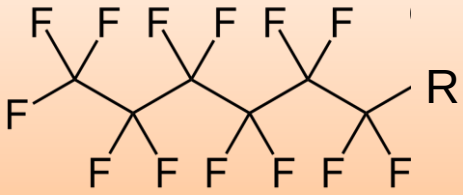
Compound	Mean breakthrough (%)
Perfluoroalkylcarboxylic acids (PFCA)	
PFBA	1.72
PFPeA	1.26
PFHxA	0.00
PFHpA	0.26
PFOA	0.21
PFNA	0.11
PFDA	0.09
PFUdA	0.14
PFDoA	0.13
PFTrDA	0.10
PFTeDA	0.22
Fluorotelomer acrylates (FTAcr)	
8:2 FTAcr	1.73
Fluorotelomer alcohols (FTOH)	
4:2 FTOH	0.29
6:2 FTOH	1.80
8:2 FTOH	1.89
10:2 FTOH	3.08
Perfluoroocatanesulfonamides (FOSA)	
Me-FOSA	0.15
Et-FOSA	0.19

High sensitivity

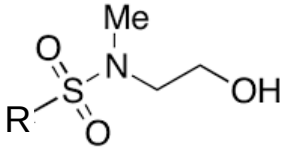
Achieving good detection limits



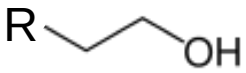
PFCAs
MDL <3 ppq



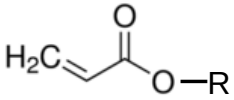
Fluorinated tail



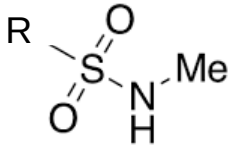
N-MeFOSE-M
MDL <2 ppq



FTOHs
MDL <5 ppq



FTAcr
MDL <1.18 ppq

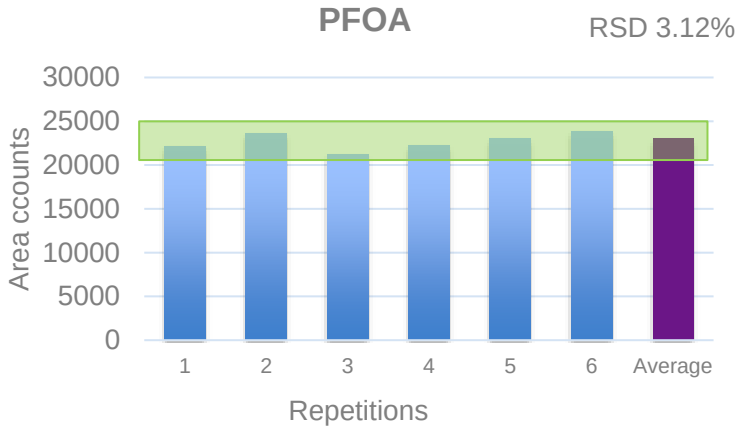


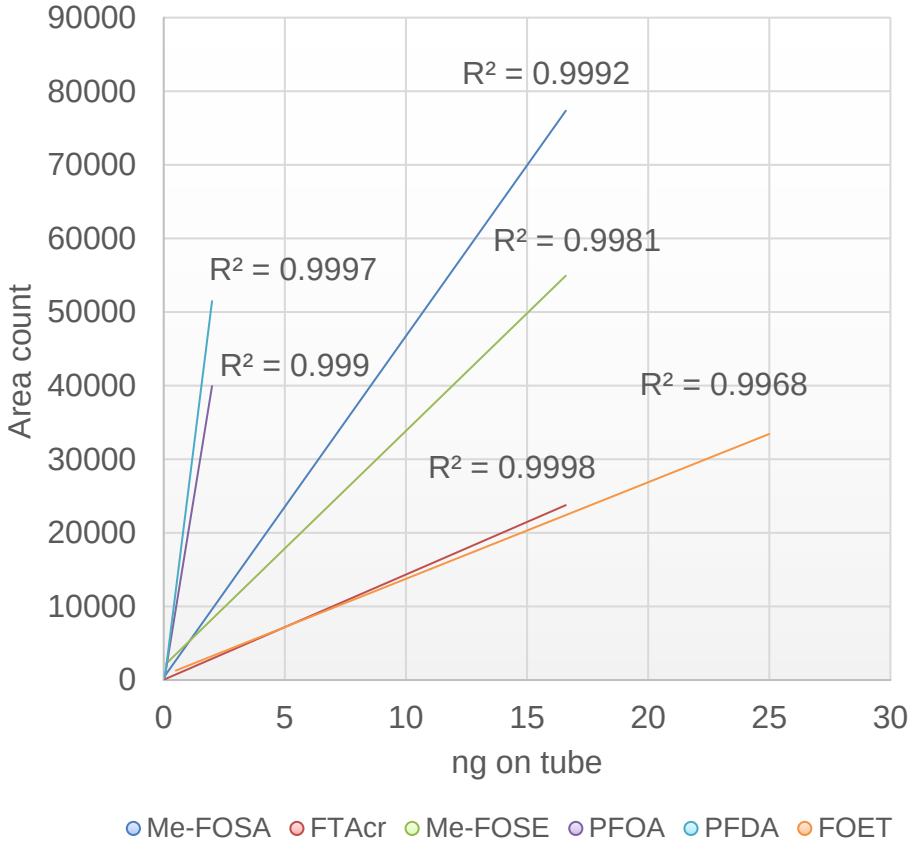
N-MeFOSA-M
MDL <2 ppq

Linearity and reproducibility

Implementing a robust method

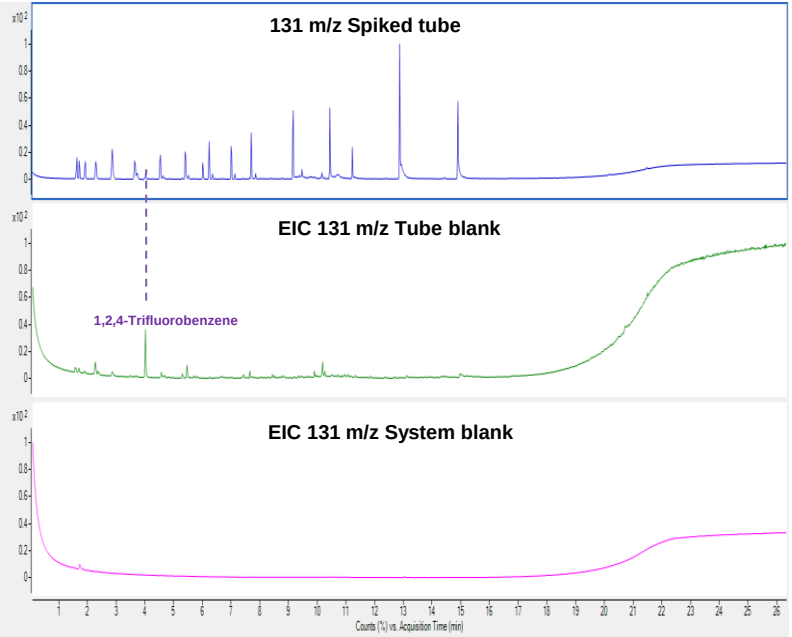
- Excellent linearity and reproducibility obtained
- No carryover
- No system contribution

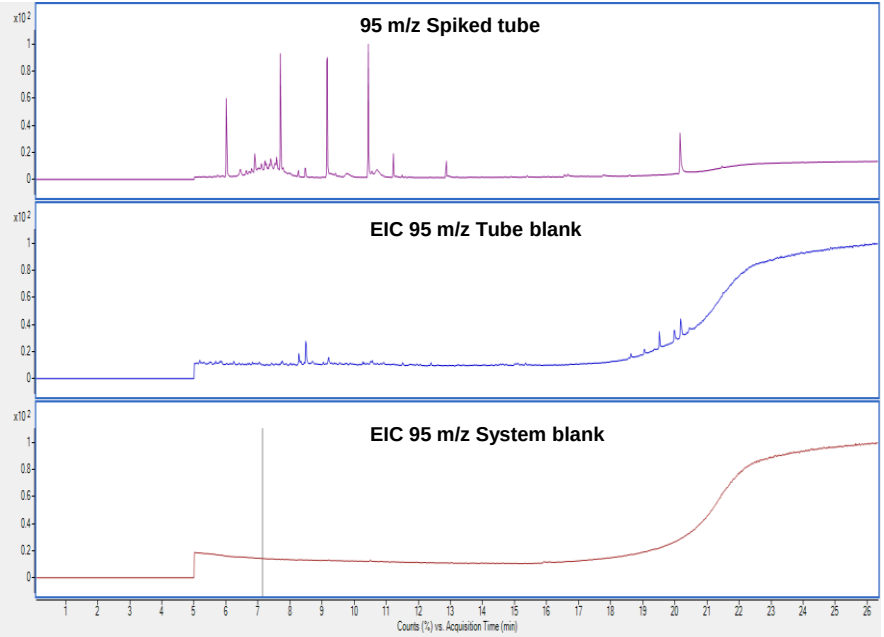




TD–GC–MS system blanks

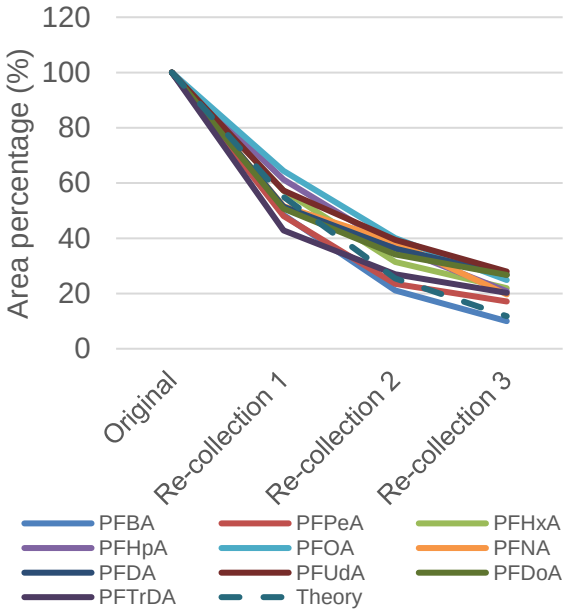
No PFAS contribution from the system

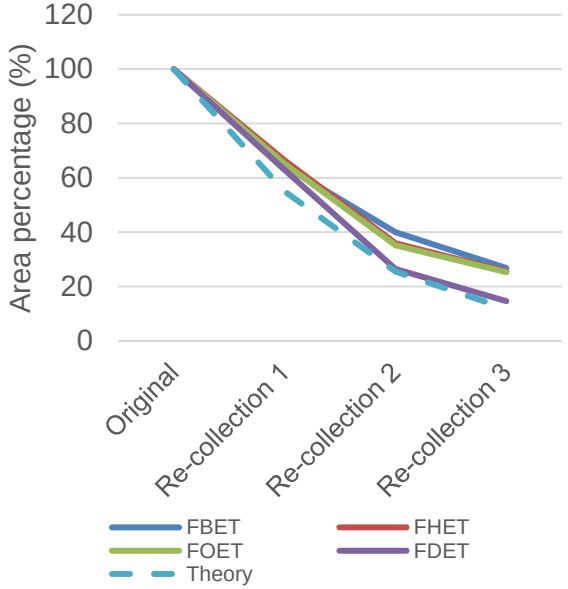


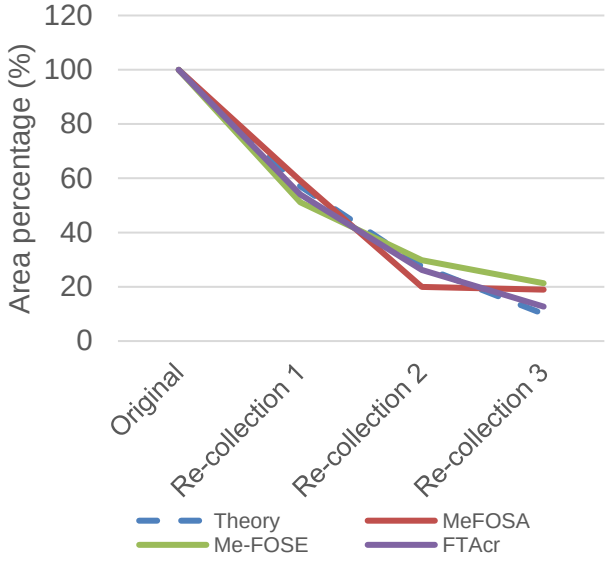


Advanced data validation techniques

Excellent analyte recovery demonstrated by re-collection



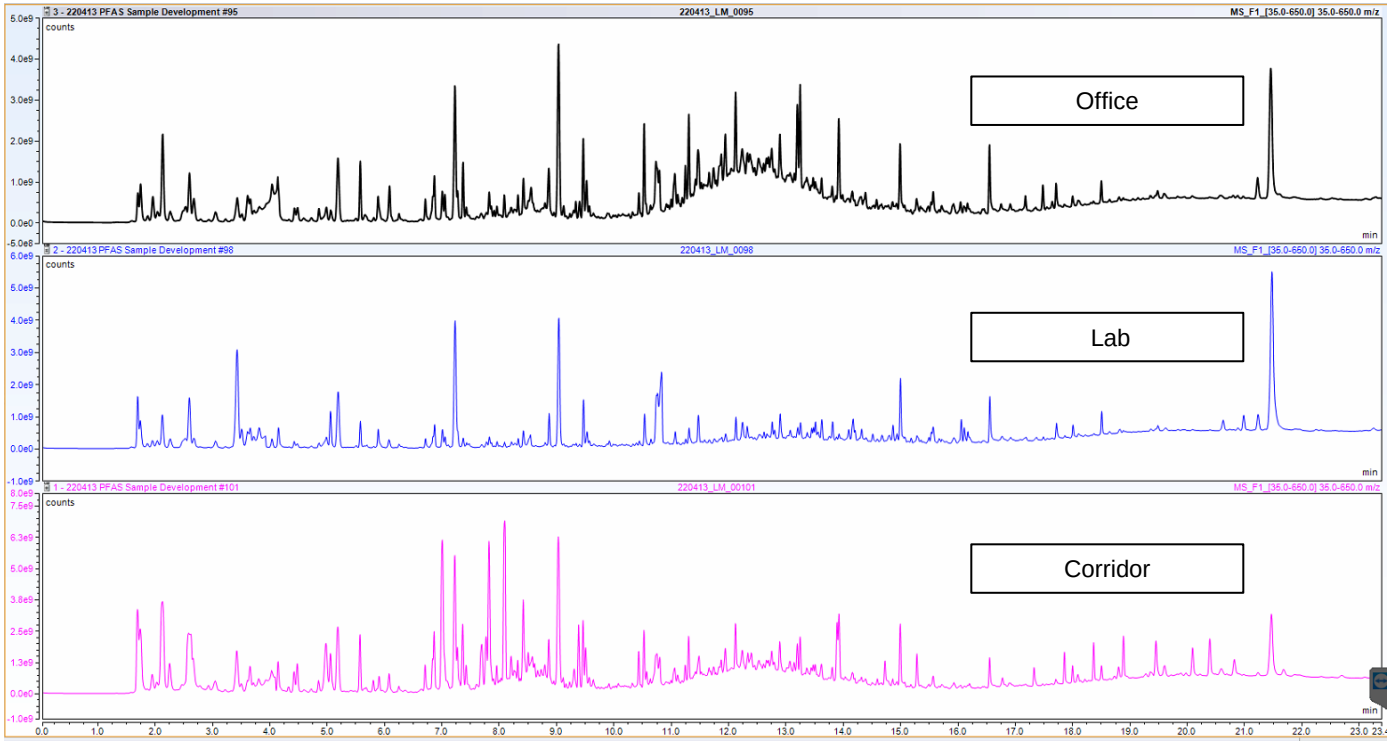




No PFAS losses with the optimized method

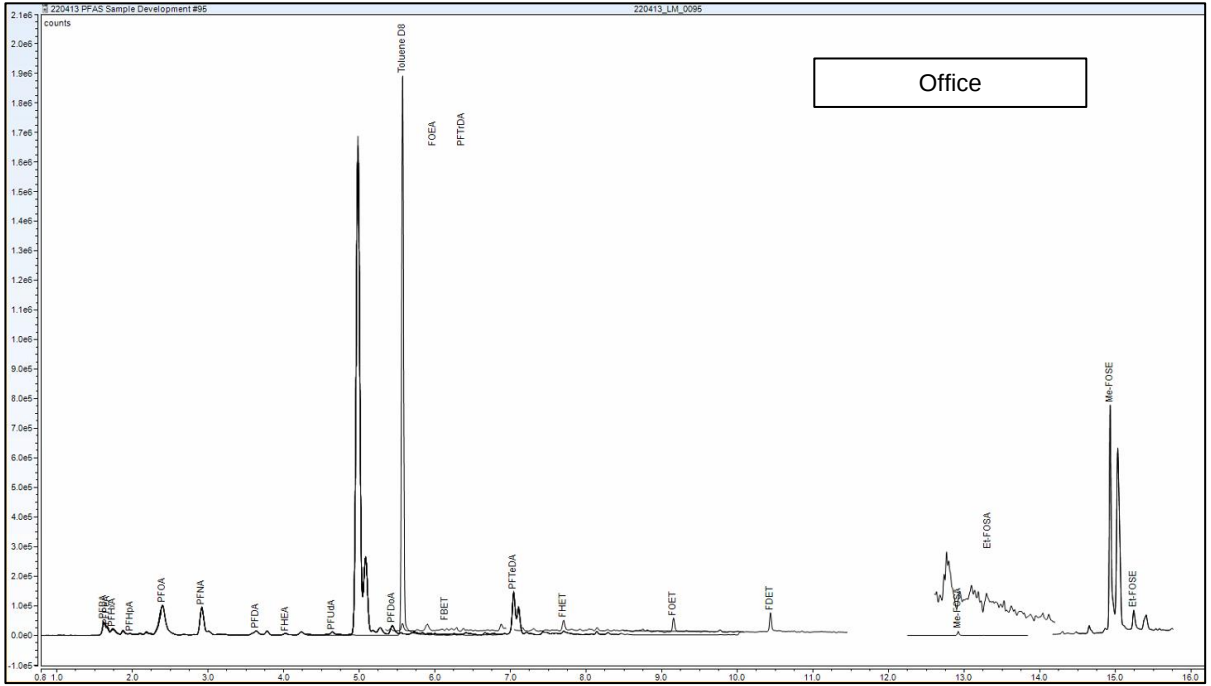
Simultaneous targeted and untargeted analysis

- Wide volatility range sampled in various indoor air environments
- Enables untargeted screening of air samples for PFAS and beyond



Simultaneous targeted and untargeted analysis

- Whilst maintaining high sensitivity for target PFAS compounds.
- All in one sample and one analysis



Summary

Sampling and analysis of a challenging range of trace-level volatile and semi-volatile PFAS vapours in air

- TD–GC–MS is a robust technology for analysis of VOCs and SVOCs in air including PFAS compounds

- Using advanced air monitoring sampling and analytical TD–GC–MS systems we've demonstrated:
  - Excellent linearity and repeatability
  - Low ppq detection limits for all compounds
  - Large degree of flexibility for sampling volume

- Future development work will focus on configuring the thermal desorbers are also routinely coupled with advanced GC–MS and GC-MSMS technology for targeted analysis and discovery work.