# Improving Discovery of Volatile Per- and Polyfluoroalkyl Substances (PFAS) in Landfill Gas

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# Who is SepSolve Analytical?

## Experts in analytical chemistry

SCHAUENBURG Analytics

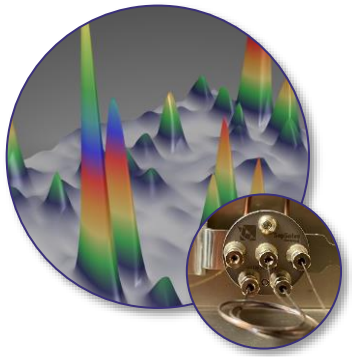
MARKES international

SepSolve Analytical

Sample extraction & enrichment

Thermal desorption

Sampling technologies

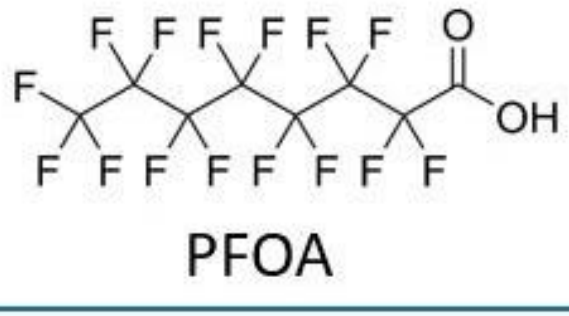


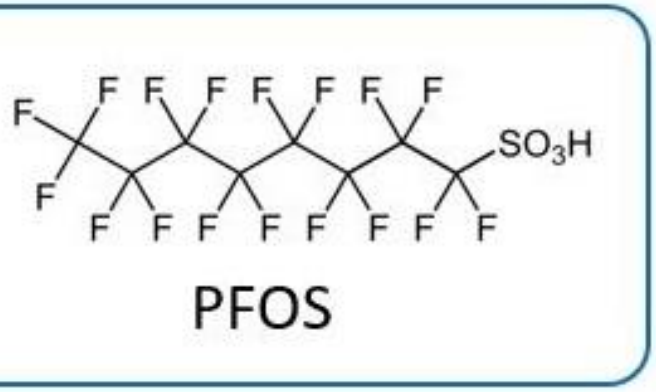
GC×GC separation

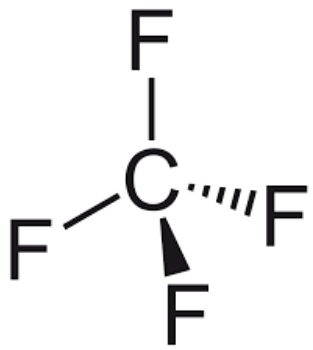

Time-of-flight mass spectrometry

Data mining & chemometrics

# Poly/Perfluoroalkyl substances (PFAS) are…




*"… highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents… have been replaced by fluorine (F) atoms"*

Buck et al., Integrated Environmental Assessment and Management (2011)

# Why are we talking about PFAS?

- PFAS are persistent in the environment
  - Classed as Persistent Organic Pollutants (POPs)
  - Hyper mobile within the environment
  - Persistent within the human body

- 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

# PFAS sources and exposure routes

Primary source

PFAS production

Secondary sources

Chemical and product Manufacturing

Industrial products

Consumer products

Occupational exposure

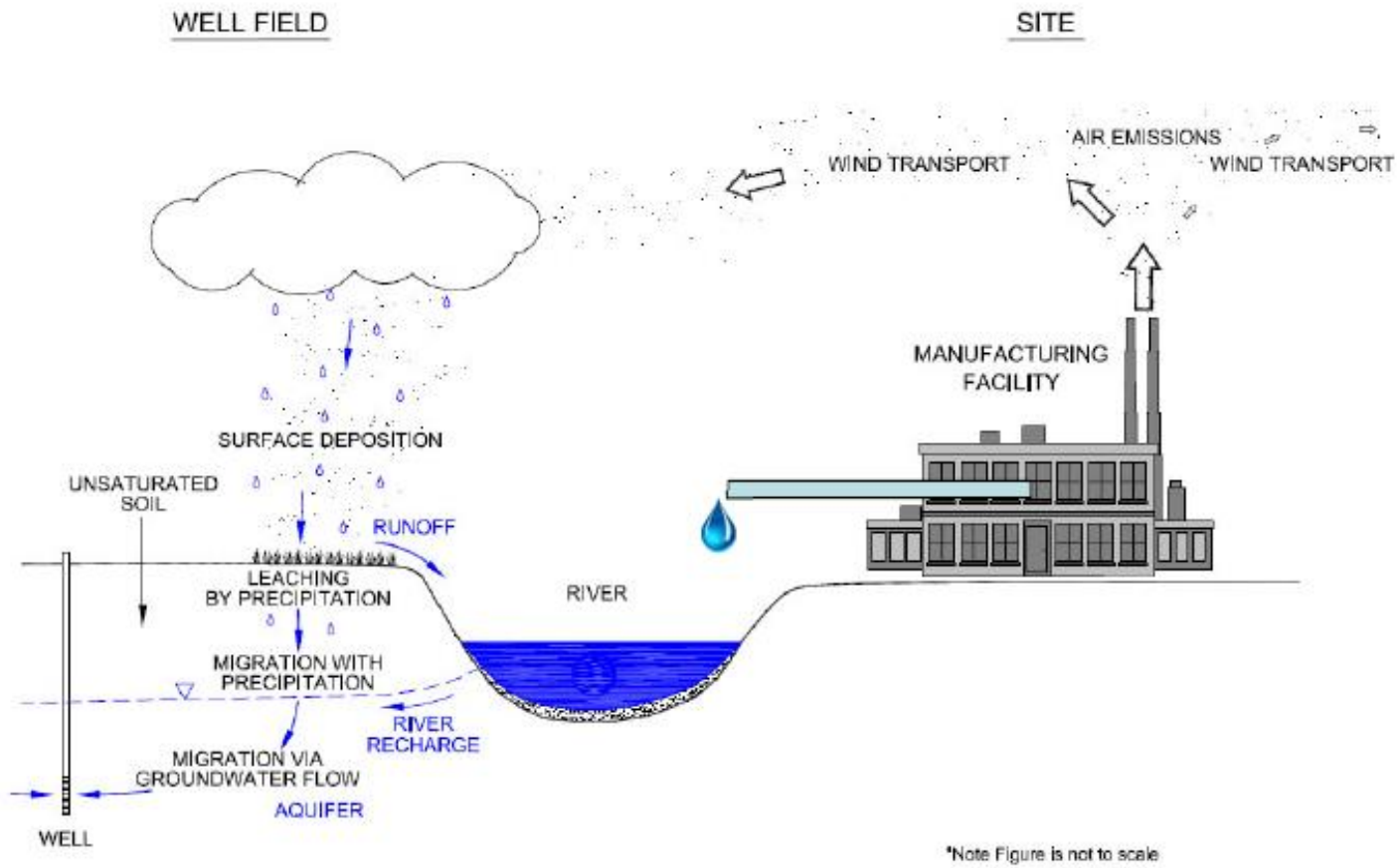
Environmental occurrence

Ecological exposure

Consumer/residential exposure

# Why is monitoring air for PFAS important?

- Air is a significant source of PFAS
  - Manufacturing
  - Product emissions
  - PFAS product incineration
  - Landfill gas
- Spreads PFAS over wide areas quickly
  - Including into residential areas
  - Transcontinental transport
- Not yet regulated




Davis et al. Chemosphere 67 (2007) 2011–2019

# Challenges of PFAS monitoring

1. Wide range of chemicals (>6000) with greatly differing properties
   - Functional groups
   - Volatility
   - Ionic and neutral species

*No single method can analyse all PFAS compounds*

2. Concentration levels within the environment
   - ppt levels
   - Bio-accumulation means even small quantities are dangerous
   - Analytical equipment must not contribute

*Requires sensitive analytical techniques*

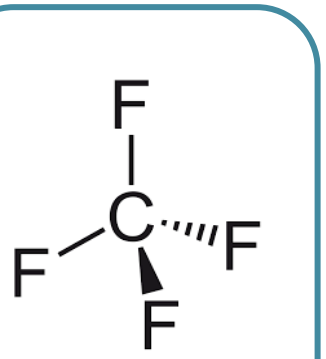
3. No analytical standards available for the majority of compounds
   - ~90 available
   - Unknown PFAS just as important

*Can we limit ourselves to target compounds?*

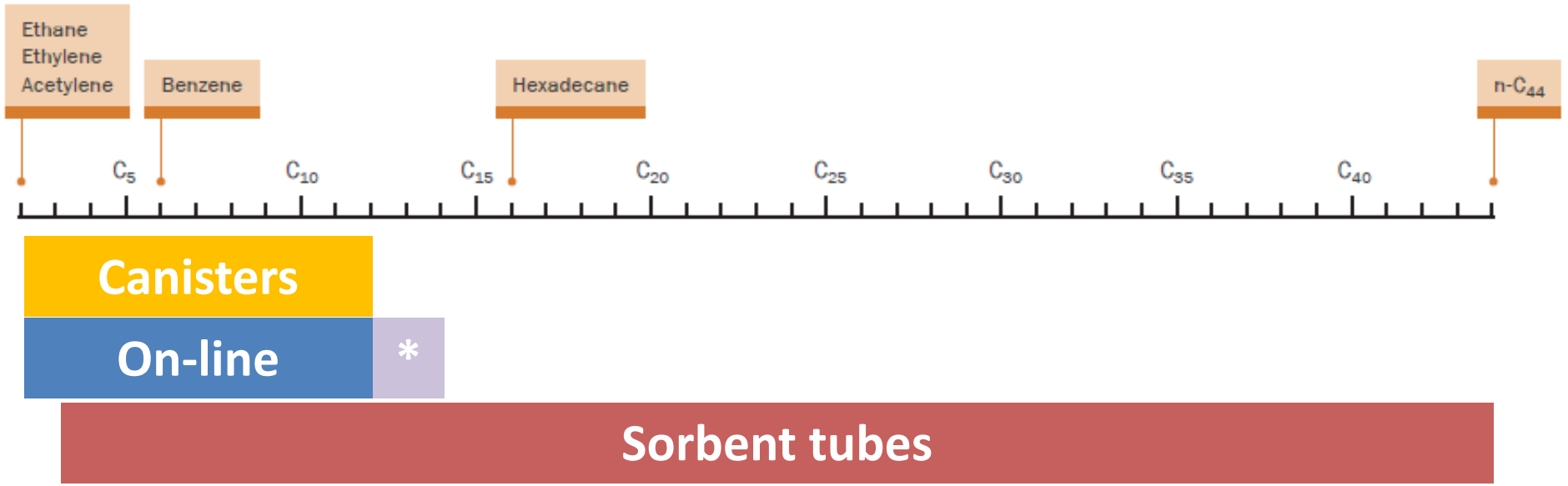
# Why use thermal desorption for PFAS analysis?

## Challenge #1: Wide range of chemicals

- Large number of chemicals (over 6000 currently classified) which means a wide volatility range
- TD–GC–MS can analyse compounds ranging in volatility from $C_2$ – $C_{44}$ straight chain hydrocarbons




Freon 14



# Air sampling techniques


## 1 Particulate sampling

A **Direct desorption of filters**

## 2 Gas phase sampling

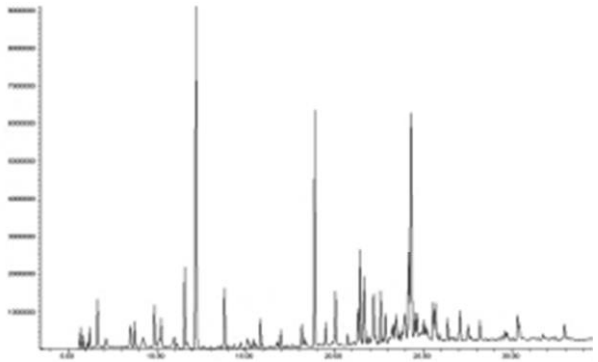
A **Pumped sampling onto sorbent tubes**

B **Passive sampling onto sorbent tubes**

C **Canisters and bags**

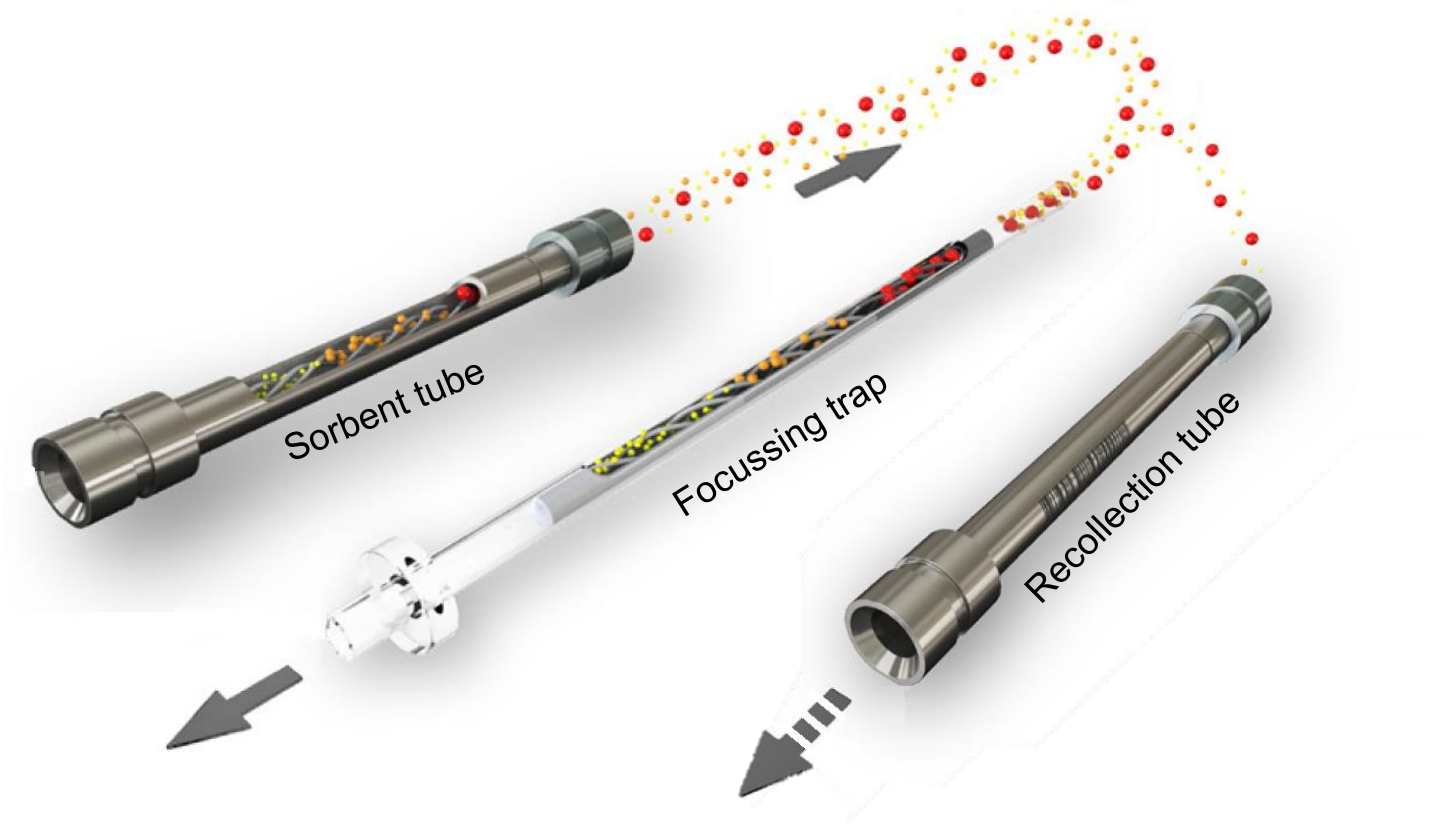
D **On-line monitoring**

**Thermal desorption (TD)**



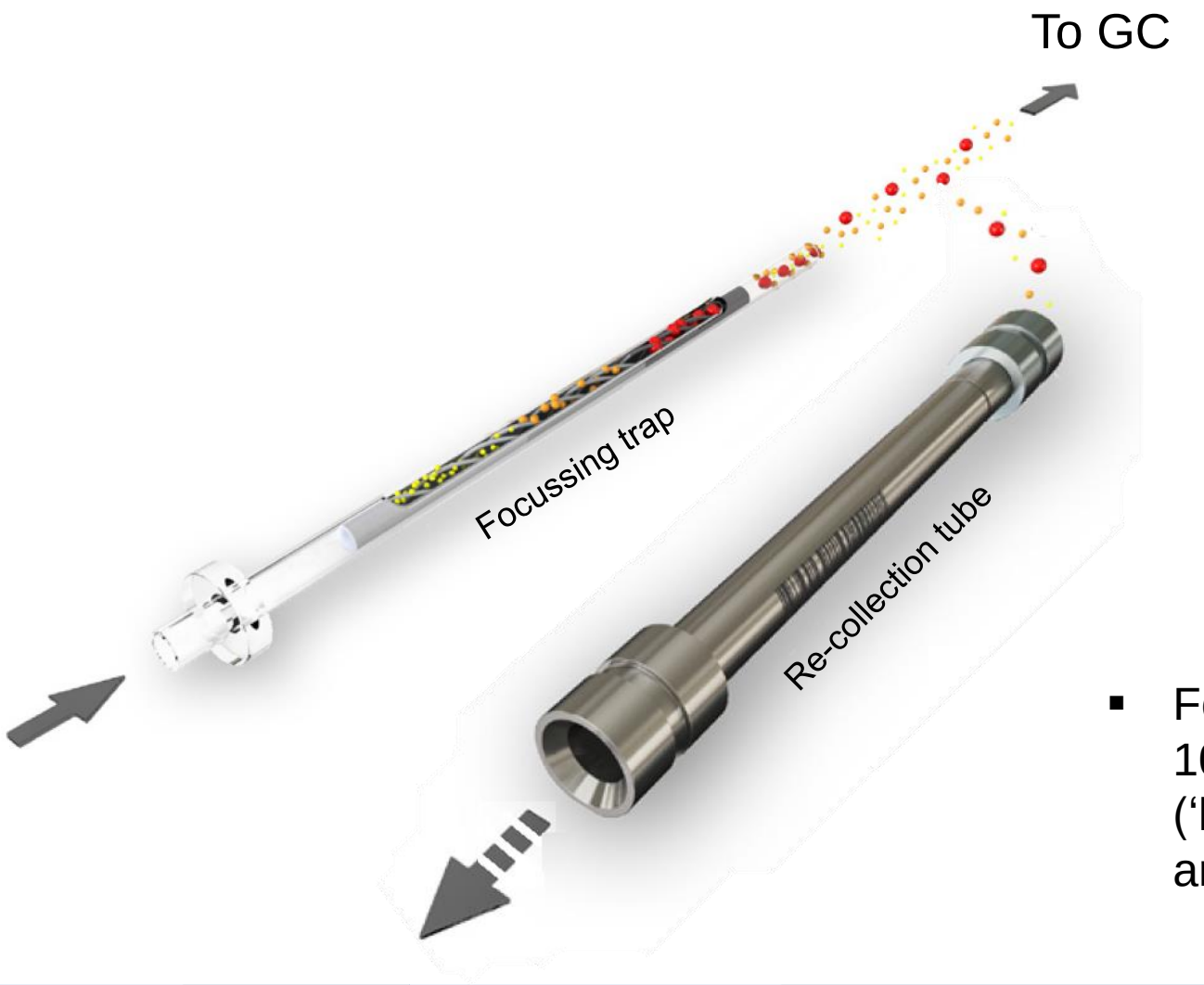
**GC–MS**

# How does thermal desorption work?




- Sample tube heated in flow of carrier gas
- Analytes swept onto an electrically cooled focusing trap (held between ambient and –30 °C)
- Focusing trap can be packed with multiple sorbents to retain target and non-target compounds

# How does thermal desorption work?

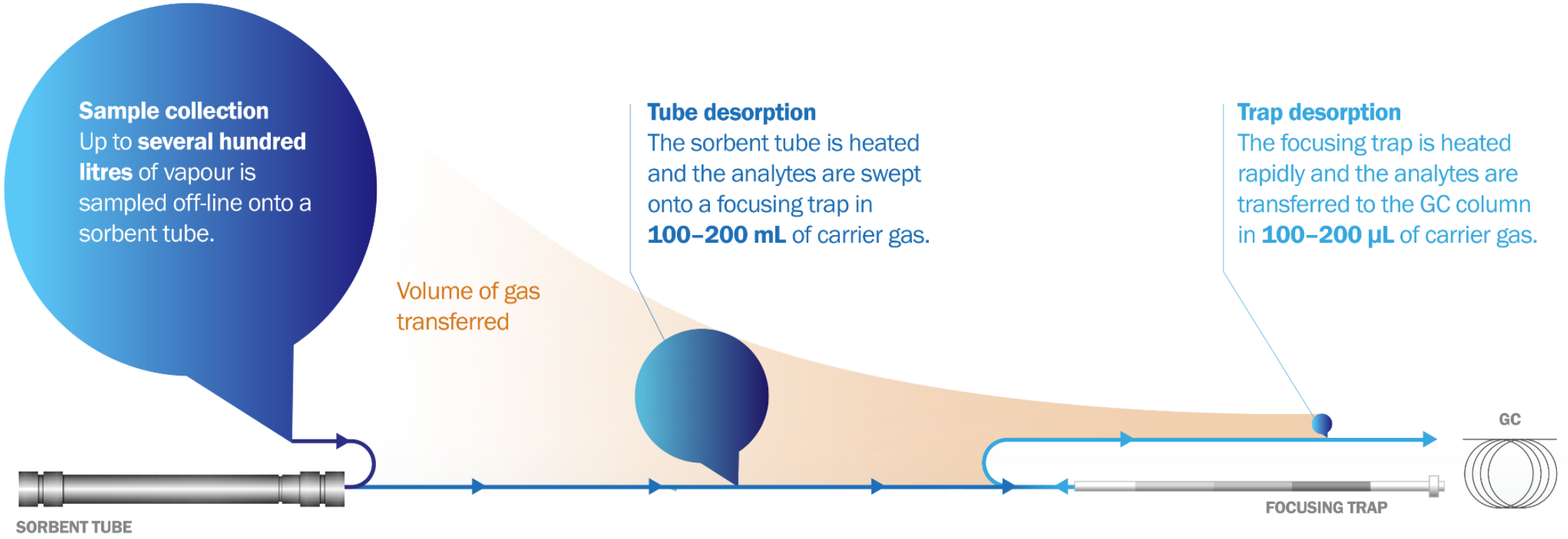



- Focusing trap is rapidly heated (up to 100°C/s) in a reverse flow of carrier gas (‘backflush’ operation), to transfer the analytes to the GC column.

# Why use thermal desorption for PFAS analysis?

## Challenge #2: Concentration levels within the environment

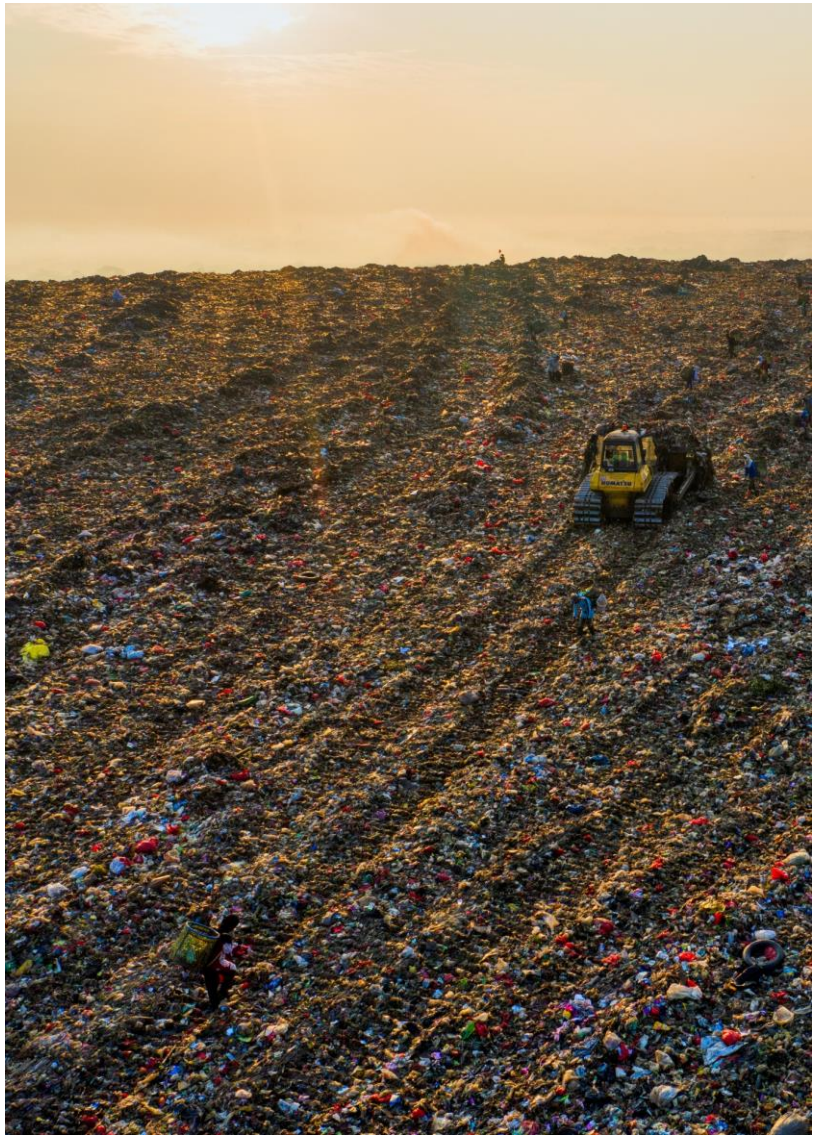
- PFAS are persistent and toxic - must be detected at very low levels (ppq)
- TD is a preconcentration technique capable of analysing ppq level components in air



# Finding PFAS within landfill gas

## PFAS disposal

- Landfill is often used for disposal of PFAS containing products
- Primary bi-product of landfill is landfill gas (LFG)
- PFAS is amongst the VOCs in LFG
  - Samples can be very complex
- LFG can emit PFAS into the environment through:
  - Flaring
  - Re-use for energy production



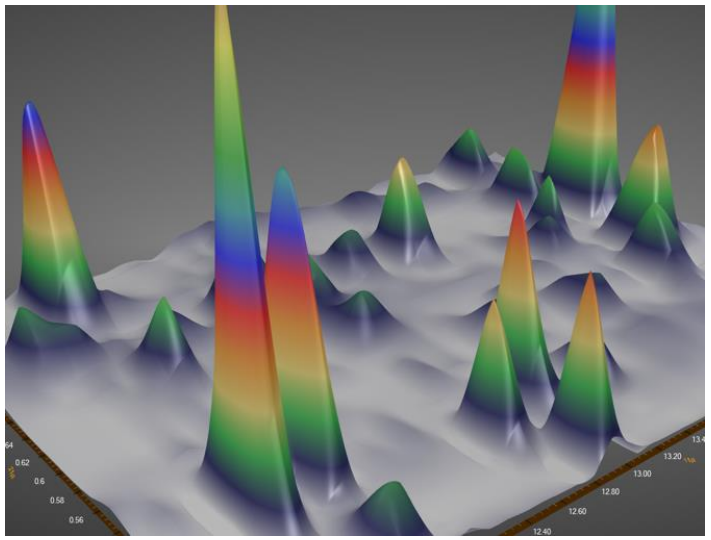
# What about the matrix?

## Challenge #2: Concentration levels within the environment

- PFAS species detected at low fg/L (pg/m$^3$) in some samples
- Sample matrix could be at µg/L or higher

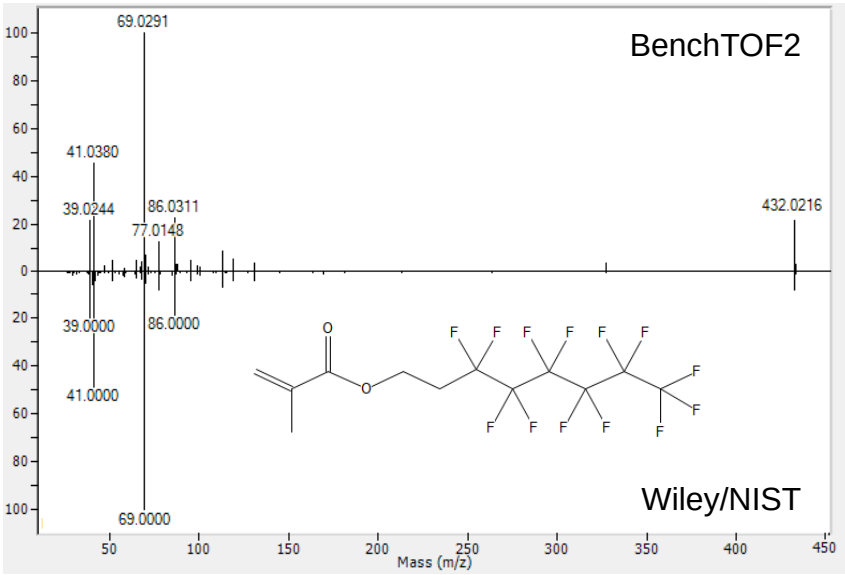
Thermal desorption (TD)

+

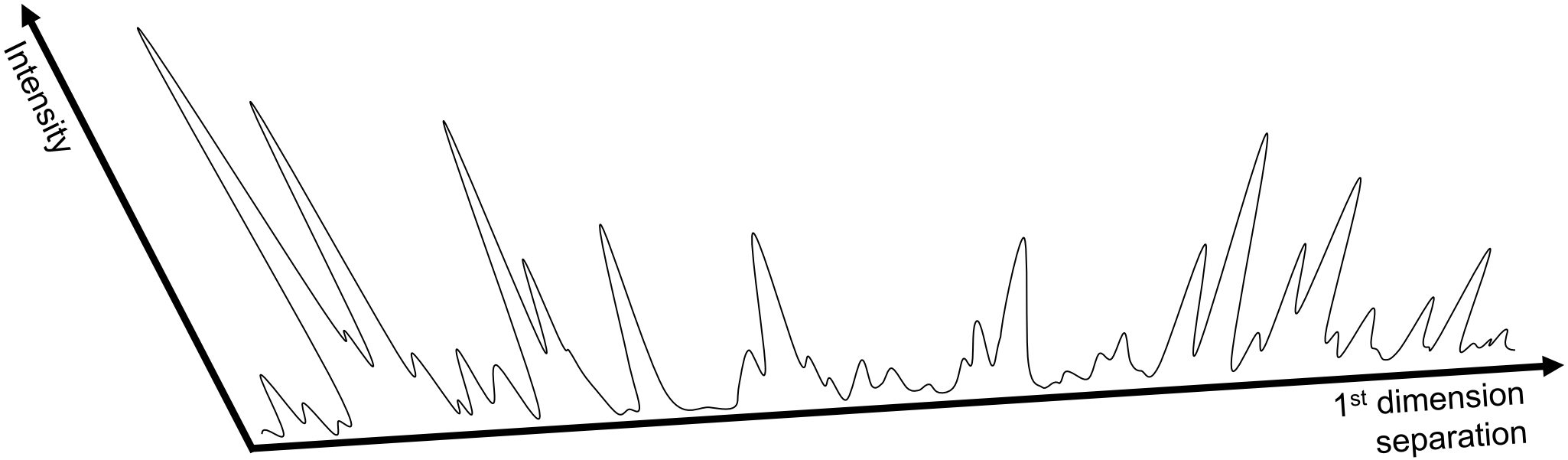


Comprehensive two-dimensional GC (GC×GC)

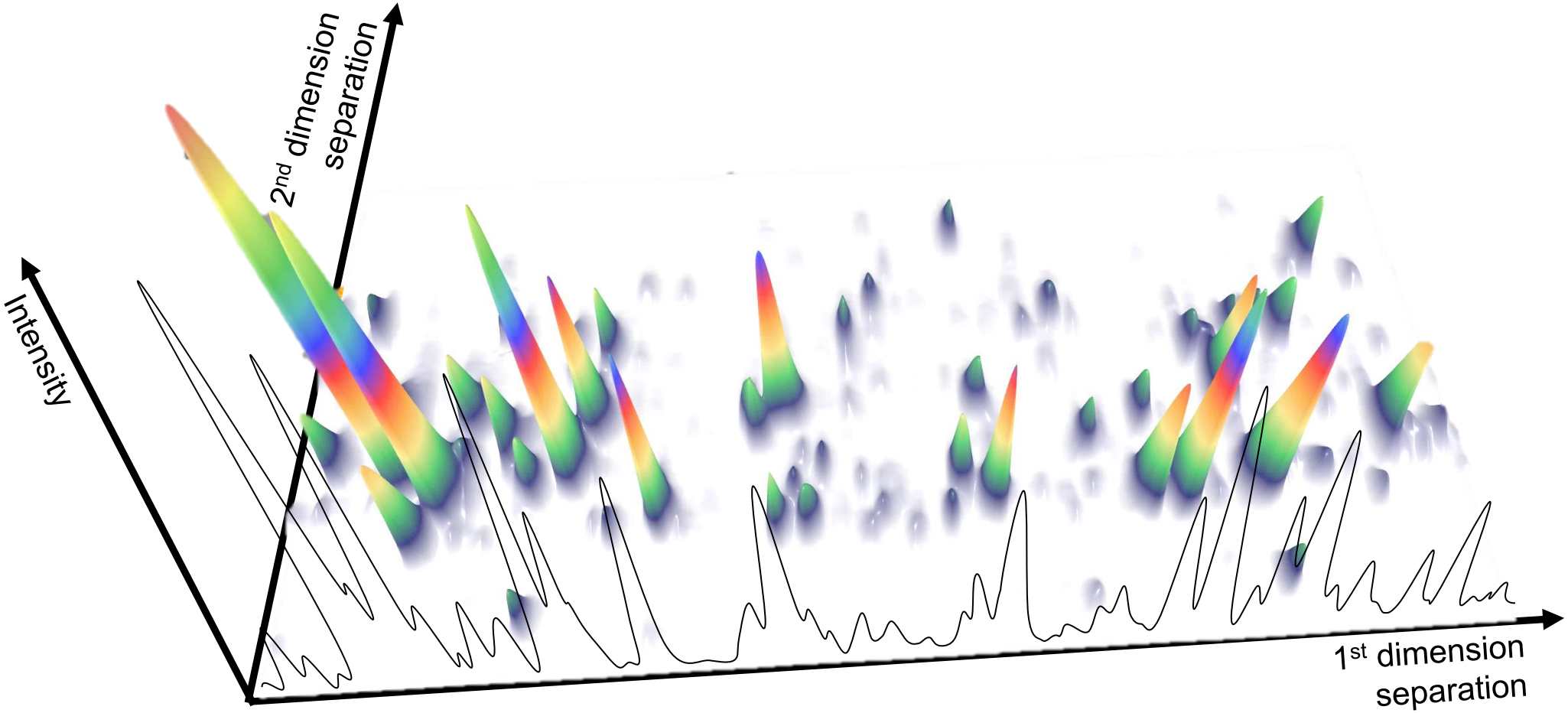
+



# What is GC×GC?

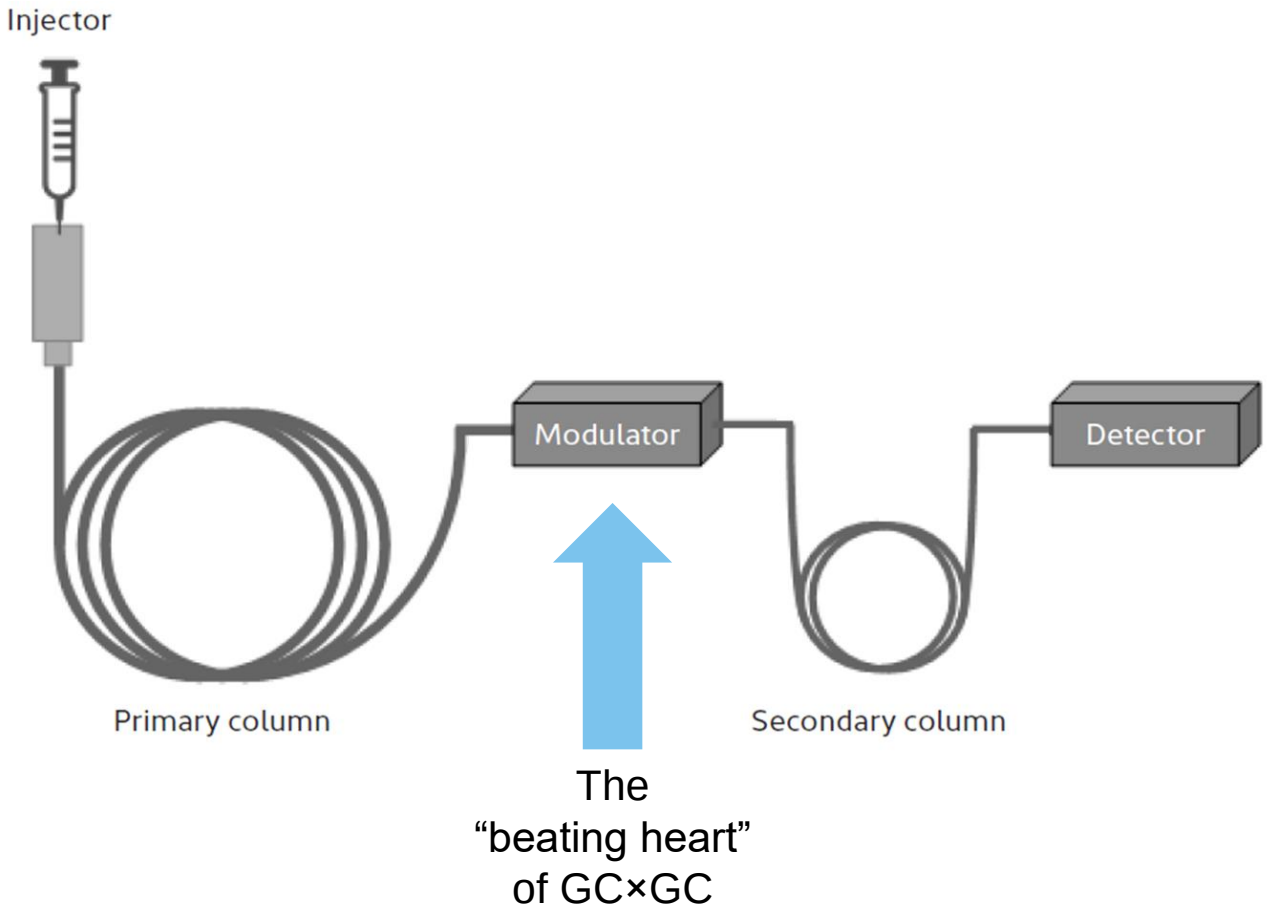


# What is GC×GC?


2nd dimension separation
Intensity
1st dimension separation

# How does GC×GC work?

## Analytical system



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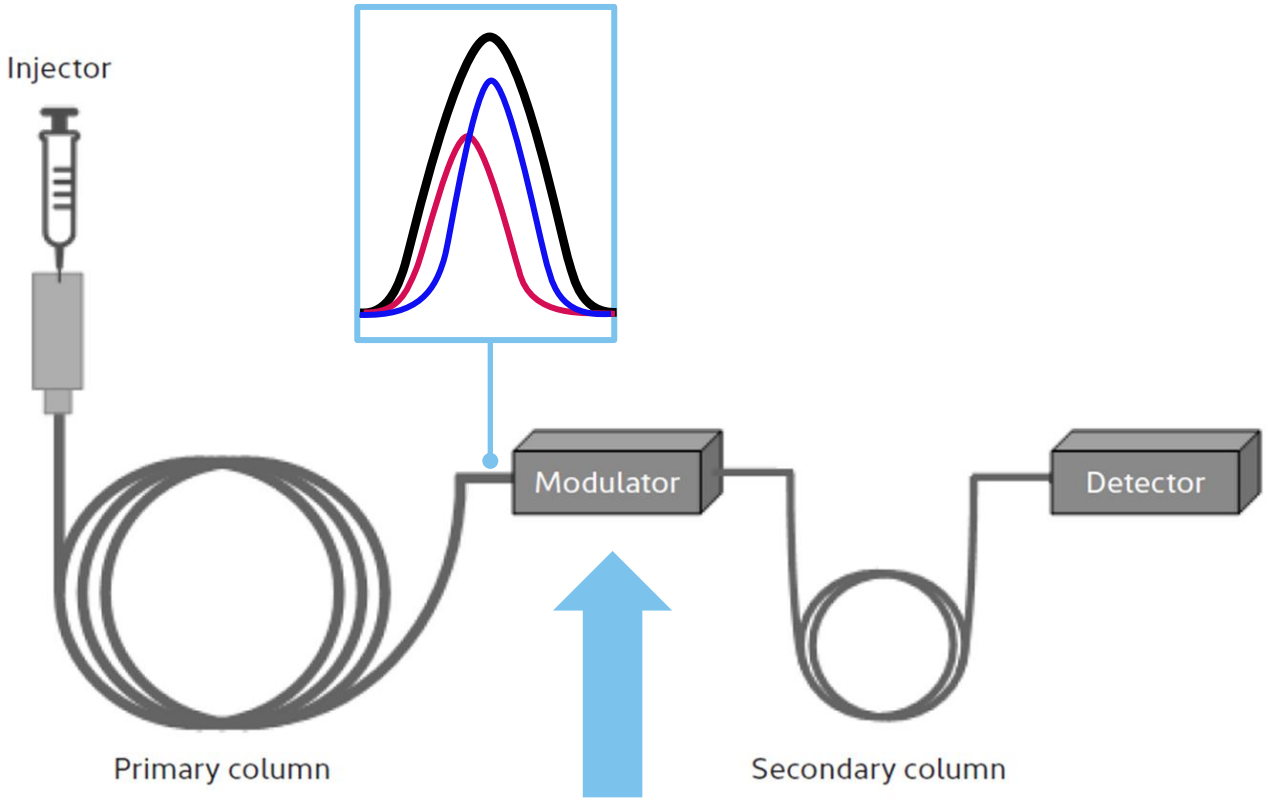


The
“beating heart”
of GC×GC

# How does GC×GC work?

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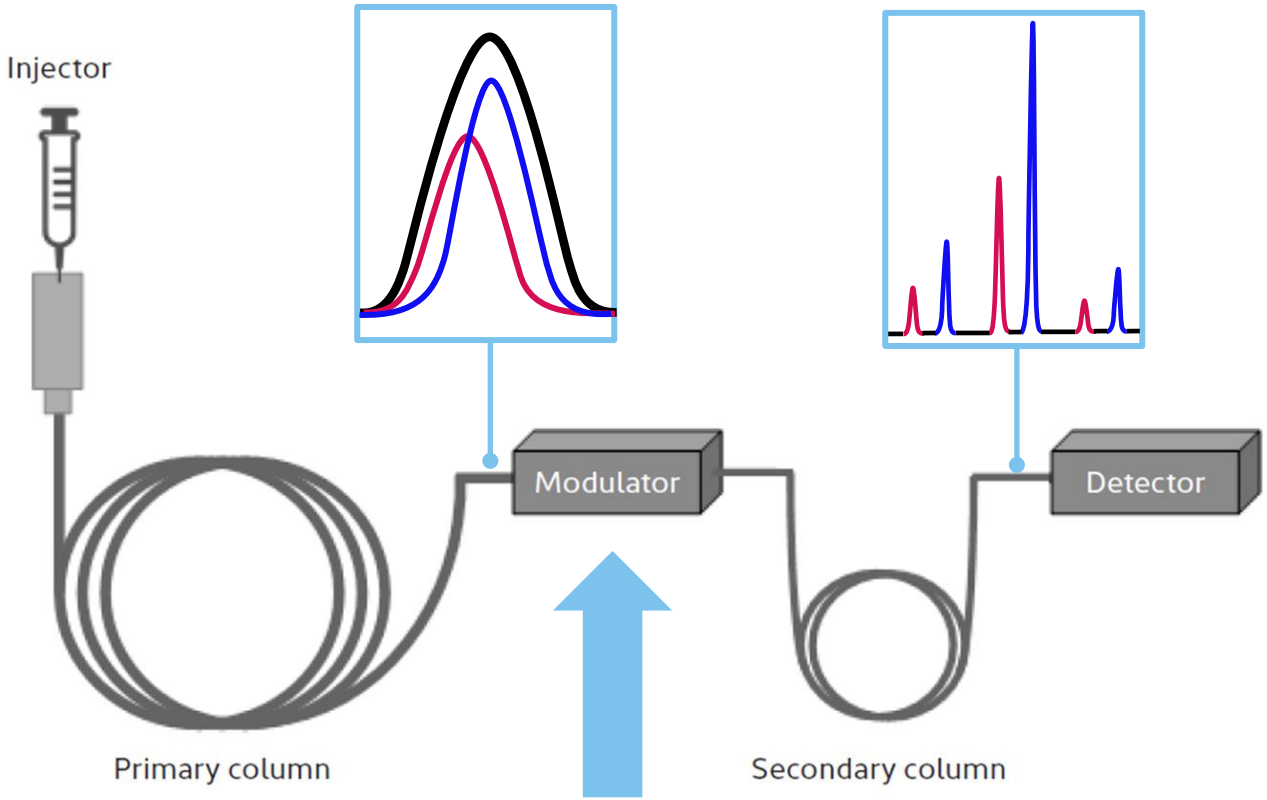


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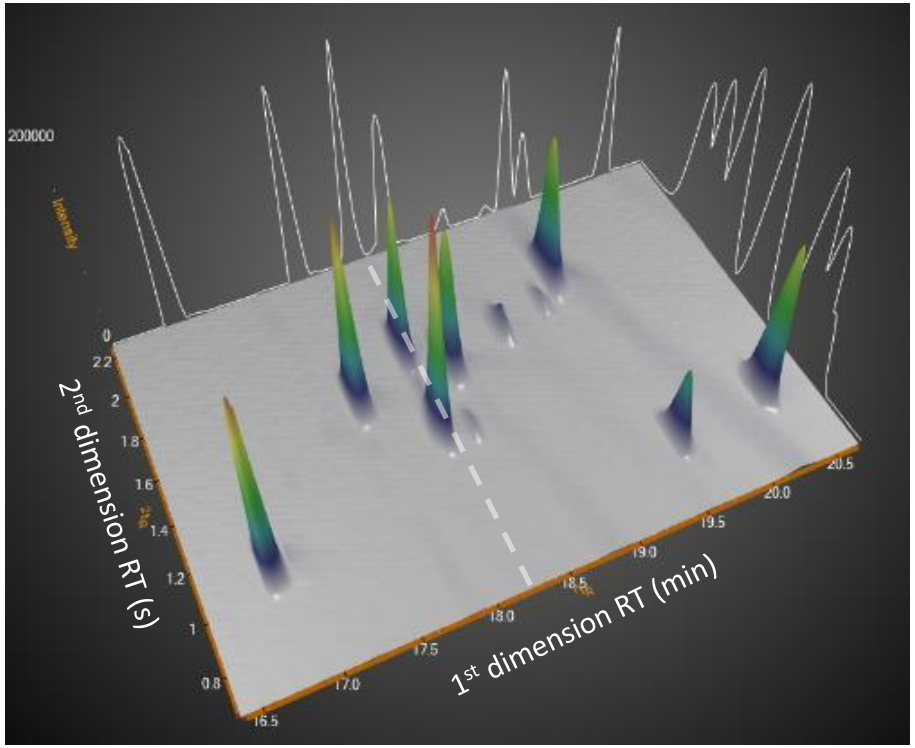
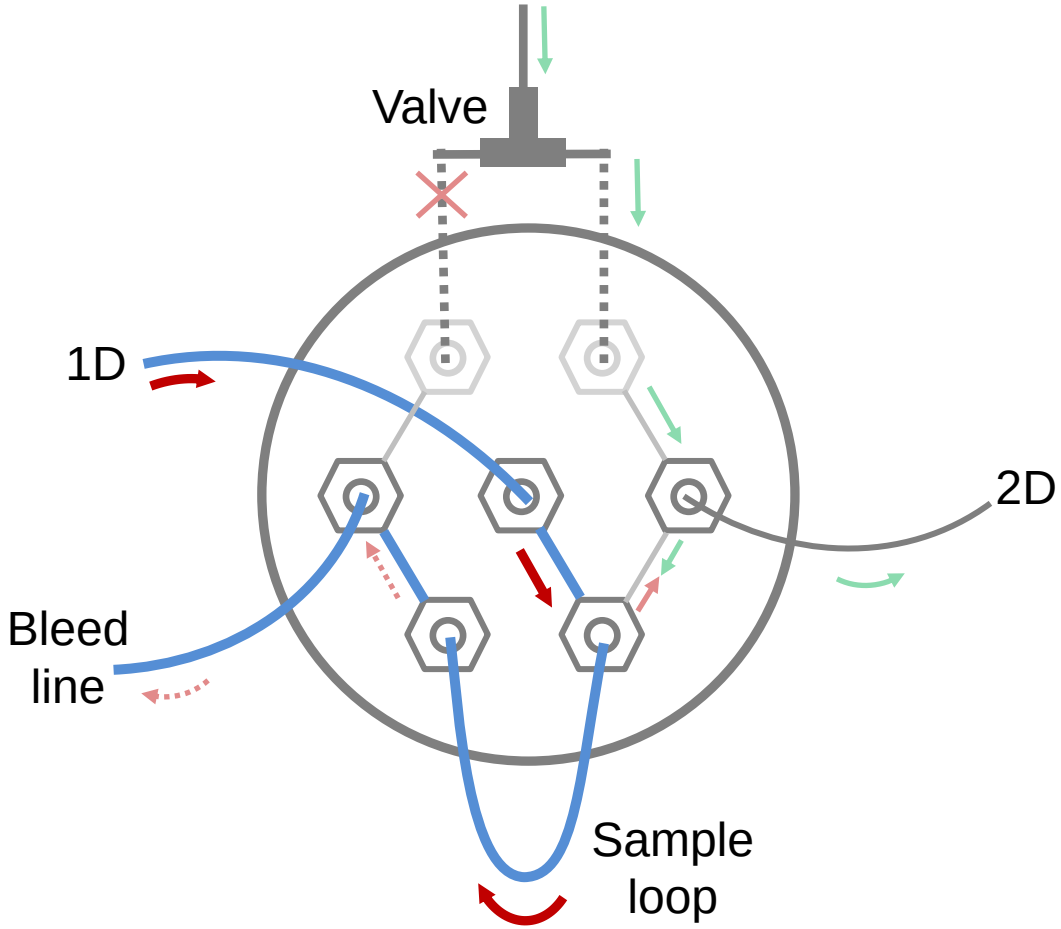


# Reverse fill/flush flow modulation

**‘Fill’** mode

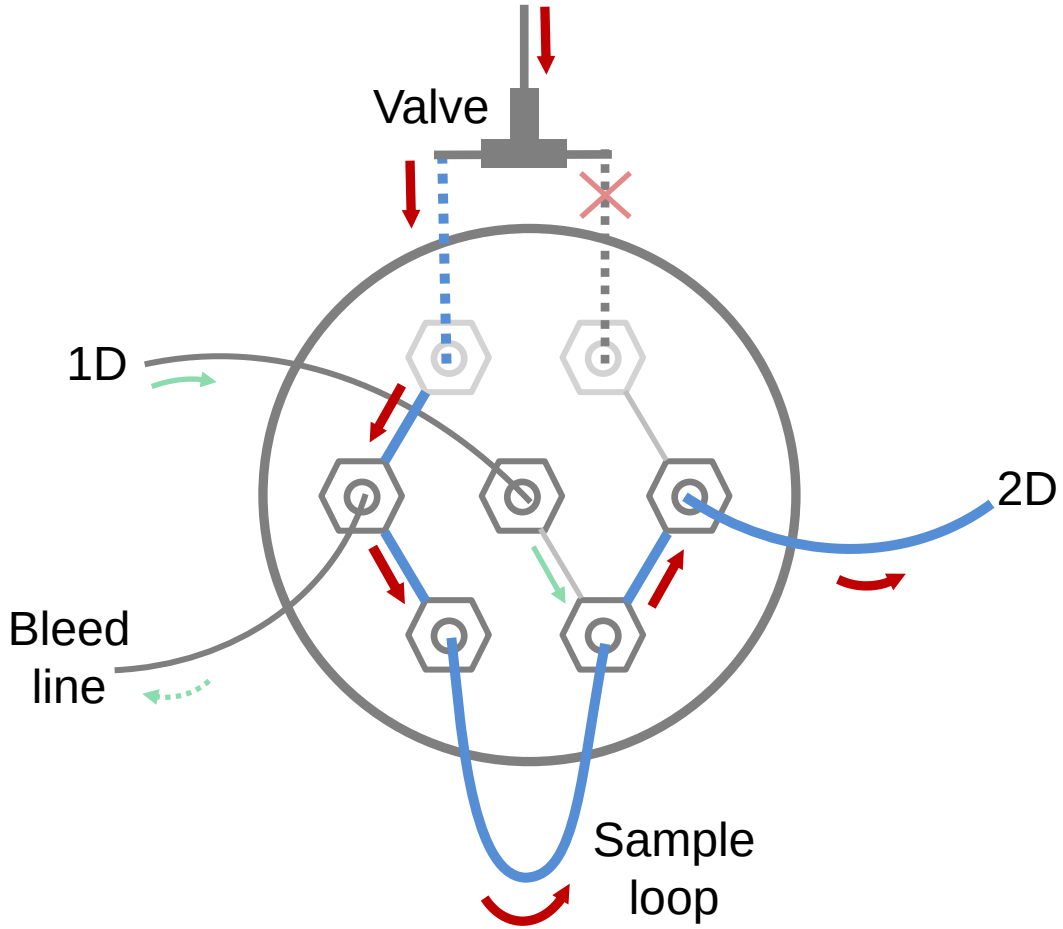





For more on the development of RFF flow modulators, see Griffith et al, J. Chromatogr. A, 1226 (2012) 116– 123

# Reverse fill/flush flow modulation

**‘Flush’** mode

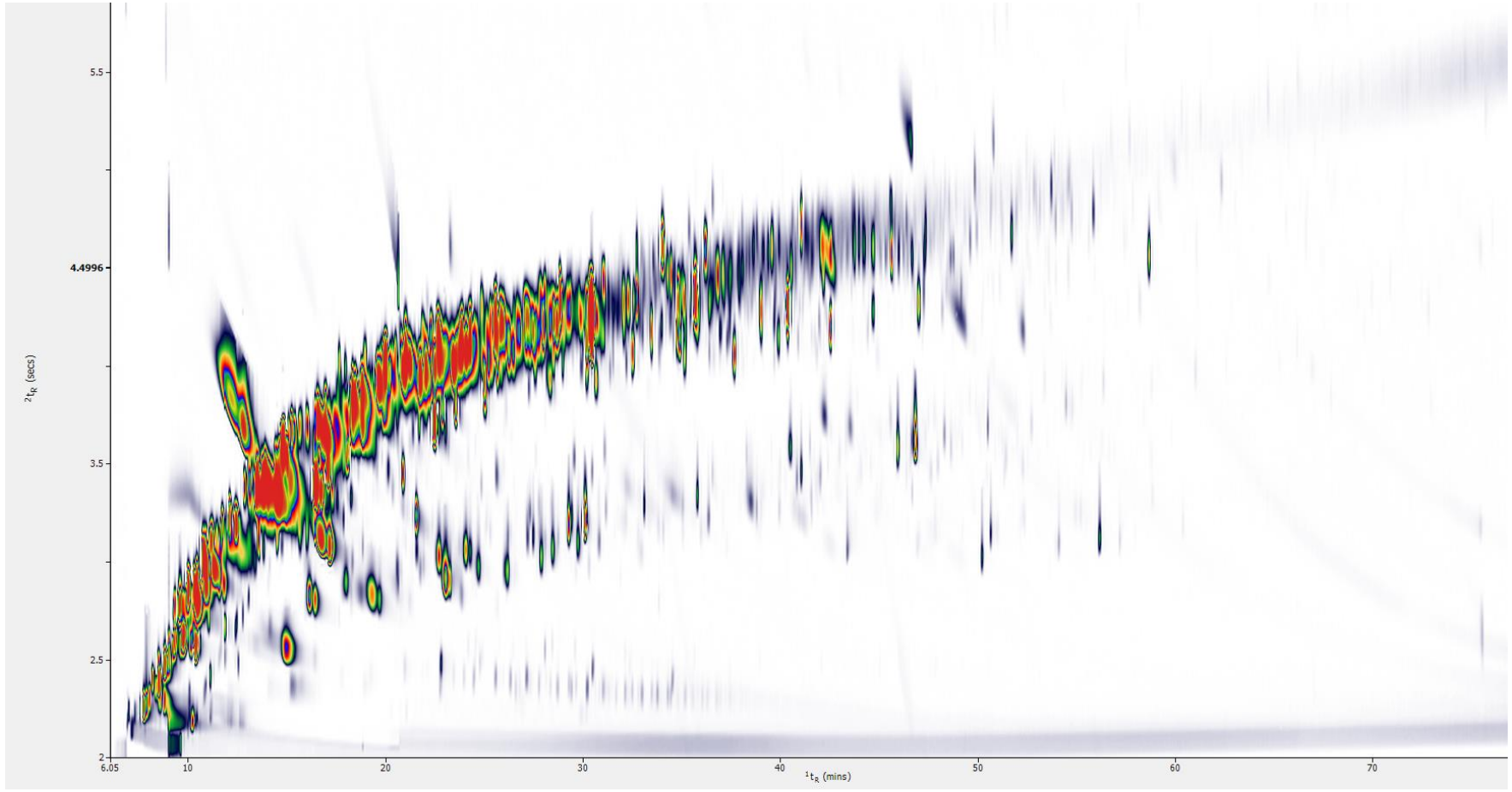





For more on the development of RFF flow modulators, see Griffith et al, J. Chromatogr. A, 1226 (2012) 116– 123

# Landfill gas is an extremely complex matrix

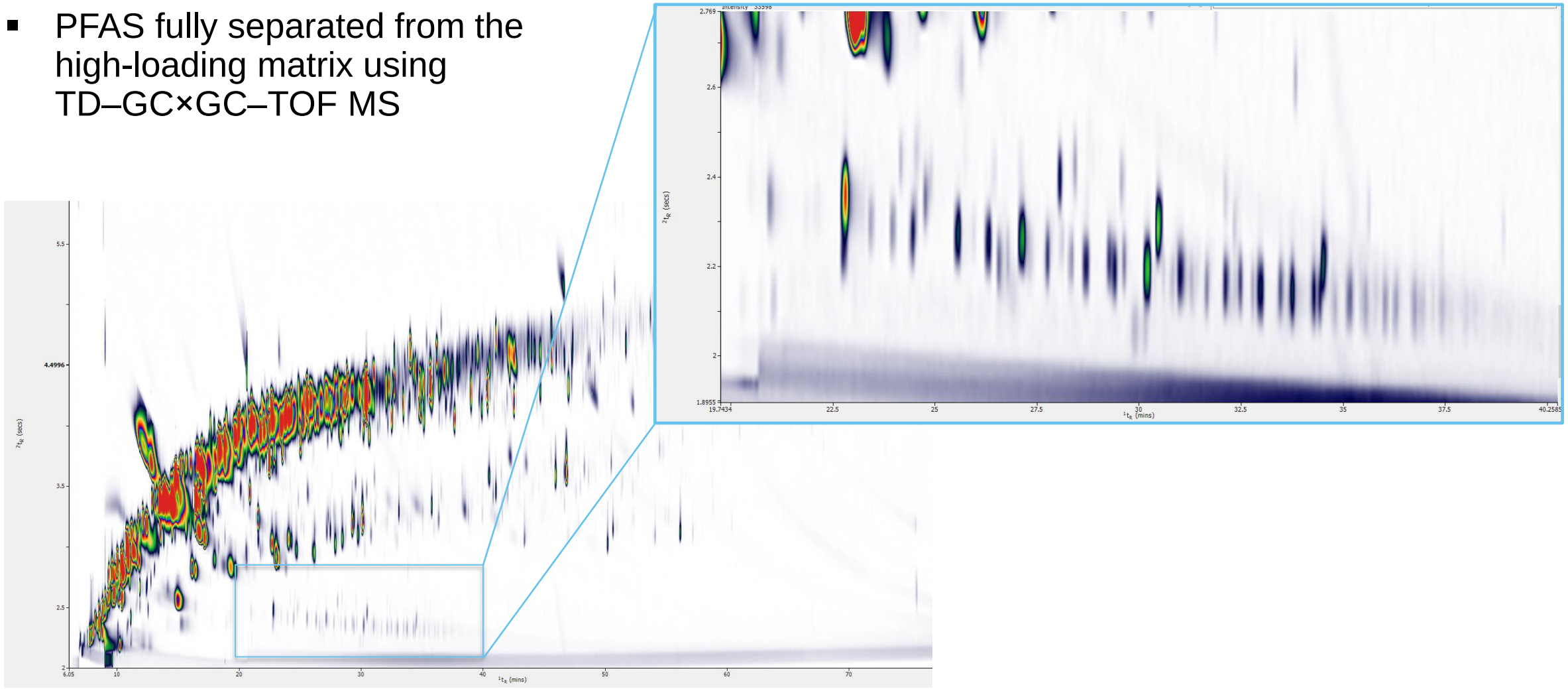
## 800 mL landfill gas sample analysed by TD–GC×GC–TOF MS




- Hundreds of compounds in the sample
- It would be challenging (or impossible) to find trace PFAS by 1D GC

# Using column selectivity to separate PFAS

- PFAS fully separated from the high-loading matrix using TD–GC×GC–TOF MS



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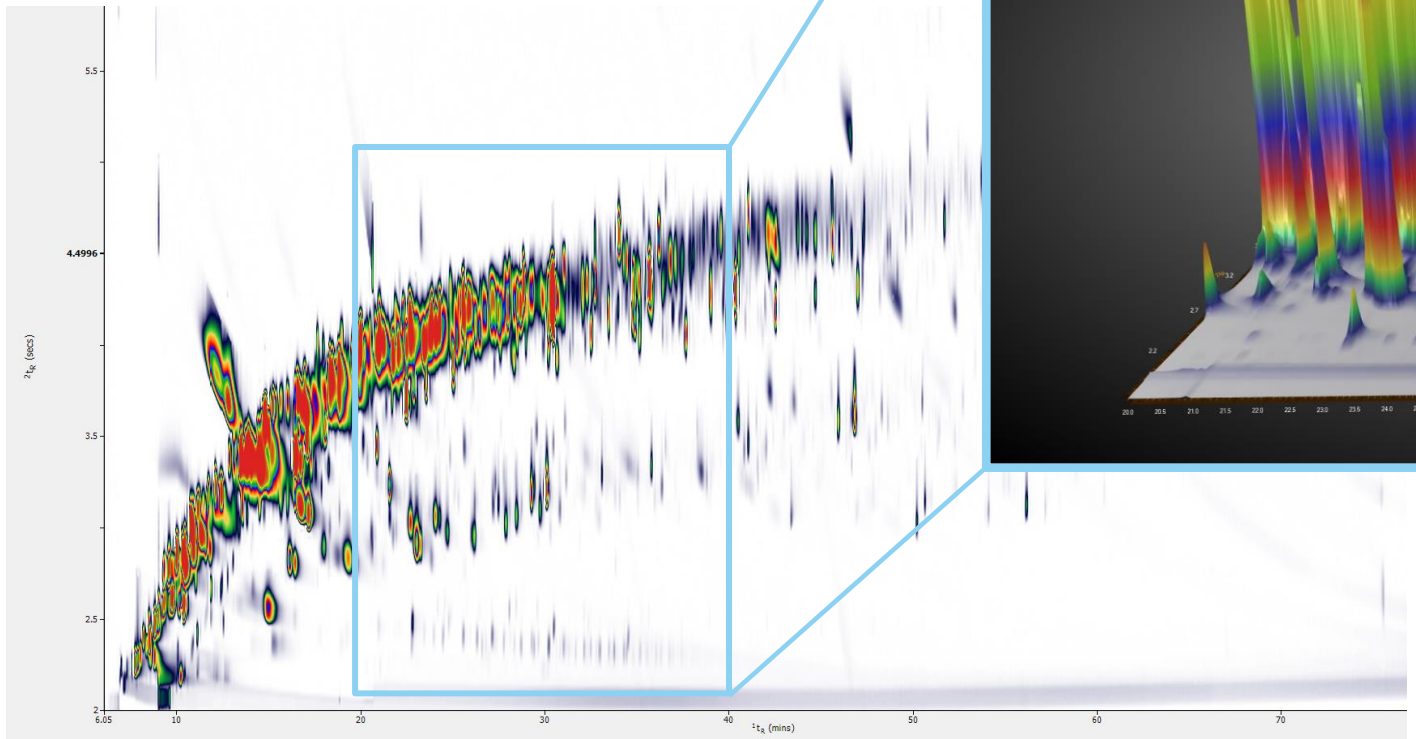
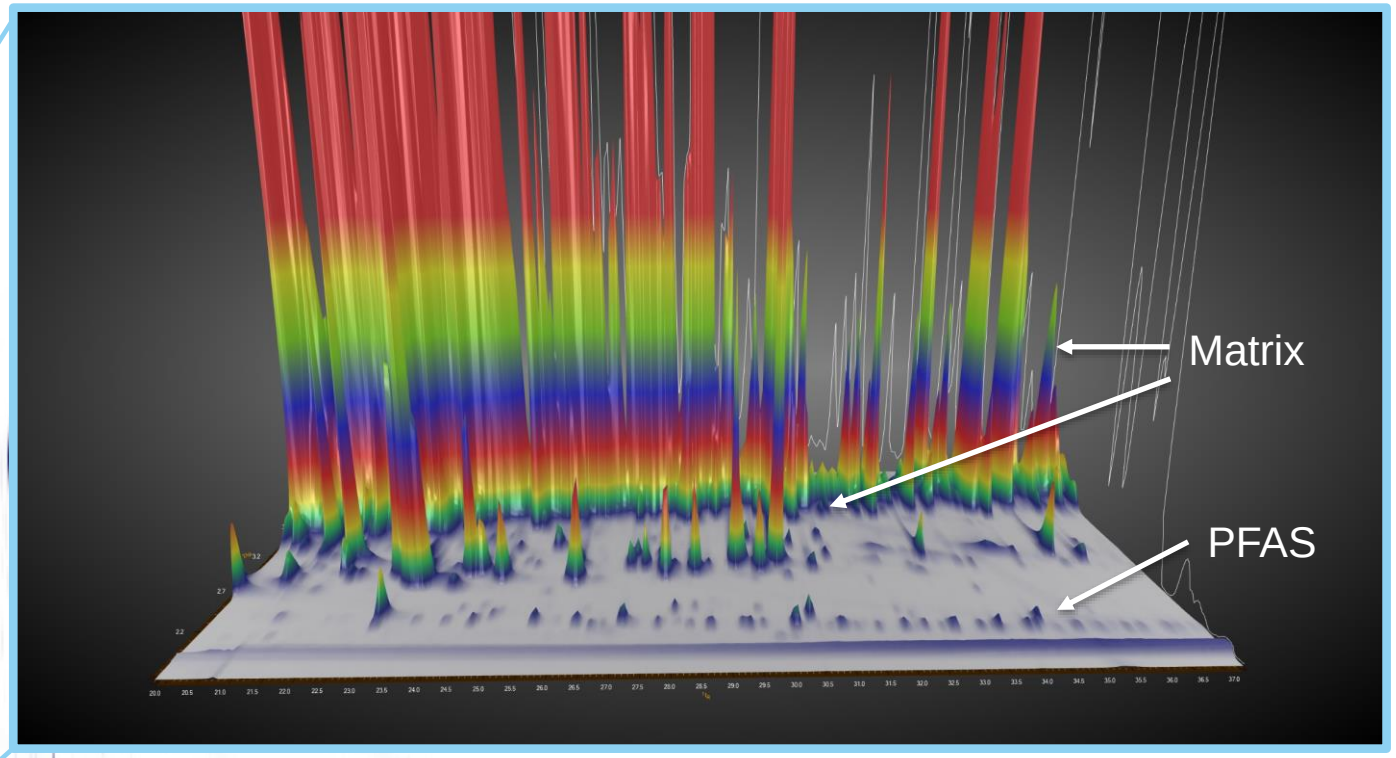
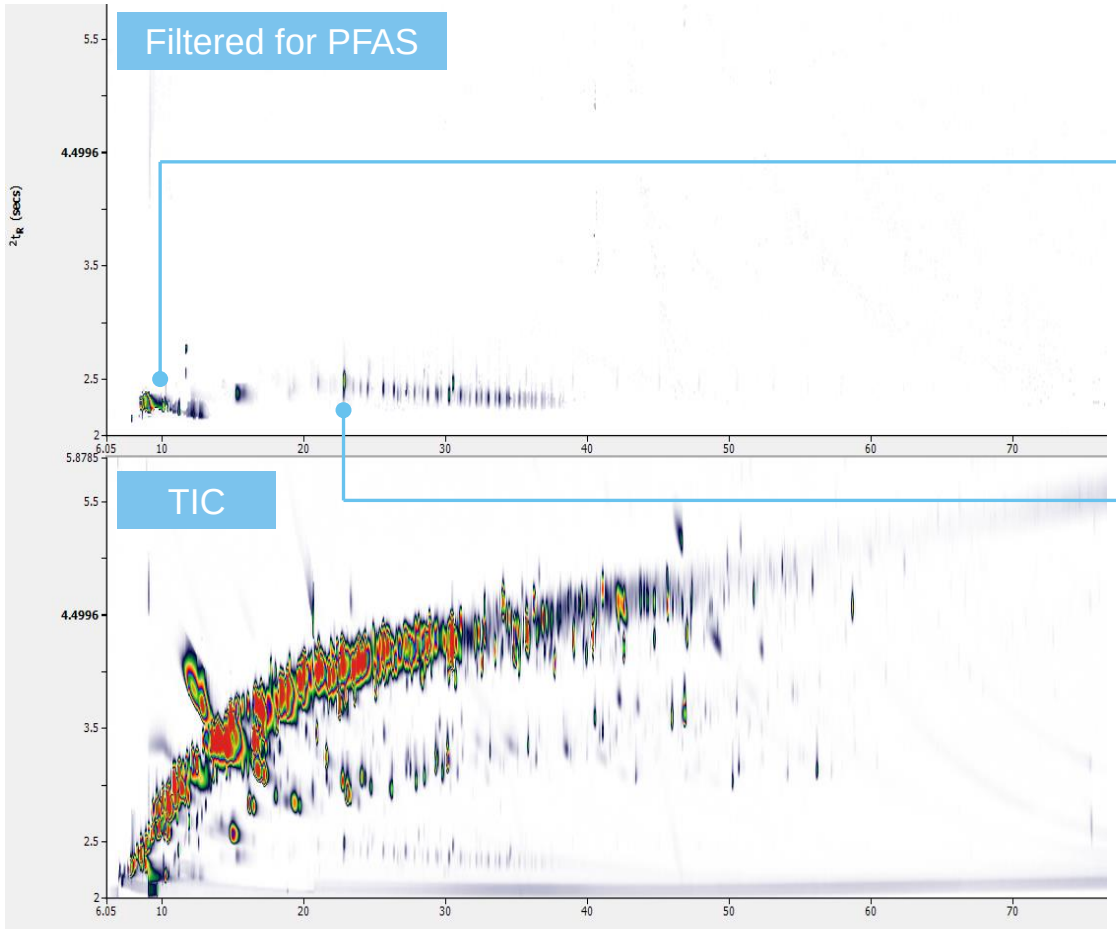
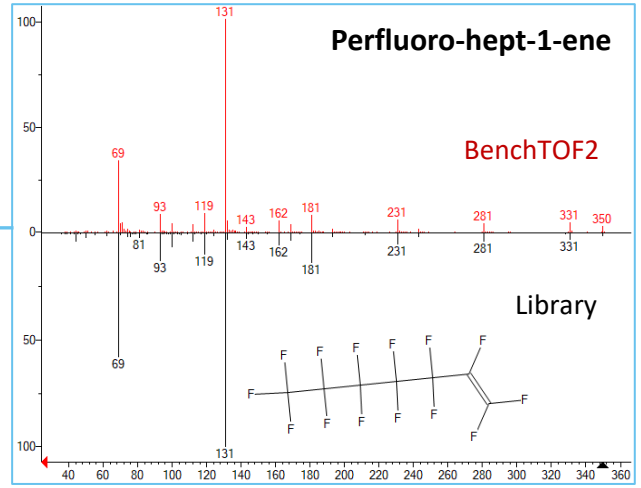


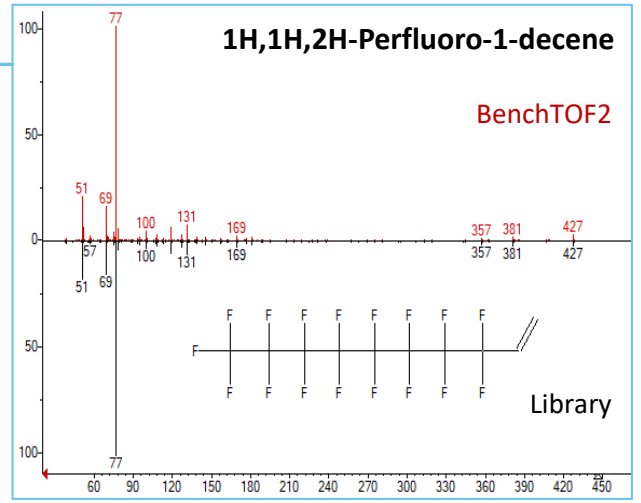



# Non-target screening of PFAS in landfill gas

## Challenge #3: No analytical standards available for the majority of compounds

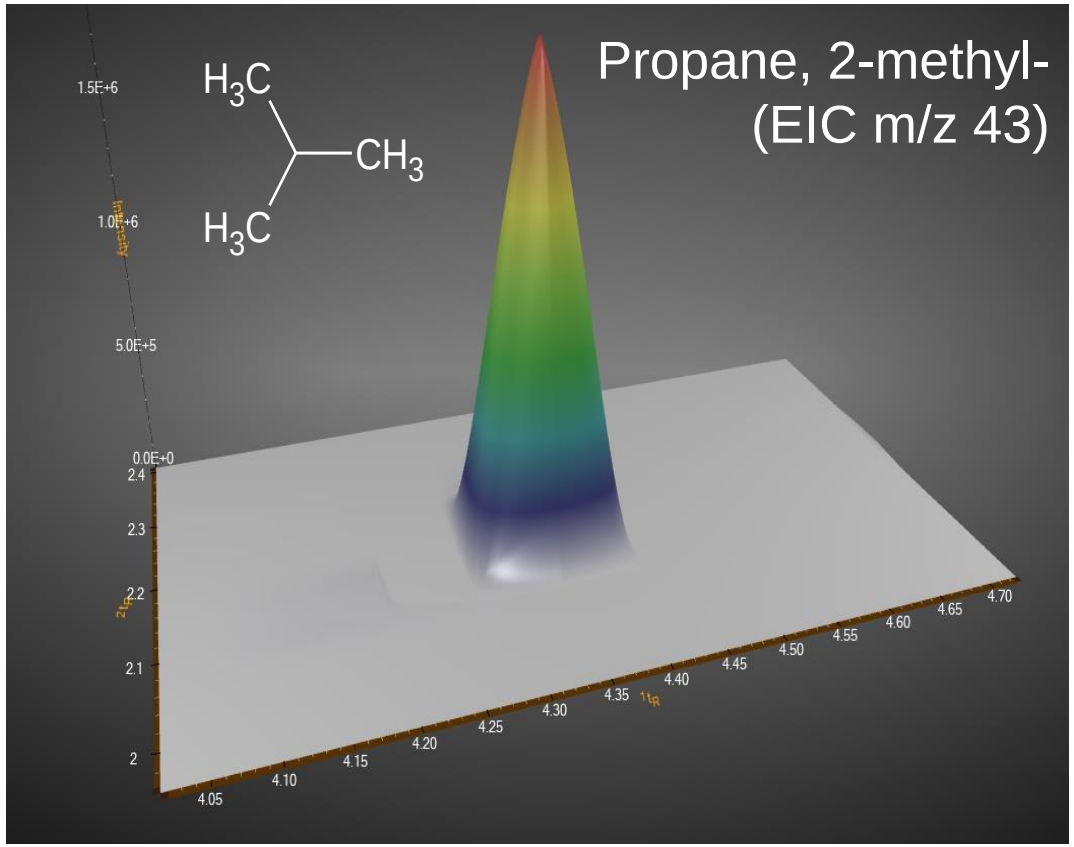


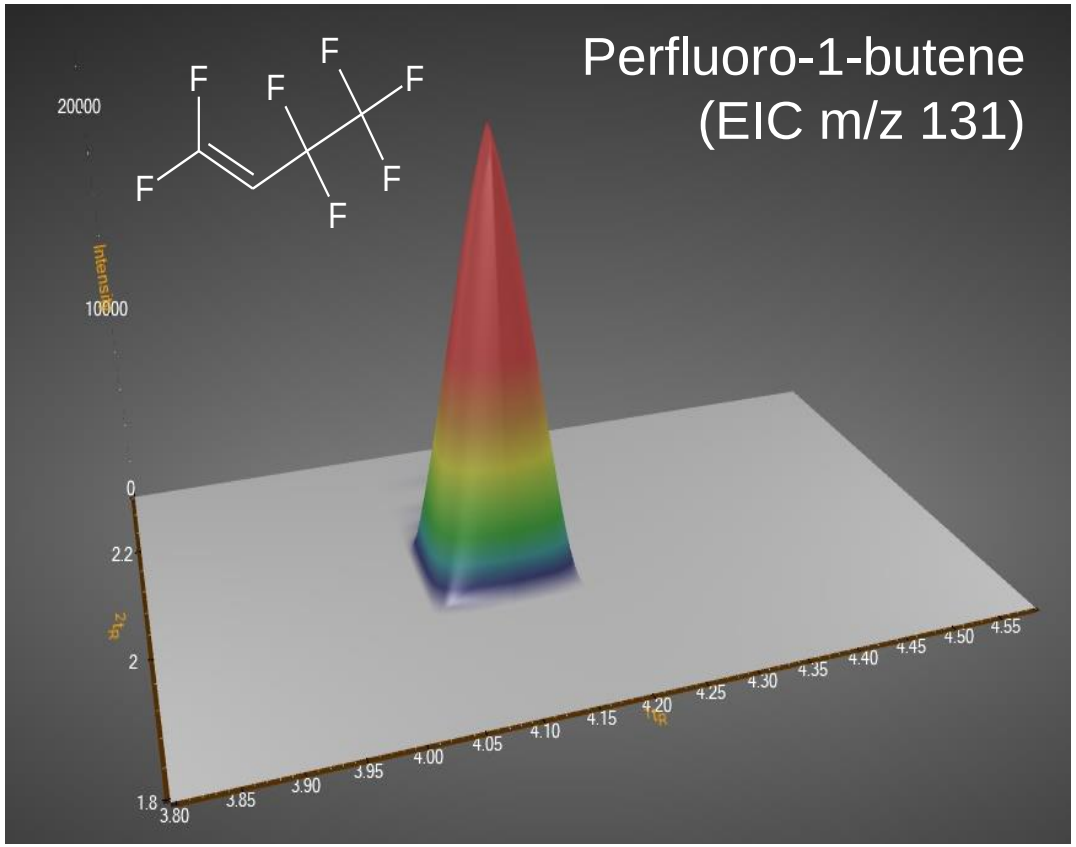




- Filter chromatograms based on spectral characteristics to easily uncover PFAS species
- 98 PF-related compounds were detected

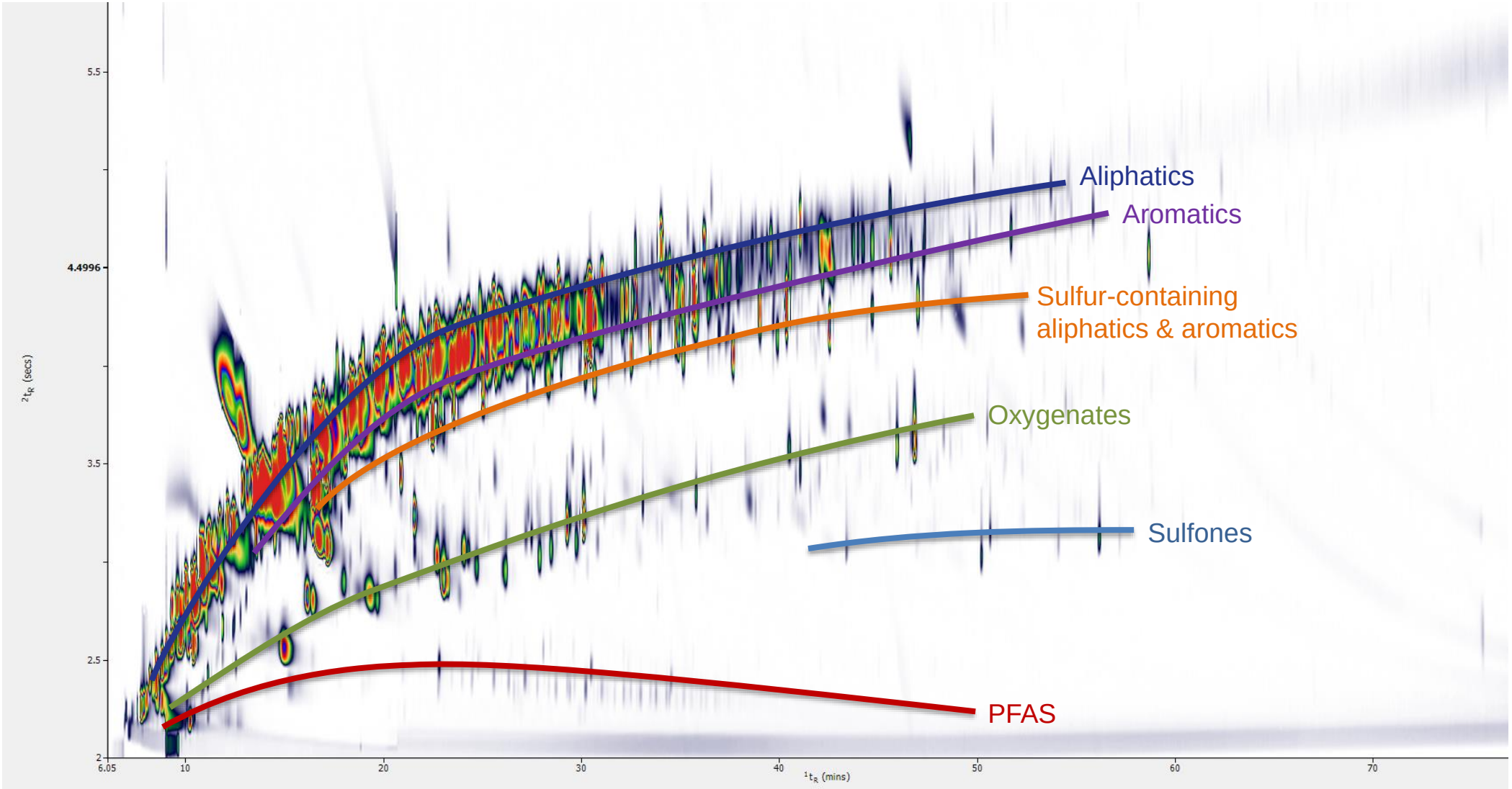
# Efficient modulation of volatiles



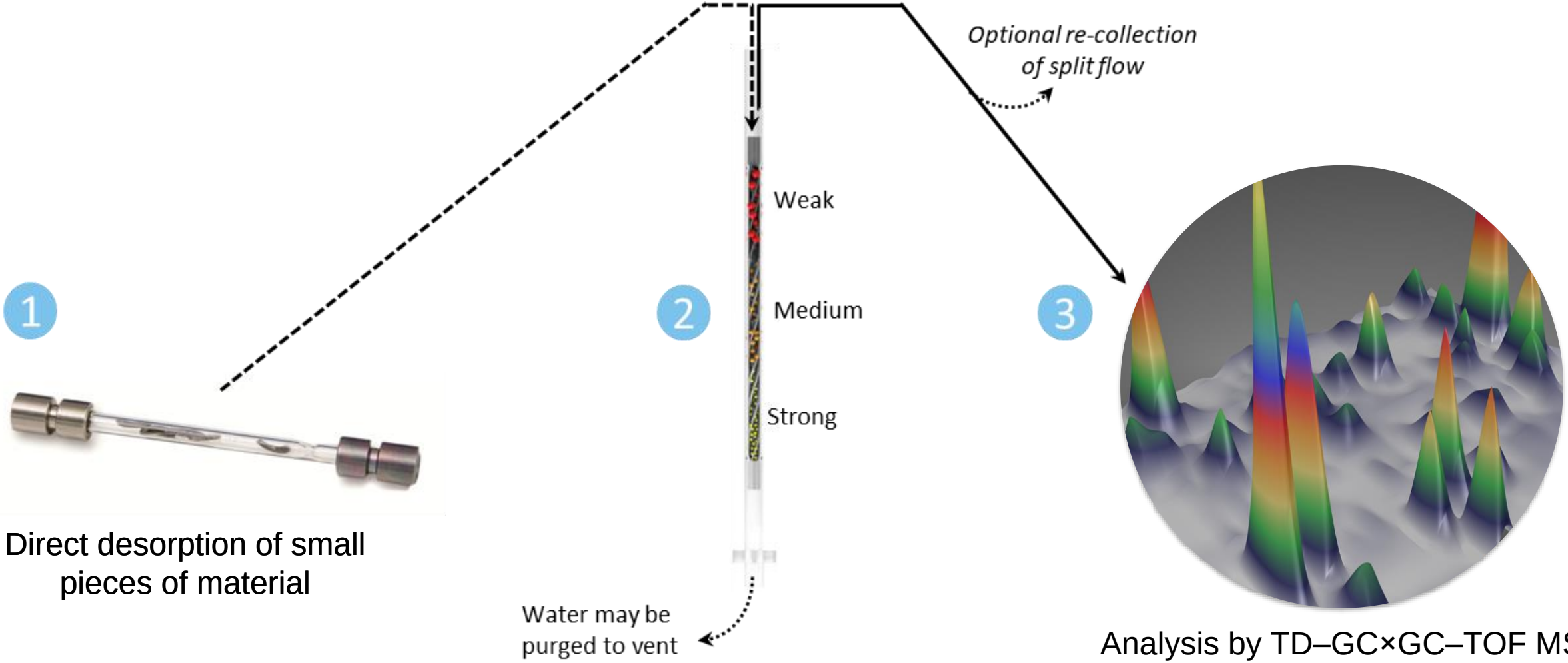

- INSIGHT flow-modulated GC×GC enables efficient modulation of VOCs and SVOCs

# Non-target screening of PFAS and other VOCs of relevance



# Screening PFAS in other complex matrices?

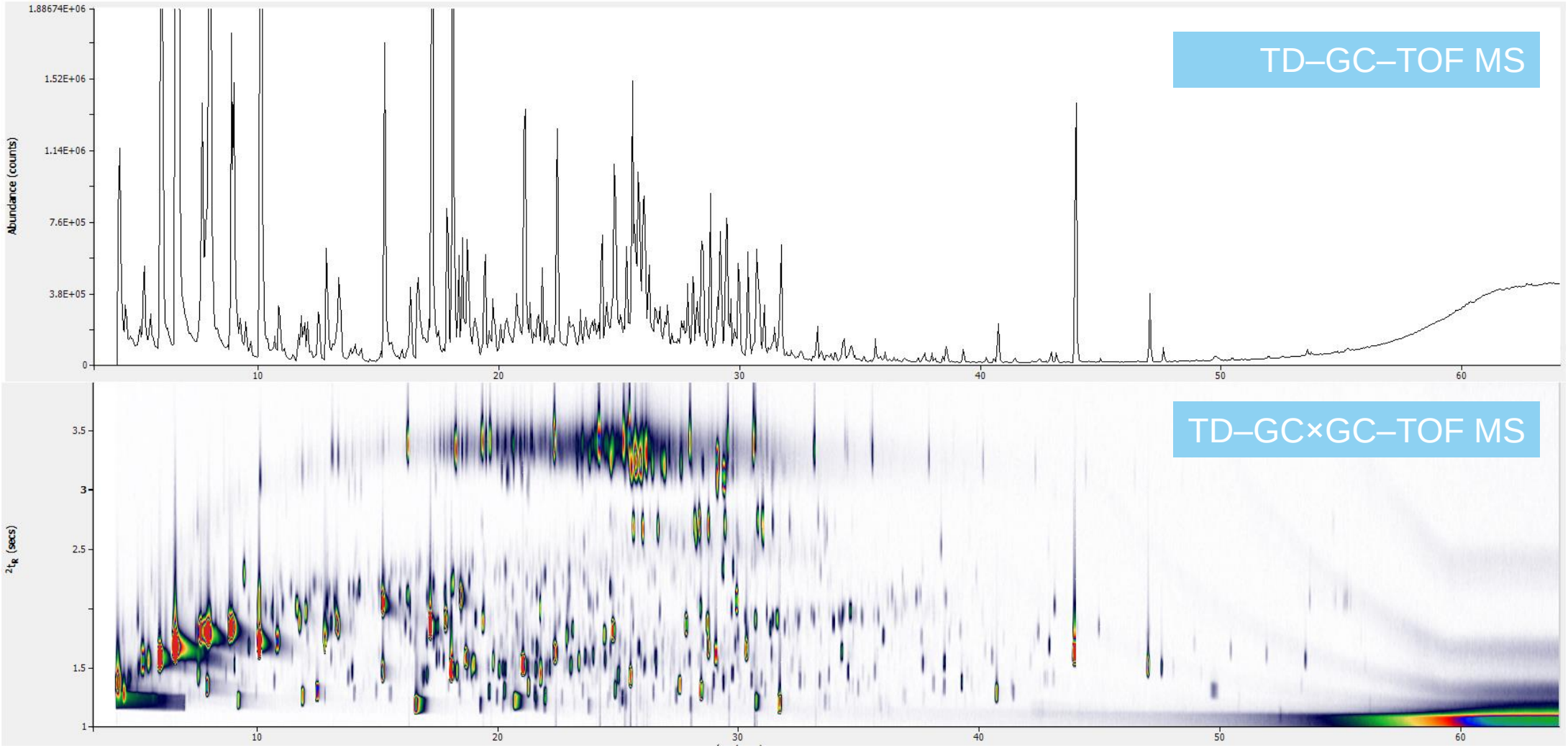
## Understanding PFAS in indoor air




Direct desorption of small pieces of material

Analysis by TD–GC×GC–TOF MS

# Emissions from a composite foam



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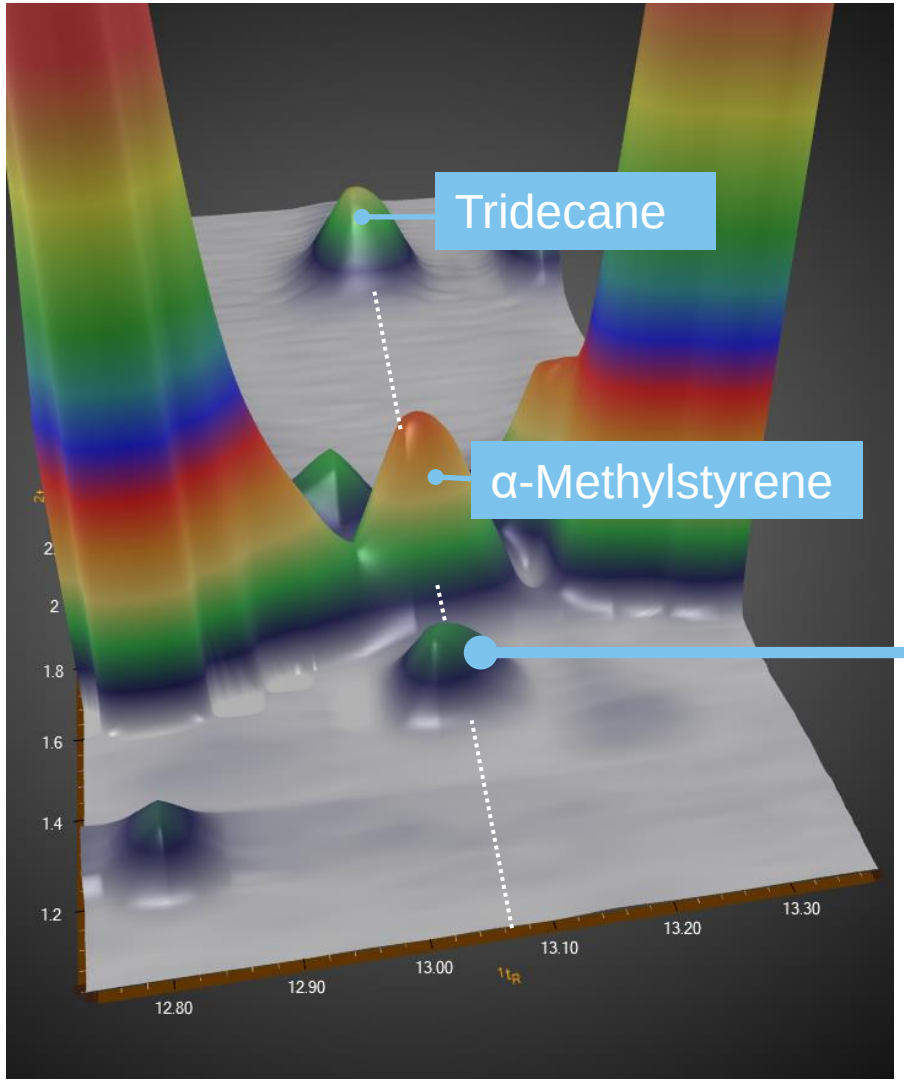
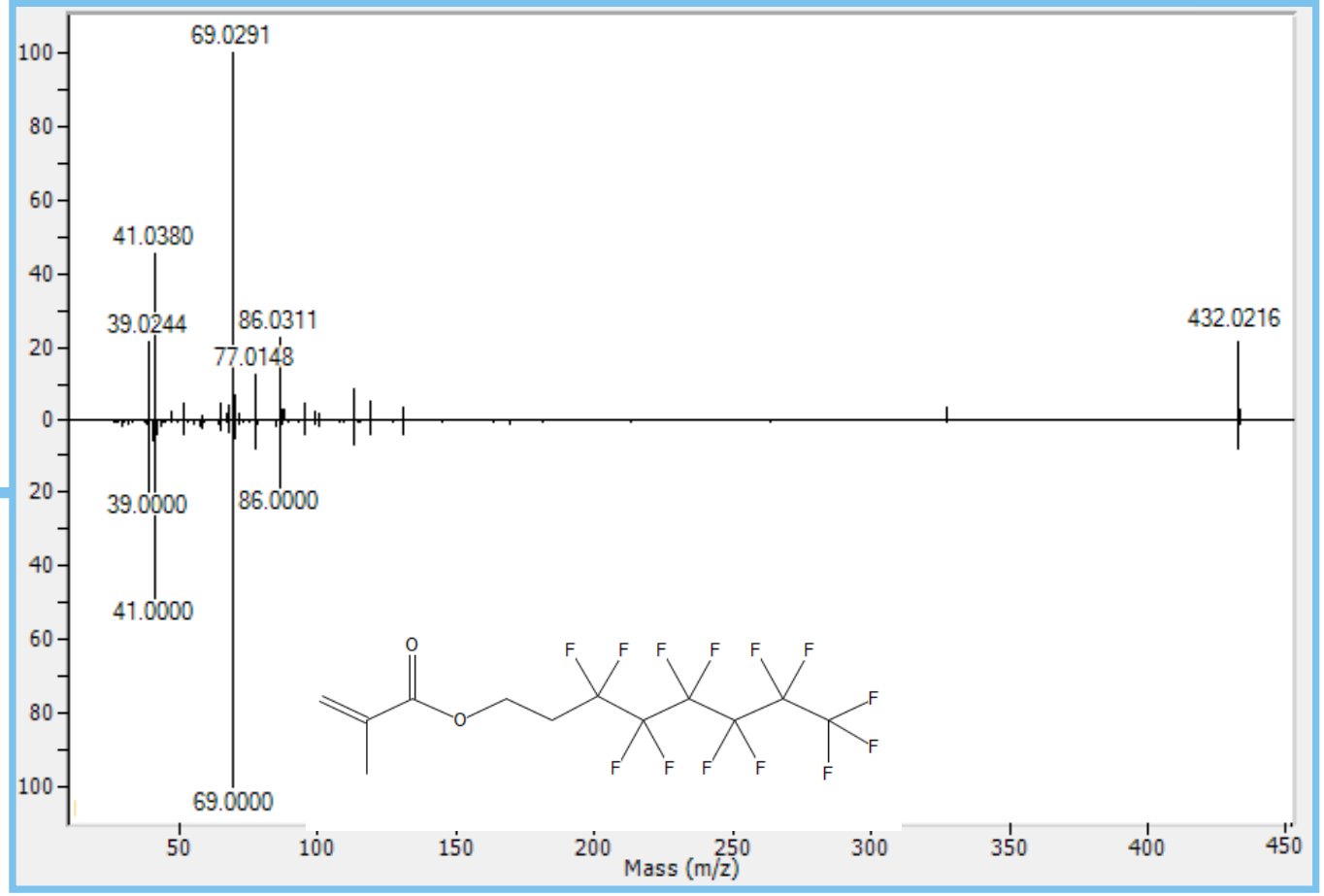



Tridecafluorohexylethyl methacrylate
($C_{12}H_9F_{13}O_2$)

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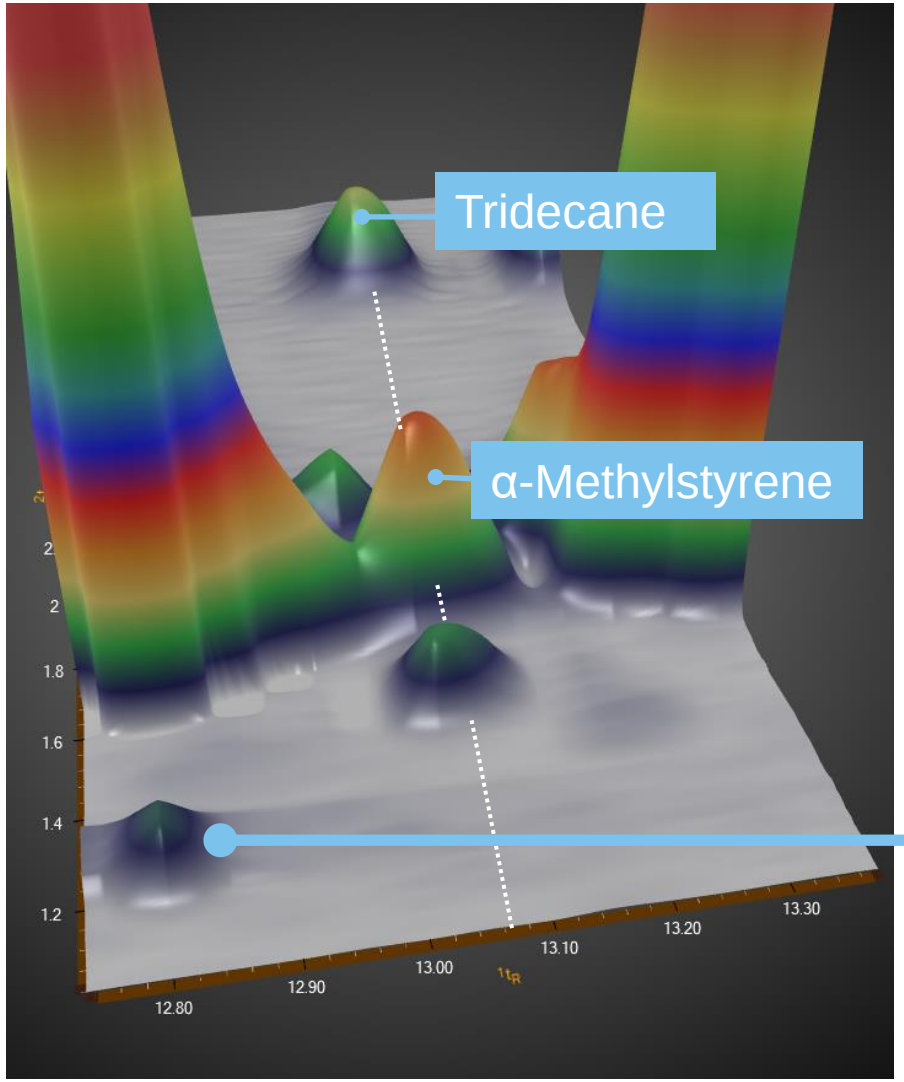
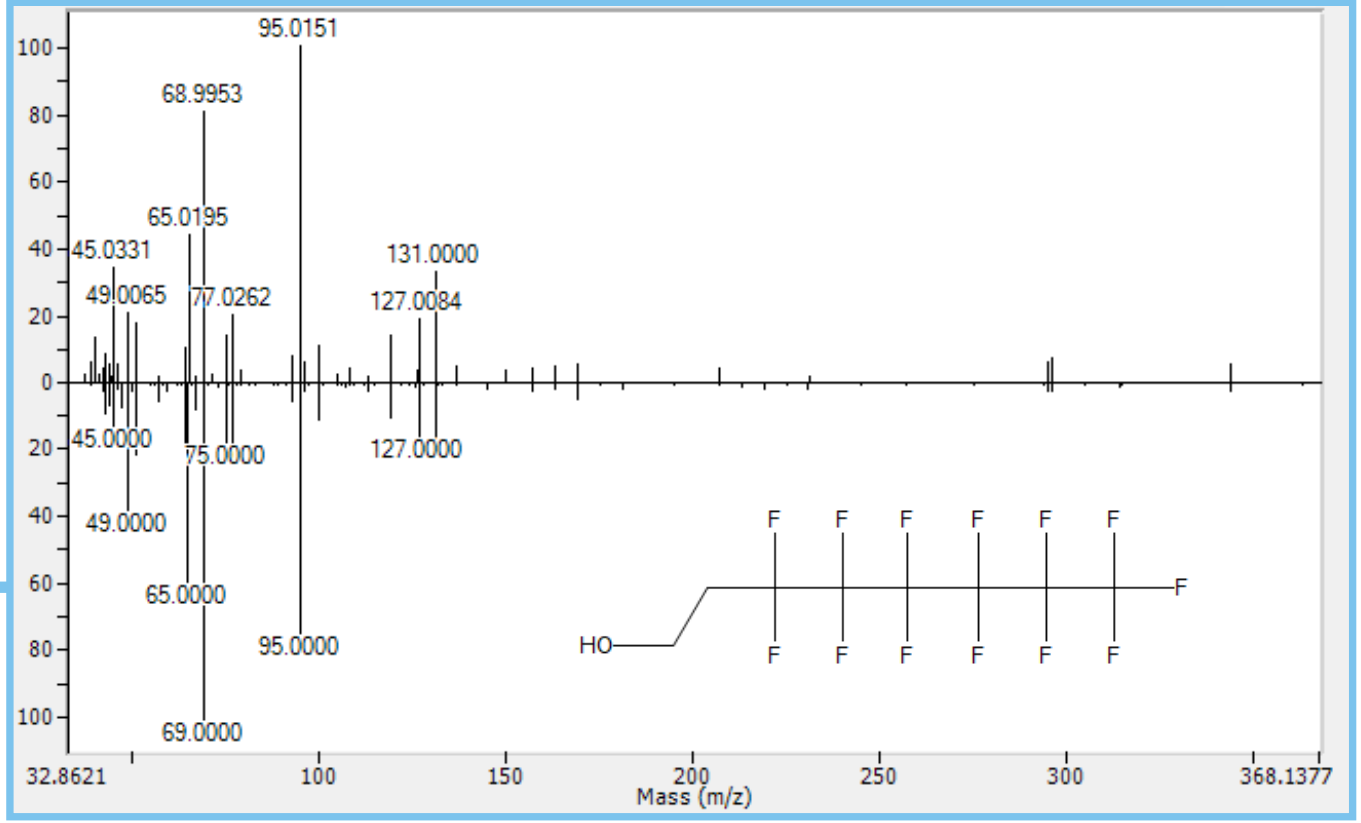



1H,1H,2H,2H-Perfluorooctan-1-ol
($C_8H_5F_{13}O$)



# Summary

- Thermal desorption (TD) provides a robust method for sampling of target and non-target PFAS, as well as other VOCs of relevance
- The flexibility of the sampling technique means that it can be applied to many PFAS-containing matrices
- TD preconcentration of the sample enables ppt-level detection
- Re-collection enables precious samples to be run again
  - Unknowns can be assessed in further detail
  - Samples can be archived for legal reasons
- GC×GC–TOF MS can help to separate PFAS from high-loading matrix for non-target screening applications

## Contact SepSolve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