Finding PFAS in a haystack: Analytical tools to identify trace PFAS in complex matrices

Matthew Edwards
Business Development, Americas (SepSolve Analytical)

Who is SepSolve Analytical?

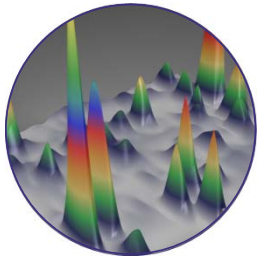
Experts in analytical chemistry

SCHAUENBURG Analytics

MARKES international

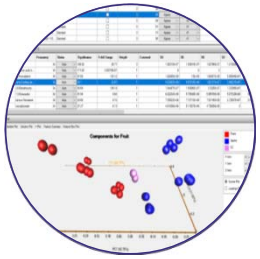
Sample preparation

SepSolve Analytical



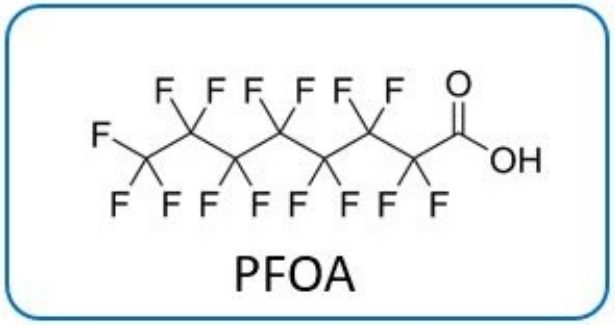
Separation

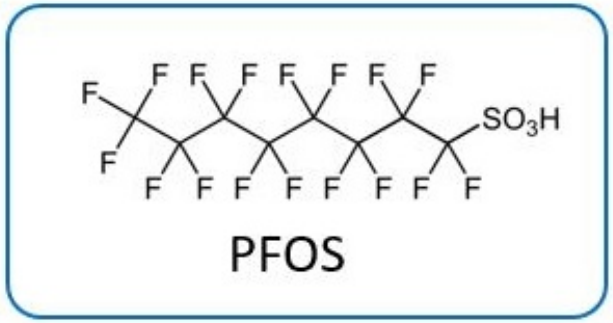
Identification

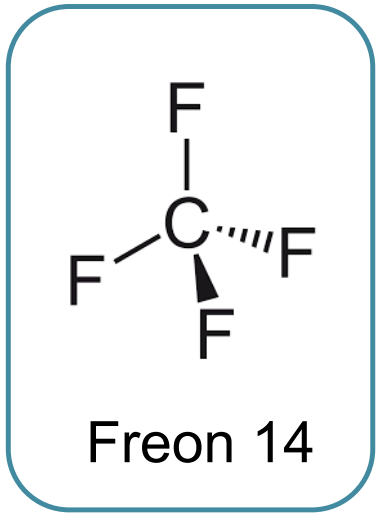


Data analysis

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aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents… have been replaced by fluorine (F) atoms"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

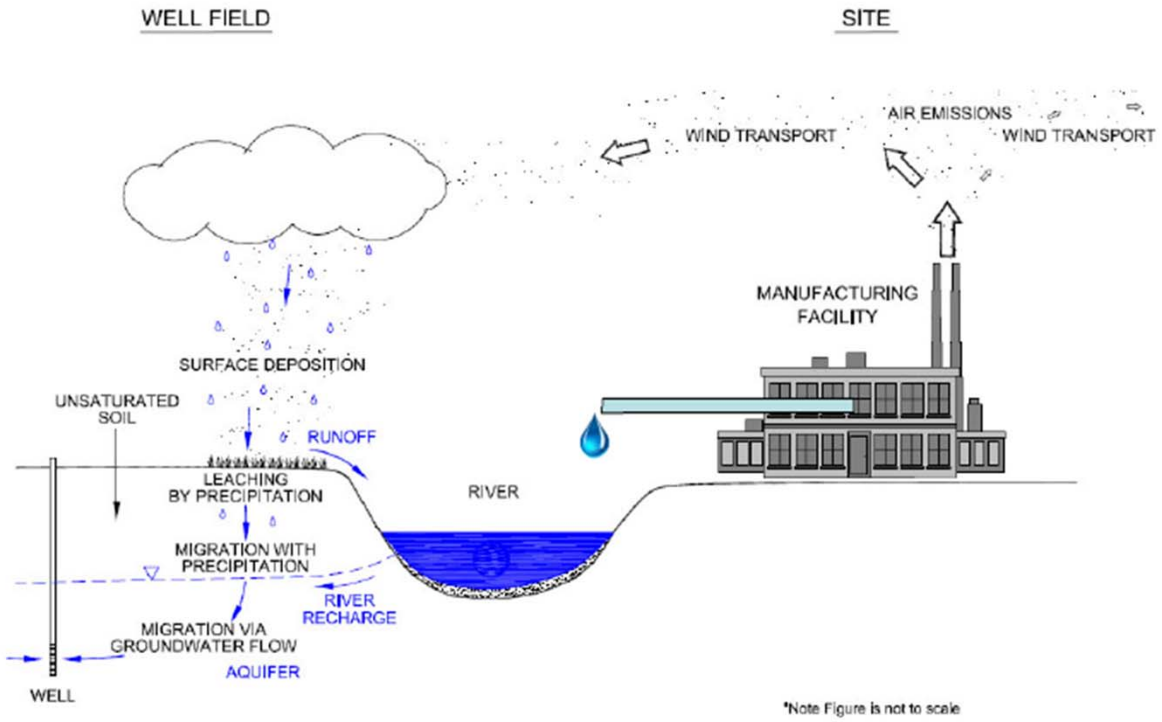
Environmental occurrence

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

How are PFAS currently measured?

- There are no set methods specifically for analysis of PFAS in air

- Modified or heavily modified methods are being investigated, but no one ‘catch all’ is available
  - Many labs use sorbents with solvent extraction and then LC

- Type of sampling depends on a number of factors such as:
  - Compound range
  - Sensitivity required
  - Matrix/potential interferents




Challenges of PFAS monitoring

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

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

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

Challenges of PFAS analysis

Challenge #1: Wide range of chemicals

- GC based methods:
  - Perfect for analysing the **volatile PFAS** species – key groups include the fluorotelomers
  - Struggles with some of the ionic species

- LC based methods:
  - Great for non-volatile
  - Struggle with volatile species with chain lengths below C_8 and certain classes like fluorotelomer alcohols

- No single method can analyse all PFAS compounds

Air sampling techniques

1 Particulate sampling

A **Direct desorption of filters**

2 Gas phase sampling

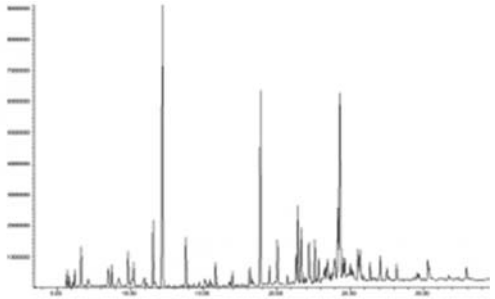
A **Pumped sampling onto sorbent tubes**

B **Passive sampling onto sorbent tubes**

C **Canisters and bags**

D **On-line monitoring**

Thermal desorption (TD)

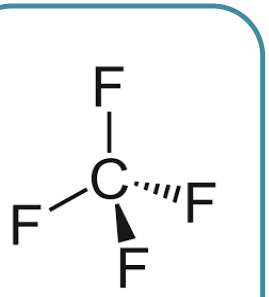


GC–MS

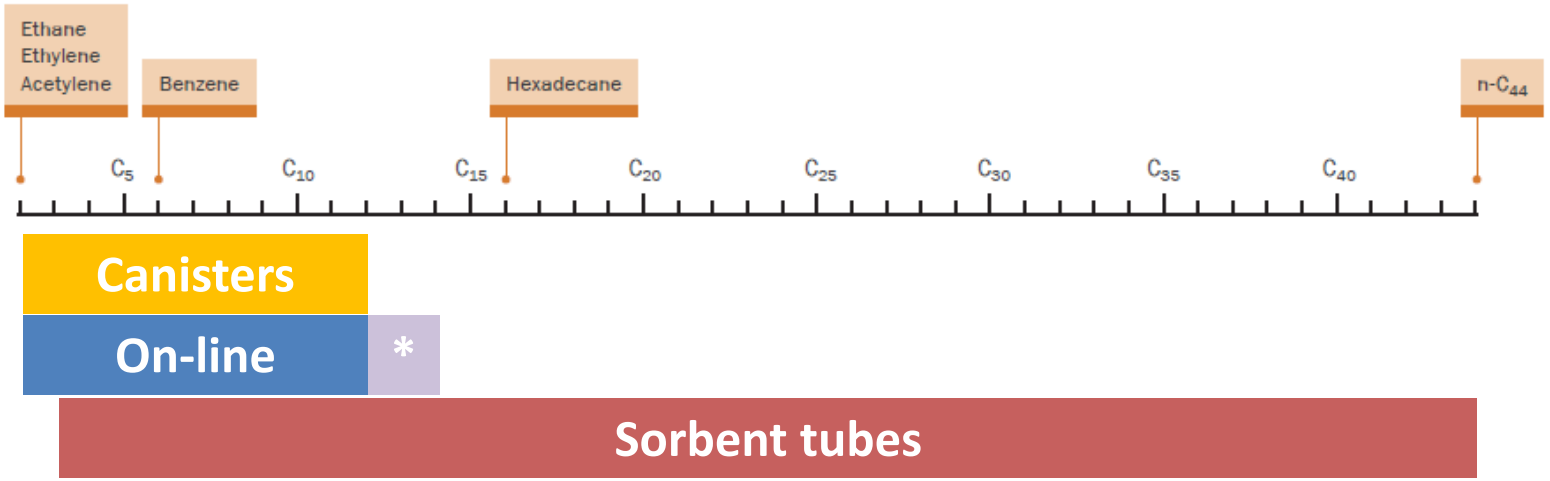
Why use thermal desorption for PFAS analysis?

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



What is thermal desorption?

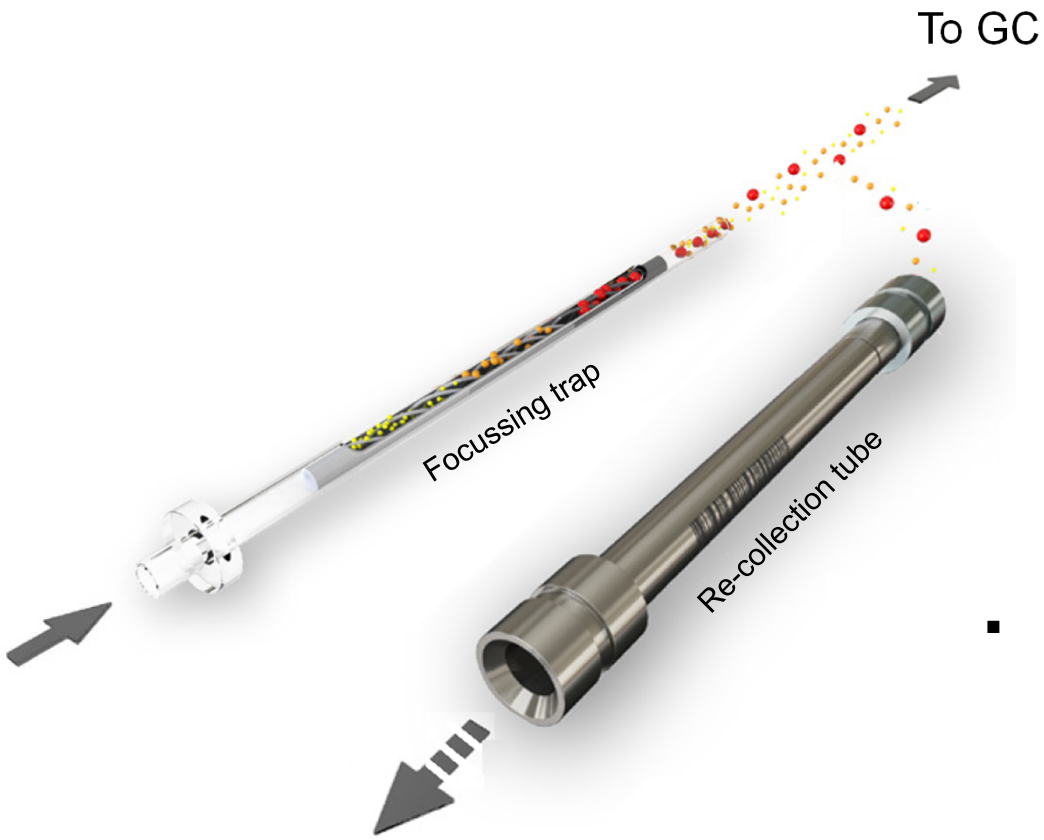
- Sample tube heated in flow of carrier gas
- Analytes swept onto an electrically cooled focusing trap (held between ambient and –30 °C)
- Focusing trap can be packed with multiple sorbents to retain target and non-target compounds

What is thermal desorption?

Why re-collection?

- ✓ Method validation
- ✓ Samples can be run on a different detector
- ✓ Hi/Lo analysis – removes risk of contamination
- ✓ Sample storage

What is thermal desorption?



- 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.

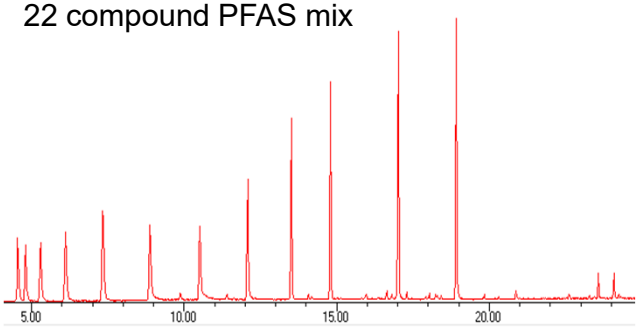
Why is this flexibility particularly important?

Challenge #1: Wide range of chemicals

Tube methodology

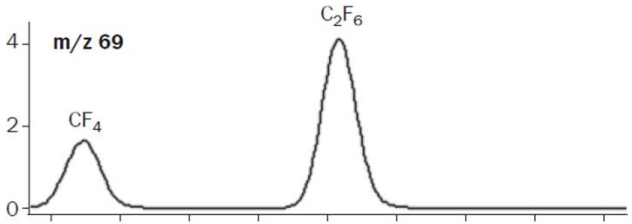
- PFAS and other VOCs
- B.P. -50 °C – 550 °C

22 compound PFAS mix



Canister/Bag methodology

- PFAS (CFCs) and other VOCs
- B.P. -130 °C – 220 °C

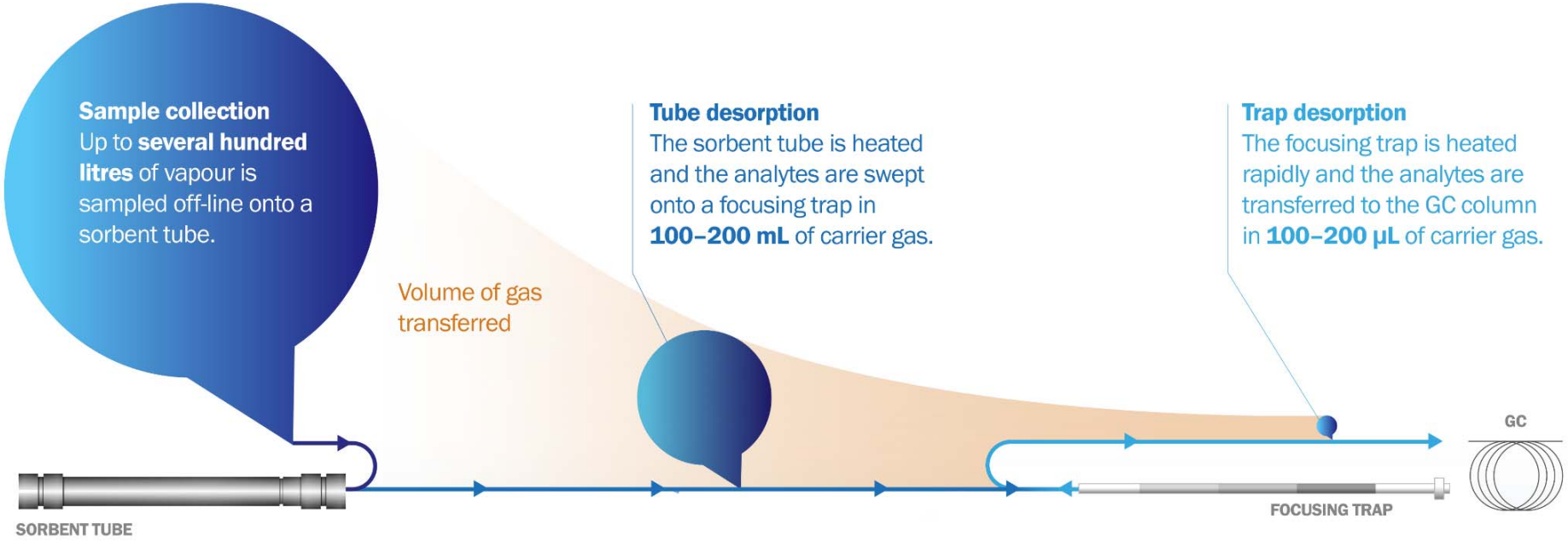


- For PFAS and PFAS breakdown products a combination approach is sometimes required

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 (ppt)
- TD is a preconcentration technique capable of analysing ppt 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?

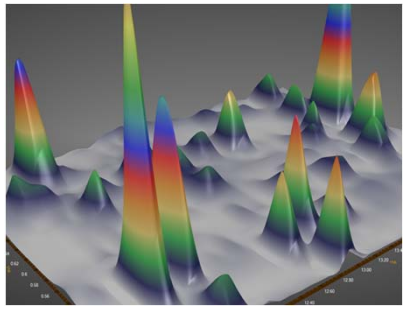
Challenge #2: Concentration levels within the environment

- PFAS species detected at 100s fg/L (pg/m^3) in some samples
- Sample matrix could be at µg/L or higher

Solution?

Thermal desorption (TD)

+

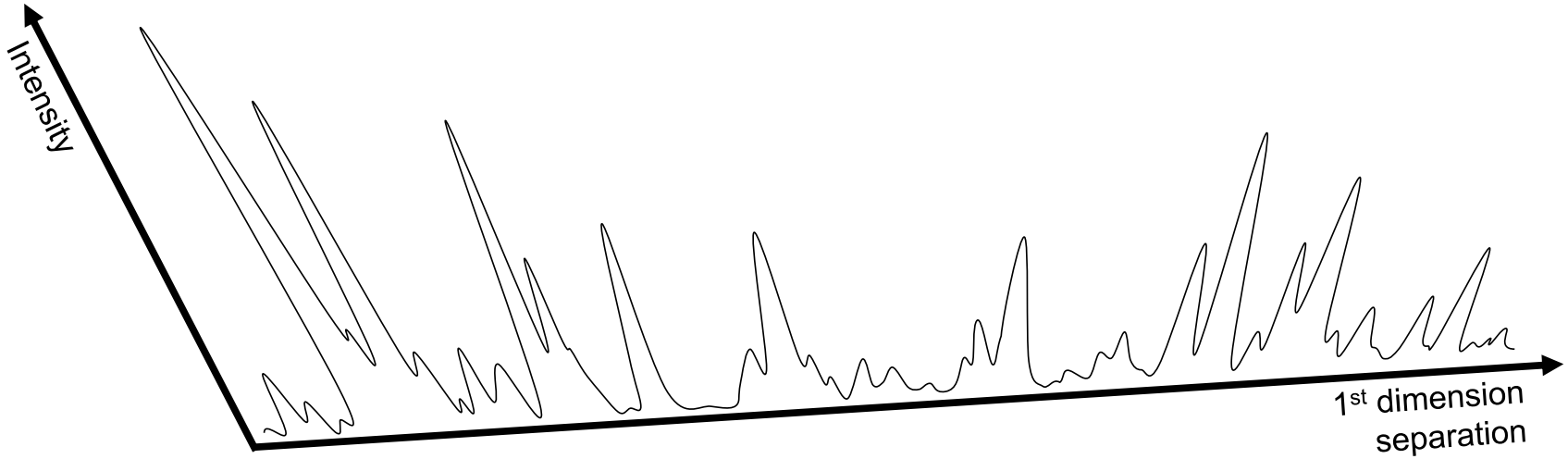


Comprehensive two-dimensional GC (GC×GC)

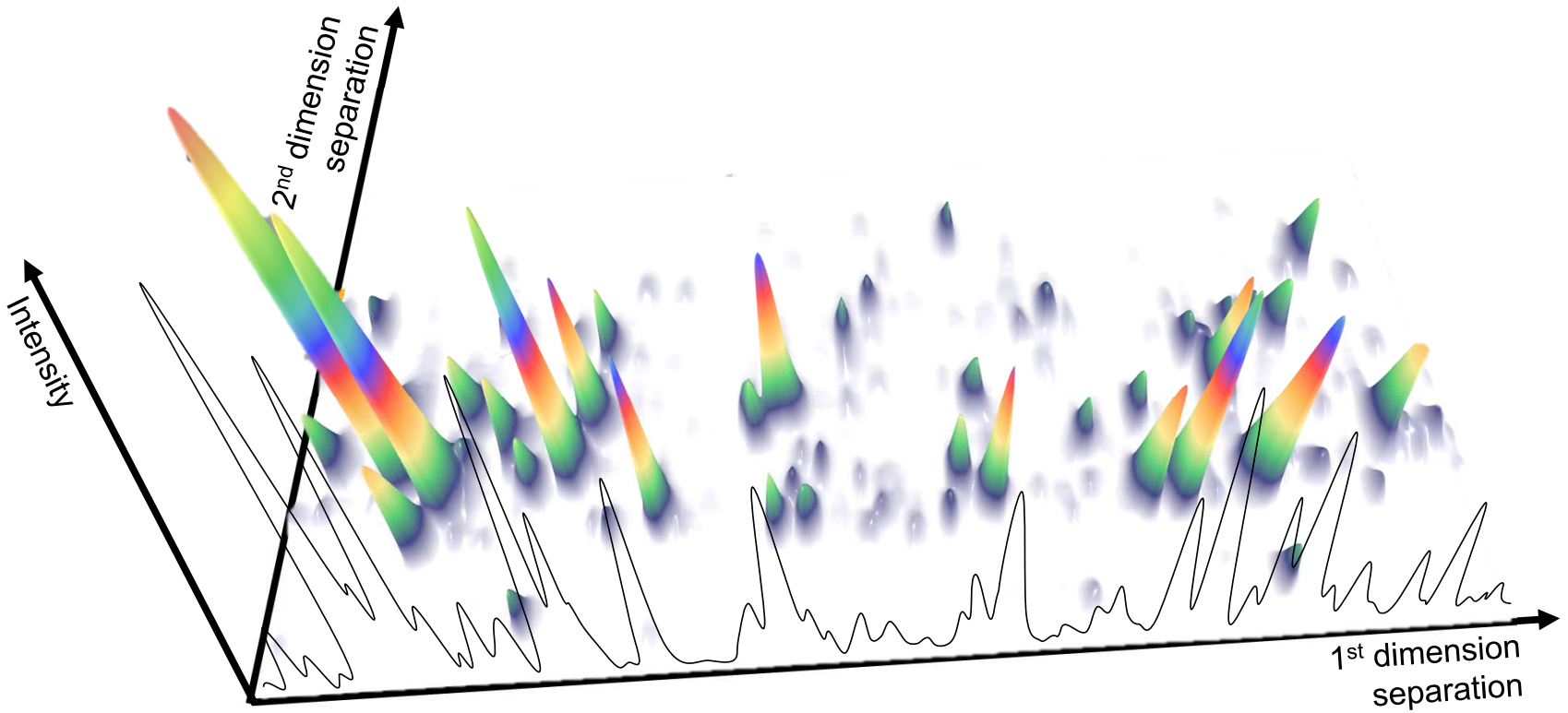
+

Time-of-flight mass spectrometry (TOF MS)

What is GC×GC?

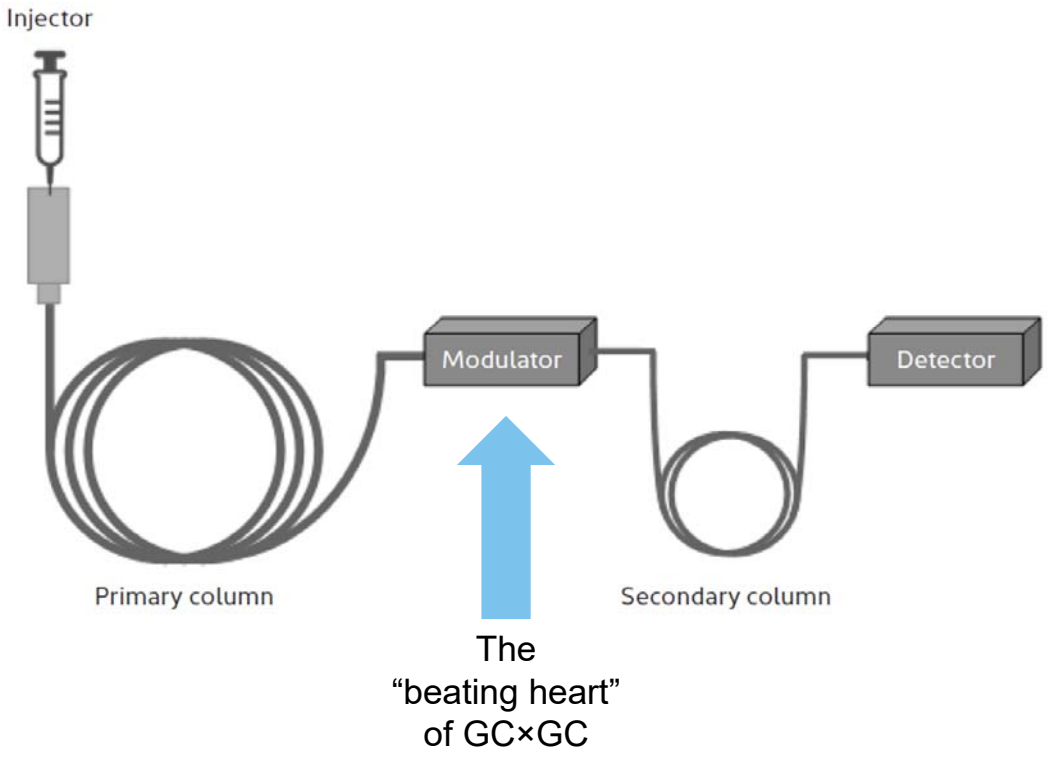


What is GC×GC?


2nd dimension separation
Intensity
1st dimension separation

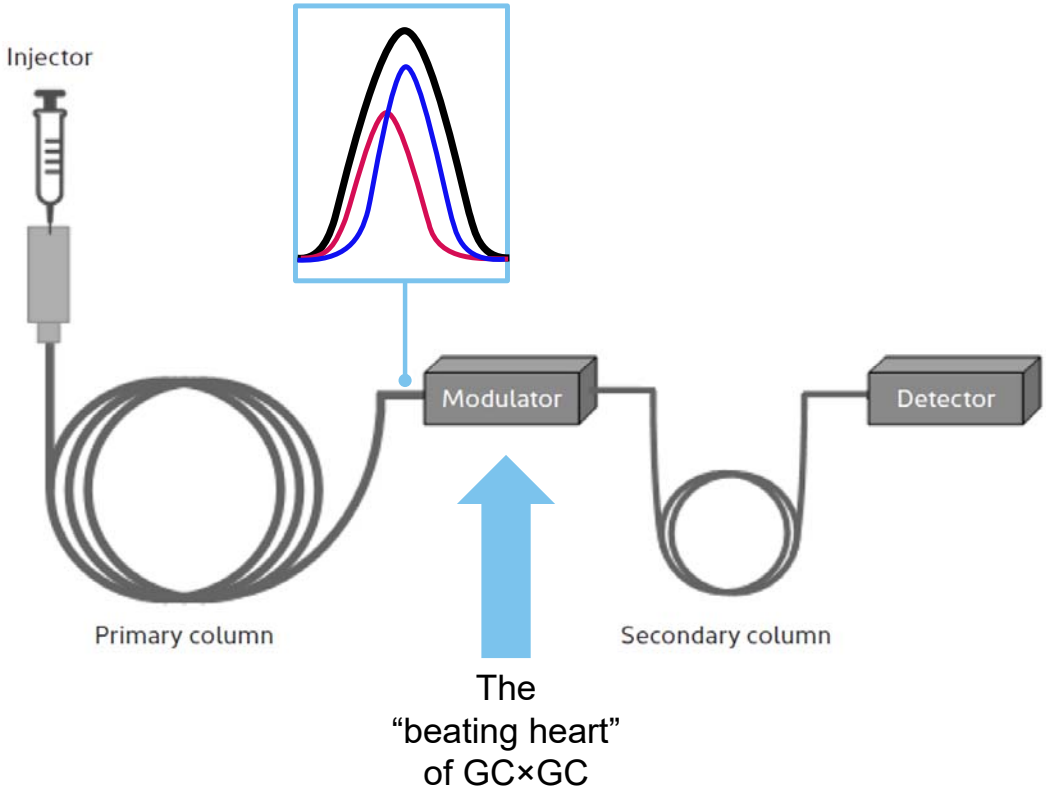
How does GC×GC work?

Analytical system



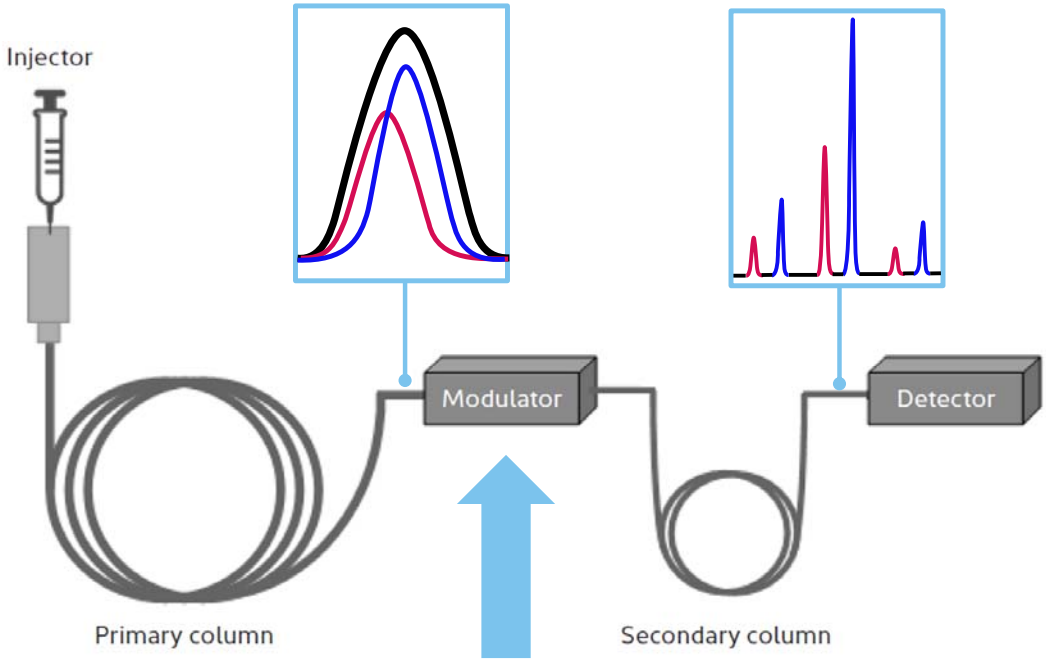
How does GC×GC work?

Analytical system

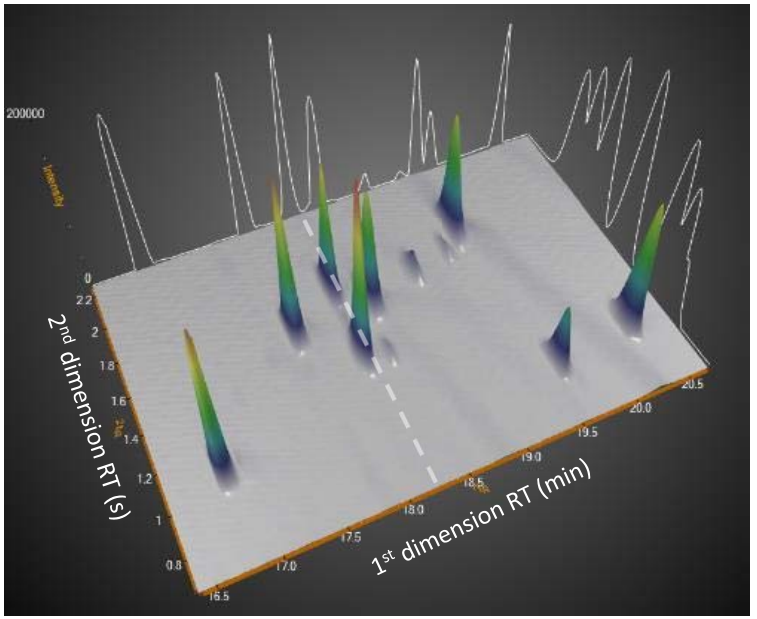


How does GC×GC work?

Analytical system



The
“beating heart”
of GC×GC

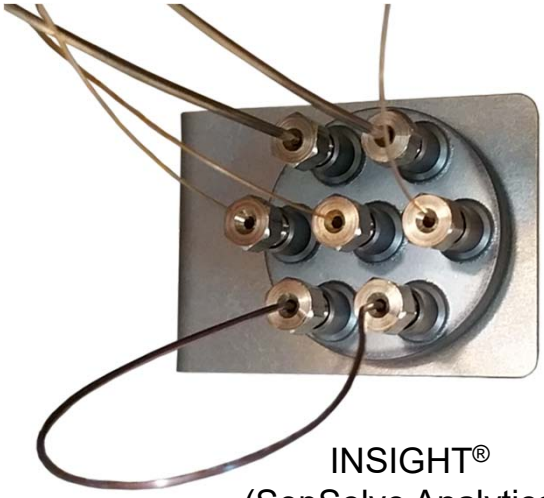


Benefits of flow modulation

- Consumable-free operation
  - Low running costs

- Efficient modulation of volatiles
  - Essential for analysis of volatile PFAS

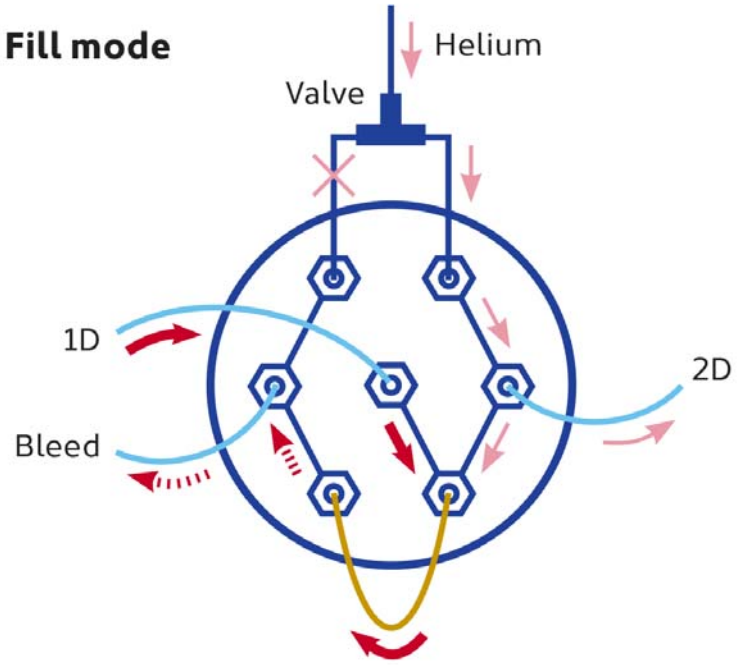
- Excellent repeatability
  - For routine analyses and large sample batches



INSIGHT®
(SepSolve Analytical)

Reverse fill/flush flow modulation

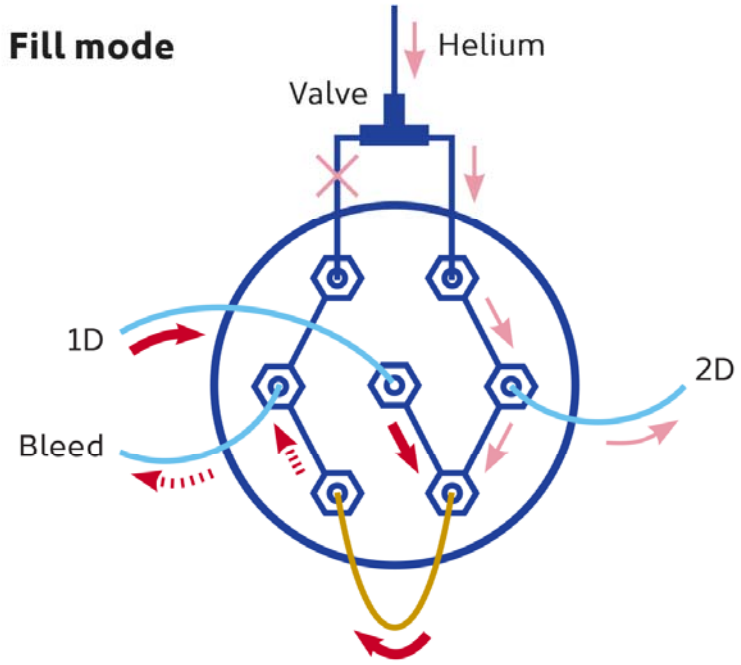
How does it work?

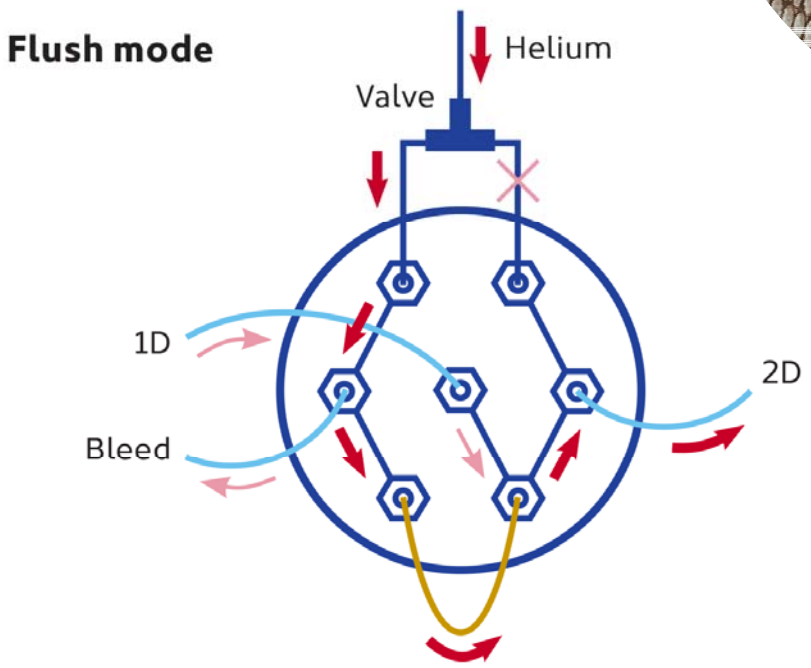


Further reading: Griffith et al, J. Chromatogr. A, 1226 (2012) 116– 123

Reverse fill/flush flow modulation

How does it work?

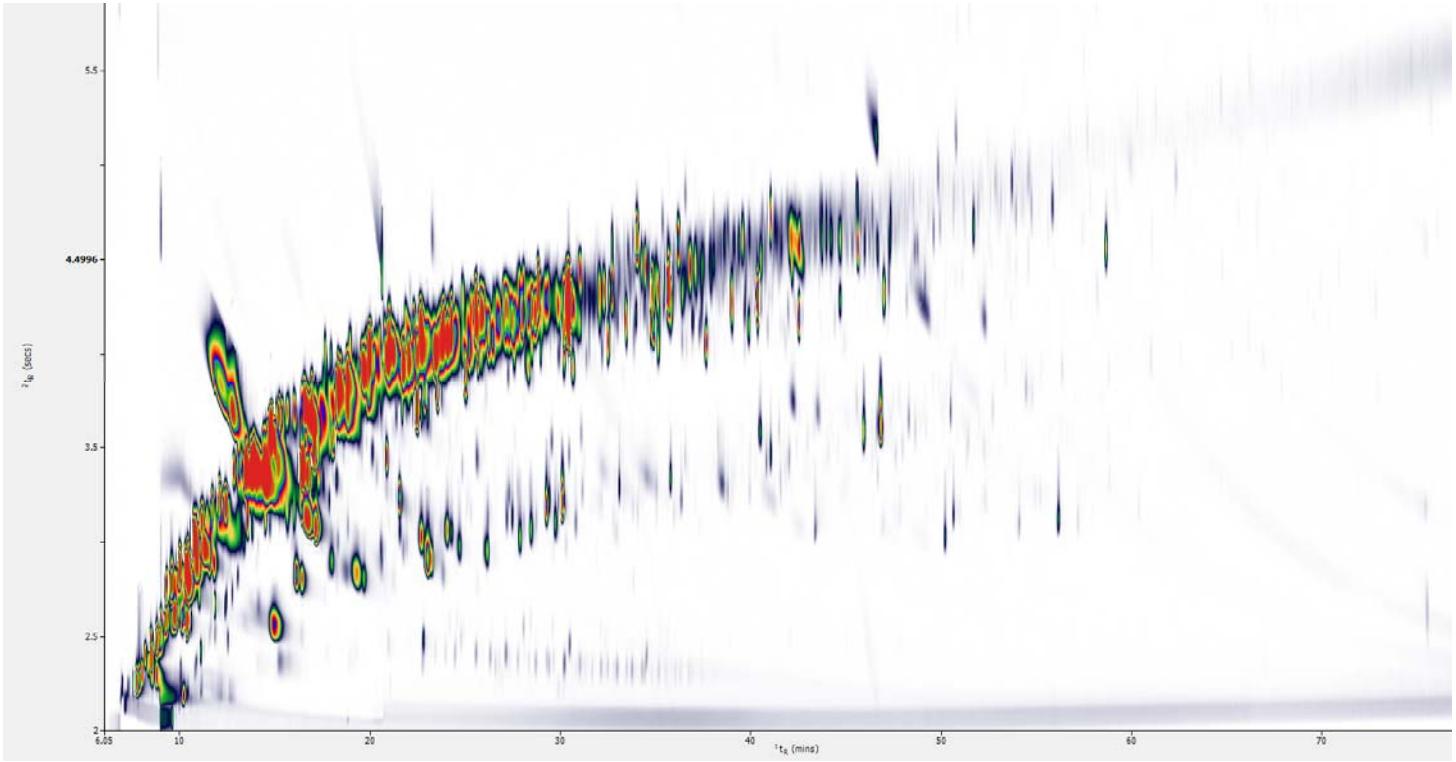




Further reading: Griffith et al, J. Chromatogr. A, 1226 (2012) 116– 123

Landfill gas is an extremely complex matrix

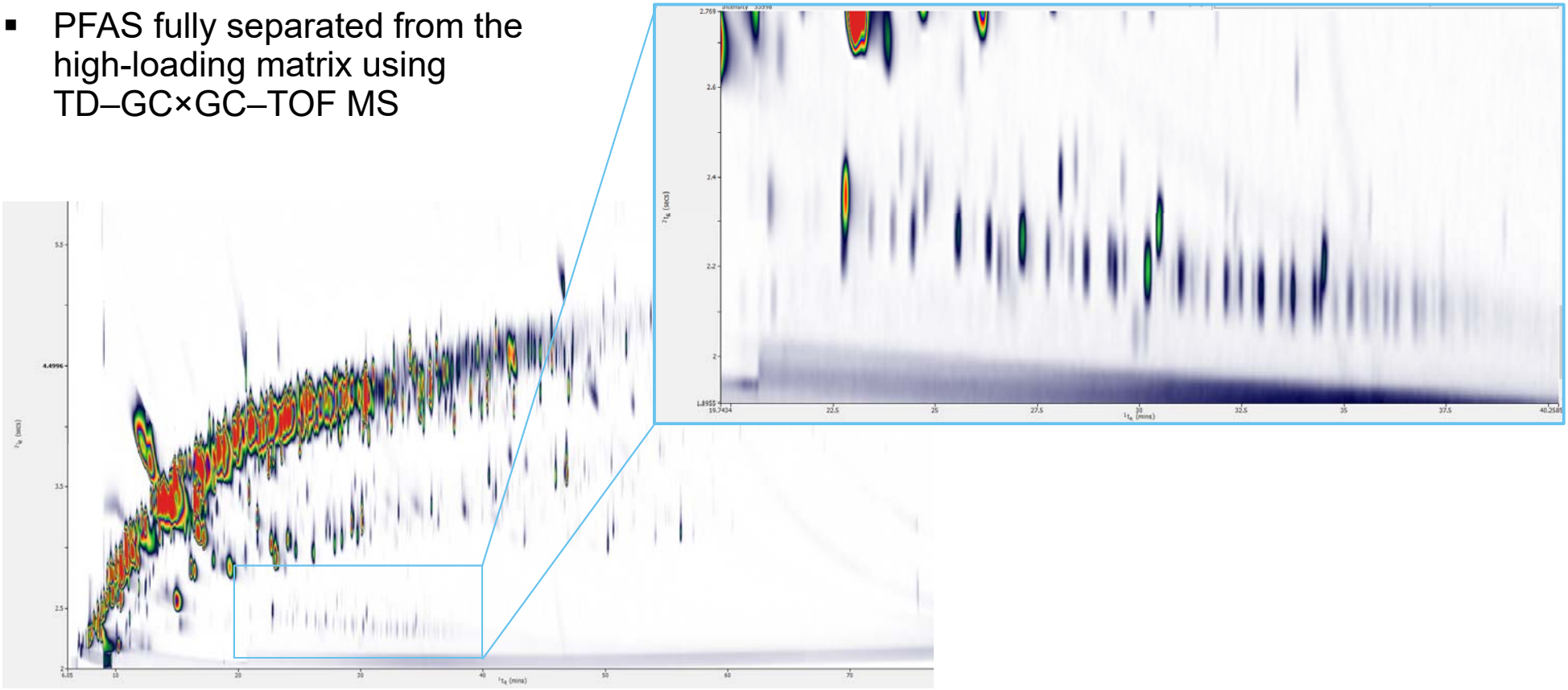
800 mL landfill gas sample analysed by TD–GC×GC–TOF MS



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

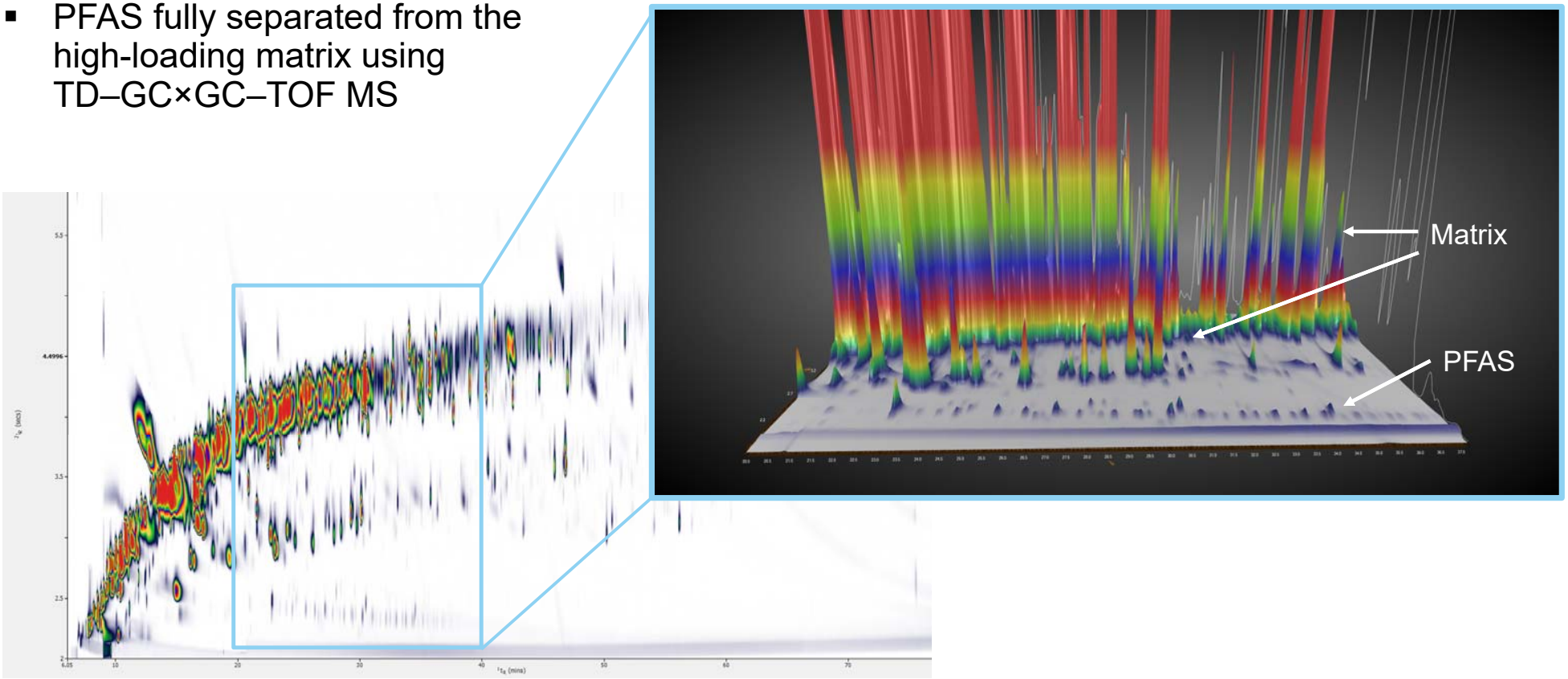
Using column selectivity to separate PFAS

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



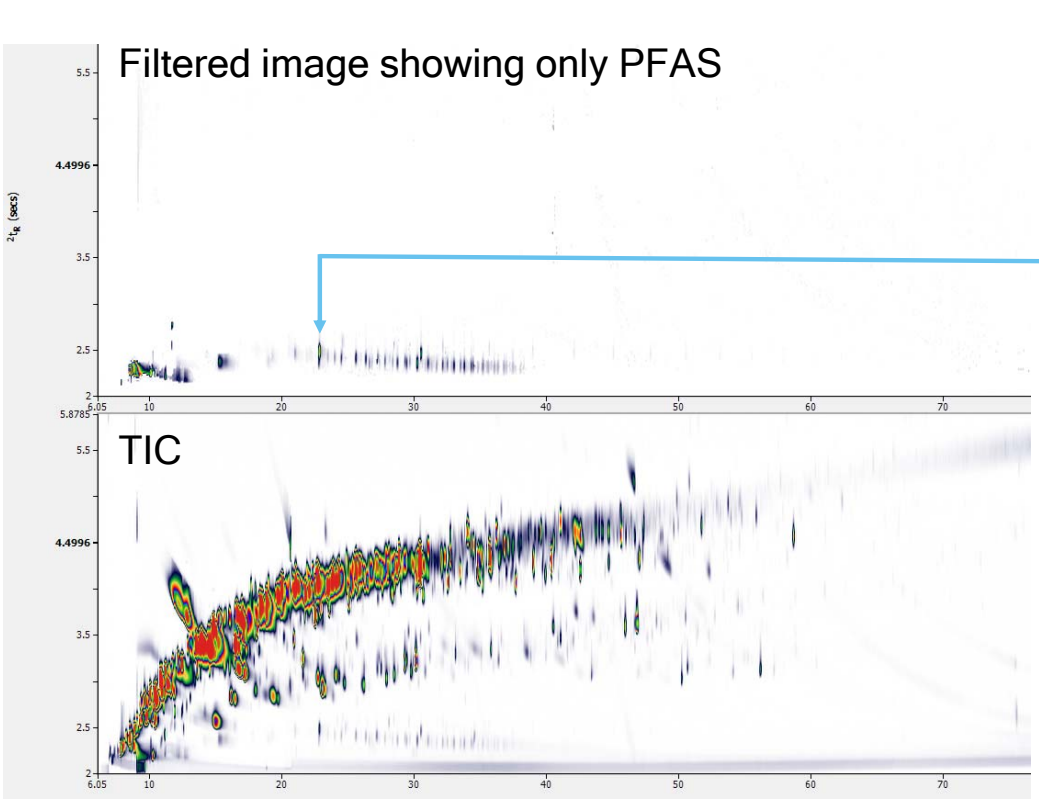
Using column selectivity to separate PFAS

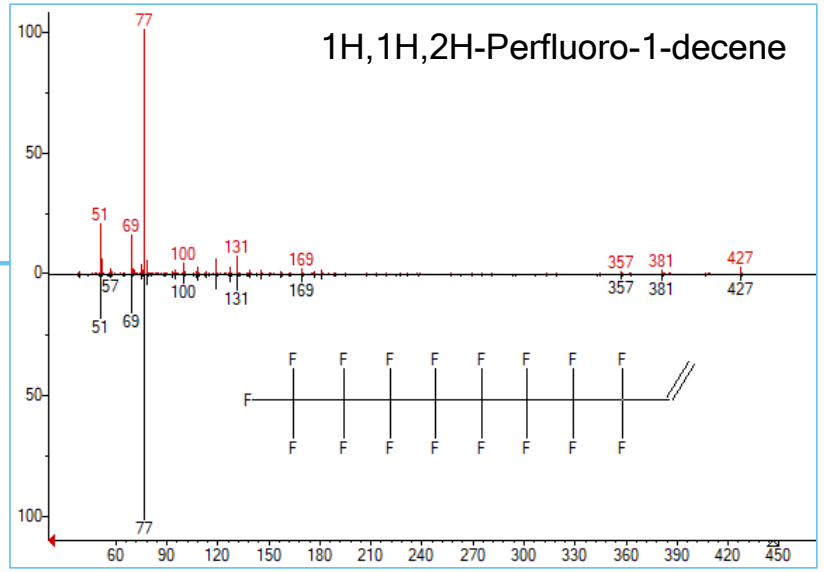
- PFAS fully separated from the high-loading matrix using TD–GC×GC–TOF MS



Non-target screening of PFAS in landfill gas

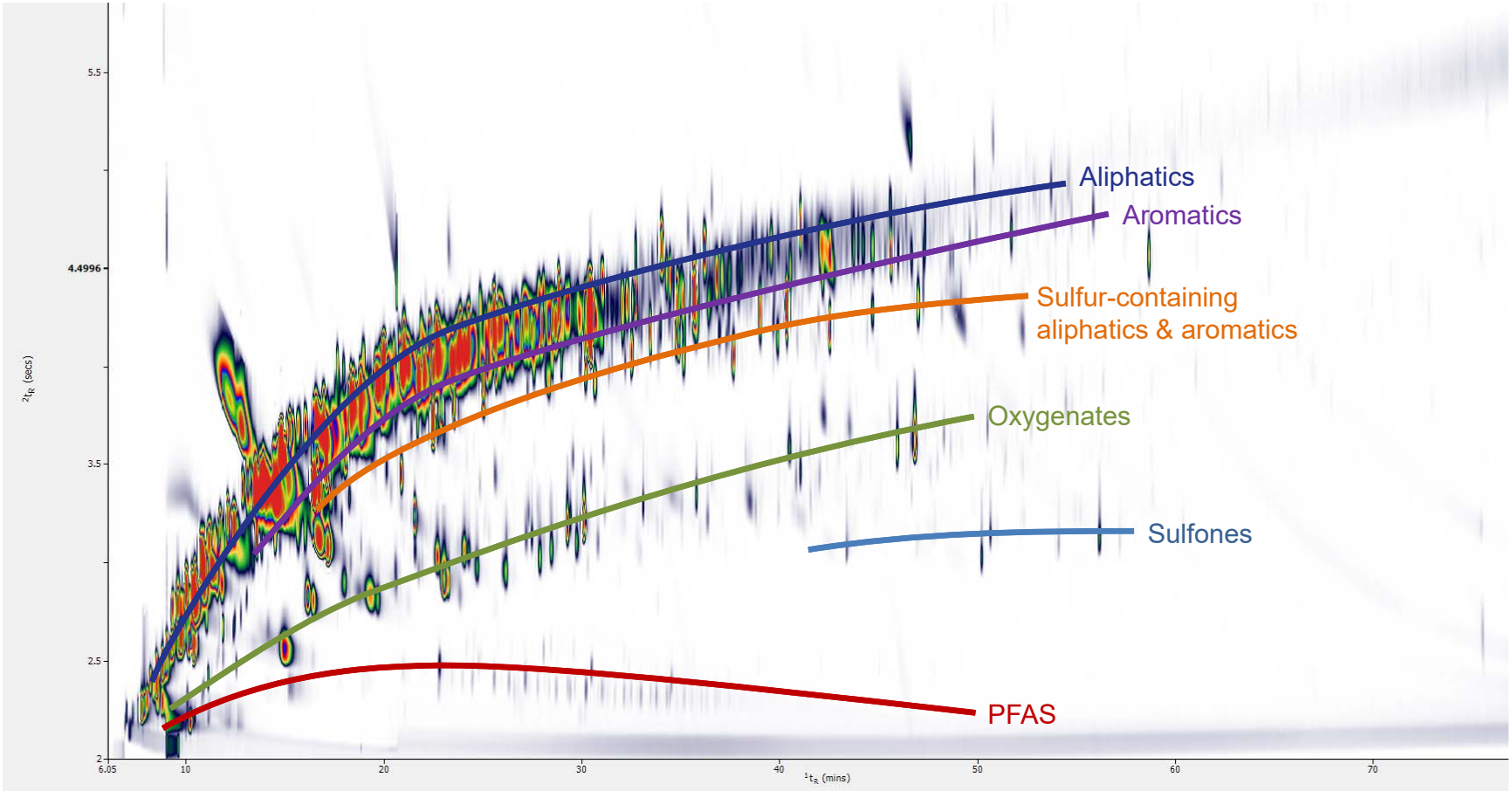
Challenge #3: No analytical standards available for the majority of compounds





- Filters (based on spectral characteristics) simplify the process of finding all PFAS species within the chromatogram
- 98 PF-related compounds were detected

Non-target screening of PFAS and other VOCs of relevance



SepSolve Analytical

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
- GC×GC–TOF MS can help to separate PFAS from high-loading matrix for non-target screening applications
- Re-collection enables precious samples to be run again
  - Unknowns can be assessed in further detail
  - Samples can be archived for legal reasons

Thank you for listening! Any questions?

Contact SepSolve

Email: hello@sepsolve.com / medwards@sepsolve.com

Tel.: UK: +44 1733 669222 / US & Canada: +1 519 206 0055 / Germany: +49 69 668 108 920

Web: www.sepsolve.com

Twitter: @SepSolve

LinkedIn: www.linkedin.com/company/sepsolve-analytical