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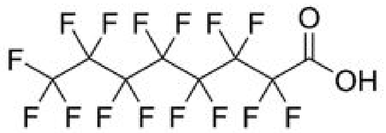
# PFAS in Air: Sampling and Analytical Techniques for the Identification of Persistent Contaminants

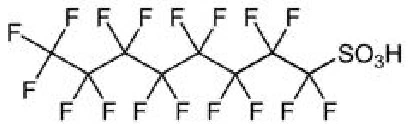
Nicola Watson Ph.D.

# What are PFAS compounds?

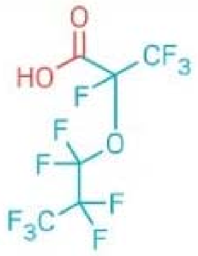
- Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that includes PFOA, PFOS, GenX, and many other chemicals.
- PFAS have been manufactured and used since the 1940s.
- PFOA and PFOS have been the most extensively produced and studied of these chemicals. Both chemicals are very persistent in the environment and in the human body.



PFOA



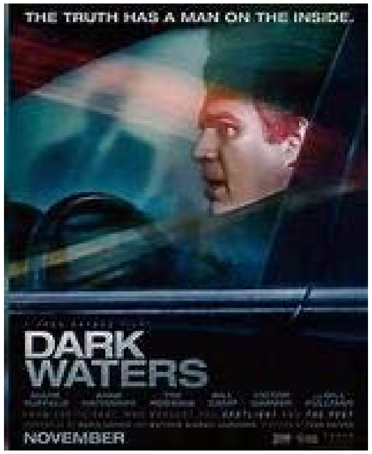
PFOS



HFPO-DA

# Why Monitor for PFAS?

- 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)
- June 22, 2020 EPA adds 173 PFAS chemicals to Toxics release inventory (TRI) of reportable chemicals. This is a small subset of the over 6000 PFAS chemicals been in use since the 1940’s
- Public awareness of PFAS has been increasing in part to the growing media coverage and true case covered in the Hollywood film Dark Waters, released in 2019



Source: US EPA (https://www.epa.gov/pfas)

# How are PFAS currently measured?

## LC-MS

- For drinking water the US EPA have methods EPA 533 & 537.1
  - Utilizes Solid Phase Extraction (537.1) or Isotope dilution anion exchange SPE (533)
  - Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) used in both methods
  - Both methods combined target 29 unique PFAS compounds
- ASTM 7979 and 7968 also exist for sludge and soil sampling
- For other matrixes/wider target list labs will use their own 537 ‘modified’ method – no universal standard
- All based on aqueous samples (water/sludge) or food tissue (fish) with LC-MS–MS analysis

# How are PFAS currently measured?

## In Air it’s a different story…

- 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
- Type of sampling depends on a number of factors such as
  - Compound range
  - Sensitivity required
  - Matrix/ potential interferents
- PFAs sources (Direct/Indirect)
  - Raw material producers
  - Use of PFAS in
    - AFFF
    - Consumer products
    - Waste infrastructure
  - Destruction of PFAS

# Air Sampling Categories

- Source emissions
  - PFAs destruction (typically burning)
  - Chemical Plants and Process vents

- Ambient Air
  - Transportation and transformation
  - Deposition
    - Multiple studies published on this e.g. Chemours/Solvay/Norlite all had significant levels of PFAs found in soil and water around the sites
  - Landfill gas

- Indoor Air
  - Deposition e.g. dust
  - Consumer product off gassing
    - Food containers
    - Cooking pots
    - Clothing

Study finds PFAS contamination in Cohoes around Norlite incinerator

Details emerge as city considers moratorium on burning controversial waste product

New contamination at an infamous N.J. chemical plant has scientists worried

Nontargeted mass-spectral detection of chloroperfluoropolyether carboxylates in New Jersey soils

John W. Washington[1,*], Charlita G. Rosal[1], James P. McCord[2], Mark J. Strynar[2], Andrew B. Lindstrom[2], Erica ...

+ See all authors and affiliations

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- Each would have to be tackled independently due to the specific nature of the problem

# Air sampling media analysis

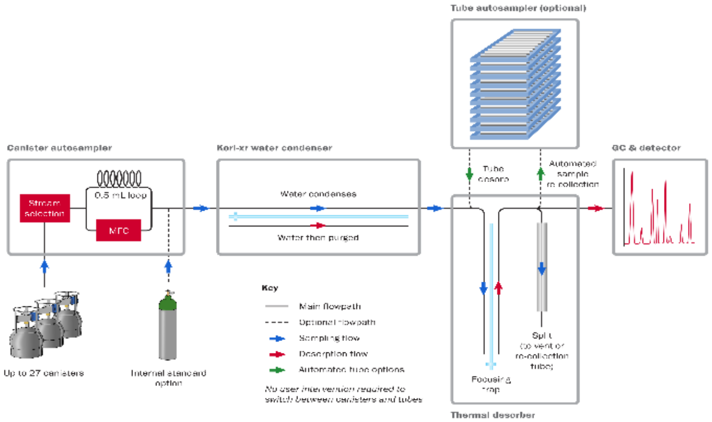
## Flexibility is key

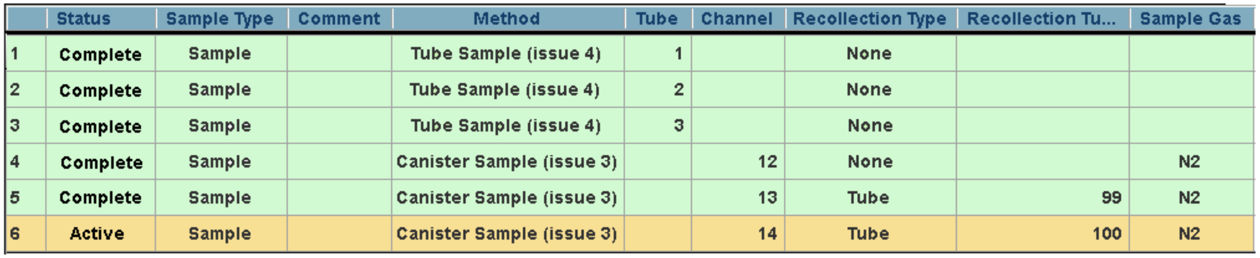
- Combination of sampling media is required to cover the range of PFAS compounds of interest in air– no one technique/collection vessel can tell you everything about the chemistry occurring
- Laboratory equipment that allows both sorbent tube/direct desorption and canister/bag samplers to be connected for analysis exists and is in use in PFAs studies across the globe

# Automation of sorbent tubes and canisters/bags

Combining tube desorption and canister (or on-line) analysis in a single sequence

- Up to 100 tubes
- Up to 27 canisters/bags
- Automated calibration – no manual intervention required
- Combining tube and canister (or on-line) analysis into a single automated sequence





| | Status | Sample Type | Comment | Method | Tube | Channel | Recollection Type | Recollection Tu... | Sample Gas |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Complete | Sample | | Tube Sample (issue 4) | 1 | | None | | |
| 2 | Complete | Sample | | Tube Sample (issue 4) | 2 | | None | | |
| 3 | Complete | Sample | | Tube Sample (issue 4) | 3 | | None | | |
| 4 | Complete | Sample | | Canister Sample (issue 3) | | 12 | None | | N2 |
| 5 | Complete | Sample | | Canister Sample (issue 3) | | 13 | Tube | 99 | N2 |
| 6 | Active | Sample | | Canister Sample (issue 3) | | 14 | Tube | 100 | N2 |

# Monitoring source emissions

# Source emission testing

Two scenarios where source emission testing could be carried out exist:

- Monitoring the production process at chemical plants and understanding what is being released into the environment
  - The PFA chemicals of interest need to be monitored
  - Other VOCs of interest would be beneficial to collect at the same time
- Monitoring PFAS destruction at incineration sites
  - The PFA chemicals of interest need to be monitored
  - Breakdown products will also need to be monitored to indicate complete breakdown

# Air Sampling Options

## Source air sampling collection

- Data on this has been published using Modified EPA 0010 collection methods
  - Capture in cooled impingers
  - Complex set up required
  - Only for Semi volatile compounds
- Modified collection method 18 has been discussed for volatile PFAs compounds, but no data has been presented publicly on this yet.

- Two separate methods,
- Lengthy extraction protocols required,
- Multiple points for contamination of sample,
- Sensitivity impacted

- European method CEN/TS 13649 has also been proposed, this would cover both volatile and semi volatile PFAS compounds, but no data has been presented publicly on this yet.

- Single method
- Minimal sample prep
- Sensitivity maximised

What about monitoring PFAS destruction?

# PFAS destruction - Is it complete?

## Considerations for source emissions

PERSISTENT POLLUTANTS

**Incineration may spread, not break down PFAS**

Preliminary data show soil and water near New York facility are contaminated

*by Cheryl Hogue*

APRIL 27, 2020

- Analysis for breakdown products for thermal destruction of PFAS compounds is essential.
- Incomplete or non destruction can lead to spread of PFAS compounds in the surrounding area
- As PFAS decompose they form other compounds.
  - The most difficult fluorinated organic compound to decompose is $CF_4$, requiring temperatures over 1,400oC, making it an ideal candidate to monitor for completion of destruction.
- $CF_4$ is typically monitored using canister or bag sampling techniques with offline analysis. $CF_4$ is too volatile to be retained on any sorbent media at ambient temperatures, so previous methods discussed would not be suitable.

# Recommendations for monitoring source emissions

## Tube methodology

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

## Canister/Bag methodology

- PFAS breakdown products
  - CF4 and other CFCs already monitored using bags, cans and online

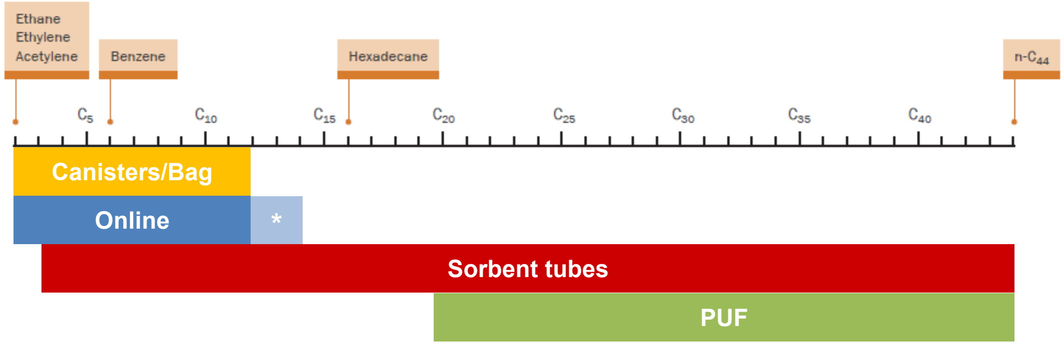
It is possible to carryout combined injection of canister and tube samples into a single injection if the samples have been co-located

# Ambient and Indoor air

# Air Sampling Options

## Ambient air sampling

- Depending on scope of compounds, multiple methods can be used e.g.
  - Modified TO-13a
    - PUF/XAD sample collection (Semi volatiles only)
  - Modified TO-17
    - Thermal desorption tube sample collection (Volatile and semi volatile compounds)
  - Modified TO-15
    - Whole air canister sample collection (Volatile and very volatile compounds)



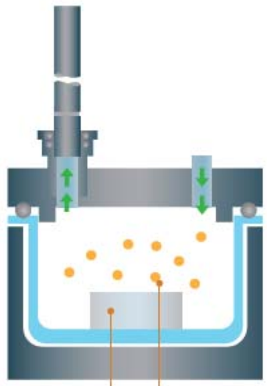
# Air Sampling options

## Indoor air/Consumer products

- Similar to Ambient air, but sampling scope could change based on longer sampling periods.
  - Introduce passive sampling utilizing canister or sorbent sampling media
    - Depending geometry, concentrations and volatility, sampling can be performed over 1 day up to months
- Sources of PFAS in indoor environment can be isolated and sampled independently using microscale thermal extraction or direct desorption

# Sampling approaches

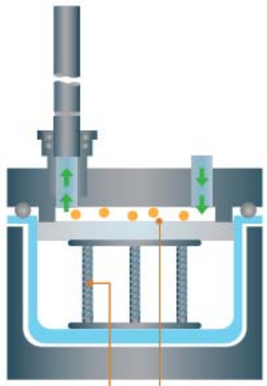
**Bulk emissions testing** is valuable for profiling odours and emissions, and for testing of raw materials and foods.



Samples are placed straight into the chambers.

Vapours swept from the entire sample are collected.

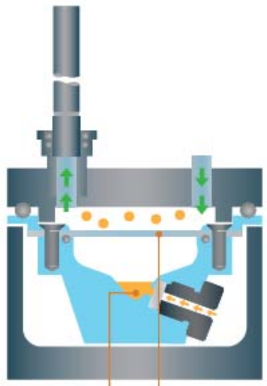
**Surface emissions testing:** This approach is suitable for determining area-specific emission rates from flat samples.



Sprung spacers raise planar samples to the top of the chamber.

A seal forms when the lid is closed, so only vapours released from the sample's surface are collected.

**Permeation testing:** A permeation accessory allows measurement of volatiles permeating through a thin layer of material.



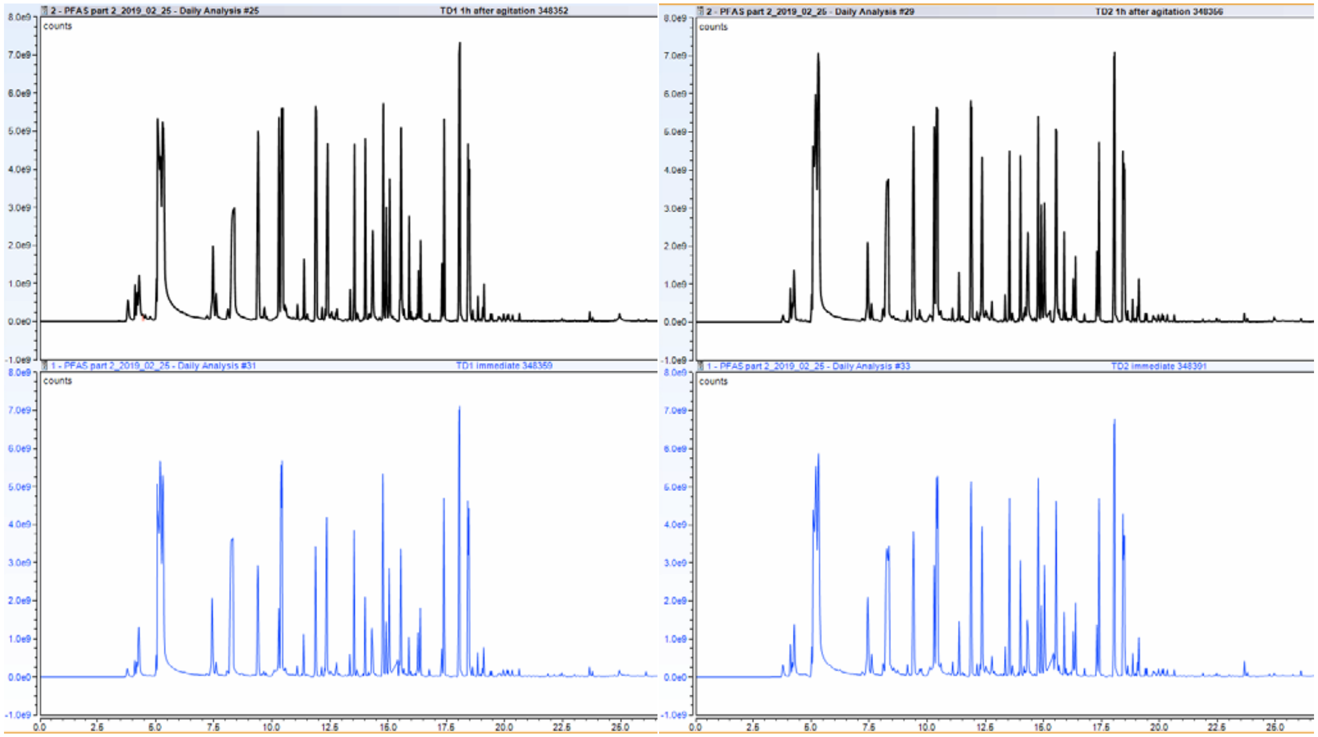
Liquid samples are injected through a septum into the well under a sealed sample of test material.

Vapours diffuse through the test material into the chamber.

# Sampling experiment – AFFF

What’s being released and how does that change over time?

- Sampled AFFF for 2 minutes at 200 cc/min
- Two repeats immediately after agitation of the AFFF mixture (black) and 1 hour afterwards (blue)

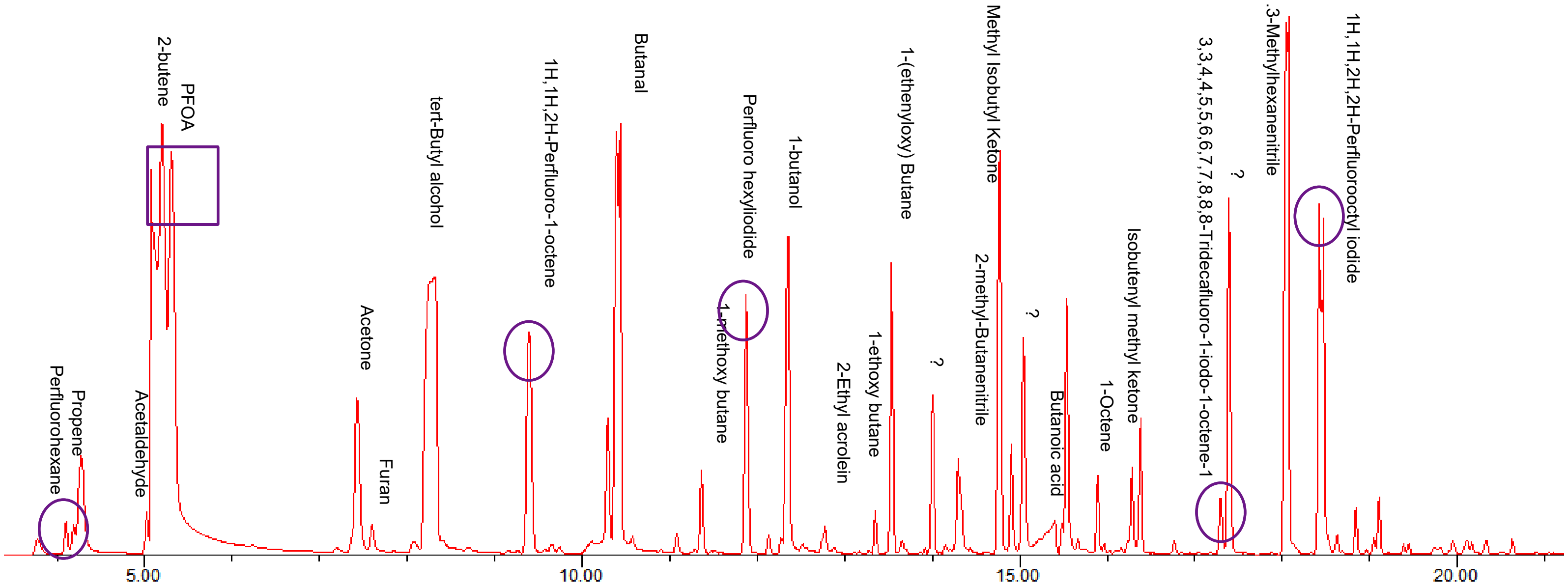


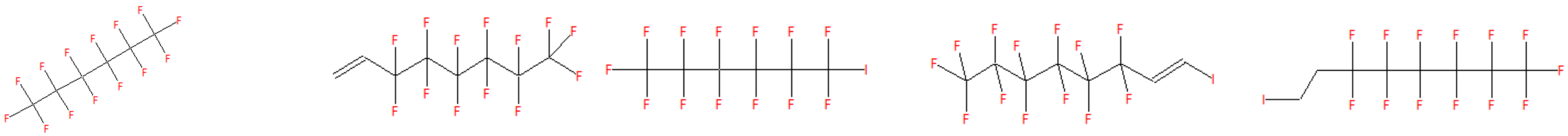
# Volatile PFAS compounds

JACOBS

Vista Analytical Laboratory

University of Nevada, Reno





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# How can monitoring be approached?

Thermal desorption offers 3 main choices for taking a sample:

- Tube
- Canister/bag
- Online

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

## Re-collection

- Confirmatory analysis can be performed on exactly the same sample.
- Samples can be archived for investigation at a later date

# Other considerations

## Detectors

# Analytical detector selection

## Considerations for selecting detectors

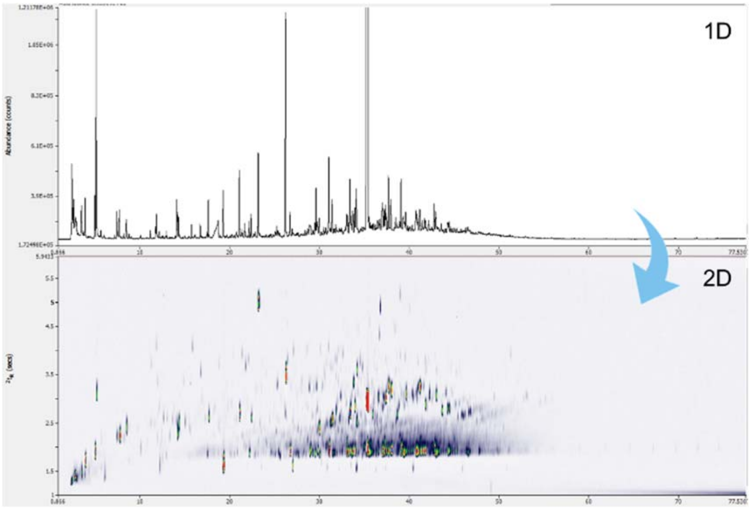
- Over 6000+ PFAS compounds, not all have been identified, nor have all of their breakdown products, many detector types exist and include, but not limited to the following
  - Accurate mass MS are essential for structural elucidation of ‘unknown unknowns’, but routine/high-throughput workflow can be challenging
  - Time-of-flight MS for screening ‘known unknowns’ with high sensitivity
  - Triple quadrupole MS for target analysis (‘known knowns’) in complex matrices
  - Soft ionisation (e.g. Tandem Ionisation or CI) can enhance MS performance
  - Electron capture detectors (ECD) can be used in more routine settings for target halogenated compounds

- Selection of a detector technique really depends on what stage of the research process you are in, and what supporting techniques can be used to boost confident identification.

# Complexities with PFAS analysis

## Chromatography enhancements

- PFAs samples for all arenas can be highly complex, so traditional 1D chromatography will not resolve all components
  - Deconvolution techniques can be used to find hidden peaks, but this is typically frowned upon in the environmental community
- Two-dimensional chromatography (or GC×GC) provides improved separation by combining two columns of different selectivity



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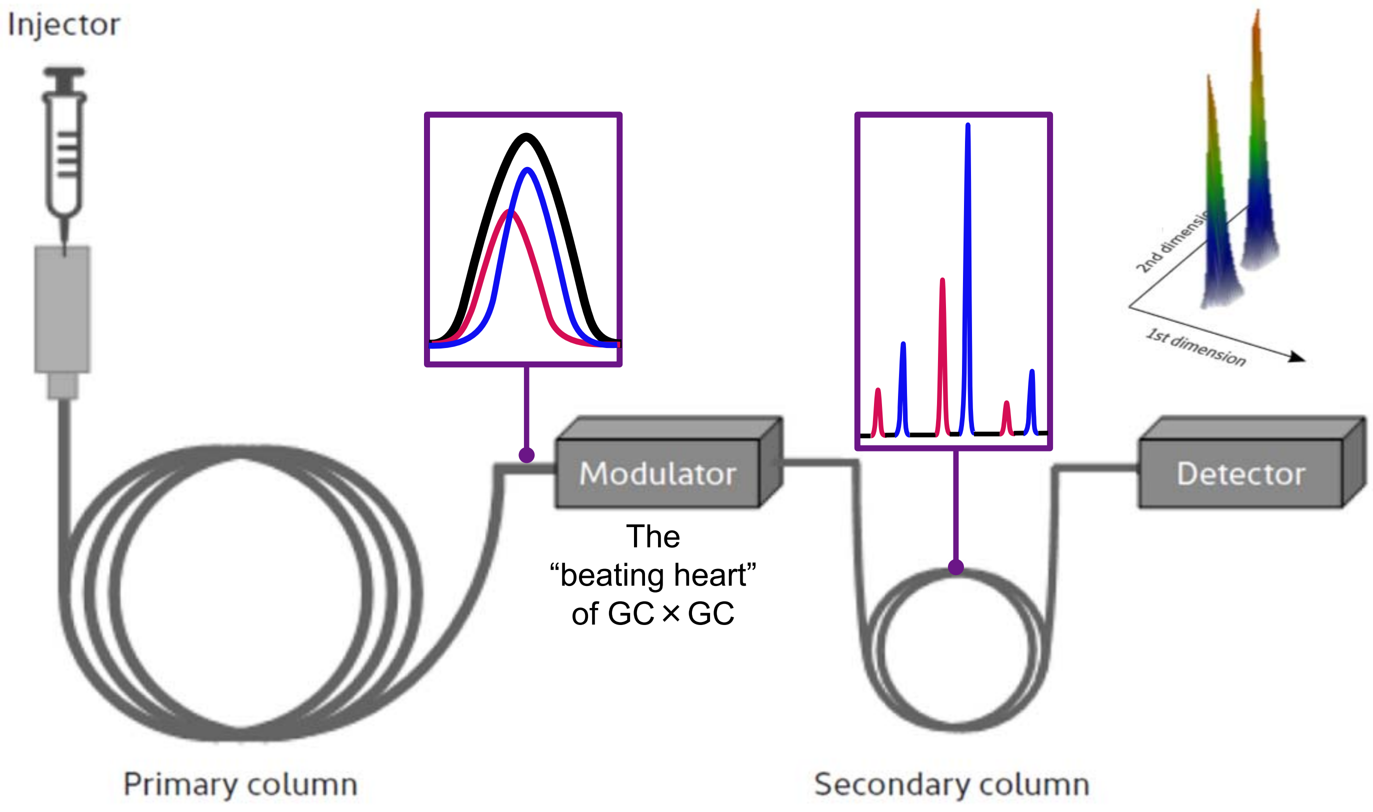
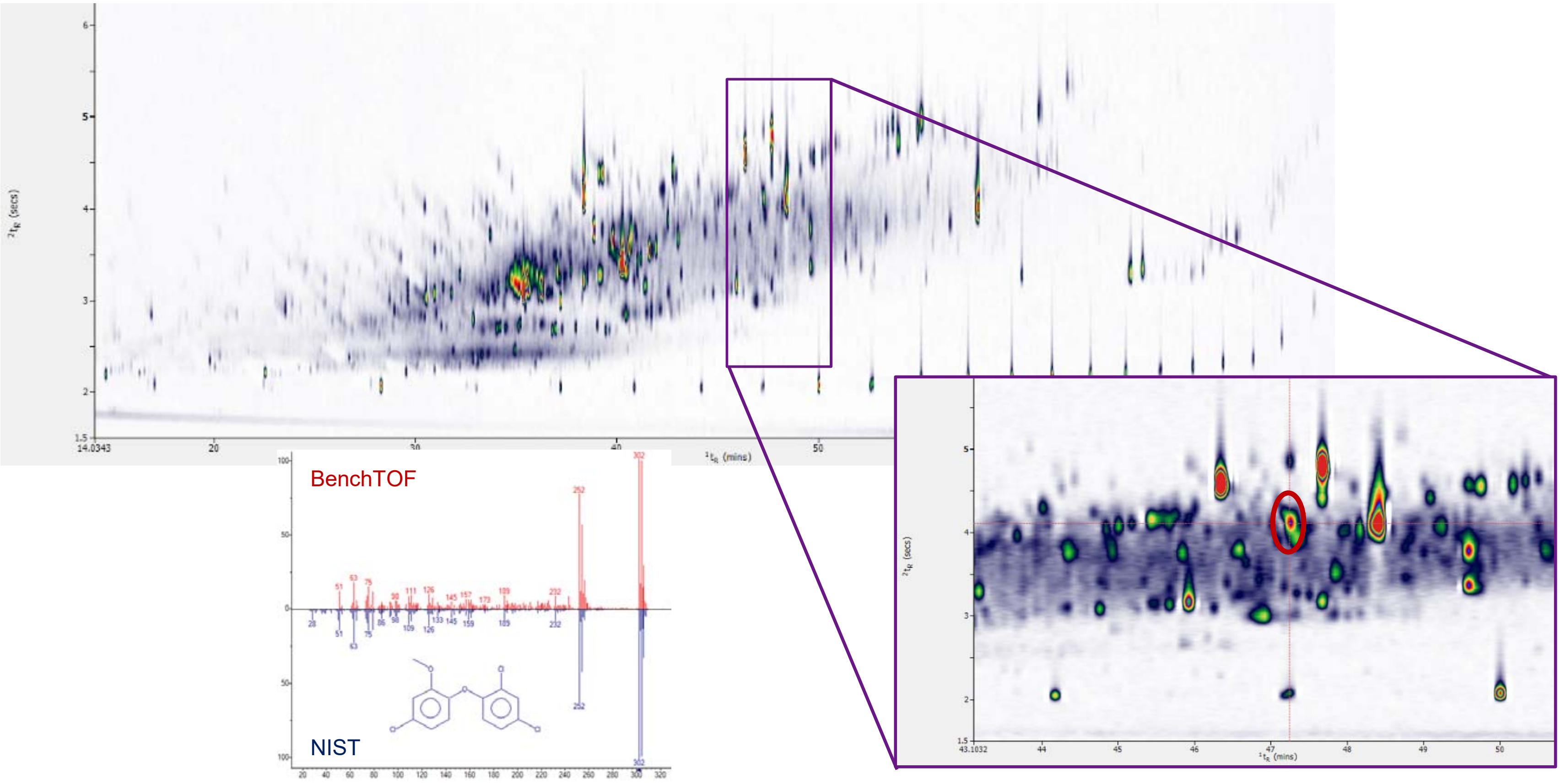
# Theory of GC×GC



The
“beating heart”
of GC × GC

# Separating the wheat from the chaff



# Conclusions

- We are at the start
  - PFAS in air research is only just beginning and I am sure we will see more on this topic as research progresses
- No one technique will do it all!
  - Combination of techniques both sampling and analytical is required to get a good picture of the chemistry of PFA chemicals in air, including exposure risks, transportation, deposition and destruction
- Collaboration is important
  - To tackle this problem collaboration between, regulatory agencies, environmental focus groups, contract laboratories and instrument vendors is a must to be successful.
- Look to the future – flexibility is key
  - Other replacement/emerging chemicals of concern – can these be monitored too?
  - Flexible analytical systems that allow multiple types of air sampling media to be analyzed, will future proof the laboratory for new concerns.
  - If non selective detectors are used, data can be re-processed to look for other chemicals of concern

# Any questions?

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