Chemical Ionization Mass Spectrometry For Real-Time Monitoring Of Semivolatile Emerging Atmospheric Contaminants:

Application Of The Aim Reactor In PFAS Detection

S. Jorga, Maya Abou-Ghanem, **V. Pospisilova**
Environmental Measurement Symposium, Anaheim CA

Per- and polyfluoroalkyl substances (PFAS)

- Man-made chemicals used in numerous industrial and consumer products
- Persistent in the environment
- Associated with adverse health effects
- Their number is growing

The New York Times

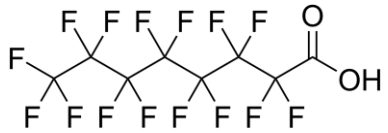
PFAS: The 'Forever Chemicals' You Couldn't Escape if You Tried

Virtually indestructible, these artificial compounds are used in fast-food packaging and countless household items, but they have been found as far away as virgin forests.

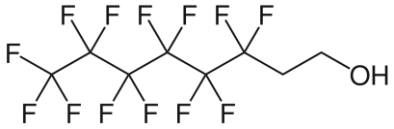
Biden-Harris Administration Announces New Steps to Protect Communities from PFAS and Other Emerging Chemicals of Concern

Proposed rules would better enable regulators to address PFAS under the nation's hazardous waste law to protect families across the nation

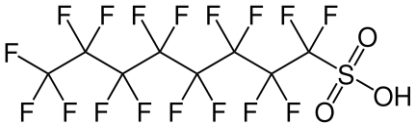
PFOA



6:2 FTOH

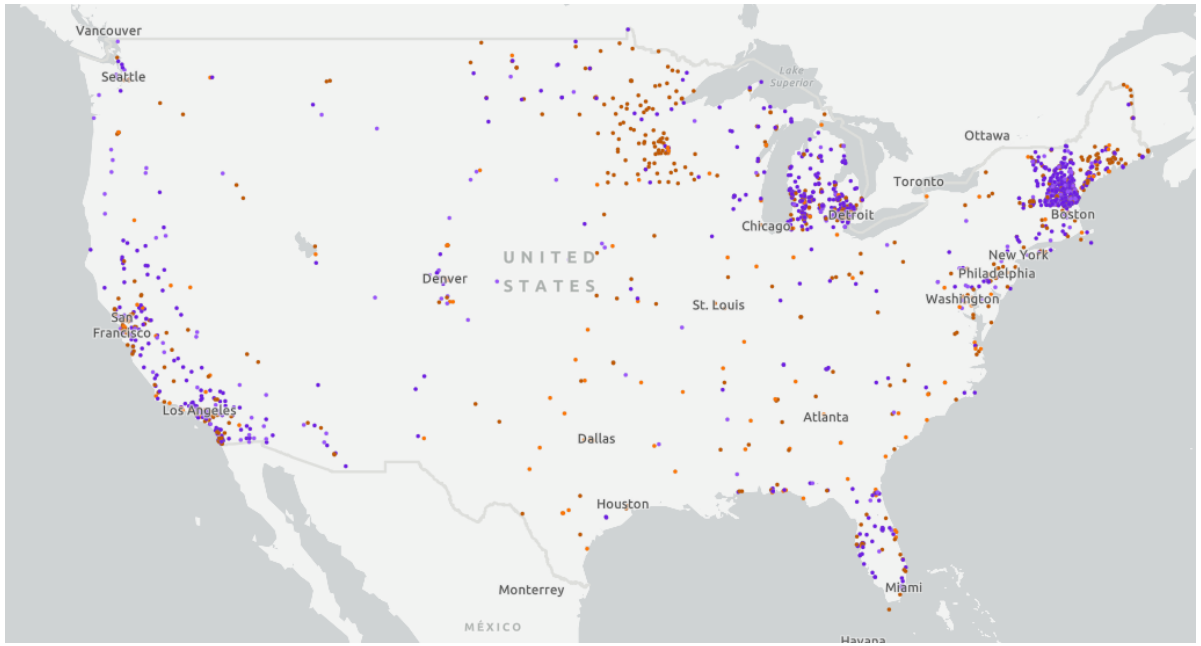


PFOS

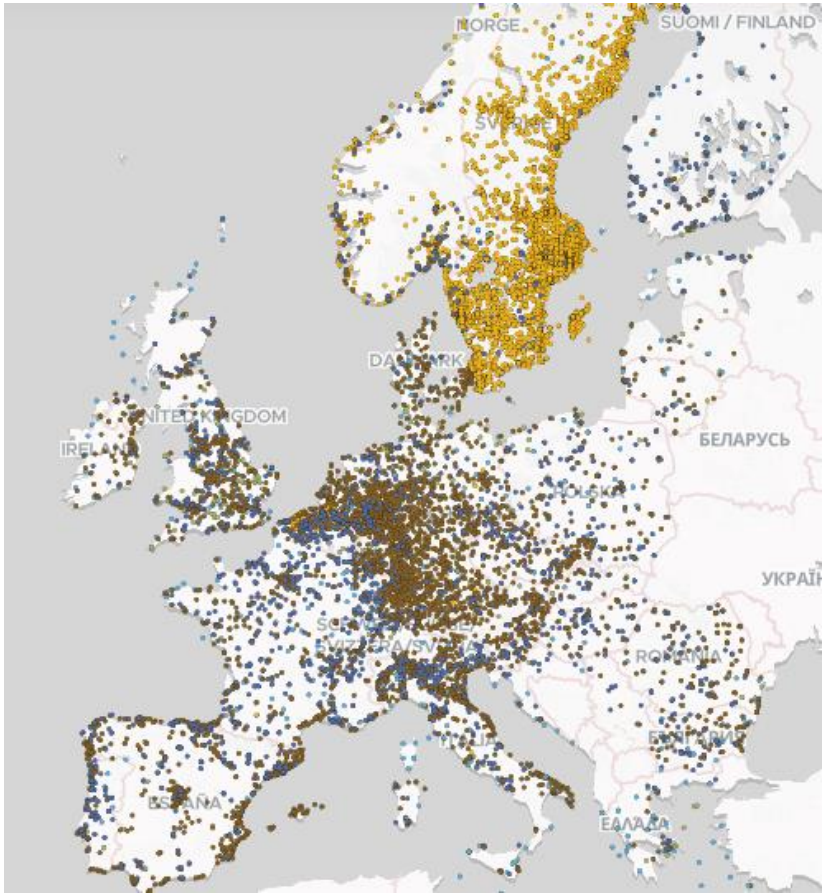


PFAS in the environment

- Have been detected in waters, soil, sediments and air
- Typically measured in water where legal limits defined for subgroup of PFAS



https://pfasproject.com/



https://www.lemonde.fr/en/les-decodeurs/article/2023/02/23/forever-pollution-explore-the-map-of-europe-s-pfas-contamination_6016905_8.html

PFAS in the air

- Currently **non-regulated in the air** despite important exposure pathway
- Absence of standardized methodology
  - Offline analysis
  - Passive X Active air samplers
  - LC-MS, GC-MS

Landfill Gas: A Major Pathway for Neutral Per- and Polyfluoroalkyl Substance (PFAS) Release

Ashley M. Lin, Jake T. Thompson, Jeremy P. Koelmel, Yalan Liu, John A. Bowden, and Timothy G. Townsend*

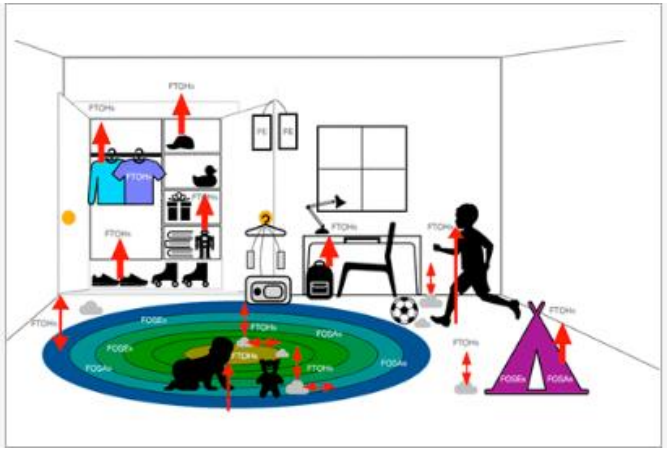
The Air That We Breathe: Neutral and Volatile PFAS in Indoor Air

Maya E. Morales-McDevitt, Jitka Becanova, Arlene Blum, Thomas A. Bruton, Simon Vojta, Melissa Woodward, and Rainer Lohmann*

INSIGHTS

EPA Issues PFAS Air Emissions Draft Test Method OTM-45

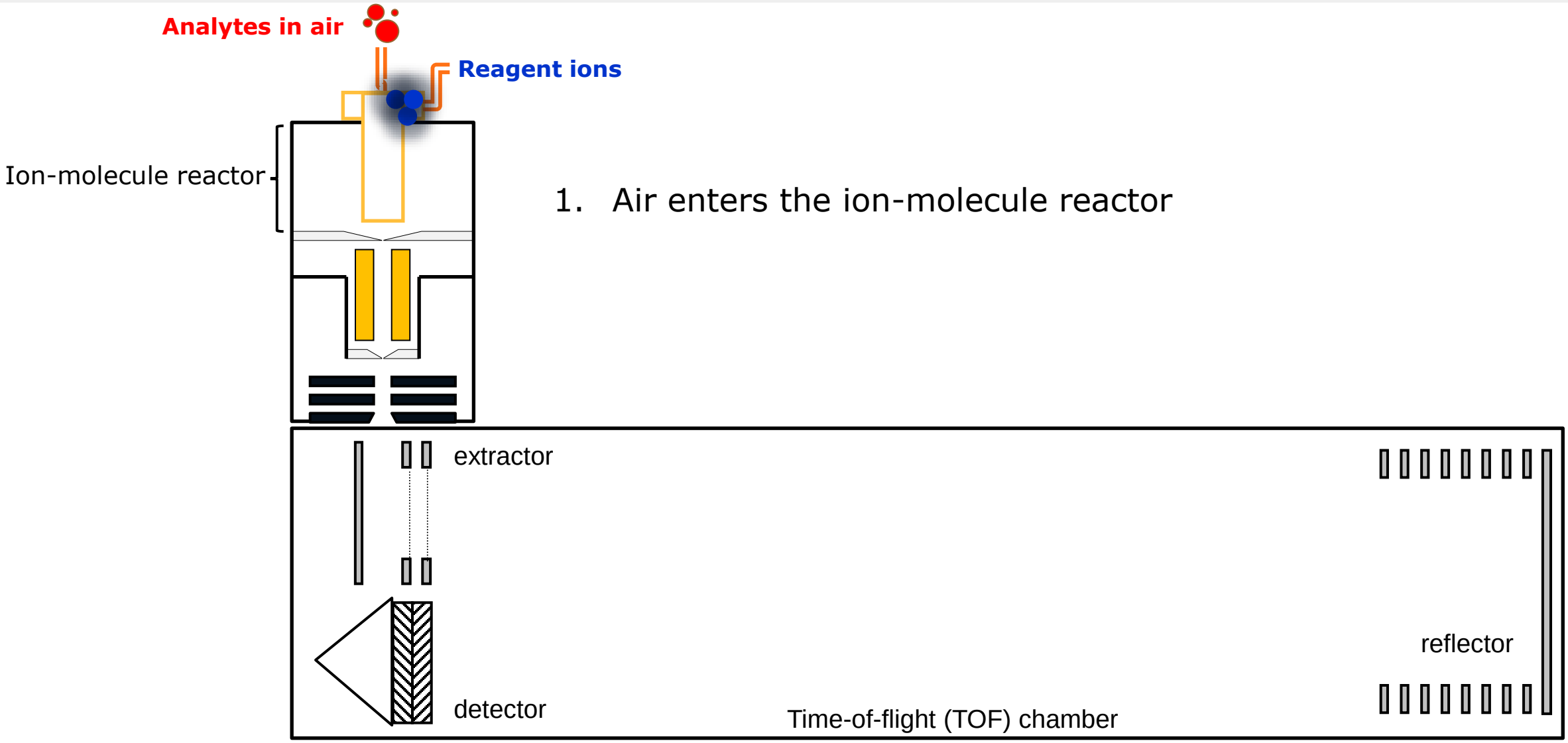
Thomas A. Dunder, Ph.D. | February 5, 2021



Drawbacks of current technology

- Limited Spatial and Time Resolution
- Only targeted analysis
- Limited understanding of emission sources, fluctuations, atmospheric fate, and transport

Our tool: Chemical Ionization TOF Mass Spectrometry



1. Air enters the ion-molecule reactor

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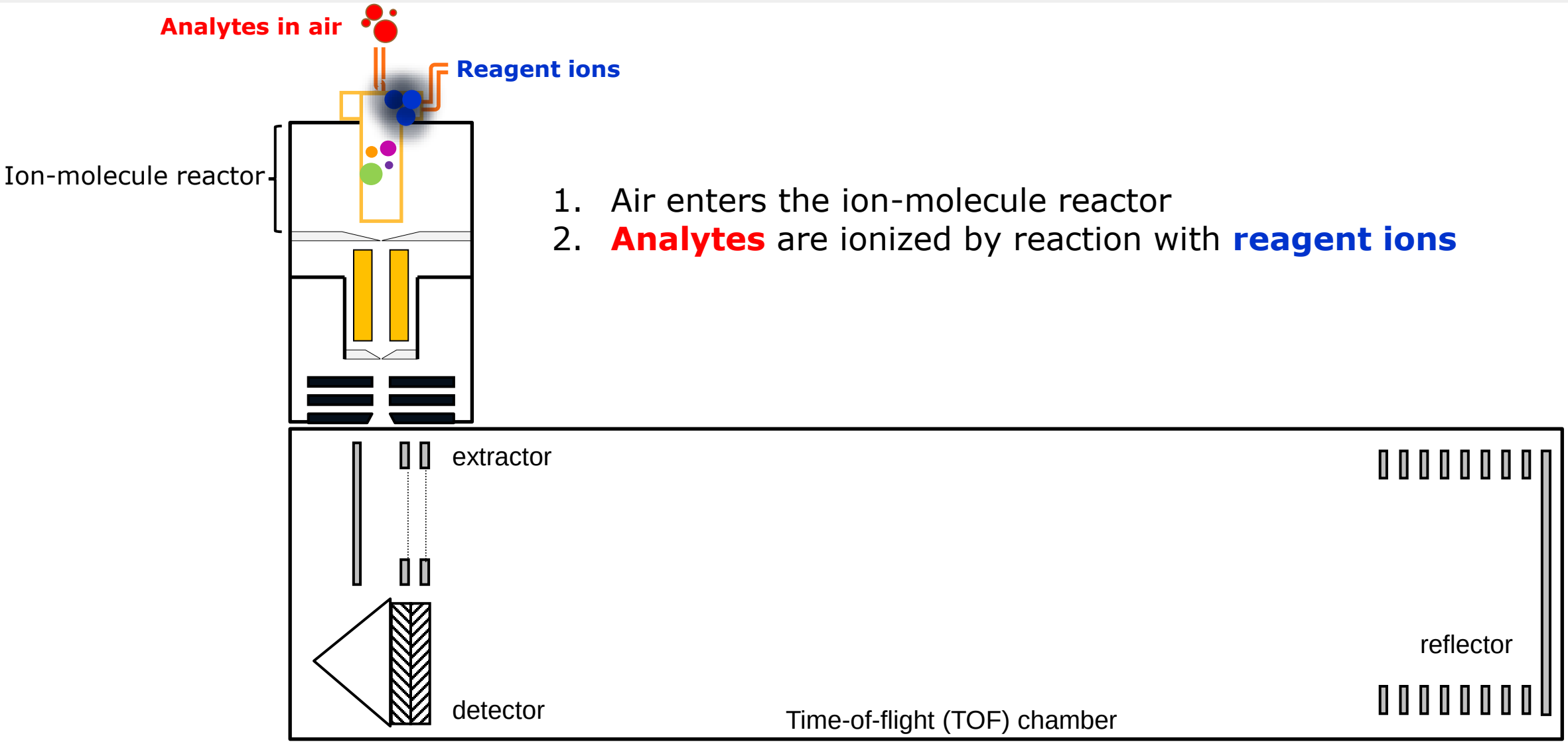

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2. **Analytes** are ionized by reaction with **reagent ions**

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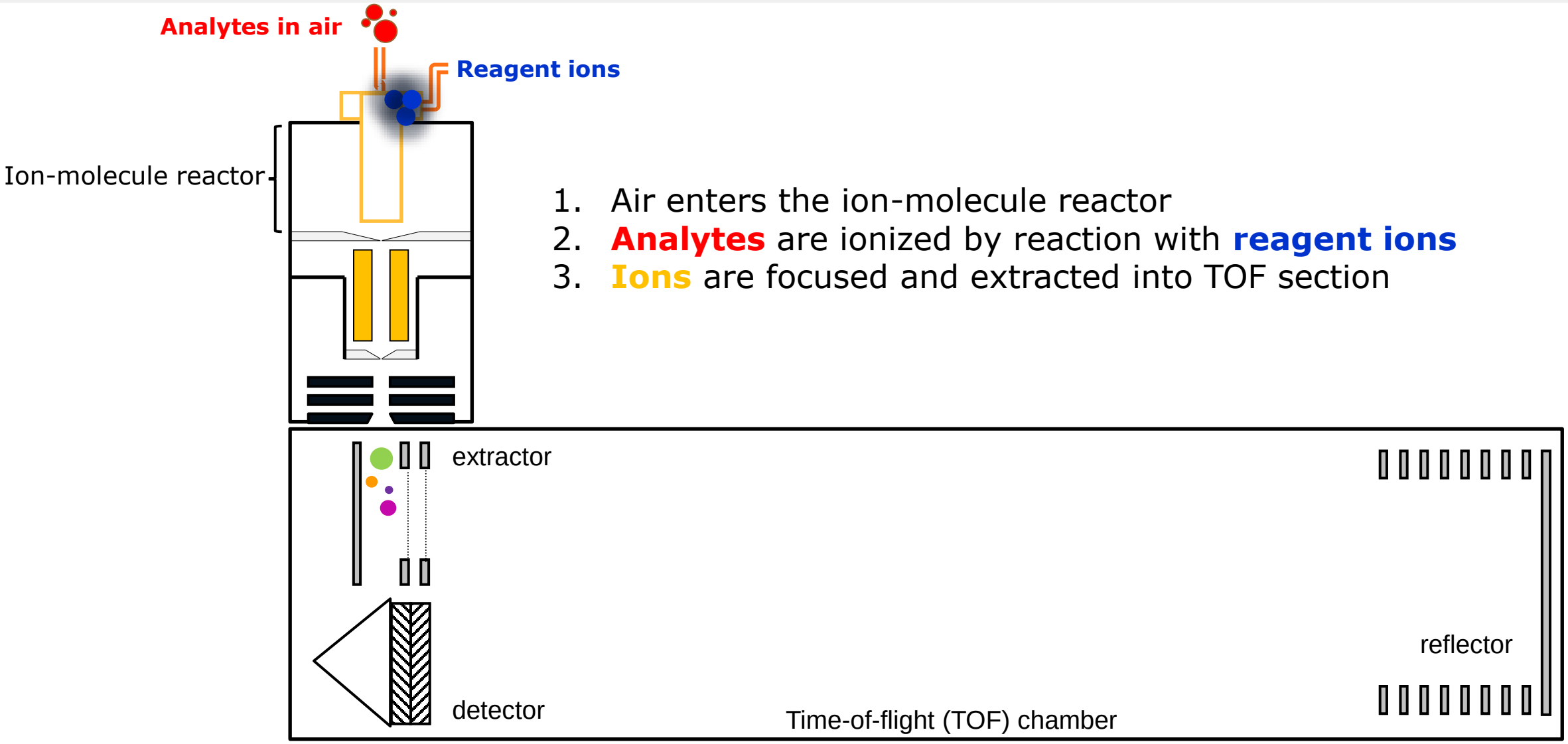

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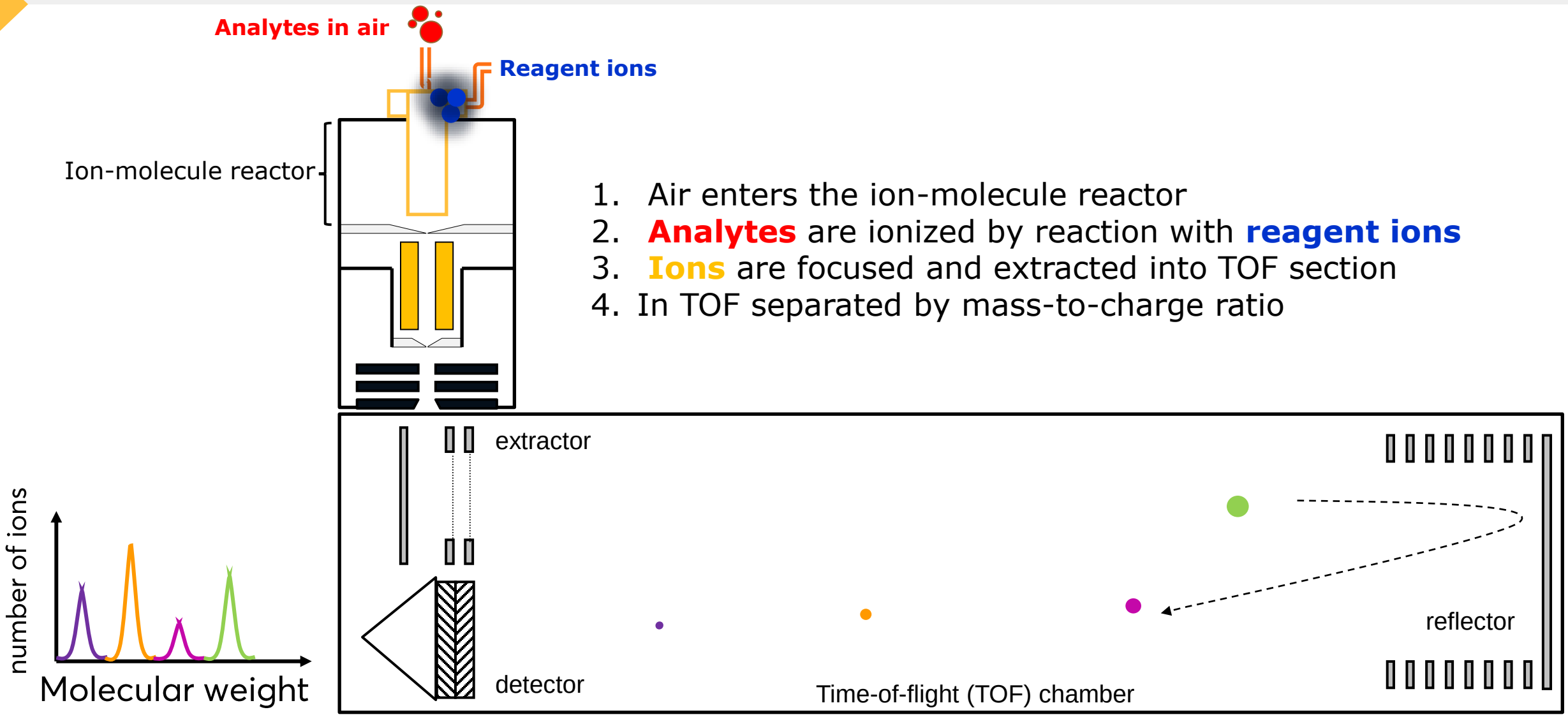
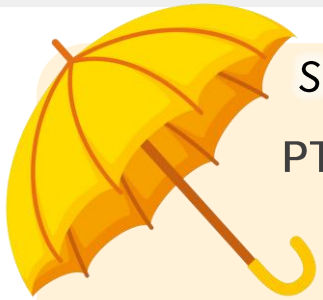


1. Air enters the ion-molecule reactor
2. **Analytes** are ionized by reaction with **reagent ions**
3. **Ions** are focused and extracted into TOF section
4. In TOF separated by mass-to-charge ratio

Target specific chemical families with different CI configurations



Soft Chemical Ionization

PTR H_3O^+ | NO^+ Iodide | O_2^+ Nitrate | NH_4^+ | $Acetone^+$ | many more…

H_3O^+ "PTR"
General-purpose
BTX, oxygenates, alkenes…

Iodide PFAS
Inorganic acids
Organic acids

NH_4^+

NO_3^-

O_2^+ Alkanes
BTX
CFC

$Benzene^+$ Solvents
Terpenes

Br^-

Acetate

NO^+ Alkanes
CFC
Alcohols

$Acetone^+$ Ammonia
Amines

Iodide CIMS seems to be a great detector for PFAS

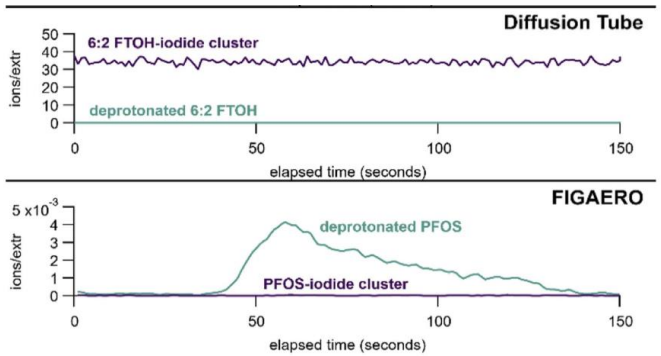
- Iodide adduct chemistry is not new
- Sensitive measurement of functionalized organic molecules, inorganic acids, halogenated species

Table 1. CIMS PFAS Calibration Summary

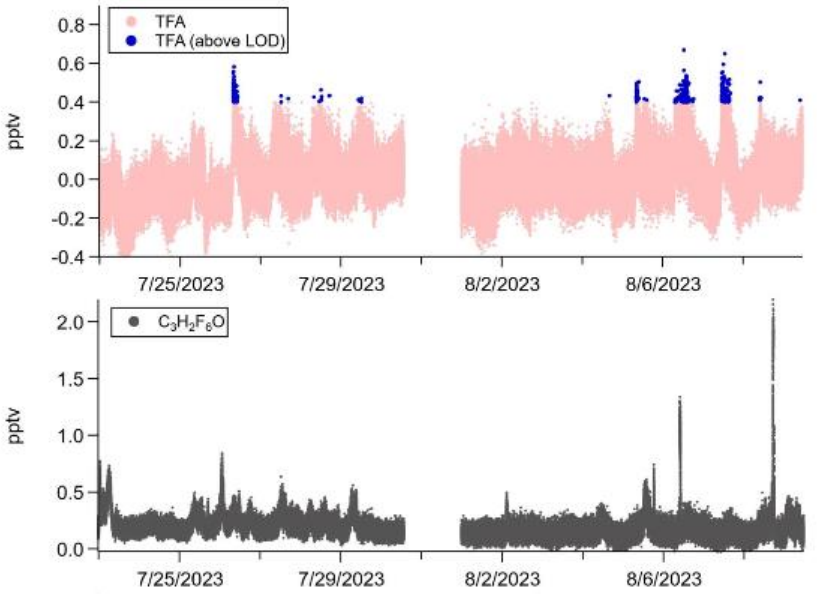
compound	structural formula	calibration factor (cps pptv^{-1})	detection limit (pptv)
4:2 fluorotelomer alcohol	$F(CF_2)_4(CH_2)_2OH$	3.0 ± 0.7	7.9
6:2 fluorotelomer alcohol	$F(CF_2)_6(CH_2)_2OH$	5.1 ± 0.3	2.1
8:2 fluorotelomer alcohol	$F(CF_2)_8(CH_2)_2OH$	9.1 ± 0.8	1.8
10:2 fluorotelomer alcohol	$F(CF_2)_{10}(CH_2)_2OH$	3.4 ± 1.1	4.8
perfluorooctanoic acid (PFOA)	$F(CF_2)_7COOH$	2.9 ± 0.6	5.9
perfluorobutanoic acid (PFBA)	$F(CF_2)_3COOH$	24.8 ± 3.9	1.4
hexafluoropropylene oxide dimer acid (HFPO-DA)	$F(CF_2)_3OC(COOH)FCF_3$	3.7 ± 1.1	7.6

Riedel et al. Environ. Sci. Technol. Lett. 2019

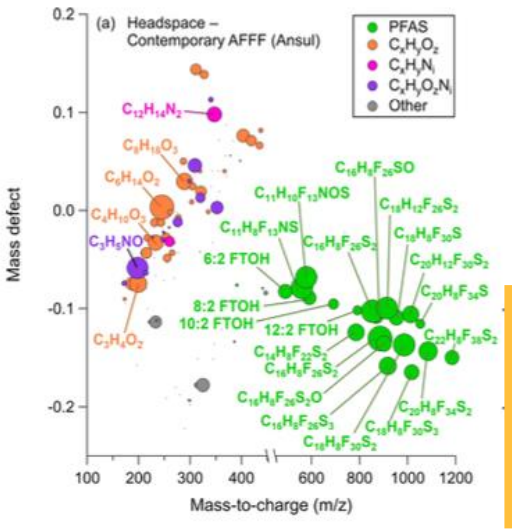
Bowers et al. Environ. Sci.: Processes Impacts, 2023



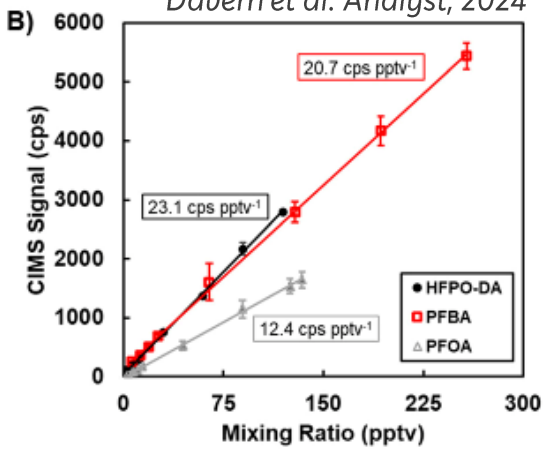
Mattila et al. Journal of the Air & Waste Management Association, 2024



Mattila et al. EST. 2024



Davern et al. Analyst, 2024



PFAS can be measured in real-time with excellent sensitivity using iodide CIMS

What has been Holding This Back?

1. Technical difficulties with 'home' made CIMS

- **CH_3I** - high consumption, toxic, polymerizes in compressed gas cylinders
- **Polonium source** - dangerous, expensive, highly regulated, hard to transport, ship to field sites
- **X-ray source** - Low sensitivity, Makes unwanted interfering ions
- High consumption of Nitrogen
- Response time - adsorption of low volatile species to the internal surfaces
- Humidity dependent

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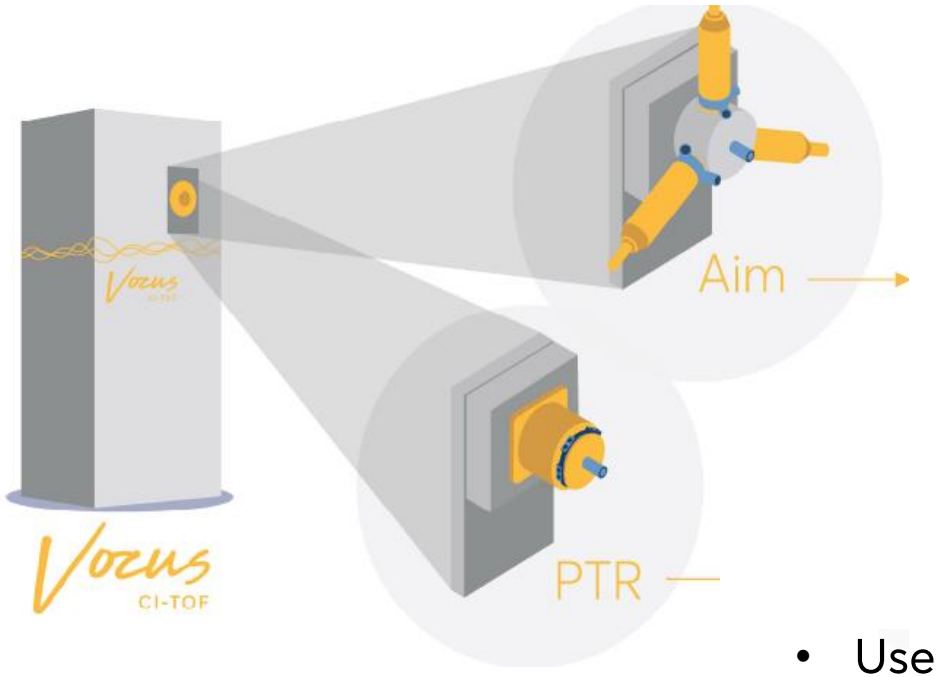
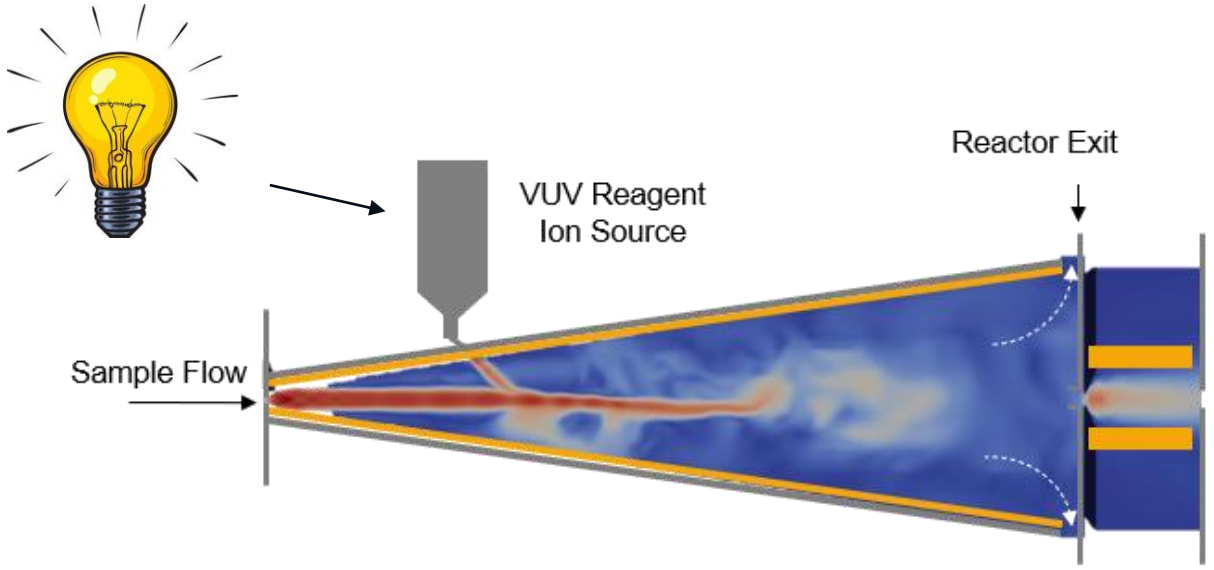
2. Calibration

- Current calibration standards are suited for GC-MS and LC-MS/MS
- Low volatile, sticky, not available in gas cylinders
- Toxic

Vocus AIM reactor





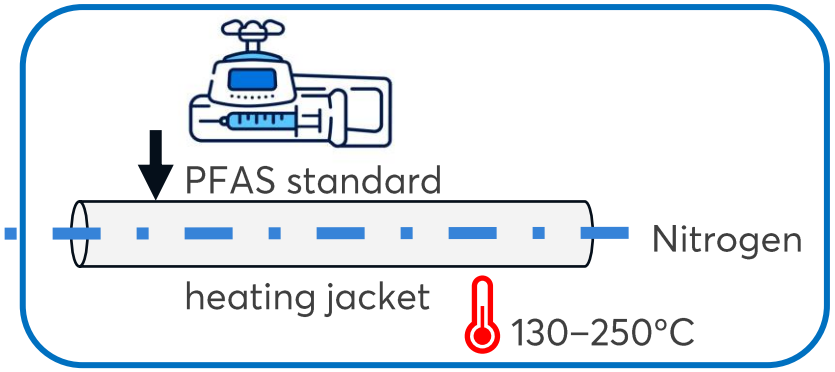
Riva, Pospisilova et al, AMT, 2024

- Use of VUV lamp as ionization source
- Operation at medium pressure (40 - 80 mbar)
- Optimized for adduct-ion chemistry with iodide as reagent ion
- Revised physical design
- Heavily suppressed **water vapor dependence**

Our solution for PFAS calibrations

- Solution concentrations ranging from 0.2 to 4 mg L^{-1} to prepared in three different solvents
- Use of a syringe pump for stable injection of analyte at flows of 20 µL/h to 800 µL/h
- Heated tube (130°C) to minimize losses to walls
- 2 Lpm flow for fast response time and quick evaporation

Calibration setup



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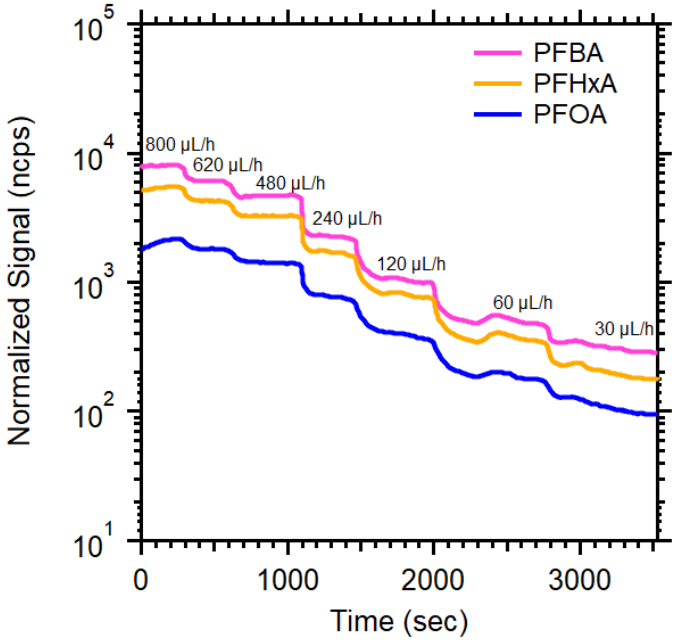

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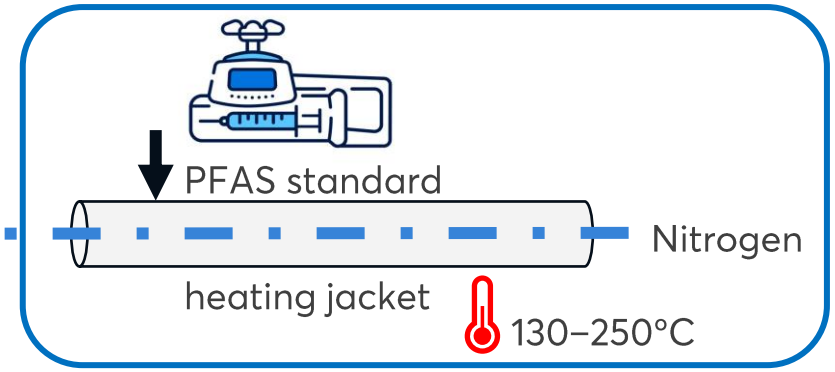
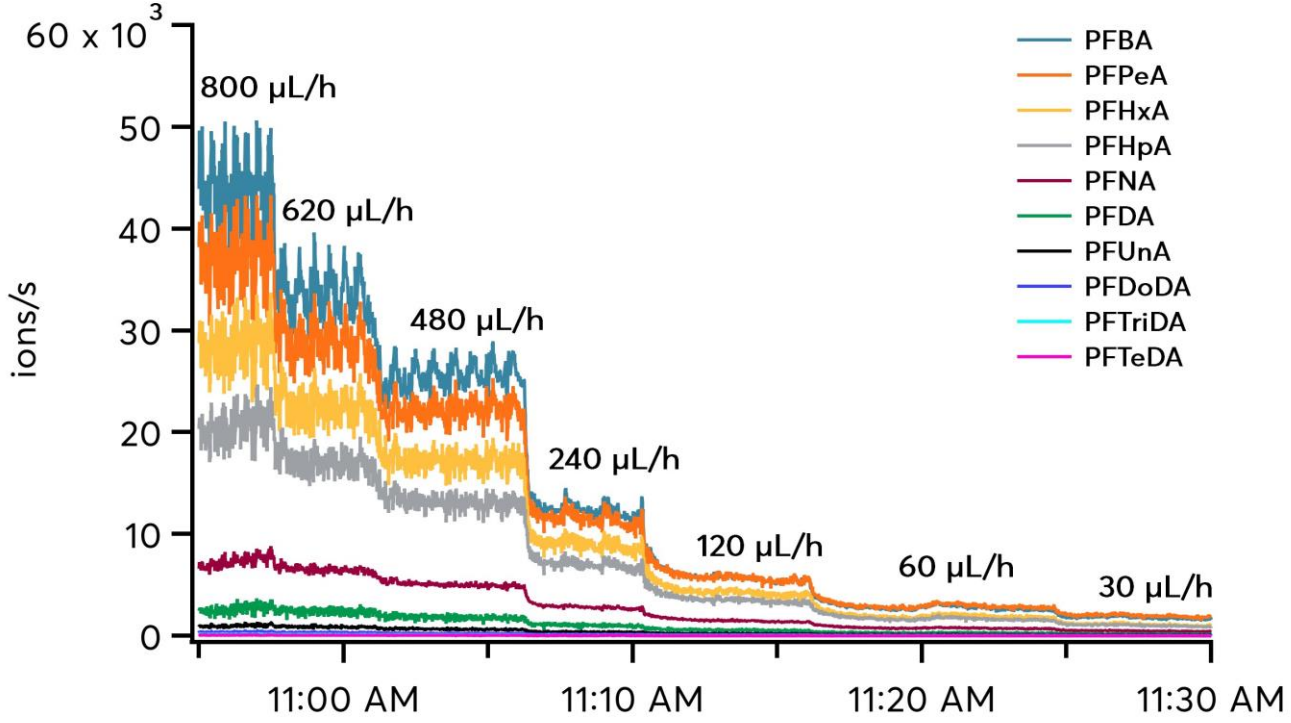
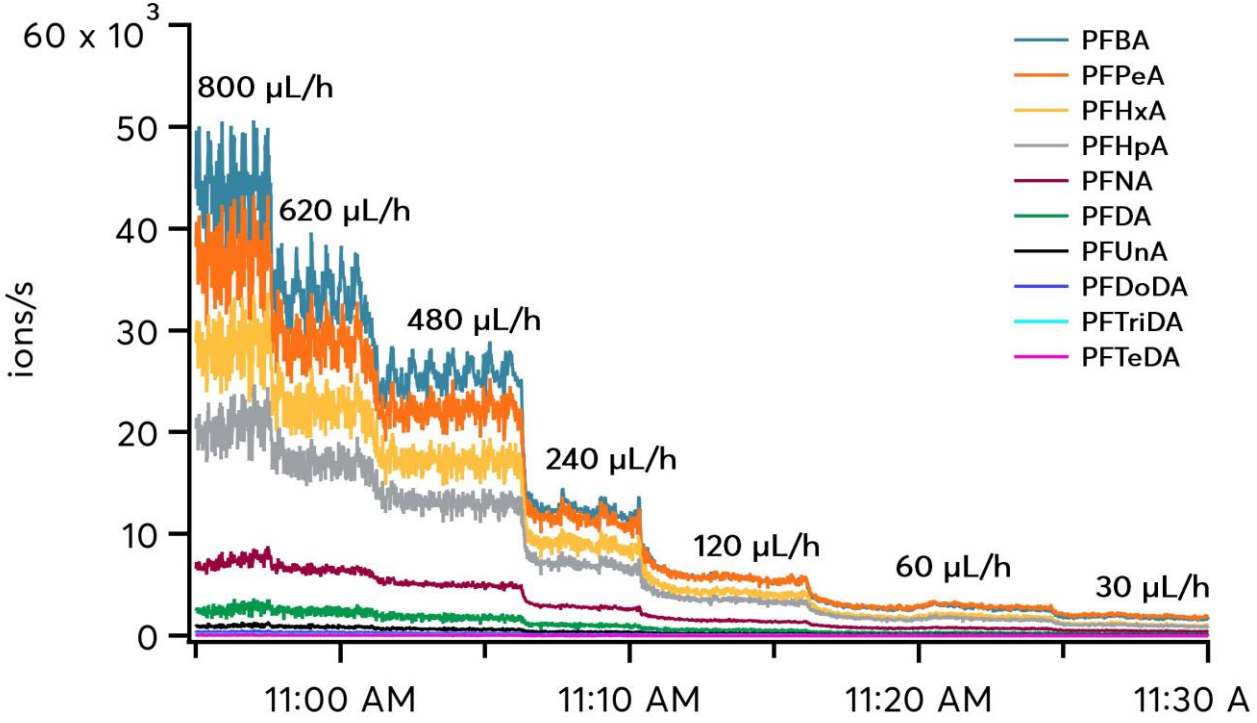


PFCAS calibrations using iodide chemical ionization mass spectrometry



Real-time, continuous measurements capture rapid changes in PFAS mixing ratio

PFCAS calibrations using iodide chemical ionization mass spectrometry



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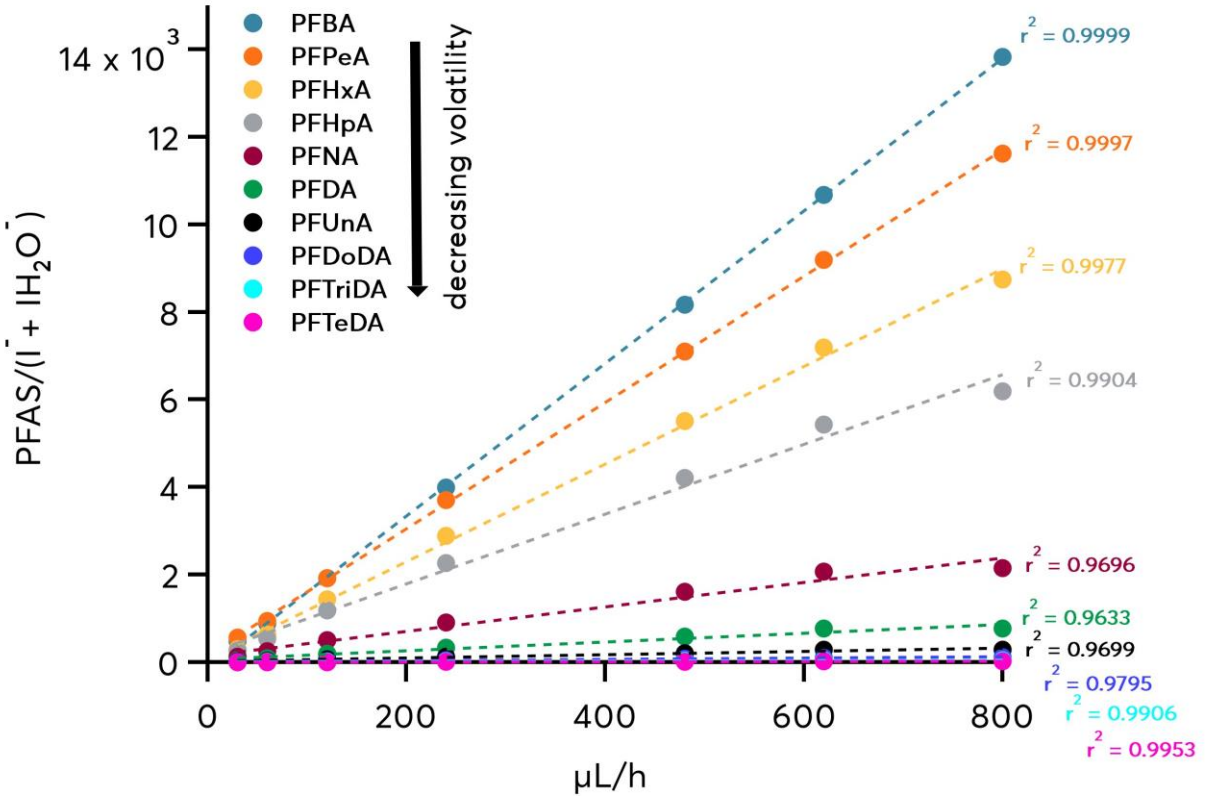
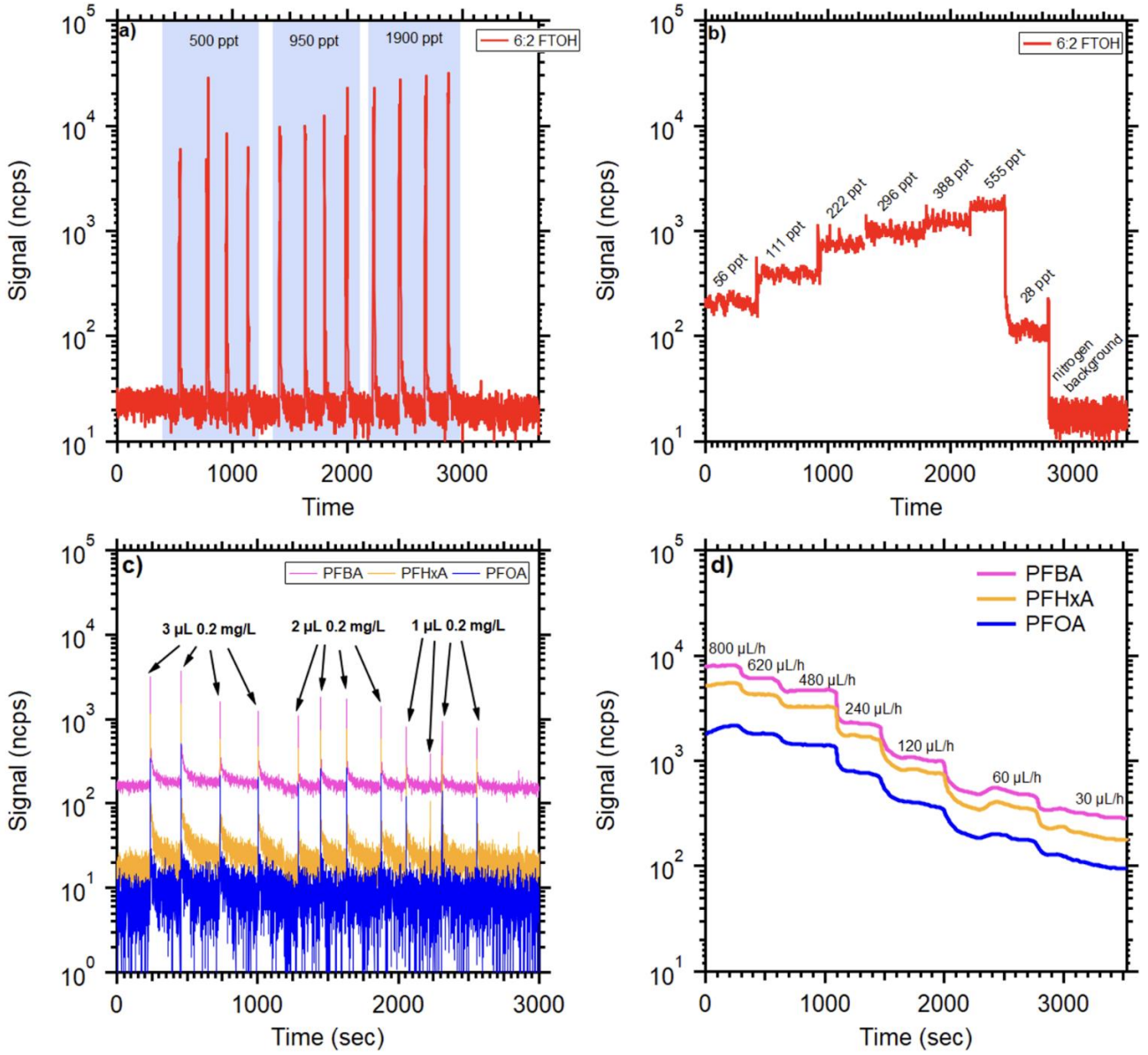


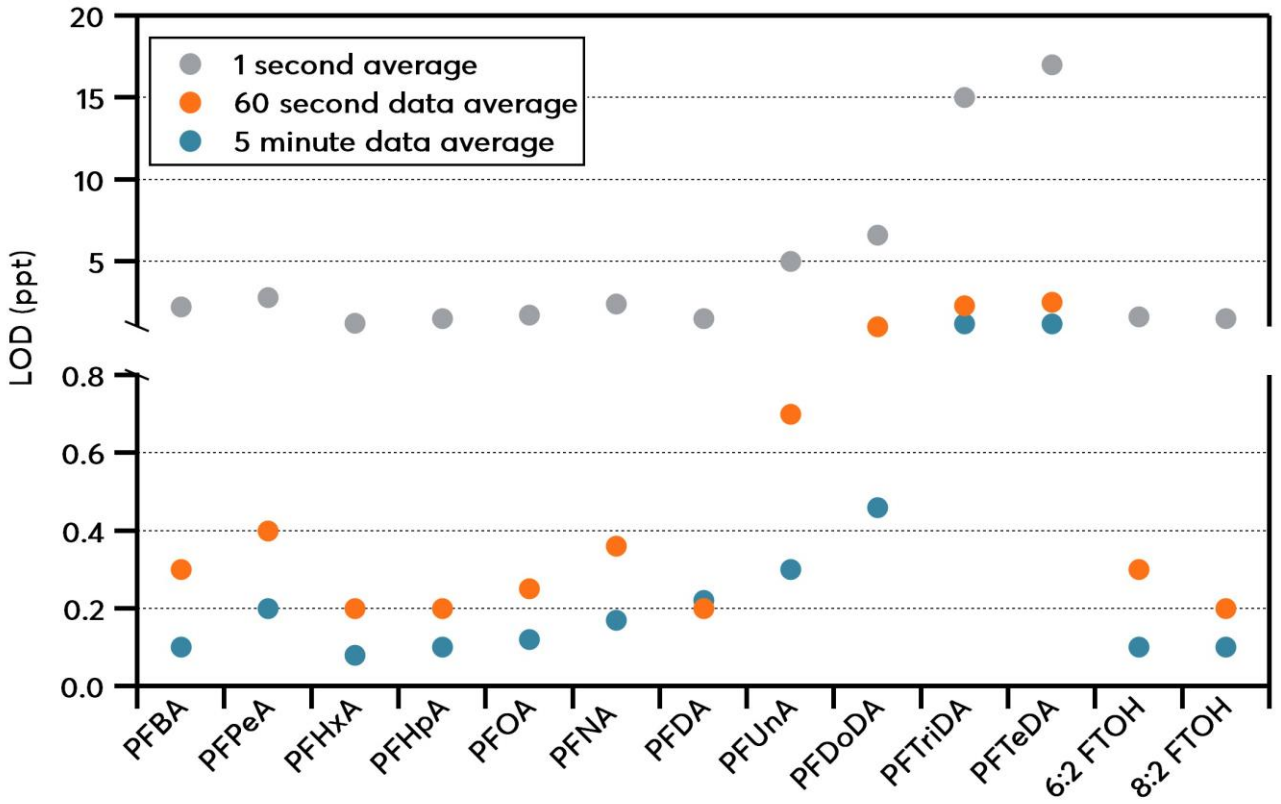
Sensitivity remains linear at low concentrations

PFCAS calibrations comparison to direct injection method

- methods agree within 30% for the volatile fraction of the PFAS
- higher variability in the signal response was observed with single injections of the same volume and concentration
- Syringe pump **showed improved stability in response** to changes in injected flow rates, and effectively mitigated operator-induced errors.



PFAS limits of detection (LOD)

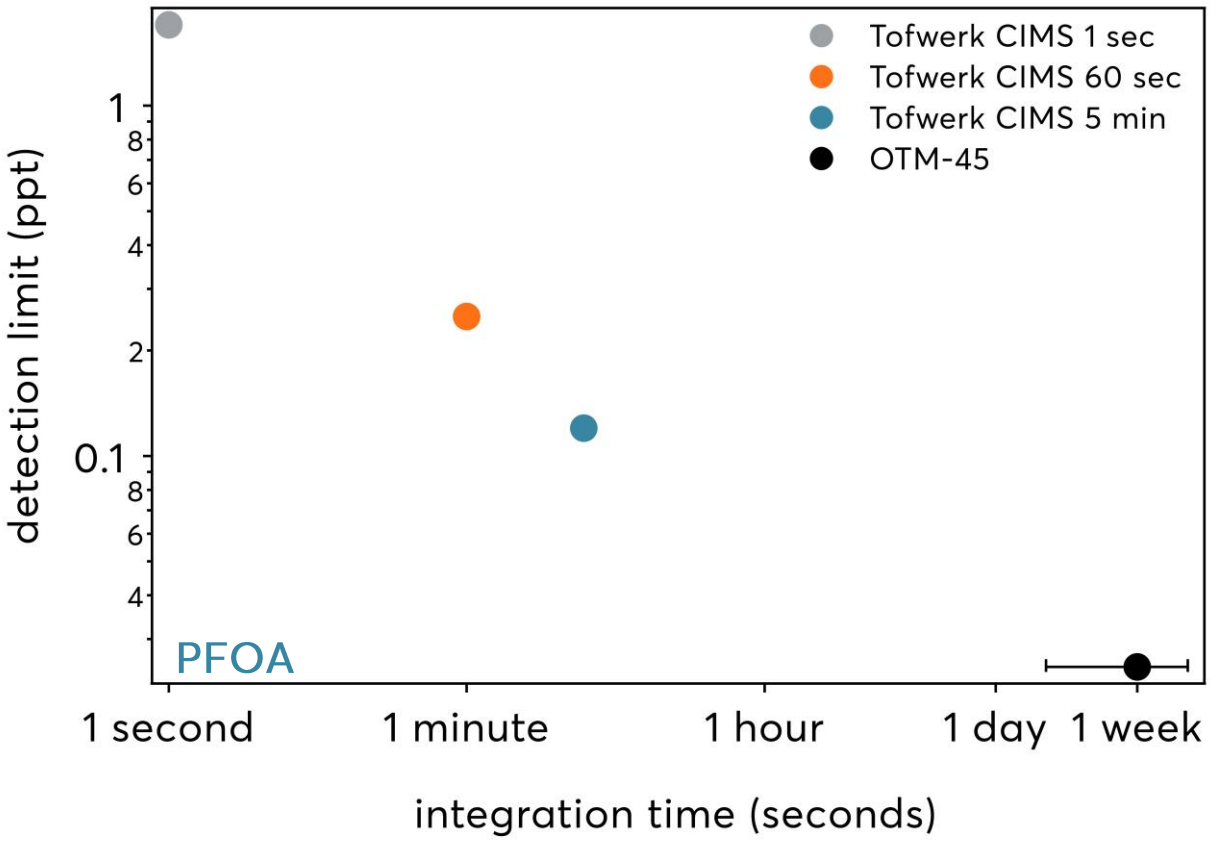


- LODs with 1 min average span between **200 ppq to 1 ppt**
- This corresponds to lower limit of ~ 2.46 x 10^6 molecules cm^{-3}
- Or **1.6 ng/m^3** for molecule at mass of 300Th

PFAS limits of detection (LOD) and comparison to other methods

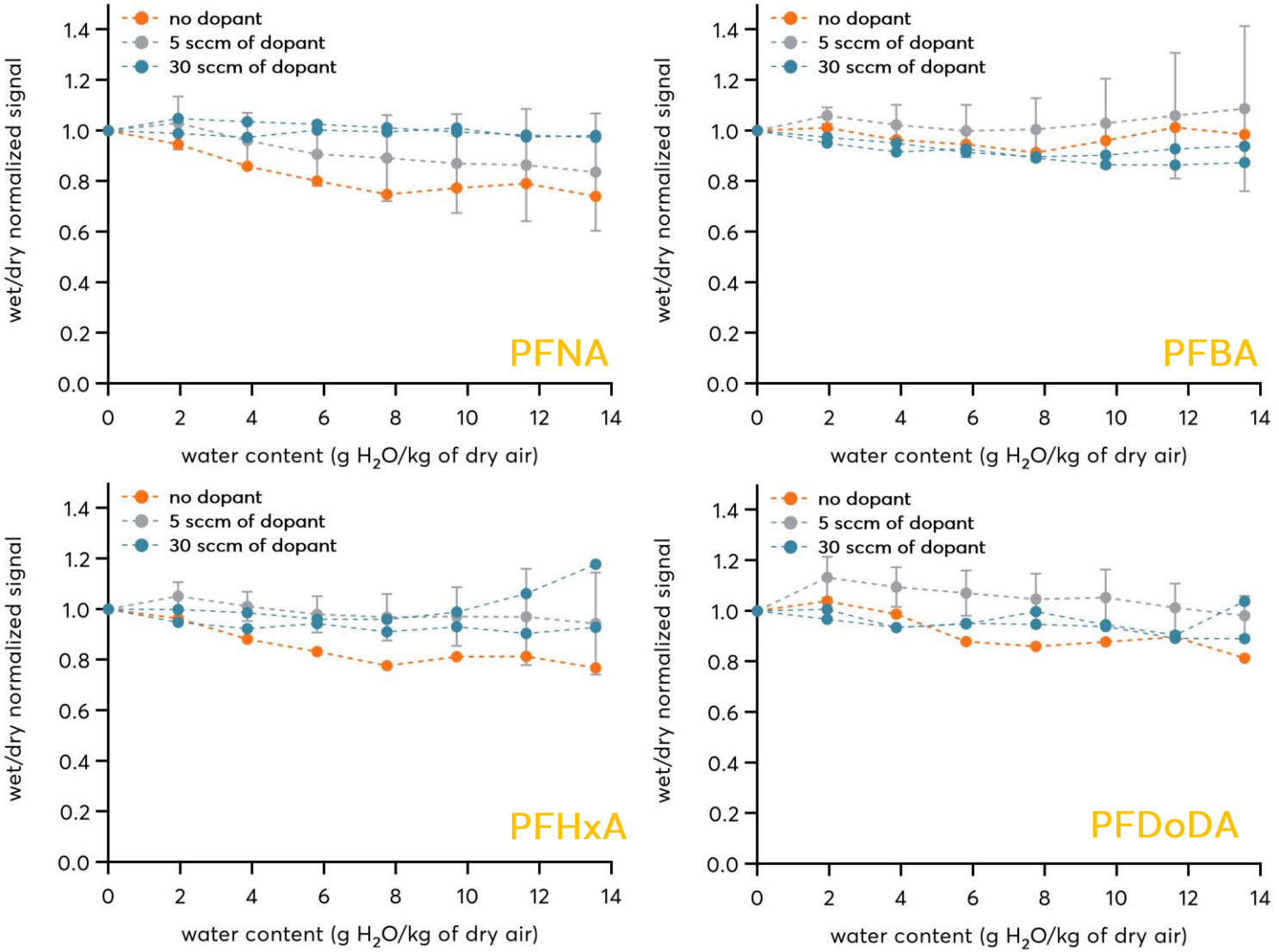
Compound	*OTM-45 MDL (ppt)	TOFWERK LOD (ppt)
	1 week of collection	1 min collection
PFBA	0.234	0.2
PFPeA	0.018	0.2
PFHxA	0.023	0.1
PFHpA	0.014	0.2
PFOA	0.025	0.3
PFNA	0.008	0.3
PFDA	0.006	0.5
PFUnA	0.014	0.5
PFDoDA	0.005	0.7
PFTriDA	0.004	1.2
PFTeDA	0.006	1.0
6:2 FTOH	0.016	0.3
8:2 FTOH	0.012	0.2

- OTM-45 achieve lower LODs due to longer averaging time (stationary measurements collected several days to weeks)
- sacrifice data acquisition speed for sensitivity

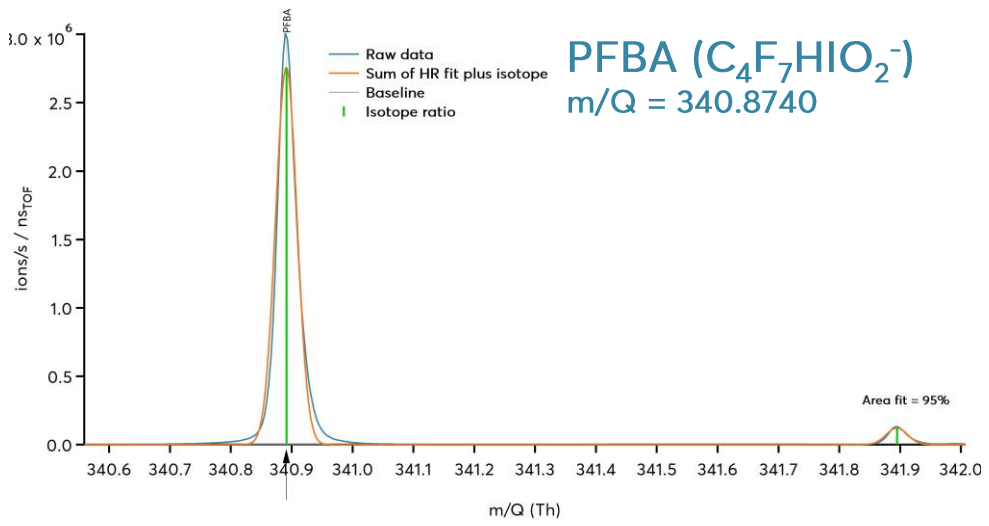


*In-Stack Detection Limits from Other Test Method 45 (OTM-45) Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources

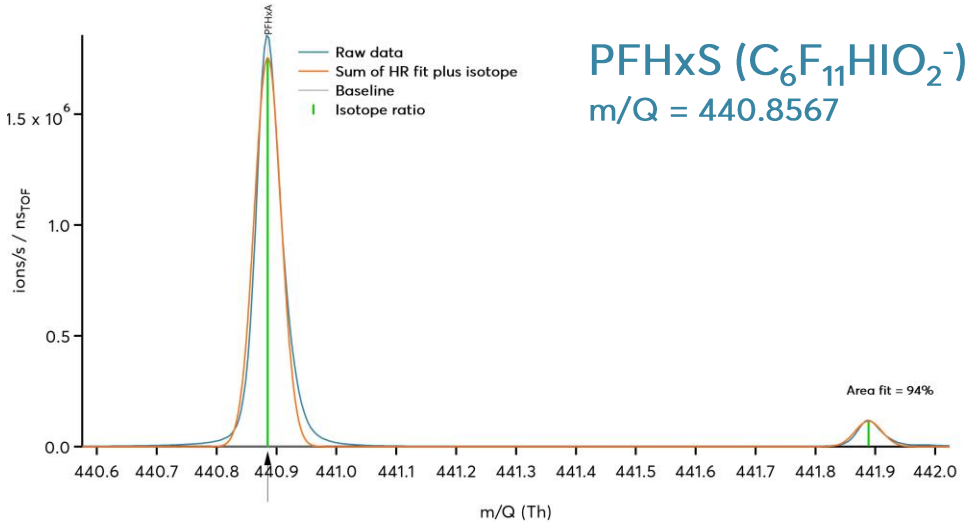
RH can influence sensitivity, but less than experimental variability



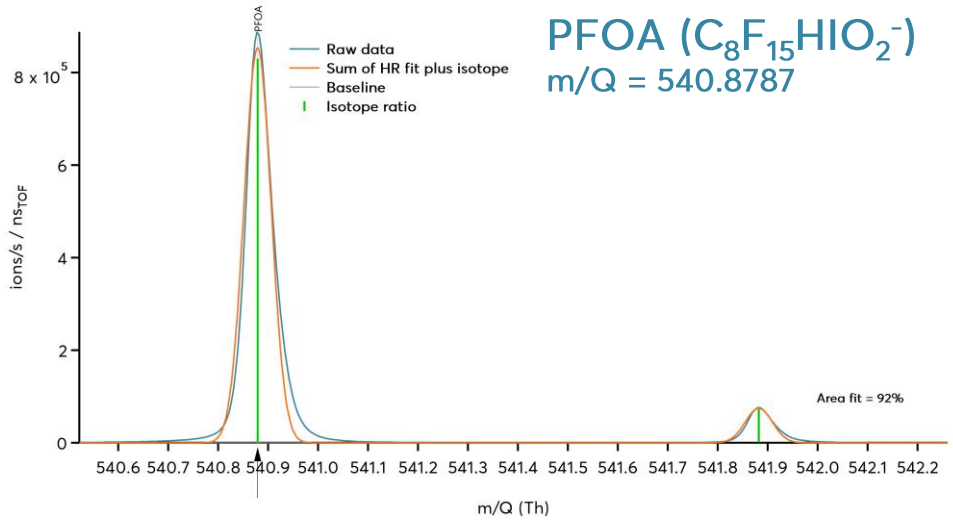
PFCAs identification with iodide chemical ionization mass spectrometry



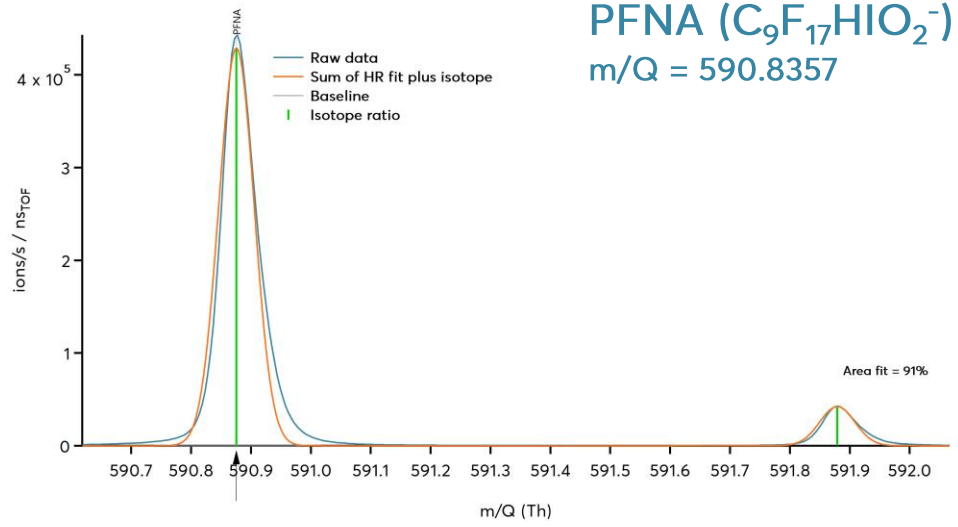
PFBA ($C_4F_7HIO_2^-$)
m/Q = 340.8740



PFHxS ($C_6F_{11}HIO_2^-$)
m/Q = 440.8567



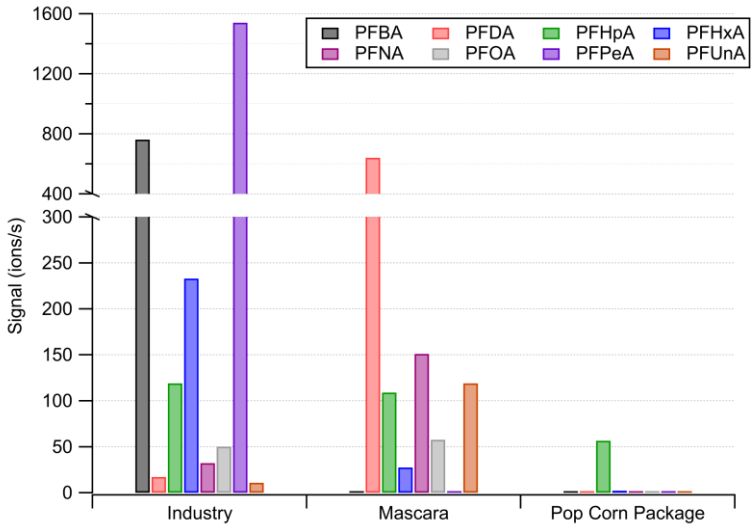
PFOA ($C_8F_{15}HIO_2^-$)
m/Q = 540.8787



PFNA ($C_9F_{17}HIO_2^-$)
m/Q = 590.8357

Real time measurements of emissions from consumer products

- **Direct untargeted 'headspace sniffing'** - water proof mascara, popcorn packaging

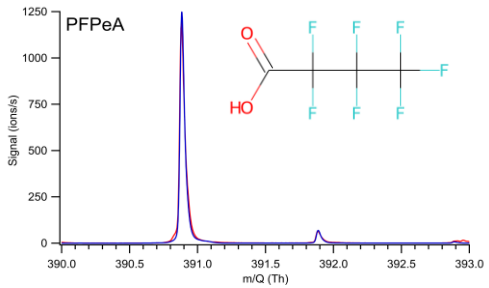


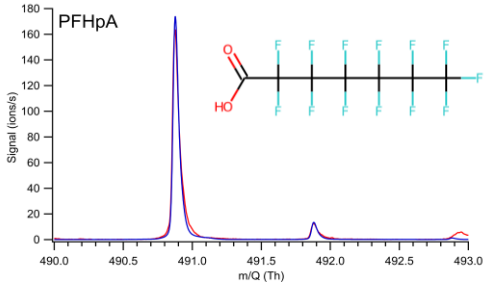
Source

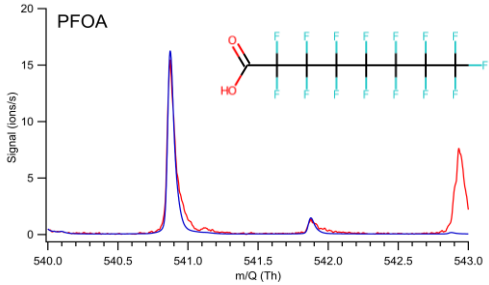
Industrial Processes

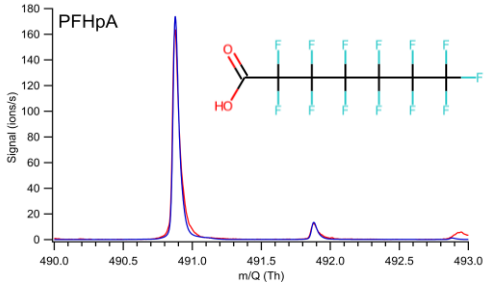
Cooking Materials

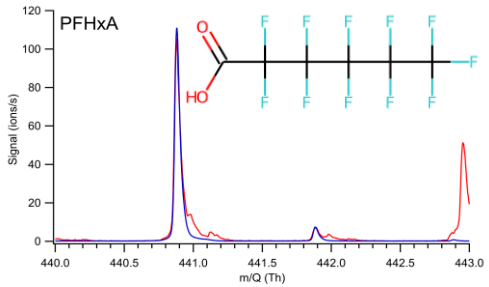
Personal Care Products







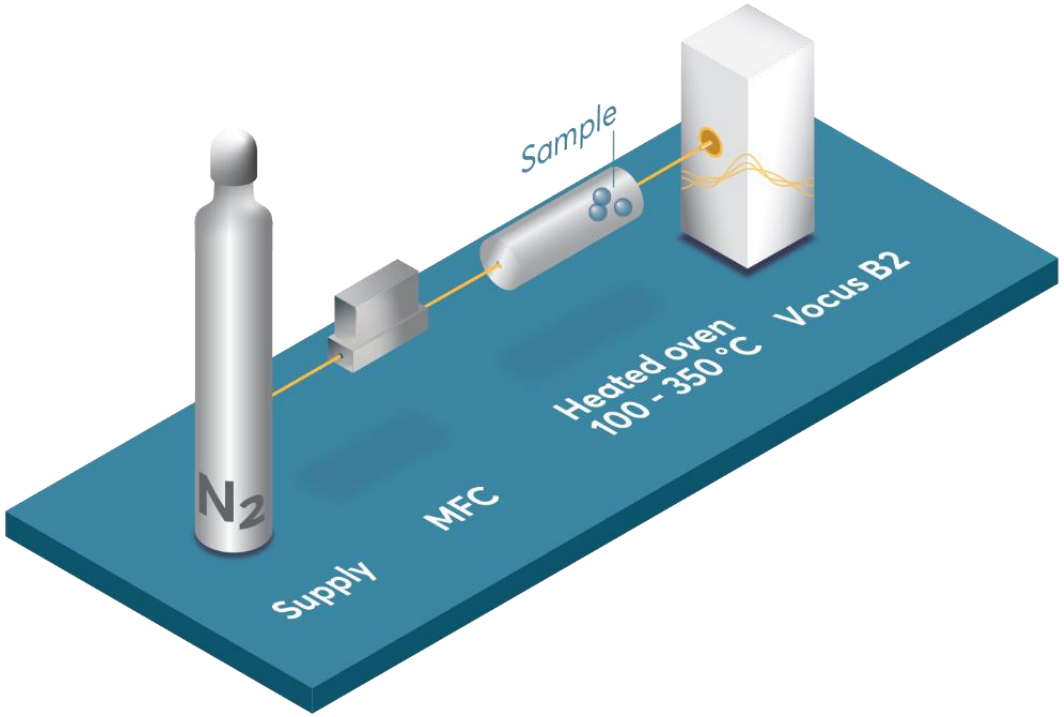




Materials offgasing

- real-time monitoring of PFAS emissions from PFA tubing at different temperatures

Experimental Setup



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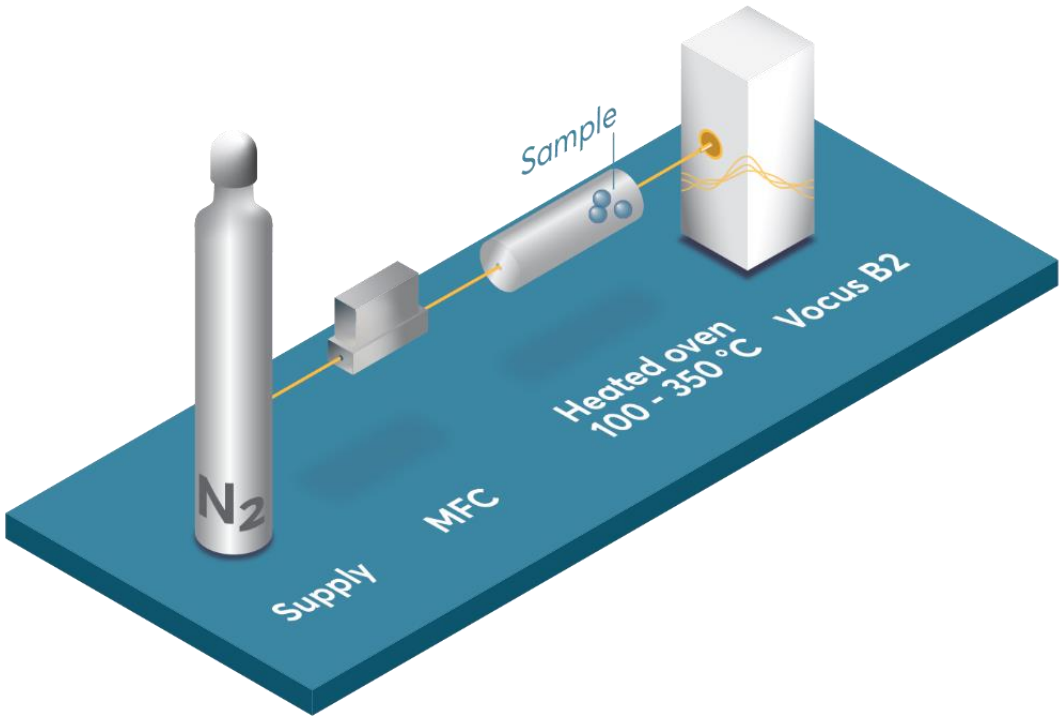
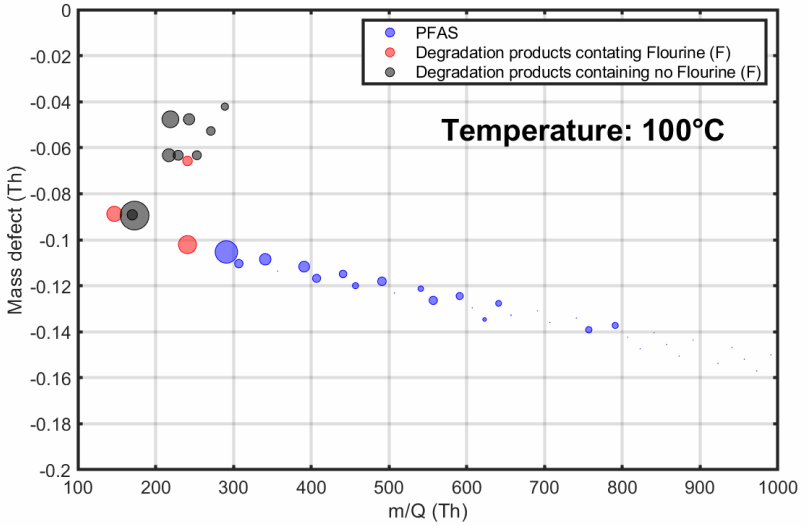
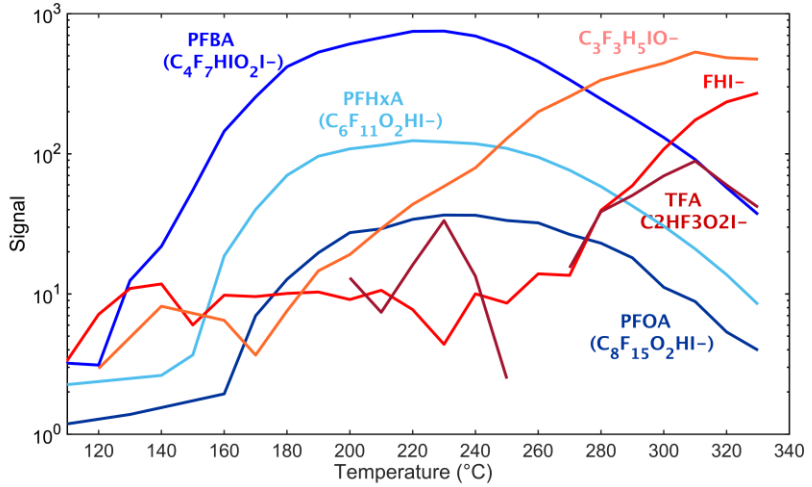


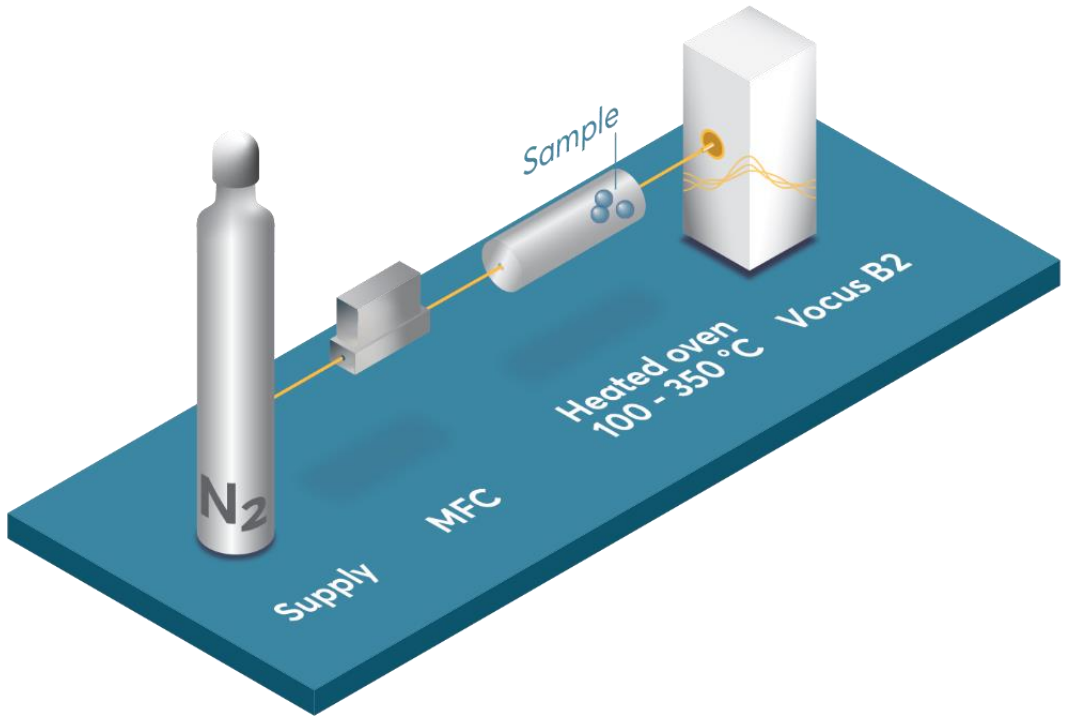




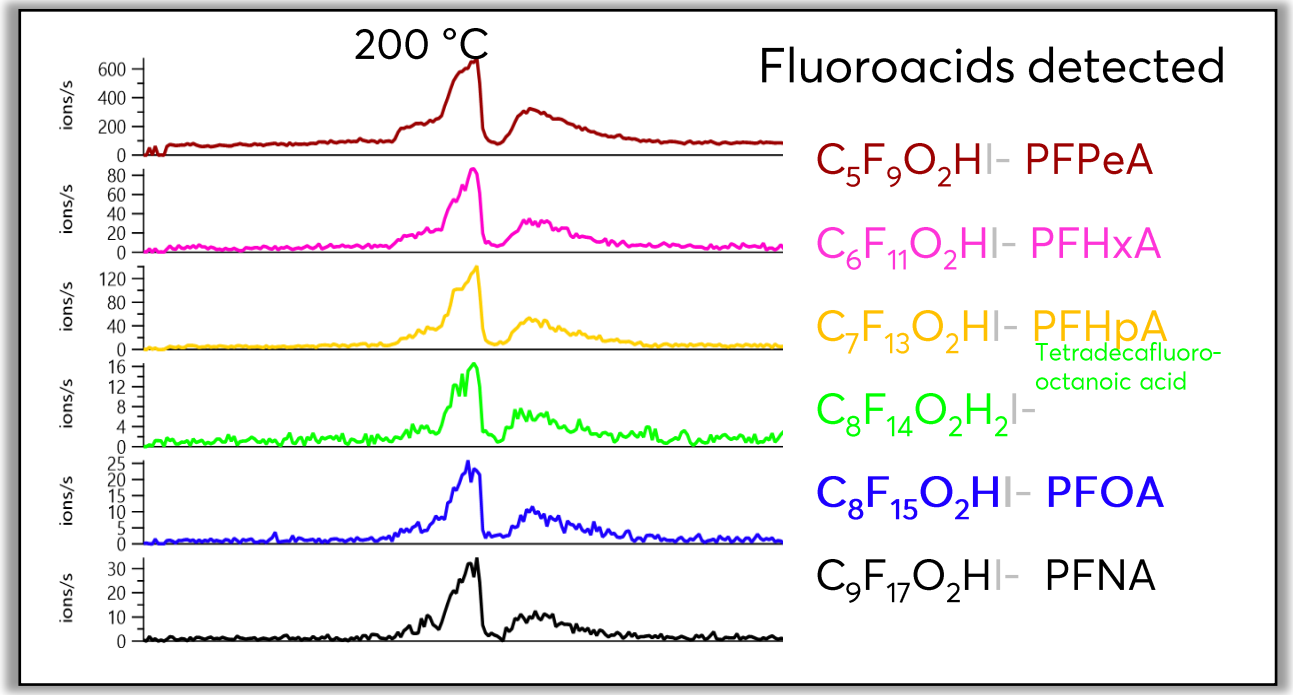
Materials offgasing - PFAS emissions from 'PFAS free' material

- 5g of unknown industrial sample typically experiencing higher temperature was heated to 250 °C and cooled down

Experimental Setup



Increasing Temperature

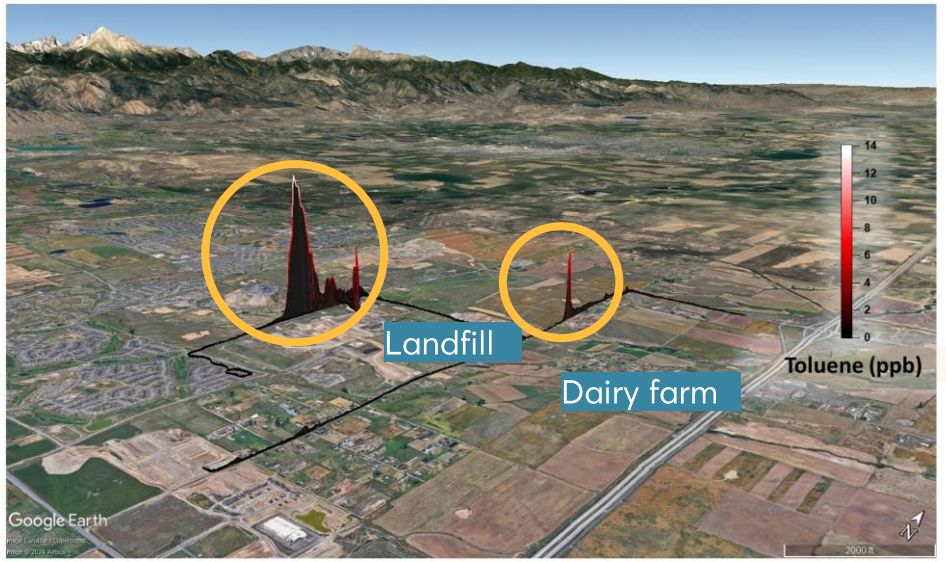


- PFAS emissions question of temperature

Ultimative goal - Searching for PFAS Sources in Ambient Air

Indoor air

Industrial facilities, stack emissions, fenceline monitoring (compliance)



Experts in mobile monitoring and characterising odour emissions and its sources

Thank you for your attention!

Veronika.pospisilova@tofwerk.com