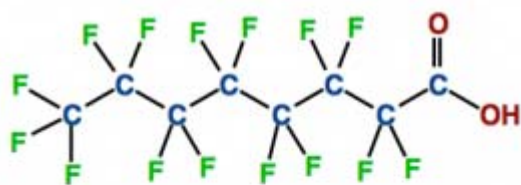


Sampling and Analysis of Perfluoroalkyl Substances in Air Using TD–GC–MS

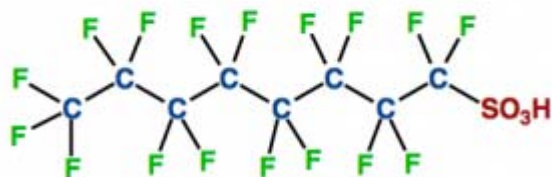


What are PFAS compounds?

- 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 - perfluorooctanoic acid

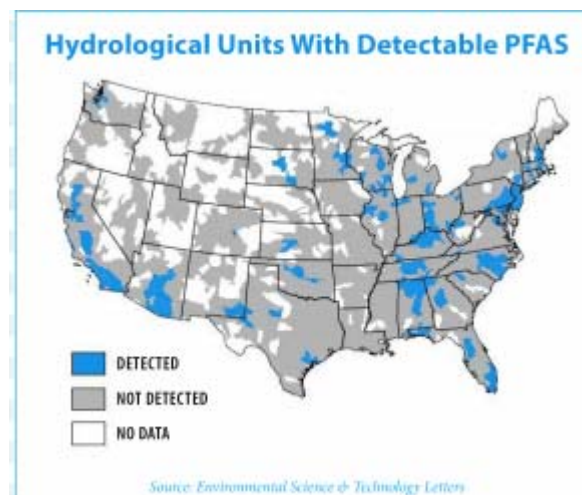


PFOS - perfluorooctanesulfonic acid



Exposure risks of PFAS

- There is evidence that exposure to PFAS can lead to adverse human health effects, such as:
 - low infant birth weights
 - effects on the immune system
 - cancer (for PFOA), and thyroid hormone disruption (for PFOS).
- PFAS are present in firefighting foams so high levels are found near military sites, where they have been used for firefighting drills
- This is one pathway for PFAS to enter the drinking water supply



How are PFAS currently measured?

- For drinking water the US EPA have method EPA 537.1
 - Determination of Selected Perfluorinated Alkyl Acids (PFAA) in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)
 - Only targets 18 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



Where does thermal desorption fit in?

- Markes Inc. is working with a local lab contracted with Jacobs (government contactor) to develop sampling and analytical methods for volatile PFAS
- Limited previous work;
 - 2008 paper on fluorotelomer alcohols (FTOHs) identified in Japan using a newly developed passive air sampler containing activated carbon felts.
 - 8:2 FTOH ranged from <32 to 2466 pg m^{-3} and was ubiquitous in the environment in Japan.
- EPA study on FTOHs in 54 consumer products
 - The content of 6:2 FTOH ranged from n/d to $331 \text{ } \mu\text{g g}^{-1}$, 8:2 FTOH from n/d to $92 \text{ } \mu\text{g g}^{-1}$, and 10:2 FTOH from n/d to $24 \text{ } \mu\text{g g}^{-1}$.
 - In addition, two consumer products from the home textile category were tested in the washing-drying process **in the micro-scale chamber** under elevated temperatures.
 - The experimental data show that the washing-drying process with one cycle did not significantly reduce the FTOH concentrations in the tested consumer products.
 - Future tests should include air sampling to allow determination of the absolute emission rates at different temperatures.

Project Team



Julia Roth

Tiffany Hill

James Hatton

Chris Lutes

Bill Diguiseppi

Chase Holton, PhD *(now at Geosyntec)*



Chris Heron

Martha Maier



David Wevill, PhD, MRSC

Wade Bontempo

Nicola Watson, PhD



University of Nevada, Reno

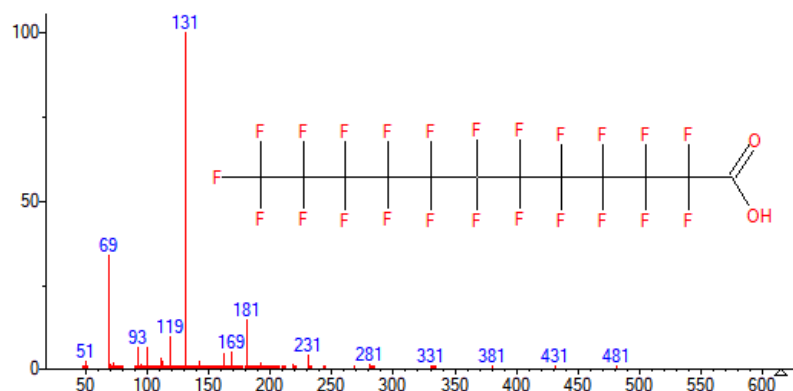
David Hanigan, PhD

Utsav Thapa, PhD

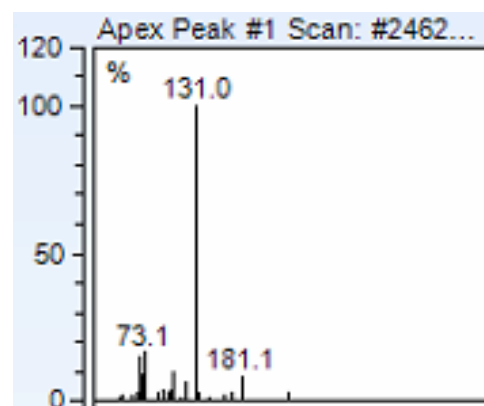
Thermal desorption method development

- Local lab, Vista, provided individual standards for 34 PFAS compounds (50 ng/μL in methanol) used in their current LC–MS/MS method
- 1 uL of each was loaded in turn to stainless steel Markes 'Universal' sorbent tubes
- 22/34 compounds gave a discernable peak
 - Acids, alcohols and sulfonamides did work
 - Sulfonic acids and sulfonates didn't work

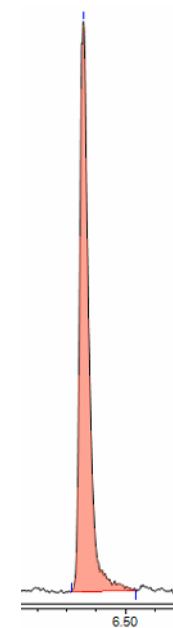
PFDoA standard



NIST Reference spectra



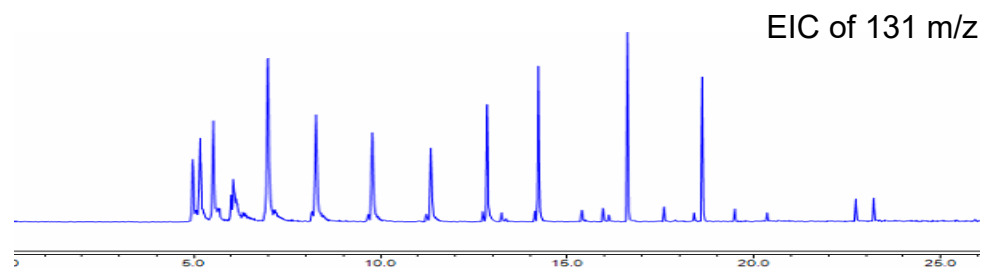
Acquired Spectra



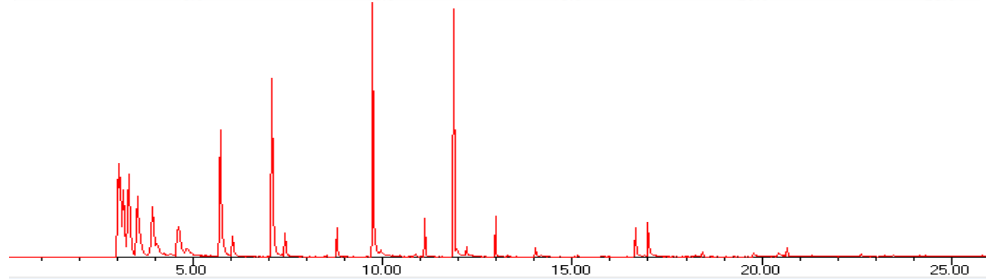
GC separation

- 22 compounds were mixed together to create a ~ 2.2 ng/μL mixed standard.
- This mix was used to refine the GC column and method.
- The 'VRX' 60 m x 0.25 mm x 1.4 μm column was found to give the best separation

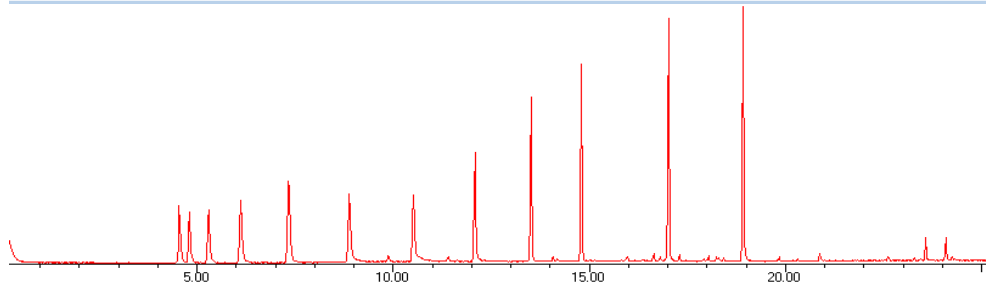
100% Dimethyl Polysiloxane
60 m x 0.25 mm x 1.00 μm
1.2 mL/min constant flow



(5%-Phenyl)-methylpolysiloxane
30 m x 0.25 mm x 0.25 μm
0.9 mL/min constant flow

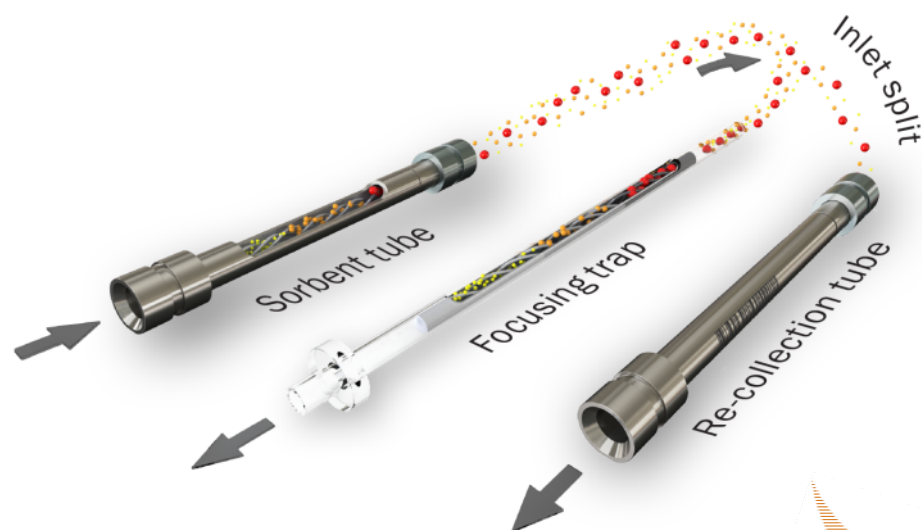


VRX type
60 m x 0.25 mm x 1.4 μm
1.2 mL/min constant flow



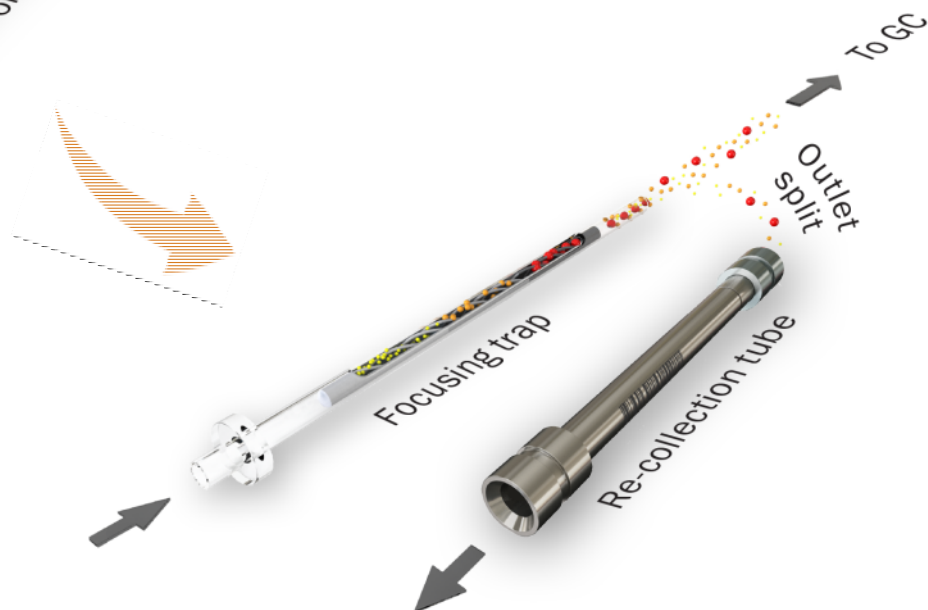
Re-collection and re-analysis of sample by TD-GC-MS

How it works



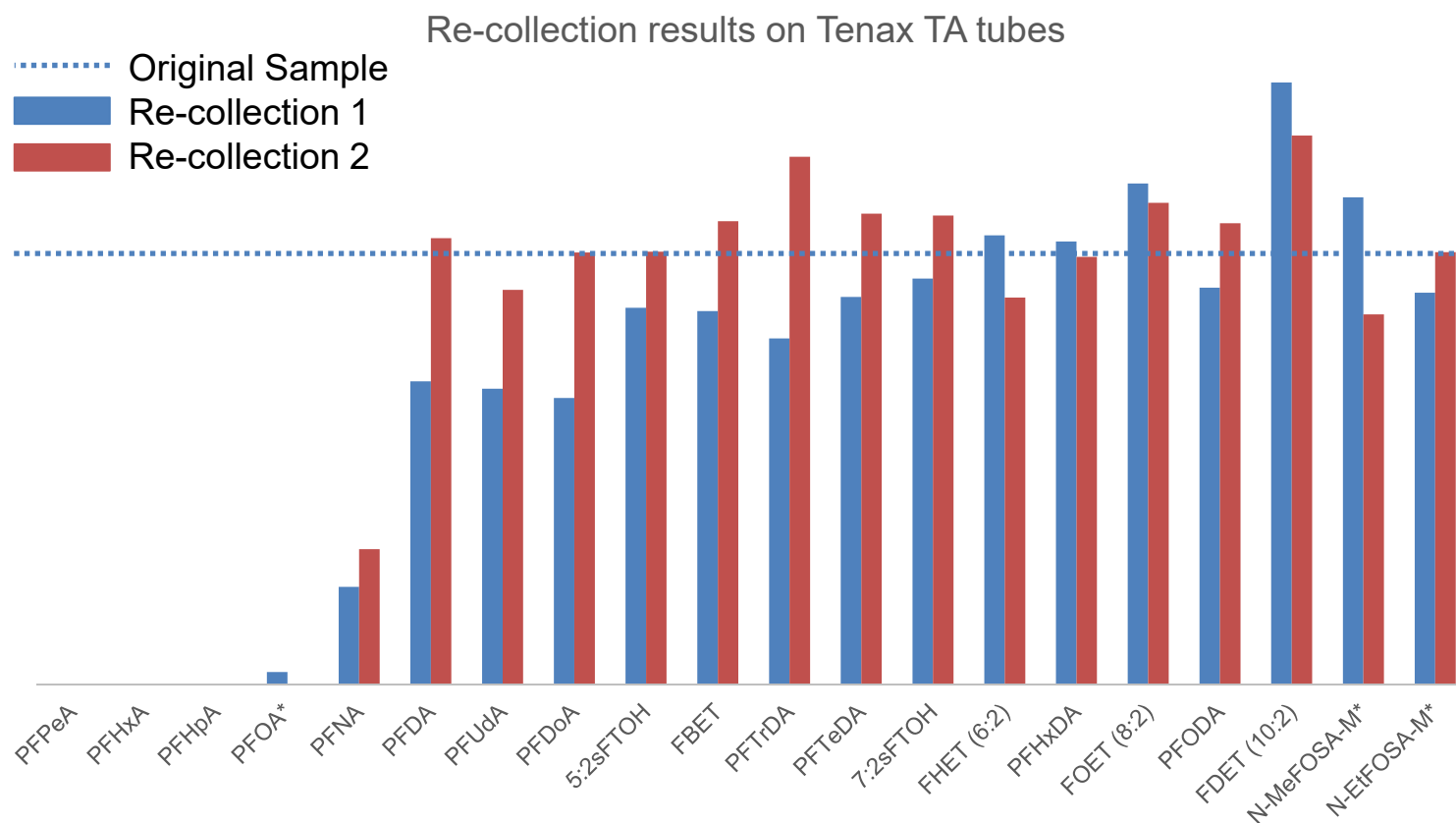
1. Volatiles transferred from sorbent tube to focusing trap in flow of gas.
 - Optional inlet split.

2. Focusing trap heated rapidly \Rightarrow analytes desorb and are injected to GC.
 - Optional outlet split.



Re-collection (recovery) tests

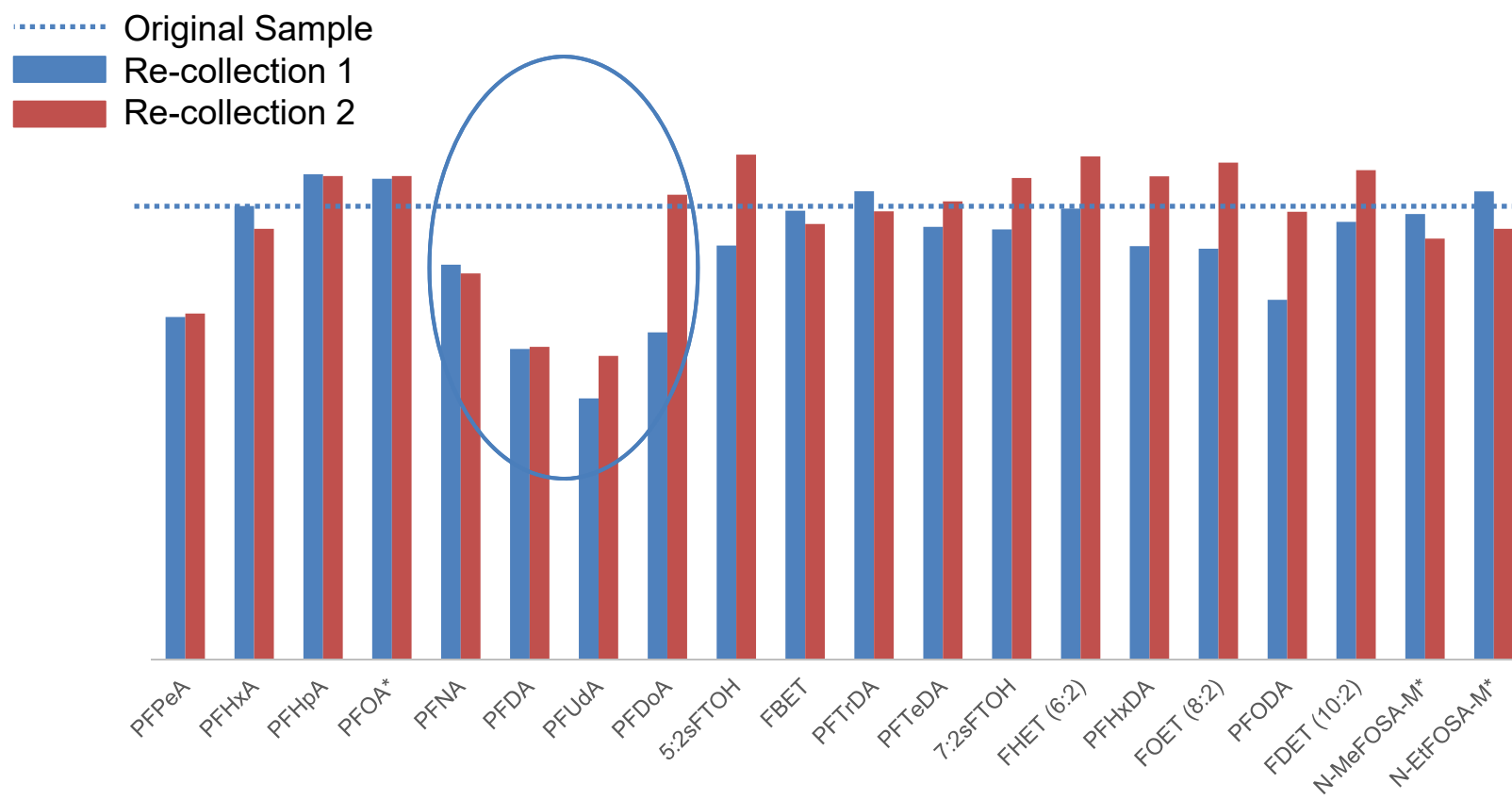
- Re-collection experiments were run using Markes' Universal and Tenax TA stainless steel tubes.
 - 5 lightest acid compounds were lost (due to breakthrough) on Tenax TA tube.



Re-collection (recovery) tests

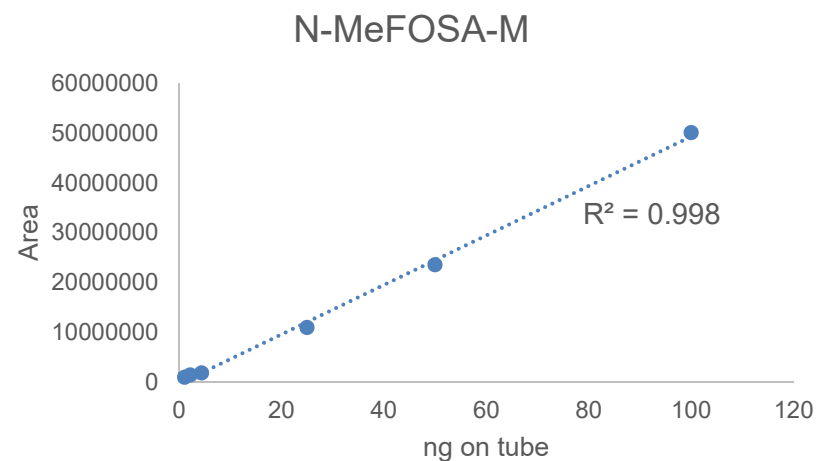
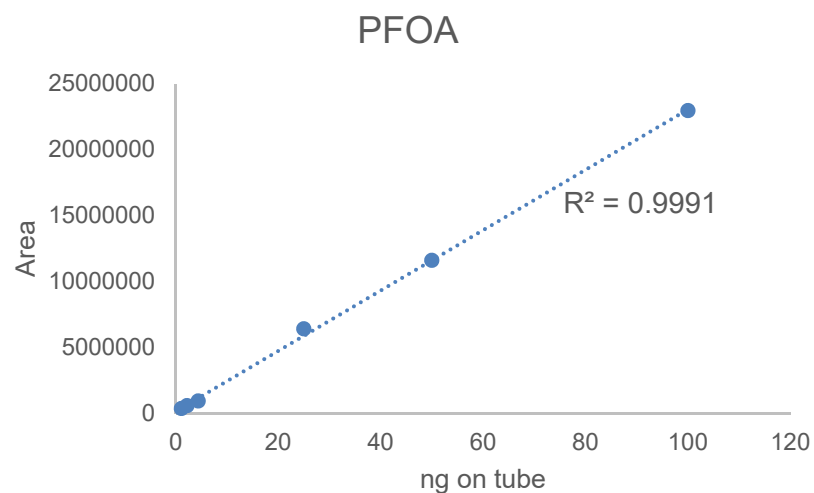
- No breakthrough seen on Markes Universal stainless-steel sorbent tube.
- Consistent drop in recovery for PFNA, PFDA and PFUdA indicated in circle

Re-collection results on Markes 'Universal' tubes



Calibration and Repeatability

- Calibration and repeatability tests were carried out using stainless steel 'universal' tubes
 - Calibration relative response factor (RRF) % RSD averaged 23.0% (ok)
 - Repeatability (1 uL injection) in full scan mode averaged 13.2% n=3 (ok)



Breakthrough

- Basic breakthrough tests performed by loading standard to a Universal tube then sampling an additional volume, 400 cc and 800 cc of lab air
 - Recovery was > 90% at both volumes for all sulfonamides and acids except PFDoA (83% and 72% for 400 cc and 800 cc respectively)
 - Carryover test of the tube showed > 5% carryover for PFDoA, suggesting low recovery was due to incomplete desorption from the tube
- Based on these preliminary tests, 400 cc sample volume is suggested
- Method optimization would require improvements of desorption efficiency to increase overall recovery.

AFFF volatility box experiment

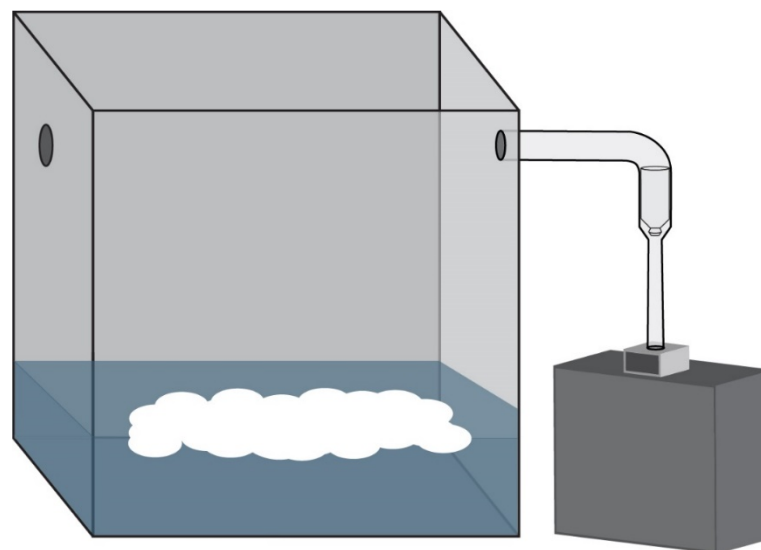


Experimental setup

| Experimental Parameters | | |
|-------------------------|-----------------------------------|----------------|
| | <i>Trial 1</i> | <i>Trial 2</i> |
| Flow Rate (cc/min) | 200 | |
| Dilution | 50% AFFF, ~2.5% active ingredient | |
| AFFF Expansion Ratio | 15:1 | |
| Sample Duration (hours) | 24 | 0.083 |

| Sample Breakdown per Event | | |
|----------------------------|-----------------|------------|
| Sample Type | XAD/PUF Samples | TD Samples |
| Equipment blanks | 1 | 1 |
| Samples | 2 | 2 |
| Duplicates | 1 | 1 |

| Materials Used | |
|----------------|----------------------------------------------------------------|
| Volatility Box | HDPE |
| AFFF | Fluorotelmorized derived foam currently available for purchase |
| Tubing | HDPE before sample, Tygon tubing after sample |
| Pump | SKC PCXR8 |



Analytical method: LC–MS–MS (MRM)

- Analyzed via QSM v.5.1 Table B-15 method
- XAD/PUF cartridges extracted for 30 PFAS
 - Reporting limit of **2 ng/sample (or ppt)**

| | | | | |
|---------|---------|---------|---------|--------|
| PFBA | PFHpA | PFOSA | EtFOSAA | PFTeDA |
| PFPeA | PFHxS | PFOS | PFUnA | EtFOSA |
| PFBS | 6:2 FTS | PFDA | PFDS | PFHxDA |
| 4:2 FTS | PFOA | 8:2 FTS | PFDoA | PFODA |
| PFHxA | PFHpS | PFNS | MeFOSA | MeFOSE |
| PFPeS | PFNA | MeFOSAA | PFTTrDA | EtFOSE |

Analytical LC–MS–MS (MRM) results



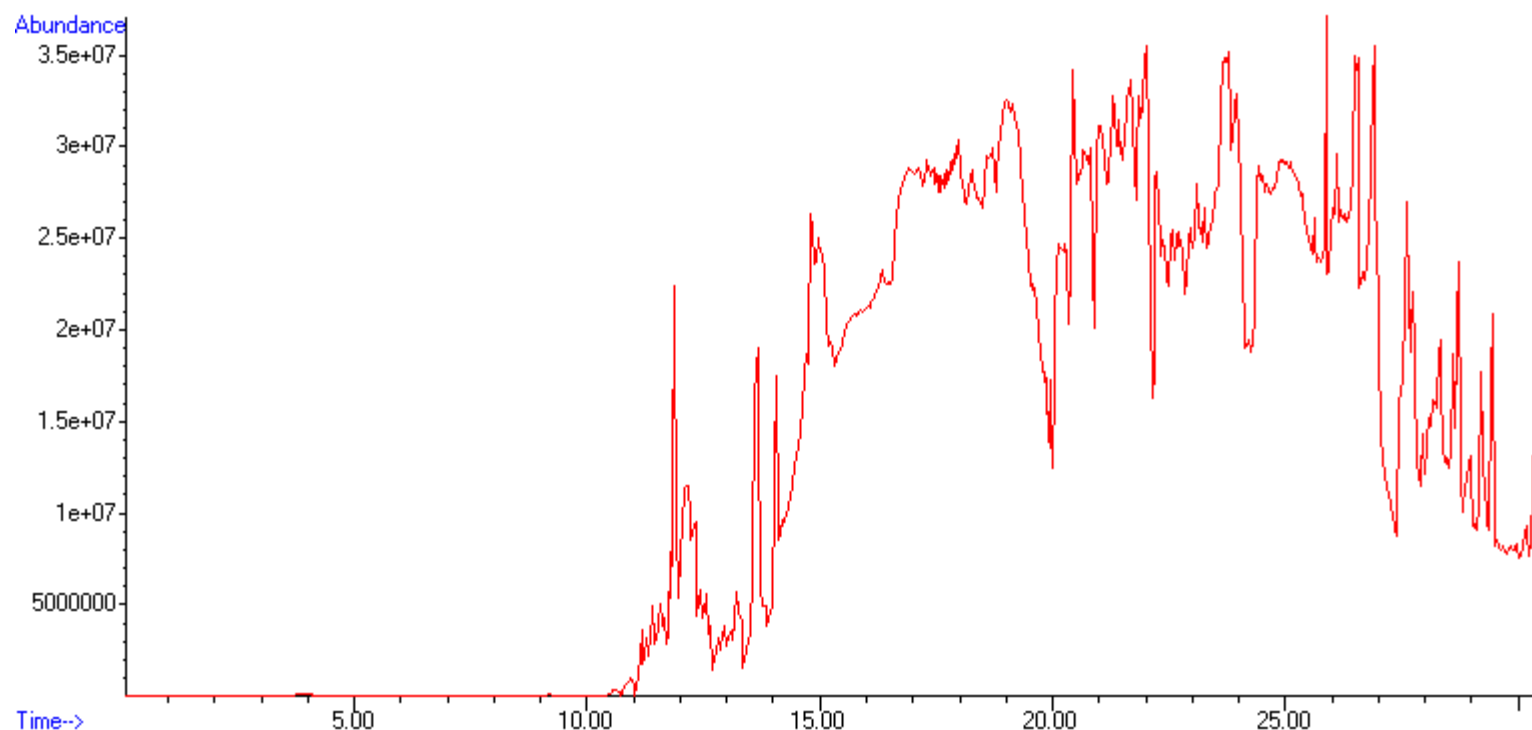
| Compound | CAS No. | Equipment Blank (ng/L) | Sample 1 (ng/L) | Sample 2 (ng/L) | Sample 3 (ng/L) |
|----------|------------|------------------------|-----------------|-----------------|-----------------|
| PFBA | 375-22-4 | 3.45 | 5.43 | 3.98 | 4.27 |
| PFHxA | 307-24-4 | ND | 41.7 | 33 | 32.1 |
| 6:2 FTS | 27619-97-2 | ND | 66.7 | 77.5 | 47.3 |

Key Takeaways:

- PFHxA and 6:2 FTS were present in AFFF emissions, but not at levels that would be of concern for vapor intrusion
- PFHxA and 6:2 FTS are intermediates in the degradation pathway
- PFBA may have been detected due to background

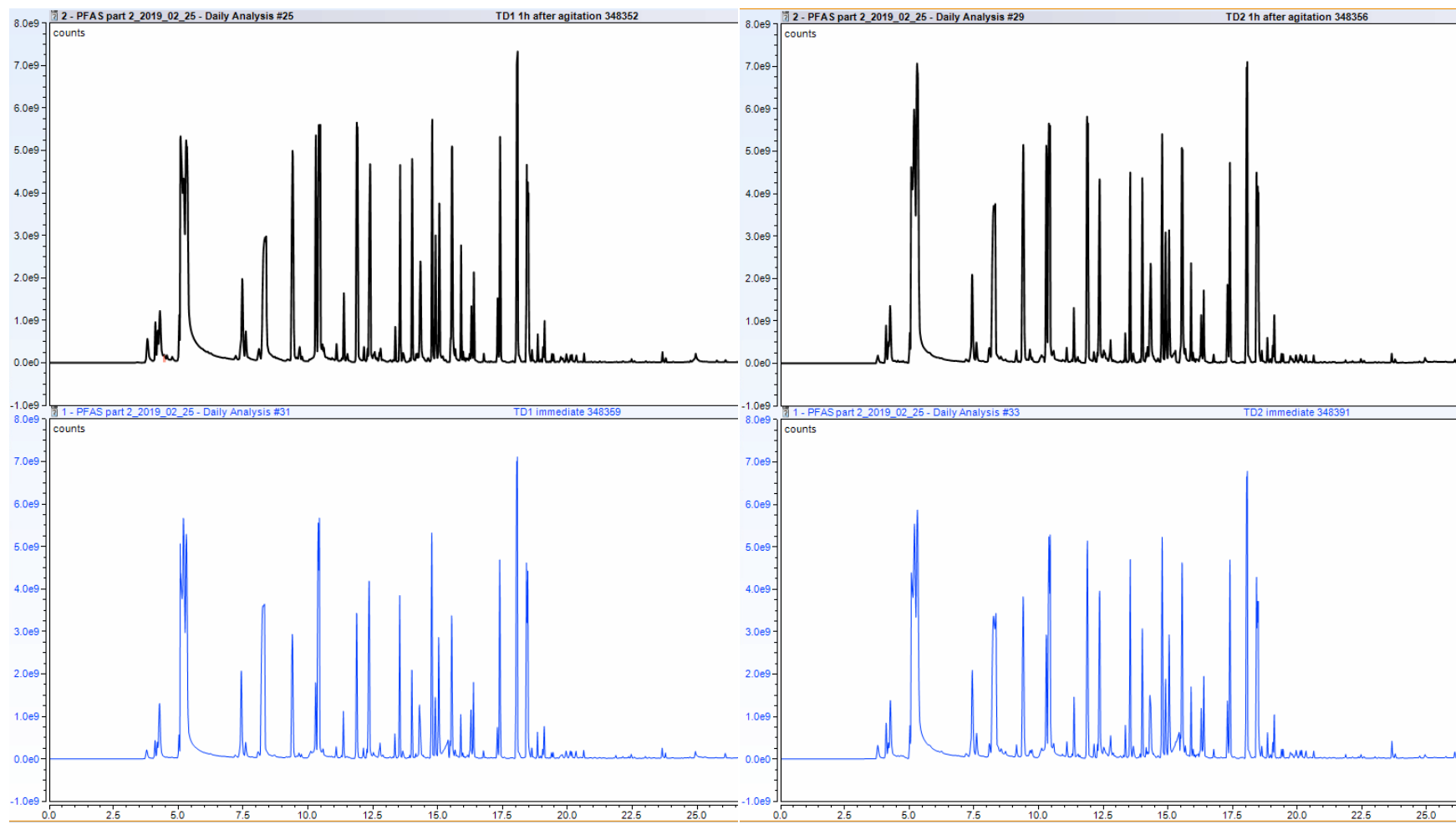
Sampling experiment results

- Sampling experiment performed using direct emissions from AFFF
- TD tube was sampled at 200 mL/min for 24 hours = 288 L of air sampled
- This exceeded by far the breakthrough volume for the PFAS compounds and overloaded the GC column and MS detector on the first run



Sampling experiment repeat

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



Target analysis results – PUF/XAD-2 comparison

Values are ppt

PUF/XAD-2 samples run by LC-MS-MS at Vista Analytical labs, CA

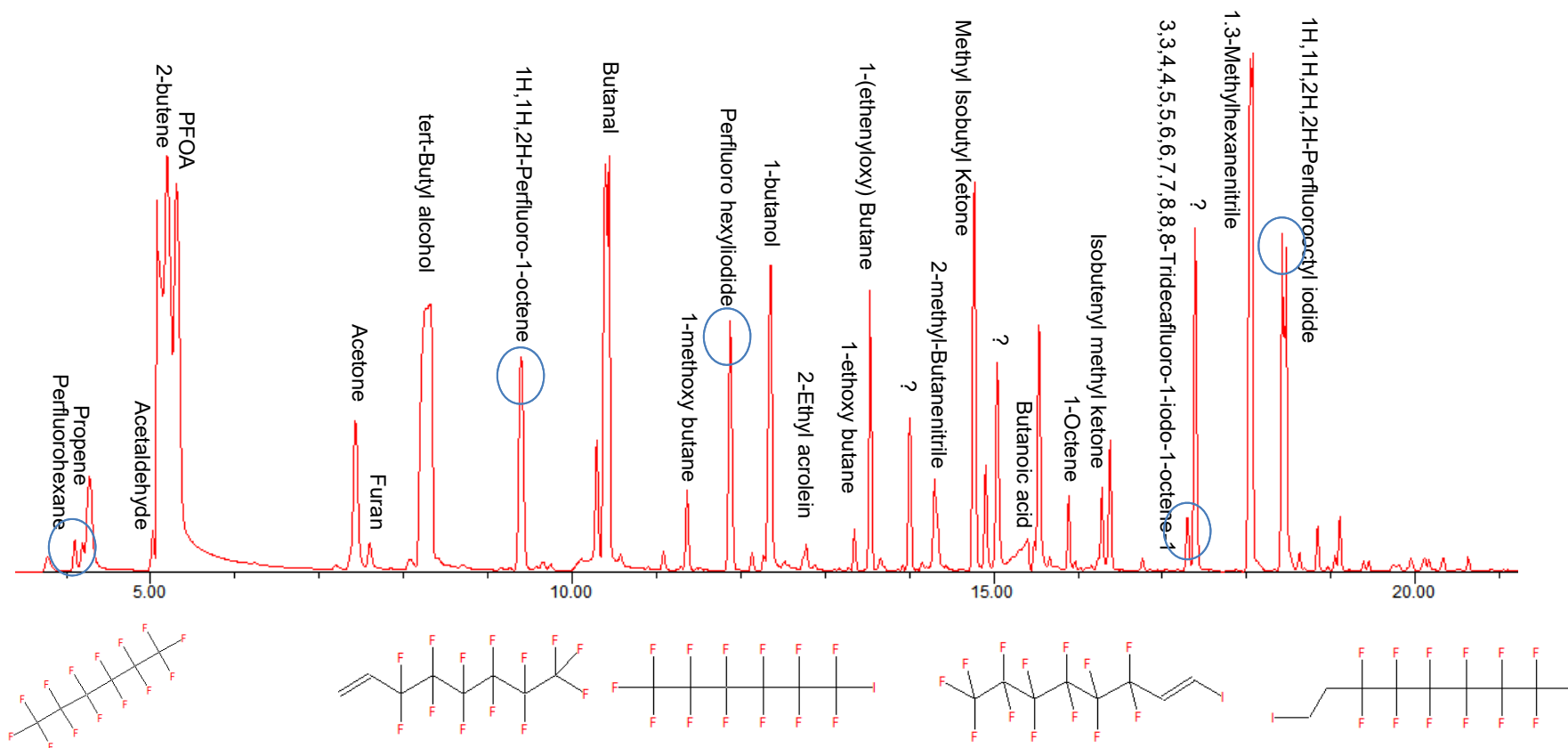
| Compound | TD tube blank | TD1 immediate | TD1 1h after agitation | TD2 immediate | TD2 1h after agitation |
|------------------------|---------------|---------------|------------------------|---------------|------------------------|
| PFPeA | n/d | 0.98 | 4.00 | 2.05 | 2.05 |
| PFHxA | n/d | 88.46 | 178.73 | 165.63 | 188.18 |
| PFHpA | 0.07 | 2.66 | 16.65 | 6.33 | 8.35 |
| PFOA | 1.69 | 6859* | 11873 | 9383* | 15468 |
| PFNA | 0.05 | 0.46 | n/d | 1.73 | 0.10 |
| PFDA | 0.10 | 17.38 | 55.53 | 36.69 | 61.50 |
| PFUdA | 0.54 | n/d | n/d | n/d | n/d |
| PFDoA | n/d | 0.59 | 1.65 | 1.68 | 2.05 |
| PFTTrDA | n/d | 0.42 | n/d | 0.28 | 0.53 |
| 5:2sFTOH | n/d | 0.50 | n/d | n/d | 1.13 |
| FBET | 4.79 | 28.76 | 45.28 | 43.75 | 40.58 |
| PFTeDA | n/d | 1.78 | 5.25 | 3.81 | 10.10 |
| 7:2sFTOH | 0.06 | 4.08 | 9.73 | 7.52 | 10.83 |
| FHET (FTOH 6:2) | 0.04 | 33.96 | 35.90 | 33.08 | 34.23 |
| PFHxDA | 0.02 | 0.56 | 1.08 | 1.05 | 1.23 |
| FOET (FTOH 8:2) | n/d | n/d | n/d | n/d | n/d |
| PFODA | n/d | n/d | n/d | n/d | n/d |
| FDET (FTOH 10:2) | 1.35 | 9.24 | 10.65 | 12.28 | 11.70 |
| N-MeFOSA-M | 0.92 | 0.19 | 0.20 | 0.14 | 0.20 |
| N-EtFOSA-M | 2.85 | 0.18 | 0.15 | 0.11 | 0.13 |
| N-MeFOSE-M | 0.35 | n/d | n/d | n/d | n/d |

* These values greatly exceed the calibration range of the system.

| Compound | PUF/XAD blank | PUF/XAD sample 1 | PUF/XAD sample 2 |
|----------|---------------|------------------|------------------|
| FTS 6:2 | n/d | 1.28 | 2.69 |

Untargeted analysis

Immediately after agitation



Micro-Chamber/Thermal Extractor

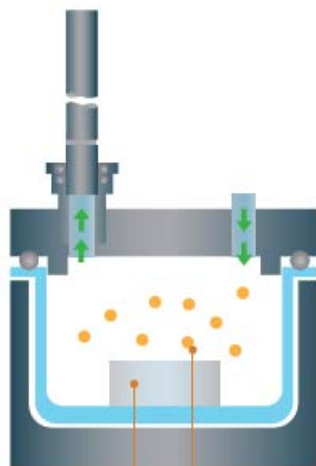
- Compact, stand-alone unit for rapid sampling of chemicals and odours released from a wide variety of products, foods and materials.
- Dynamic headspace approach, samples of VOCs and SVOCs onto sorbent tubes
- Simulates real-world ageing / formulation processes
- Ideal solution for
 - Industry – R&D, Formulation & QC screening
 - Test Labs – Certification, screening
 - Government labs – Certification and R&D
 - Universities – R&D
- Compatible with multiple sample types:
 - Sorbent tubes (industry standard and other)
 - DNPH,
 - online systems & continuous monitors



Fast, Simple, Cost-effective, Robust, Reliable, Sensitive, Versatile, Compliant

Sampling approaches

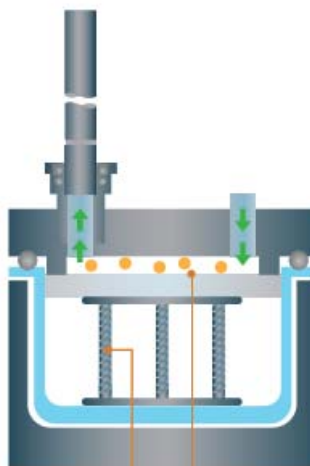
Bulk emissions testing is valuable for profiling odours and emissions, and for testing of raw materials and foods.



Samples are placed straight into the chambers.

Vapours swept from the entire sample are collected.

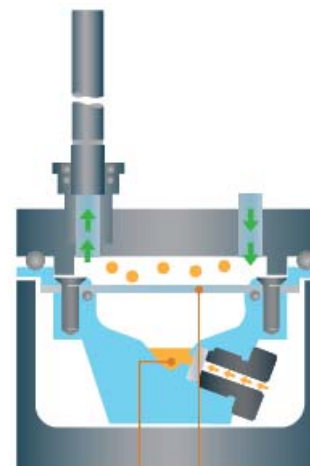
Surface emissions testing: This approach is suitable for determining area-specific emission rates from flat samples.



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.

Microchamber testing

Direct collection from source material
ng/L

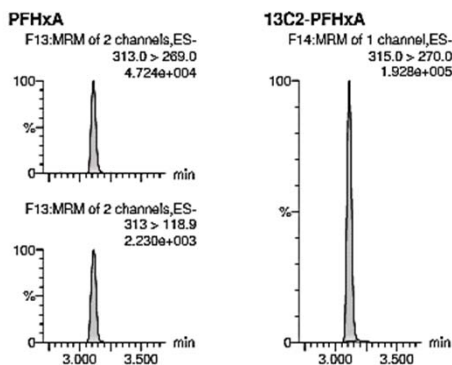
| ID | RT (min) | Tube blank | Chamber blank | AFFF 26°C | AFFF 40°C | Tube blank after desorption |
|--------------------|--------------|------------|---------------|--------------|-------------|-----------------------------|
| PFPeA | 4.32 | n/d | n/d | 6.04 | n/d | n/d |
| PFHxA | 4.56 | n/d | n/d | 10.00 | n/d | n/d |
| PFHpA | 5.02 | n/d | n/d | 6.44 | n/d | n/d |
| PFOA | 5.83 | n/d | n/d | 544 | 28.4 | n/d |
| PFNA | 6.91 | n/d | n/d | 3.03 | n/d | n/d |
| PFDA | 8.52 | n/d | n/d | 8.68 | 0.59 | n/d |
| PFUdA | 10.17 | n/d | n/d | n/d | n/d | n/d |
| PFDaA | 11.76 | n/d | n/d | 0.97 | n/d | n/d |
| 5:2sFTOH | 13.84 | n/d | n/d | n/d | n/d | n/d |
| FBET | 13.96 | n/d | n/d | n/d | n/d | n/d |
| PFTTrDA | 13.21 | n/d | n/d | n/d | n/d | n/d |
| PFTeDA | 14.49 | n/d | n/d | n/d | n/d | n/d |
| 7:2sFTOH | 15.74 | n/d | n/d | n/d | n/d | n/d |
| FHET (6:2) | 16.54 | n/d | n/d | 43.2 | 20.6 | n/d |
| PFHxDA | 16.73 | n/d | n/d | n/d | n/d | n/d |
| FOET (8:2) | 17.77 | n/d | n/d | n/d | n/d | n/d |
| PFODA | 18.63 | n/d | n/d | n/d | n/d | n/d |
| FDET (10:2) | 18.7 | n/d | n/d | 217 | 22 | n/d |

Analytical LC-MS-MS (MRM) results AFFF analysis

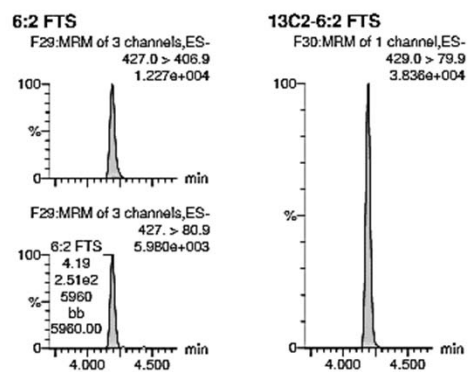
The AFFF used in the volatility box experiment was analyzed via LC/MS/MS at a 1:1000 dilution. At that dilution only PFHxA and 6:2 FTS were present above the DL of 250 ppt. These results correspond with what was seen in the XAD/PUF.

| Compound | CAS | Concentration (ppt) |
|----------|------------|---------------------|
| PFHxA | 307-24-4 | 1327 |
| 6:2 FTS | 27619-97-2 | 1512 |

PFHxA



6:2 FTS



Conclusions and future work

- The AFFF Volatility Box Experiments are the first step in understanding PFAS vapor intrusion
- AFFF feedstock impurities detected with TD–GC–MS would likely volatilize readily after release
- Two sampling and analytical methods have been tested:
 - XAD/PUF Sampling with LC-MS-MS (MRM) has been tested for 30 PFAS
 - TD Sampling with TD-GC-MS has been tested for 22 of the PFAS Standards
- Further studies to mimic real life conditions/events
- Refine sampling and analysis procedures
- Study with different starting materials

Any questions?



Contact Markes



enquiries@markes.com



+1-866-483-5684



www.markes.com



@MarkesInt



www.linkedin.com/company/markes-international



PFAS Volatility



Theoretical Henry's Law Constants and Vapor pressures

| Substance | Aqueous Solubility (g/L) | P _{vapor} (PA) | Henry's Law Constant (atm m ³ mol ⁻¹) |
|--------------------------------------|--------------------------|-------------------------|--------------------------------------------------------------|
| PFOS (K ⁺) | 5.19 E-1 | 3.31 E-4 | 3.4 E-9 |
| PFOA (H ⁺) | 9.5 | 7.0 E1 | 4.6 E-6 |
| PFOA (NH ₄ ⁺) | >5.00 E2 | <1.3 E-3/9.2 E-3 | <1.1 E-11/7.8 E-11 |
| N-EtFOSE | 1.51 E-4 | 5.4 E-1 | 1.9 E-2 |
| N-EtFOSEA | 8.9 E-4 | N.A. | -- |
| 6:2 FTOH | 1.2-1.7 E-2 | N.A. | 1 E -2 |
| 8:2 FTOH | 1.40 E-4 | 2.93 | 9.6 E-2 |

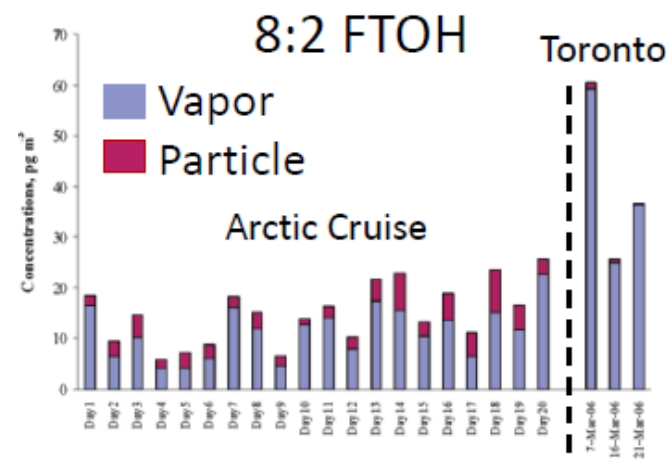
Meets USEPA's 2015 volatility criteria:
1) Henry's Law Constant
> 10⁻⁵ atm*m³/mol

Source: Hekster et al (2002)

Particle - Gas partitioning

Key Takeaway:

- **ALL** PFAS precursors analysed were vapor phase dominant



| | | 6:2 FTOH | 8:2 FTOH | 10:2 FTOH | MeFOSE | EtFOSE |
|------------------------------------------|--------------------------|----------|----------|-----------|-----------|-----------|
| Arctic Gas Phase Air Concentration | Arithmetic Means (pg/m3) | 2.65 | 11.4 | 6.57 | 8.3 | 1.87 |
| Arctic Particle Phase Air Concentration | | BDL | 3.5 | 0.8 | 3.53 | 1.05 |
| Toronto Gas Phase Air Concentration | | 17.7 | 40.2 | 21.2 | 8 | 2.33 |
| Toronto Particle Phase Air Concentration | | 0.31 | 0.71 | 1.09 | 4.2 | 0.96 |
| Arctic Particle Phase | Percentage | BDL | 23% | 15% | 32% | 22% |
| Toronto Particle Phase | | BDL | 2% ± 1% | 5% ± 3% | 30% ± 16% | 30% ± 16% |

Notes:

1) BDL = Below Detection Levels

2) MeFOSEA was analyzed for, but below detection levels

Source: Shoeib et al (2006)