

Testing of PFAA Release from Consumer Articles

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- This is an on-going research project
- Results will be made public through peer-review channels



Today's Topics

- Why testing consumer articles
- Approach
- Source study
 - ✓ Method development and evaluation
 - ✓ PFAA content in new consumer articles
- Transport study
 - ✓ Gas-phase transfer
 - ✓ Particle re-suspension
 - ✓ Other aging tests



Why Testing Consumer Articles?

- It is poorly understood remains how the general public gets exposed to PFAAs
- Fluorinated chemicals are widely used in consumer articles
- Some consumer articles contain high level PFOA: up to 2000 ng/g*
- Consumer articles are often used in close vicinity to humans

* Washburn, et al (2006)



Project Objectives

- Provide data to support OPPT's risk assessment for PFAAs and related chemicals
- Identify major PFAA sources in consumer articles
- Characterize PFAA release from articles during aging process and factors affecting the release
- Evaluate risk management options for reducing human exposure to PFAAs in homes and offices



Approach

- Source study
 - ✓ Developing methods for determination of PFAAs in consumer articles
 - ✓ Determination of PFAA content in new articles
- Transport study
 - ✓ Accelerated aging tests for gas-phase transfer
 - ✓ Aging tests under close-to-realistic conditions



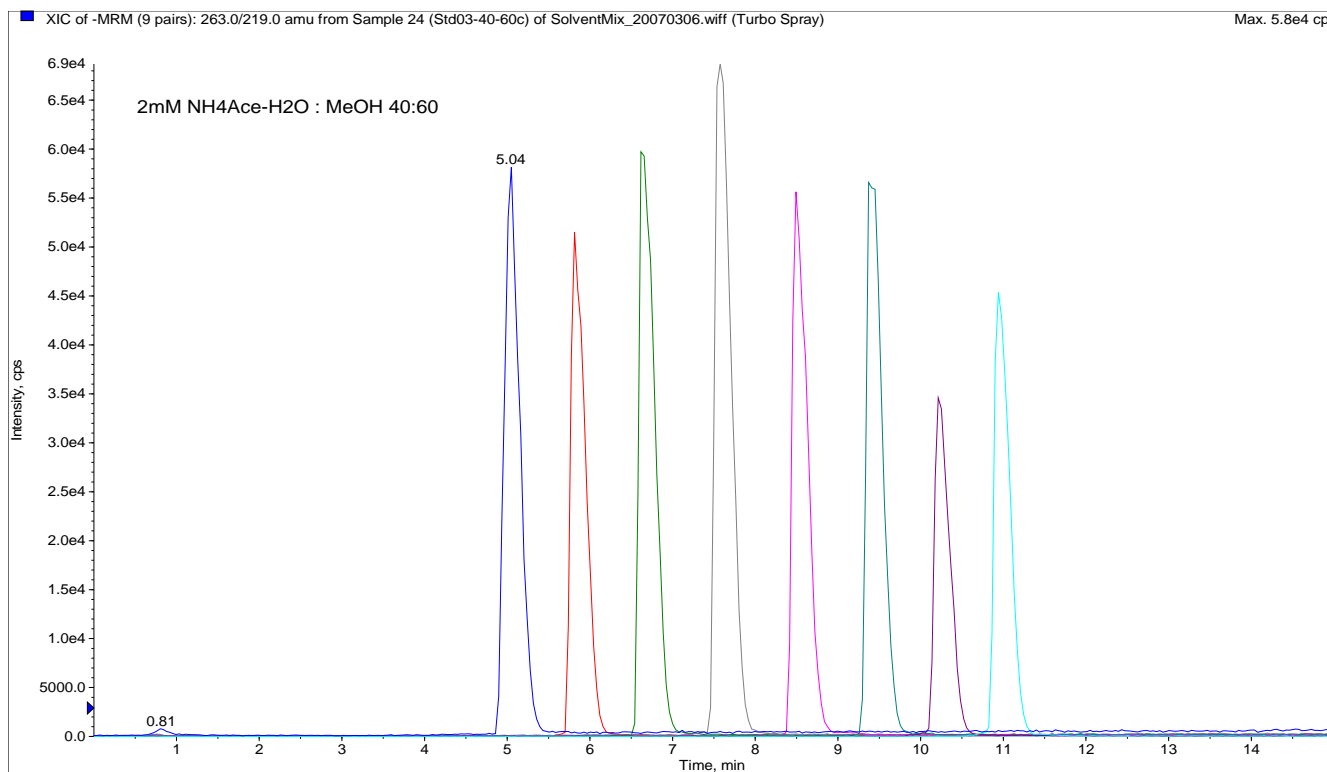
Source Study – Method Development

- Based on methanol extraction and LC/MS/MS
- Optimized for C5 to C12 PFAAs



Methods - Optimization

Chromatogram for C5 to C12 PFAAs under optimized conditions



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Factors Evaluated

- Solvent comparison
- Conventional vs. accelerated extraction
- Extraction efficiency
- Blow down
- Instrument and method detection limits
- Filtration
- Sample stability during storage



Methods – Solvent Comparison

- Compared MeOH, EtOH, ACN, MTBE, H₂O, and MeOH/ H₂O (3:2)
- Methanol was selected as the extraction solvent for its
 - ✓ High extraction efficiency
 - ✓ Good precision
 - ✓ Best compatibility with the LC mobile phase



Methods – Blow-down

RapidVap N₂ Evaporation System

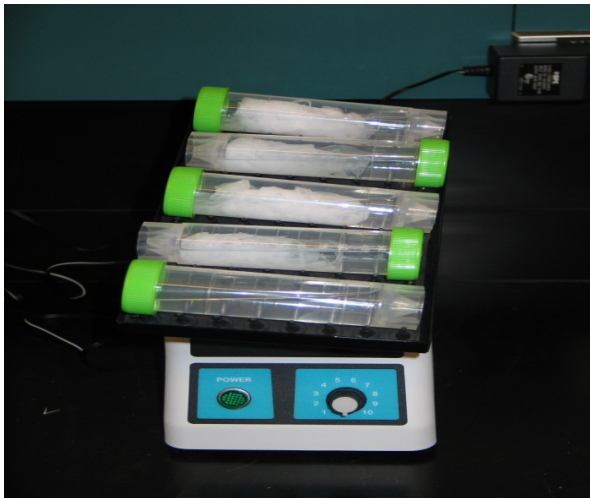


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Methods - Extraction

VSN-5 Nutating Mixer



Operating at room temperature
and atmospheric pressure

Dionex ASE 200



Operating at elevated temperature
and pressure



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Methods - Extraction

- Nutating Mixer: 24-h extraction provides adequate efficiency
- ASE System
 - ✓ Cloudy samples
 - ✓ Poor precision
 - ✓ Random carryover



Preparation of Solid Samples

Sample Coupons (1-2 g)



Add 45 mL MeOH



Add Recovery Check Standard



Extraction



Blow down to 1 mL



Rinse with 60: 40 MeOH: 2mM NH₄Ac-H₂O



Filtration



Add Internal Standard



Final volume (10 mL in 60: 40 MeOH-2mM NH₄Ac-H₂O)



LC/MS/MS analysis (0.4 mL)



Preparation of Liquid Samples

Sample aliquot (1.5 mL with known weight)



Dilute to 25 mL with 60: 40 MeOH: 2 mM NH₄Ac-H₂O



Add Recovery Check Standard



Shake and sonicate for 10 min



Filtration



Add Internal Standard



Final volume (10 mL in 60: 40 MeOH-2mM NH₄Ac-H₂O)



LC/MS/MS analysis (0.4 mL)



QA / QC

- Approved QAPP
- 22 project-specific MOPs
- Data quality criteria
 - ✓ Calibration curve: $r^2 \geq 0.99$
 - ✓ IAP %Recovery : $100 \pm 15\%$, %RSD $\pm 15\%$,
 - ✓ DCC %Recovery: $100 \pm 15\%$, %RSD $\pm 15\%$,
 - ✓ %Recovery of RCS: $100 \pm 20\%$,
 - ✓ Duplicate Samples: %RSD $\pm 20\%$,
 - ✓ Analytes in field blank: lower than PQL



PFAAs in New Consumer Articles

- Collected 130 articles from open market
 - ✓ Domestic: 65
 - ✓ Imports: 65
- Factors considered
 - ✓ Article category
 - ✓ Price range
 - ✓ Store type
 - ✓ Brand name of article
 - ✓ Trade name of fluoropolymer or fluorotelomer product
 - ✓ Country of origin



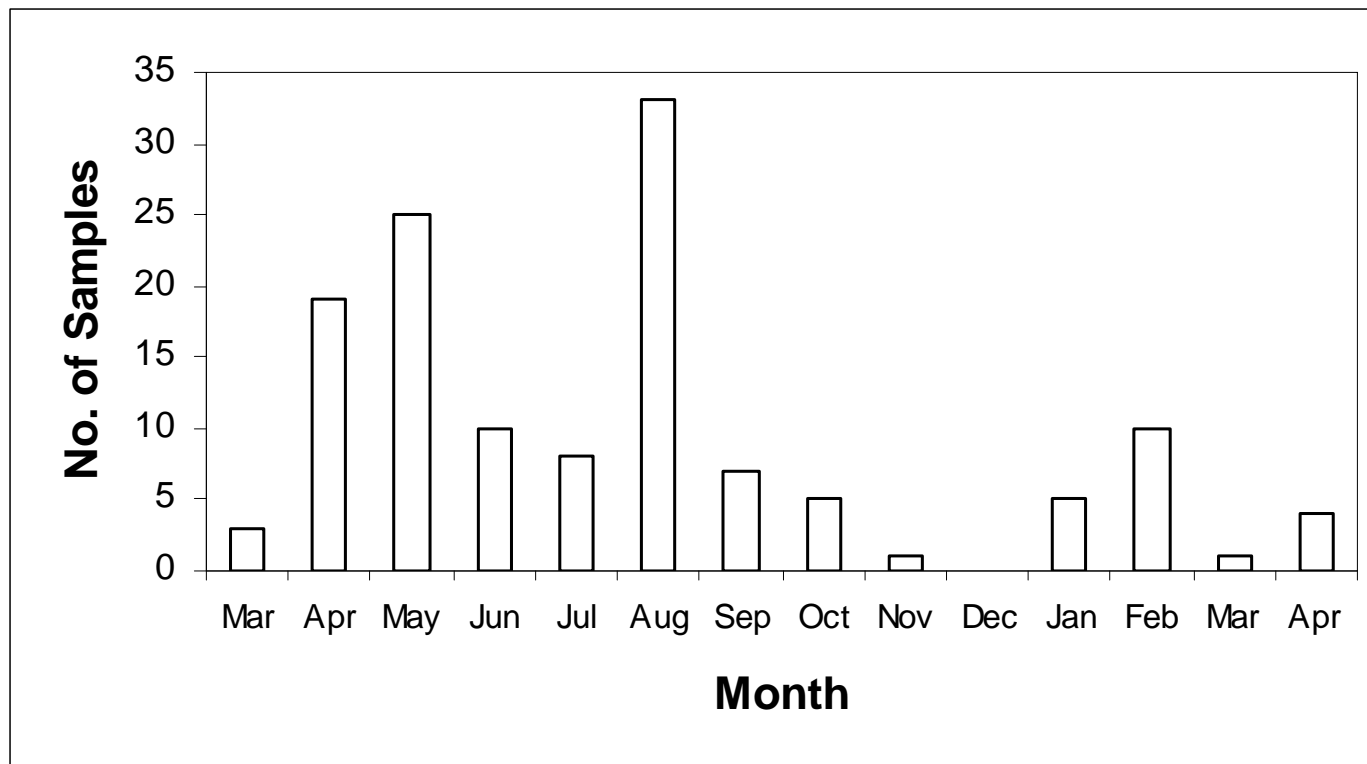
Categories of Consumer Articles

- Mill-treated carpeting
- Professional carpet care liquids
- Carpet and fabric care liquids of spot treatment
- Treated apparel
- Treated home textile and upholstery
- Treated non-woven medical garments
- Floor waxes and sealants
- Food contact paper
- Membranes for apparel
- Thread seal tapes and pastes
- Non-stick cookware
- Dental floss and plaque removers
- Miscellaneous



Sample Statistics

Sample Acquisition by Month



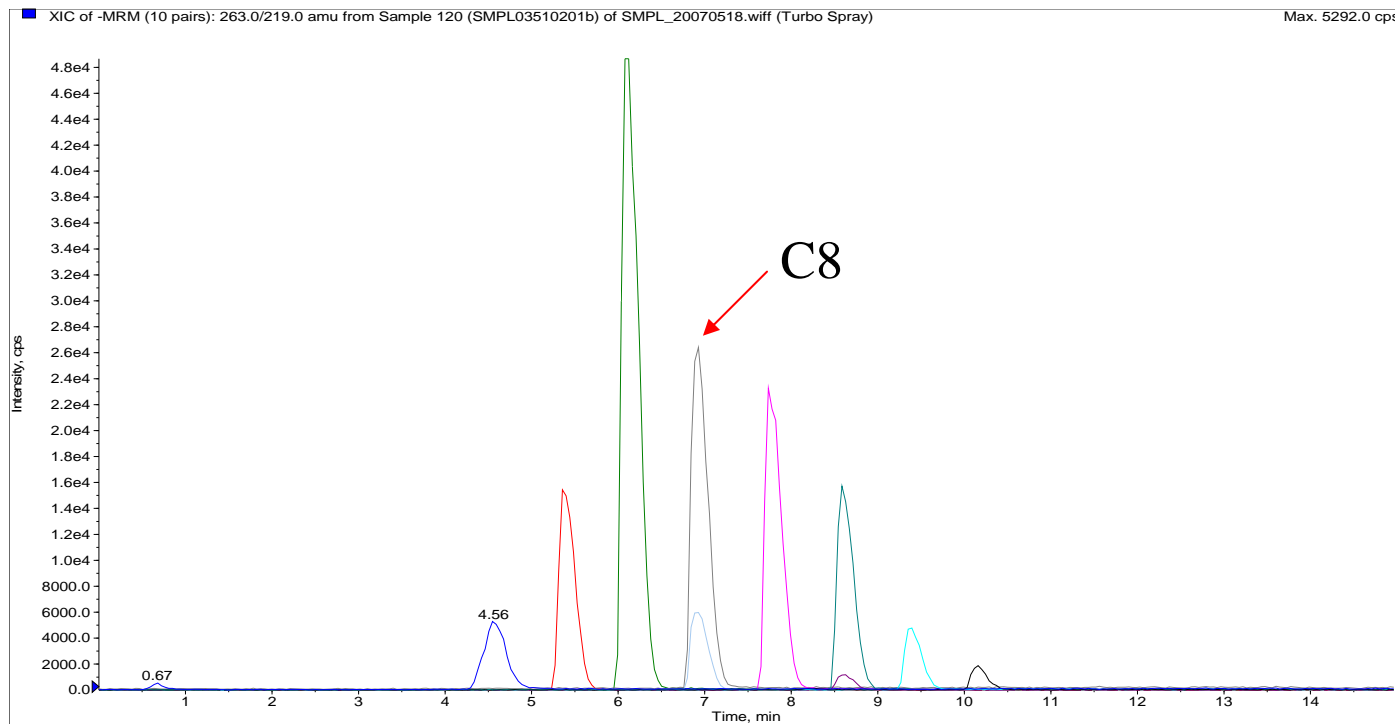
Results

- 120 out of 130 samples were analyzed successfully
- Results are based on single-step extraction



Results

Chromatogram of a carpet care liquid

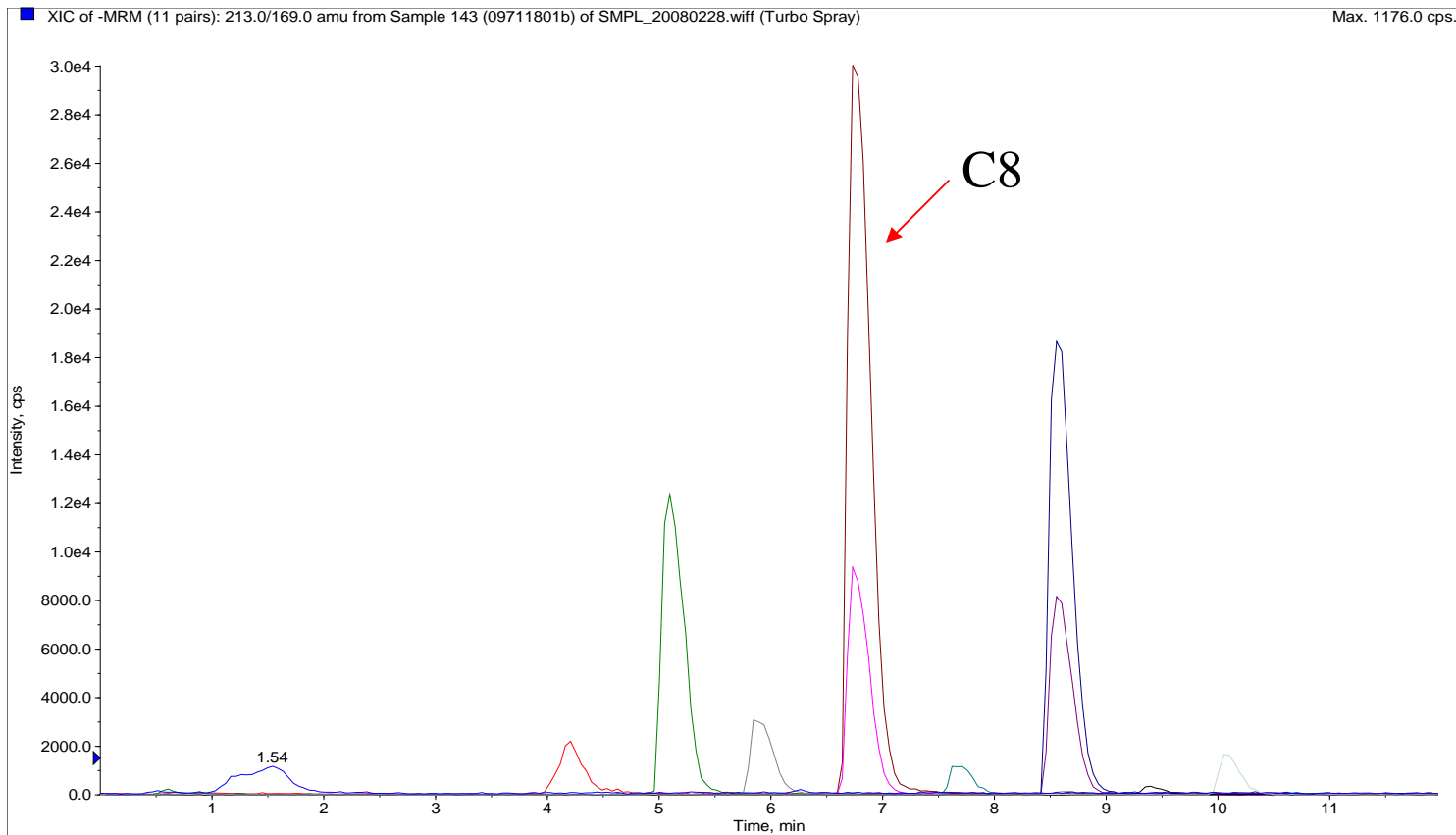


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Results

Chromatogram of a man's shirt

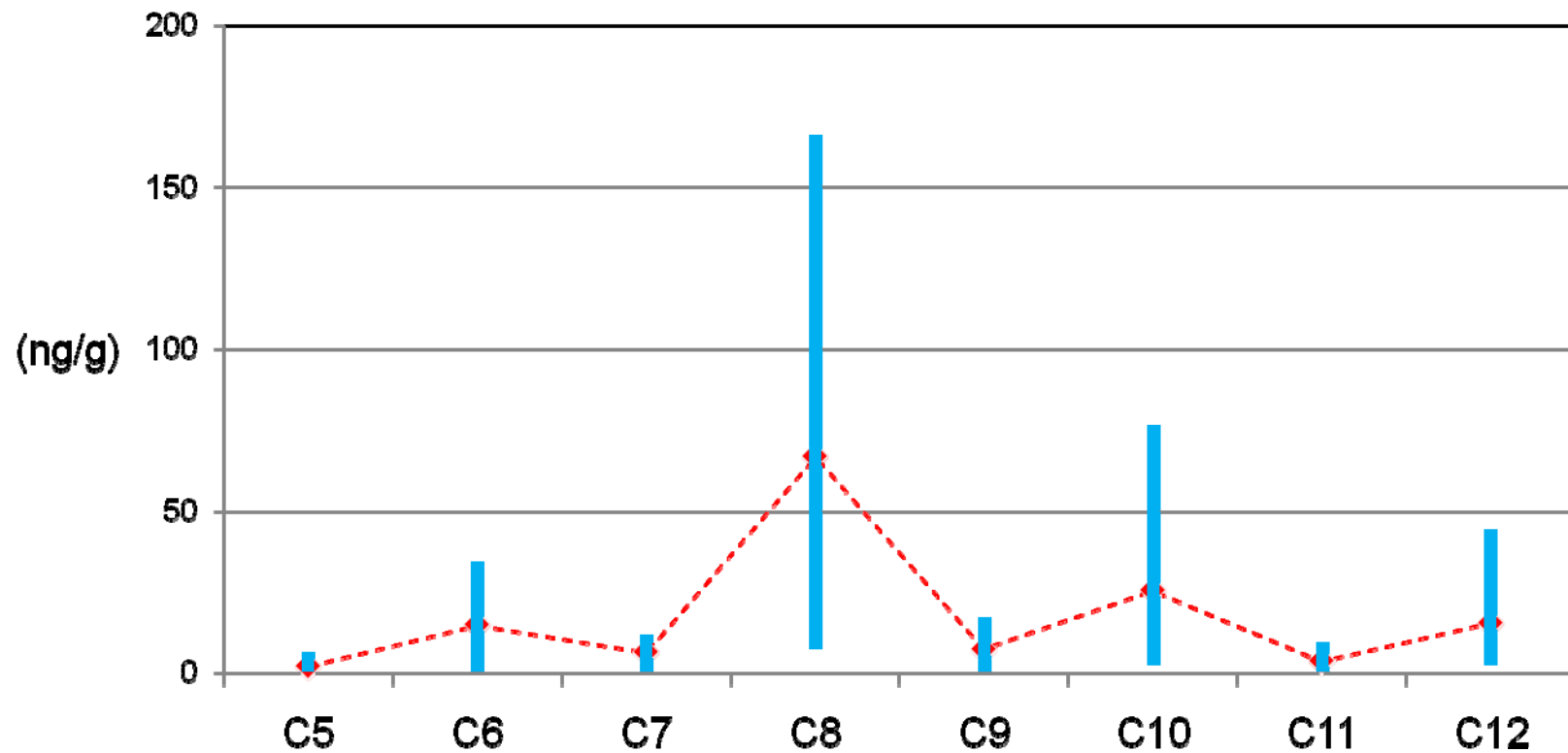


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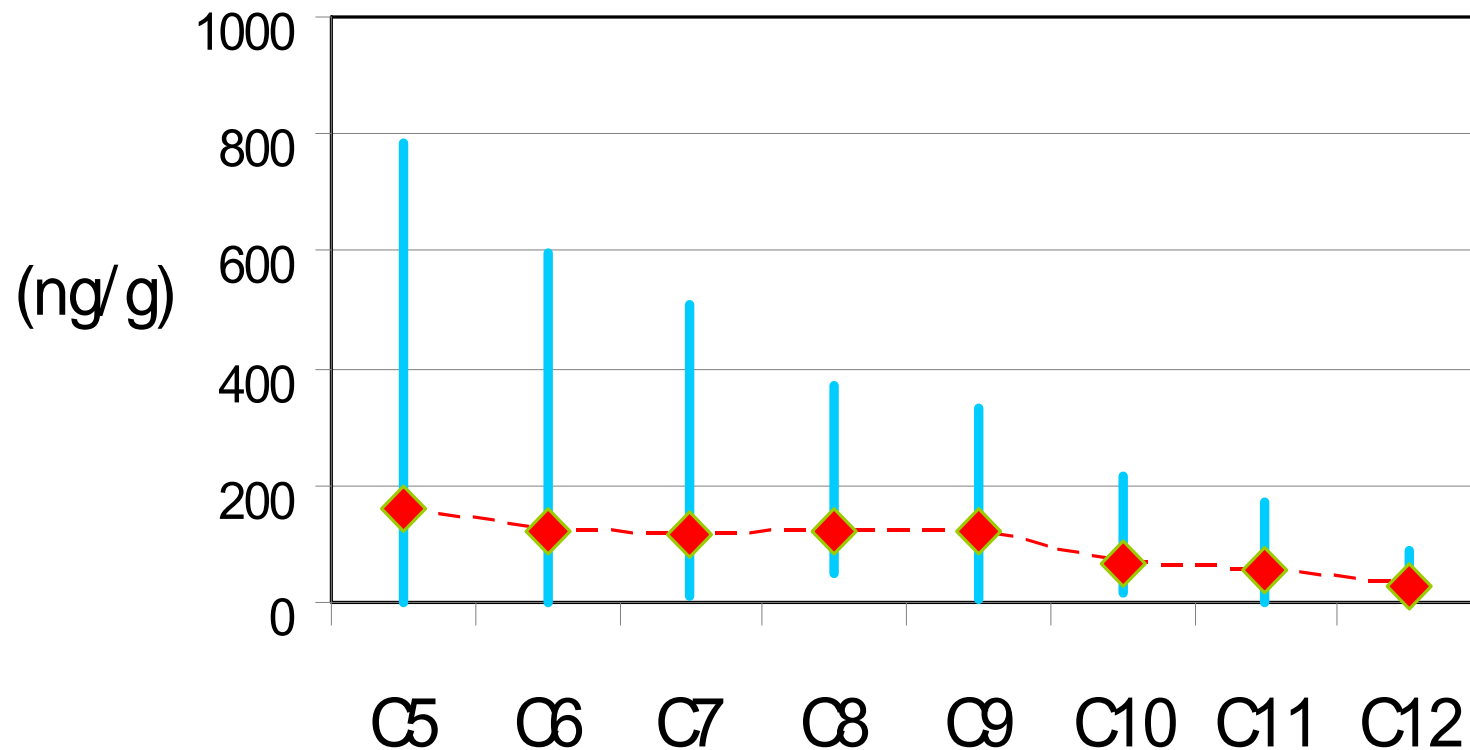
Results

Membranes for apparel



Results

Treated non-woven medical garments



Market Trends

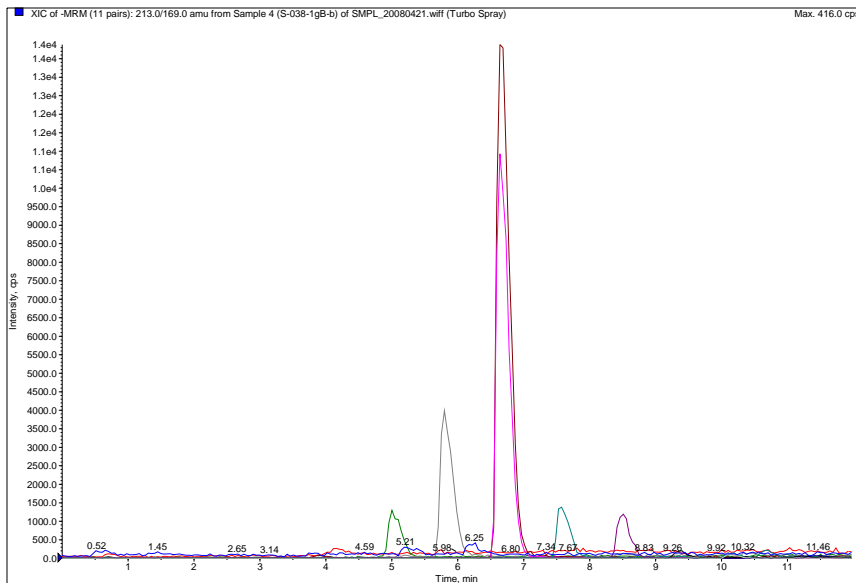
- The market has been in a transition period
 - ✓ Reformulation
 - ✓ Replacement
- PFAS content in consumer articles appears to follow a down trend
- The trends are uneven



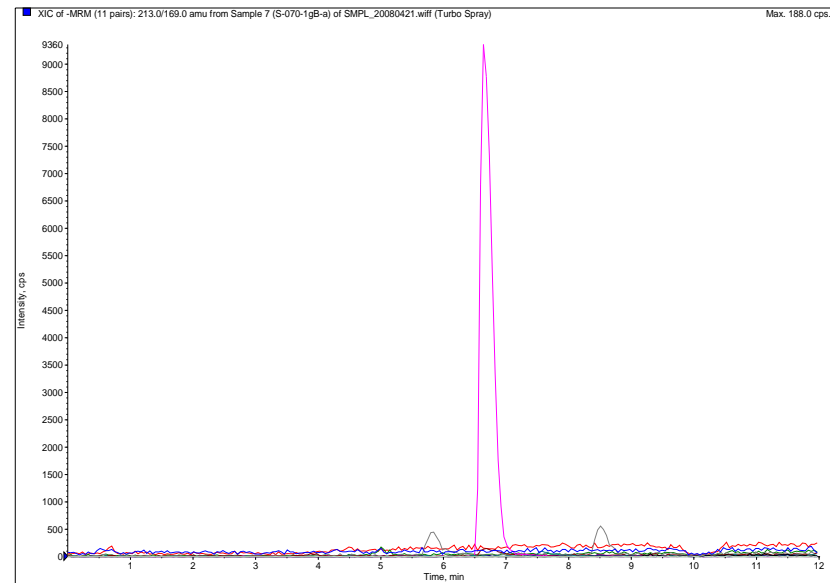
Market Trends

Example 1

Carpet A



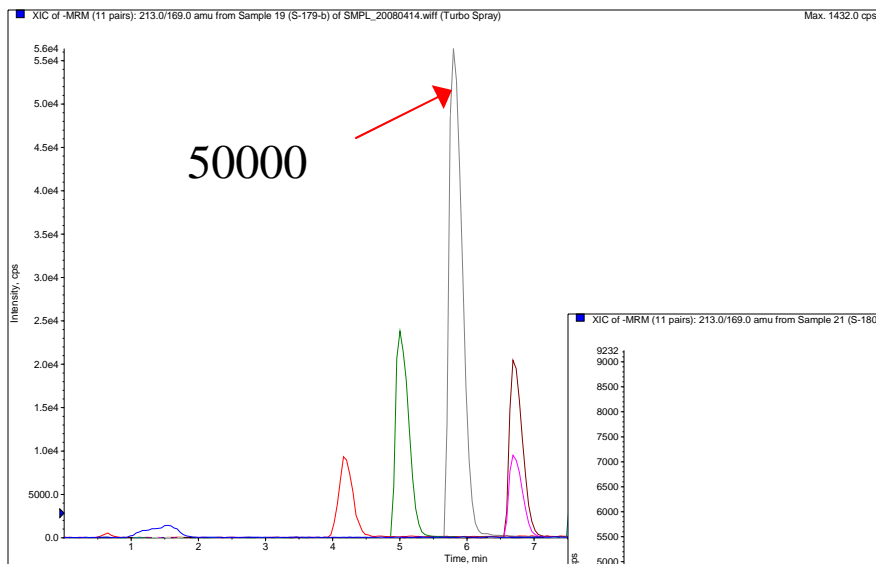
Carpet B (Replacement of Carpet A)



Market Trends

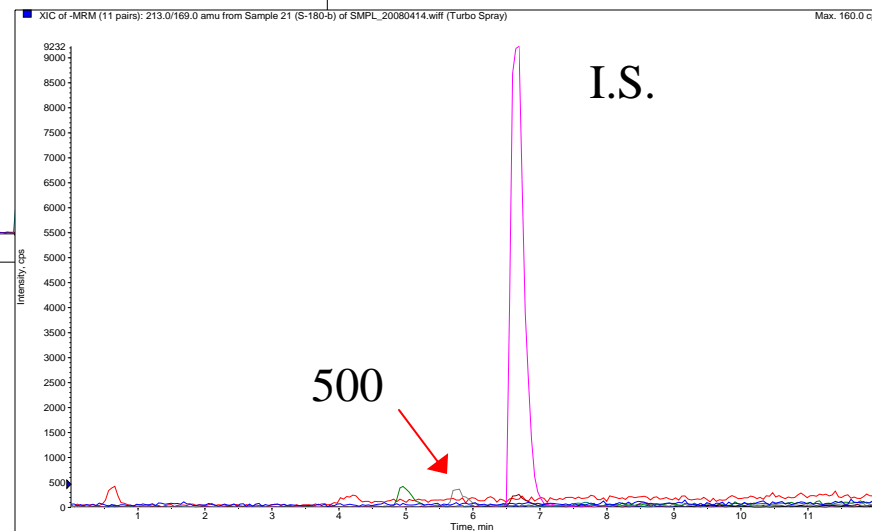
Example 2

Carpet Care Liquid A



April 2007

April 2008



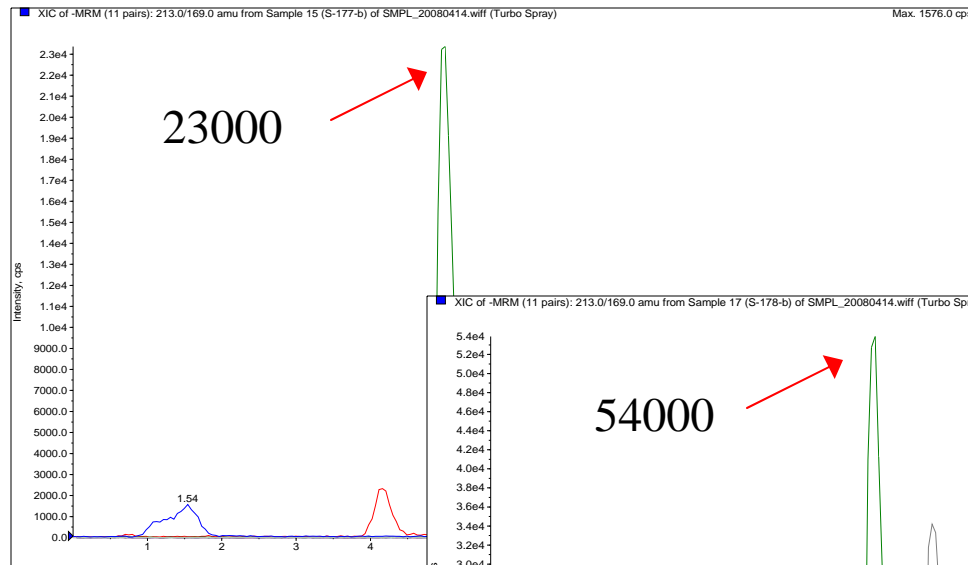
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Market Trends

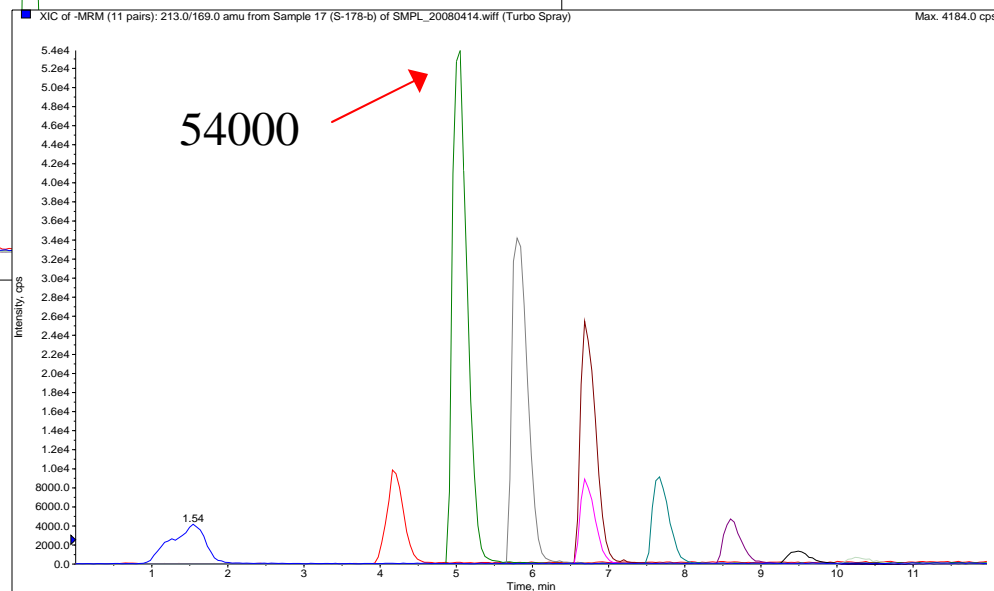
Example 3

Carpet Care Liquid B



April 2007

April 2008



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Domestic vs. Imports

- Domestic and import products are unevenly distributed among the article categories
- Some imports contain high level of PFAAs
- It requires a global effort to reduce PFAA content in consumer articles



Accelerated Aging Tests

-- Science Questions

- What is the role of consumer articles in human exposure to PFAA?
- Is gas-phase transfer significant?
- Is particle re-suspension significant?
- How can people reduce their exposure?



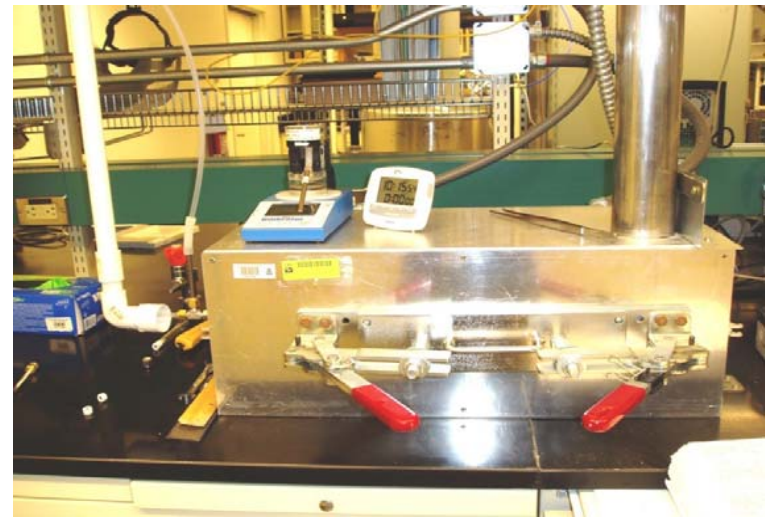
Approach

- Accelerated aging tests in small/micro chambers to estimate the significance of gas-phase transfer
- Large chamber or test house experiments to determine PFCA content in suspended particles
- Additional aging tests to address the significance of other exposure routes



Heating Tests in High-Temp Chamber

- Temperature: 80°C
- Heated nitrogen flow
- Duration: 15 hours



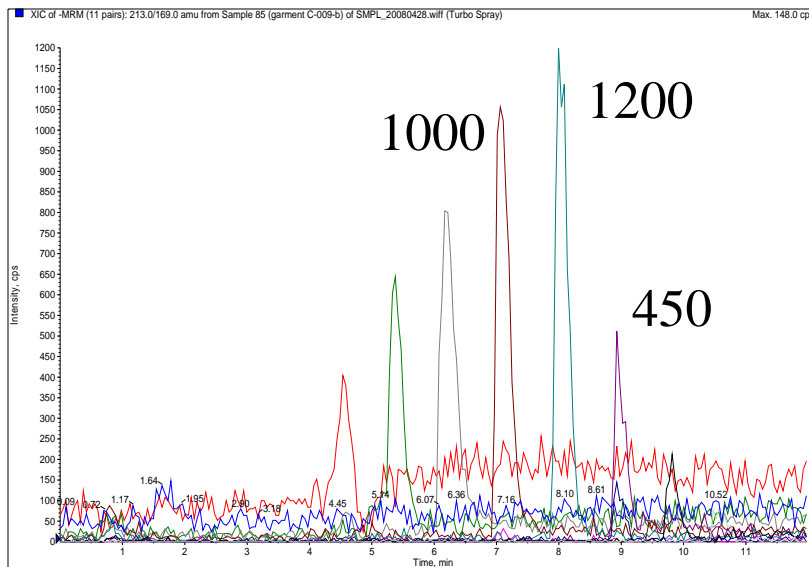
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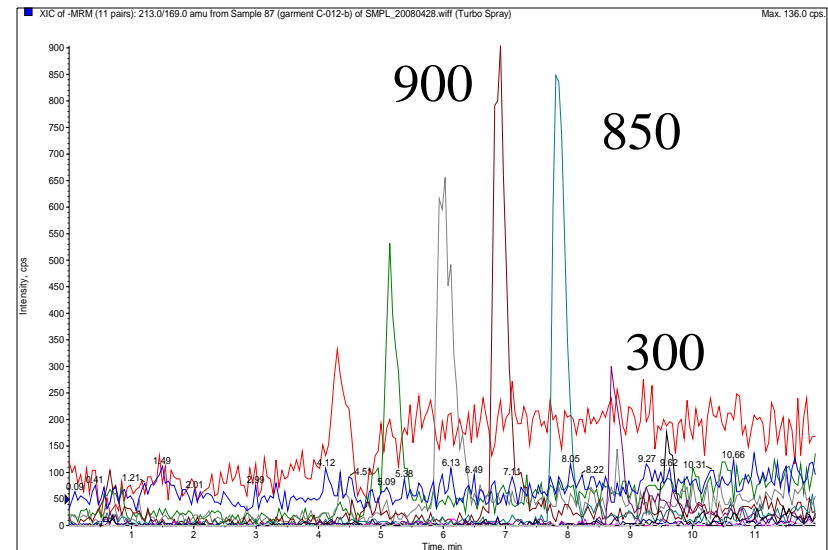
Scouting Results: Heat

Sample: Non-woven Medical Garment

Before heating



After heating



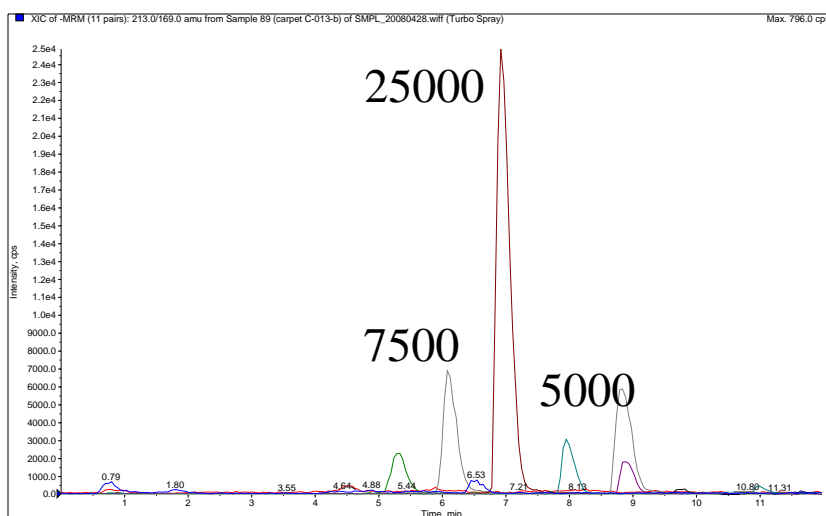
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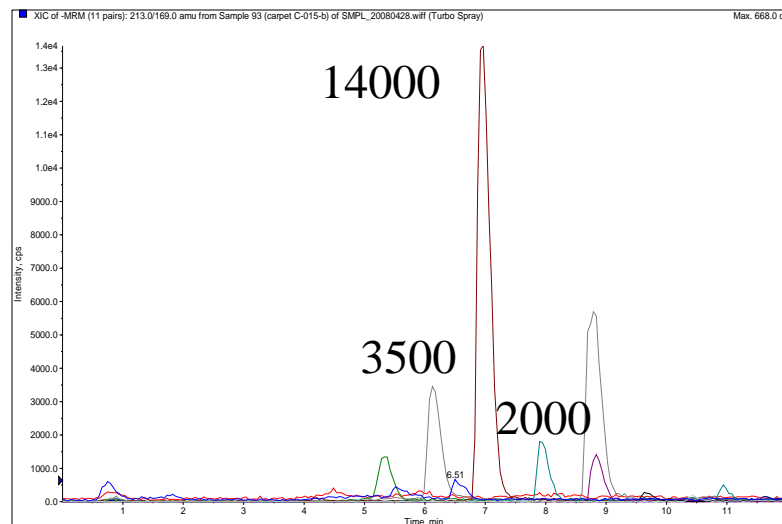
Scouting Results: Heat

Sample: Mill-treated Carpet

Before heating



After heating

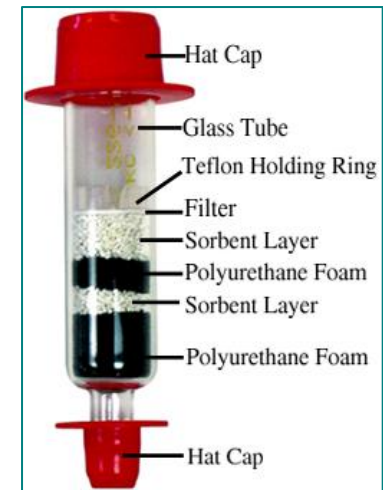


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PFAA Transfer Tests in Micro Chamber

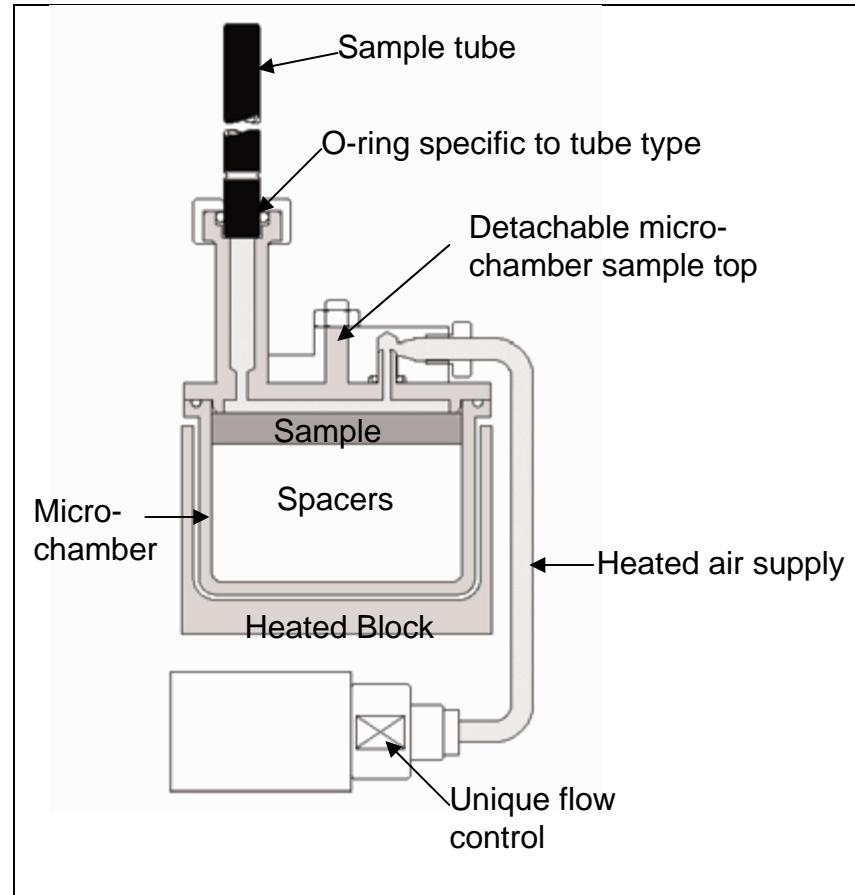
- ASTM 5116
- Elevated temperature
- Sample extraction before and after tests
- Air sampling
- Chamber surfaces: rinse



OVS Tube



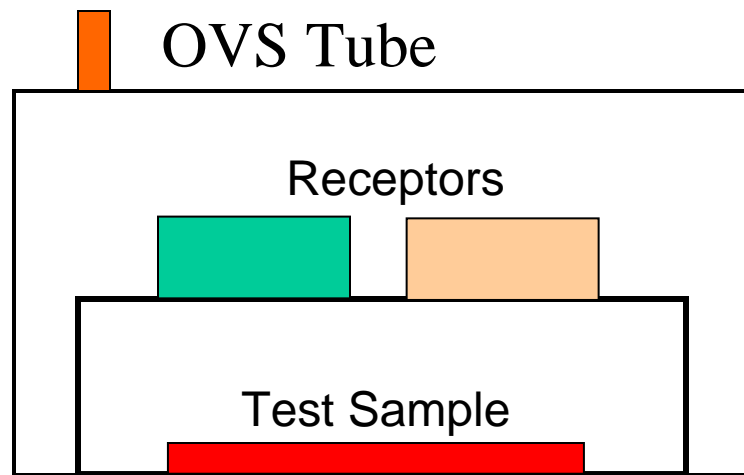
Micro Chamber



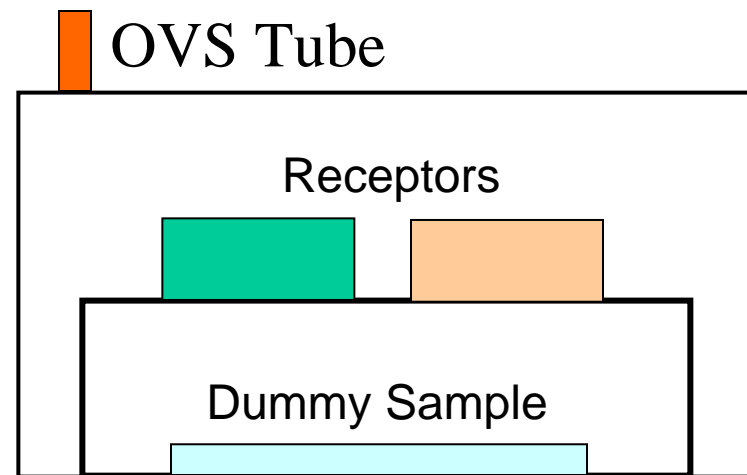
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PFCA Transfer Tests In 53-L Flow-through Chamber



Sample Chamber



Reference Chamber



Study on Particle-bound PFAAs



- ASTM 6670
- 30-m³ chamber
- Close-to-realistic use conditions
- Carpet on floor
- Dust and air sampling



Other Aging Tests

- Apparel – Washing/dry cleaning
- Apparel – Artificial sweat
- Carpet -- UV
- Dental floss -- Artificial saliva
- Liquids -- PFAA generation during aging



Acknowledgement

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