# Harmonising Analysis of VOCs from Spray Polyurethane Foam Insulation

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# Measuring Emissions from Spray Polyurethane Foam (SPF) Insulation

**ASTM D22.05 Indoor Air**

American Chemistry Council | Center for the Polyurethanes Industry

ASTM International

International Isocyanate Institute

United States Environmental Protection Agency

Bayer

Icynene

DuPont

Dow

BASF The Chemical Company

Michelin

Huntsman

CertainTeed

Honeywell

# What is SPF

## A Side

The “A” side is commonly a mixture of **methylene diphenyl diisocyanate** (MDI) and polymeric methylene diphenyl diisocyanate (pMDI).

## B Side

**Polyols** are a building block of polyurethane and react with MDI to make foam.

**Catalysts** speed up the chemical reaction.

**Blowing Agents** help the foam expand.

**Flame Retardants** increase the fire resistance of the finished Product.

# ASTM D22.05 on Indoor Air Standards

**Chamber Testing**

- ASTM D5116-10 Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions From Indoor Materials/Products
- ASTM D6670-13 Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials/Products
- ASTM D7706-11 Standard Practice for Rapid Screening of VOC Emissions from Products Using Micro-Scale Chambers

**Analytical Determinations**

- ASTM D5197-09e1 Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)
- D6196-03(2009) Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air

# ASTM Standards and Work Items

**Work Item WK40293**

- Test Method for Determination of Vapor-Phase Organic Compounds Emitted from Spray Polyurethane Foam (SPF) using Micro-Scale Environmental Test Chambers

**Work Item WK43872**

- Test Method for Determination of Emissions of Methylene diphenyl diisocyanate (MDI) from Spray Polyurethane Foam (SPF) Insulation using Emission Cells or Micro-Scale Environmental Test Chambers

**Work Item WK46527**

- Standard Method for Measuring Chemical Emissions from Spray Polyurethane Foam (SPF) in a Large-Scale Spray Booth

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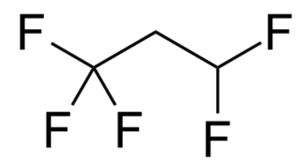
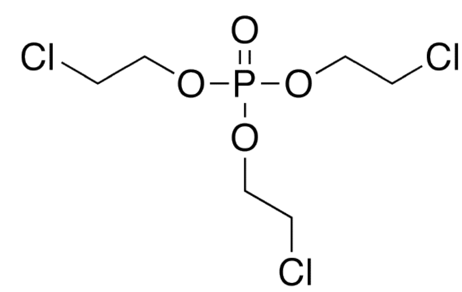
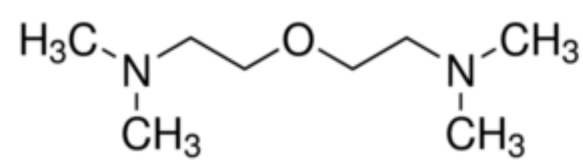
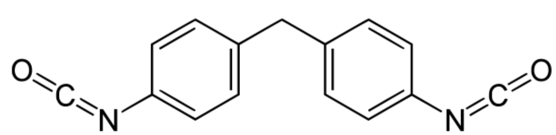
# Spray Polyurethane Foam

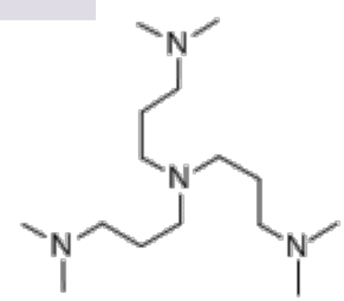


| Target Compound | Acronym | Description |
| --- | --- | --- |
| HFC-245fa | - | Blowing Agent |
| Tris-(1-chloro-2-propyl) phosphate | TCPP | Flame Retardant |
| Bis (2-Dimethylaminoethyl) ether | | Catalyst |
| Tetramethyliminobispropyl amine | TMIBPA | Catalyst |
| Pentamethyldiethylene triamine | PMDTA | Catalyst |
| Bis (dimethylaminopropyl) methylamine | DAPA | Catalyst |
| Methylene diphenyl diisocyanate | MDI | Isocyanate |









# Evaluation of TD-GC/MS Method

**Instrumentation**

**TD-100 &**

Flow path temperature: 160 °C

Sorbent Tube: Tenax TA and Carbopack X sorbent tubes (Stainless Steel)

Cold Trap: U-T12ME-2S, Materials Emissions Trap with Tenax and Carbograph 5TD sorbent

**Agilent 7890 GC and 5975 MSD**

Column: Based deactivated 5% diphenyl/95% dimethyl polysiloxane, 30 m, 0.25 mm x 0.5 µm

Column flow: 1.5 ml/min, constant flow

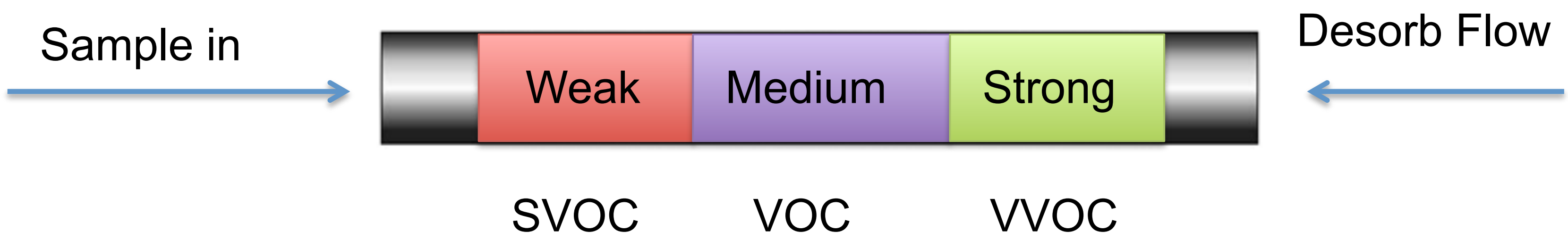
Temperature program: 40 °C (2 min), 20 °C/min to 300 °C (2 min)

Total run time: 17 minutes

MARKES international

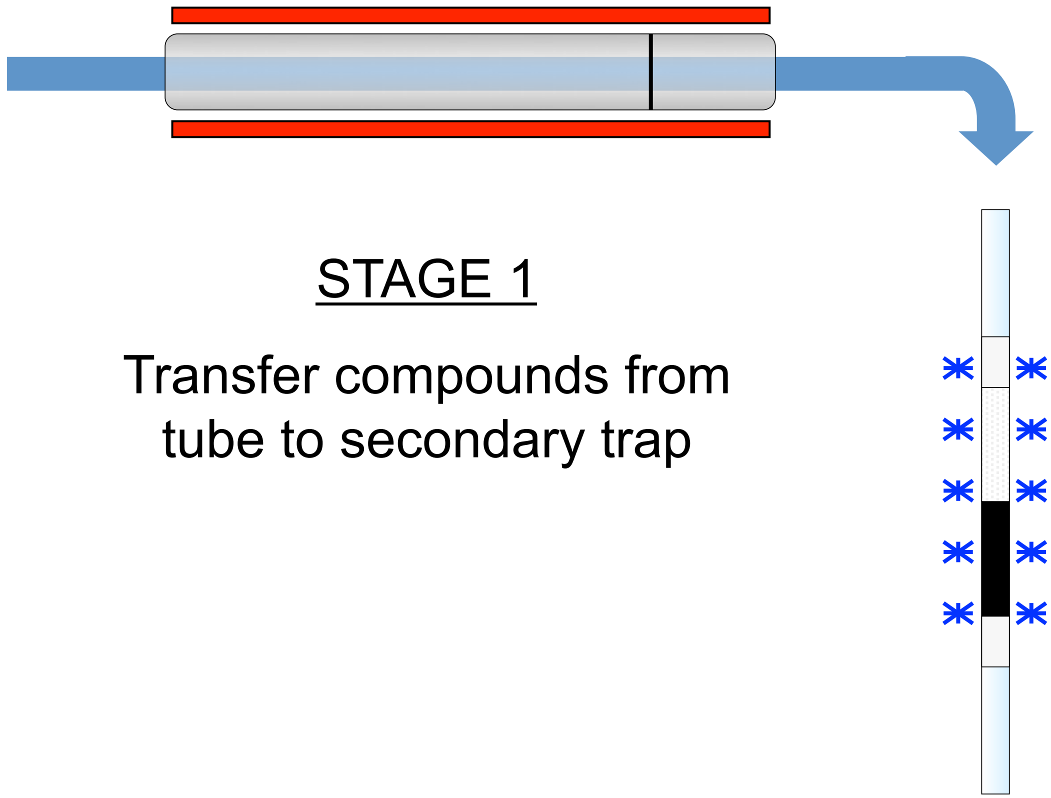
# Multibed Sorbent Tube

Enables wide volatility range



# 2 Stage Thermal Desorption

SOLUTION: Use a narrow secondary trap



STAGE 1

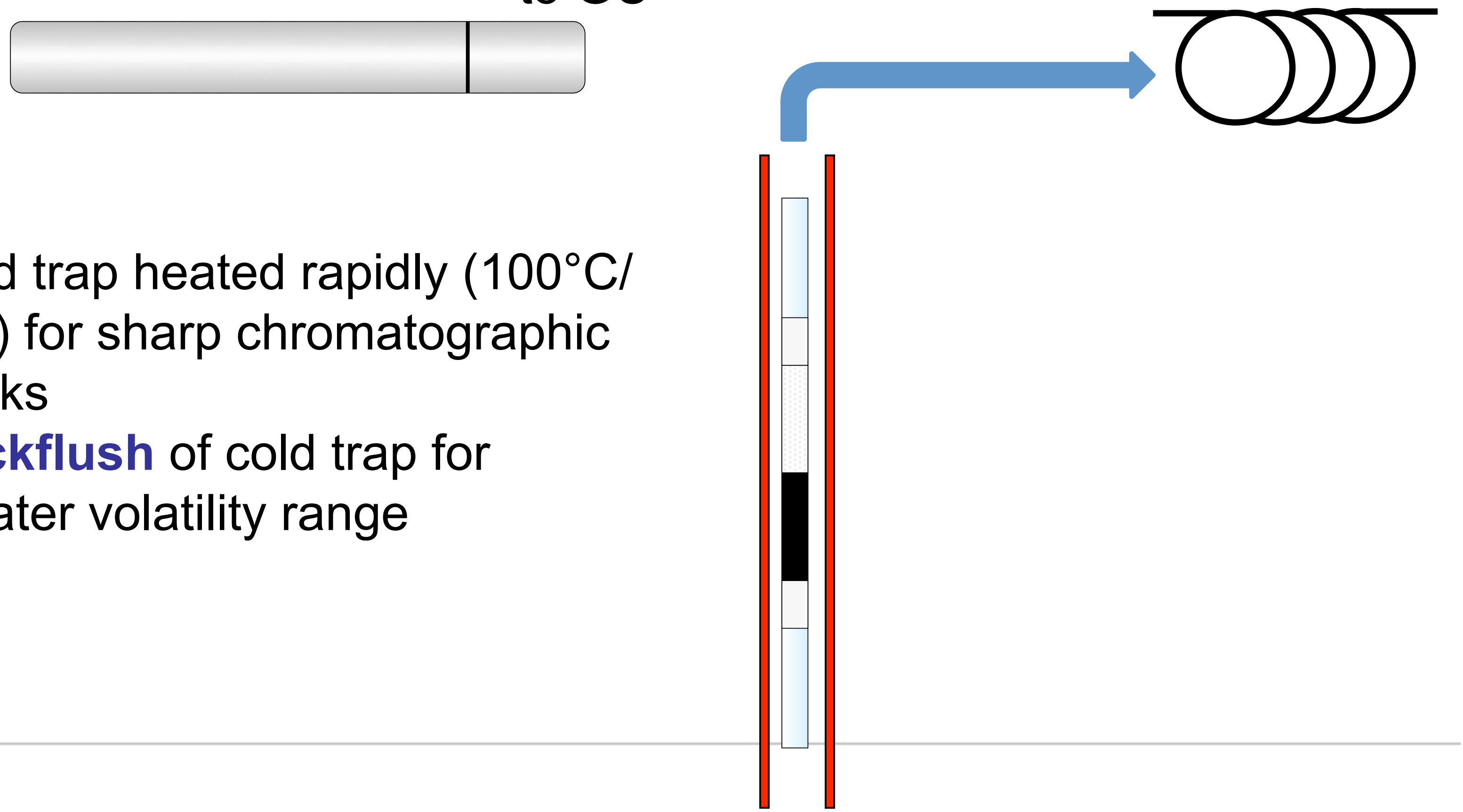
Transfer compounds from tube to secondary trap

Electrically cooled narrow bore cold trap

# 2 Stage Thermal Desorption

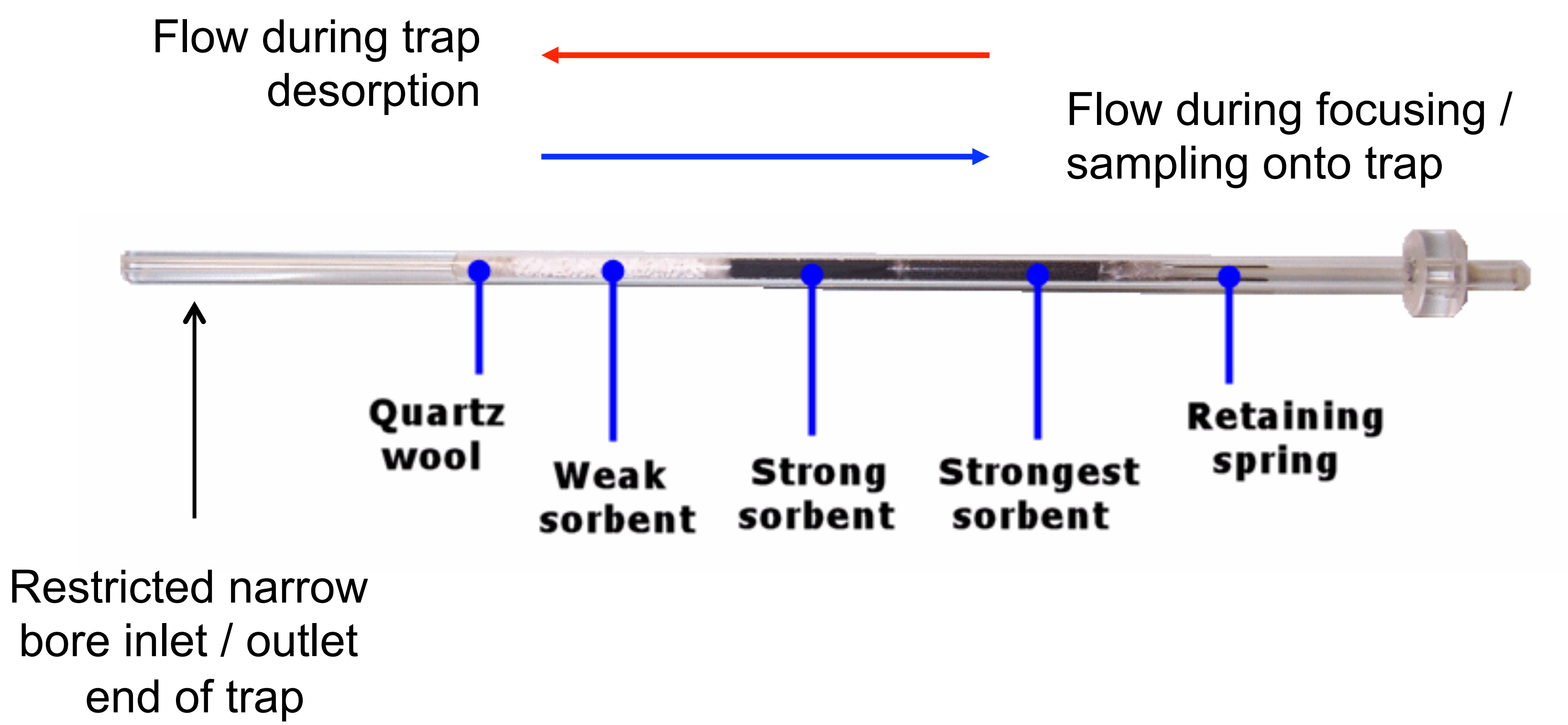
STAGE 2

Rapid transfer of compounds from cold trap to GC



- Cold trap heated rapidly (100°C/sec) for sharp chromatographic peaks
- **Backflush** of cold trap for greater volatility range

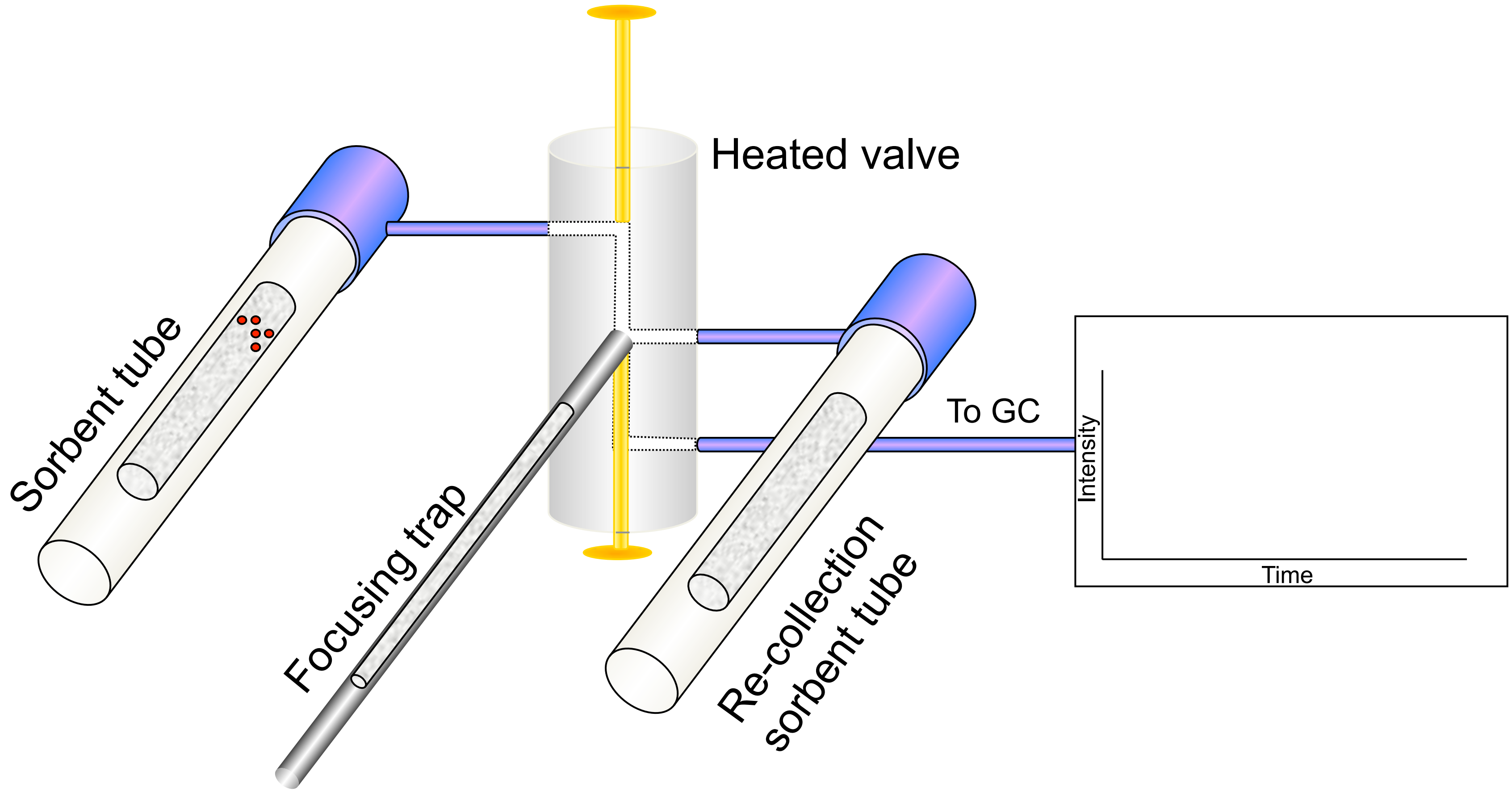
# Cold Trap




- Narrow design allows splitless injection
- Use sorbent(s) to suit specific application

# 2-stage desorption using ‘universal’ TD valve:

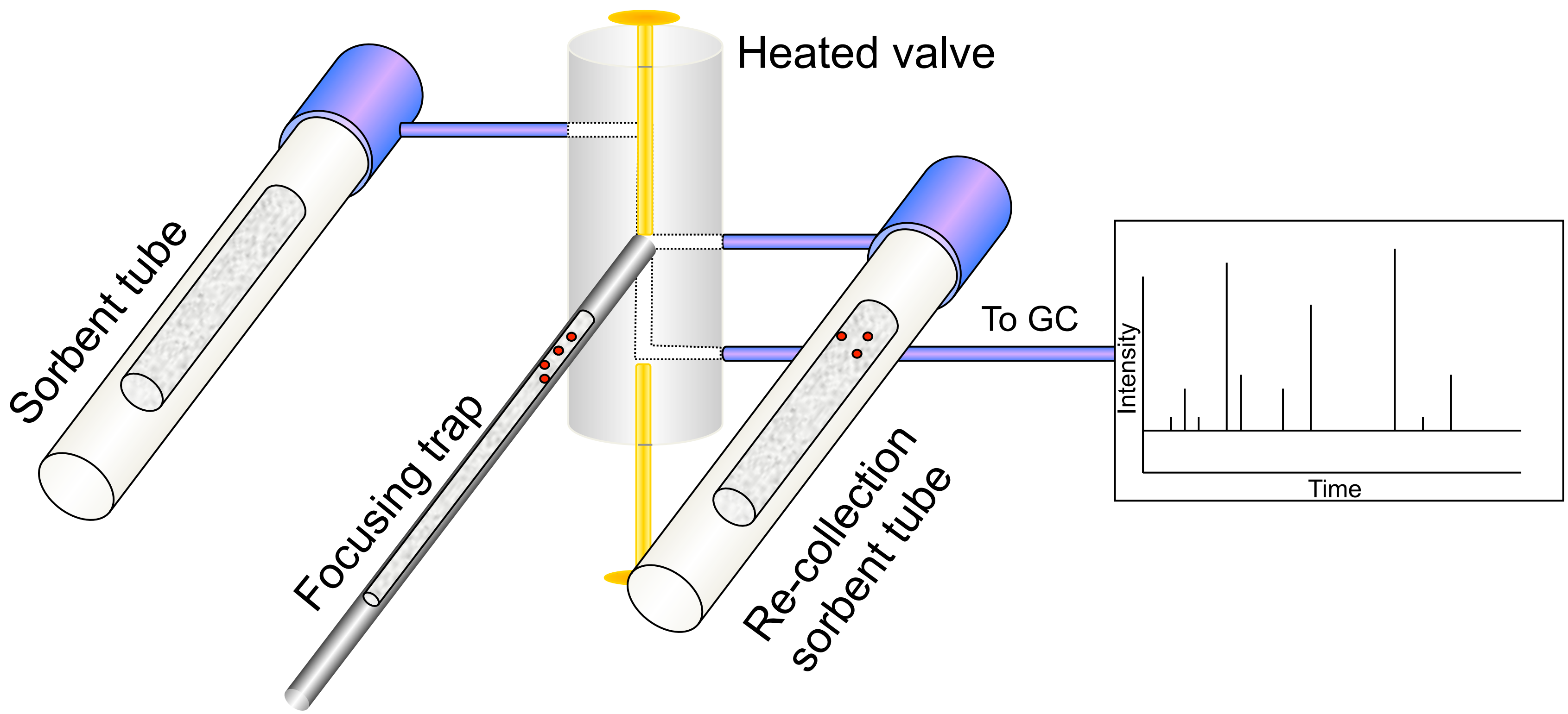
**Stage 1: Primary (tube) desorption with optional (inlet) split**




- Heated TD valve is inert and low volume: Allows quantitative recovery of high & low volatility compounds and reactive species
- The heated valve also isolates the TD system allowing: leak testing, backflush trap desorption, purge to vent, sample overlap, *etc.*

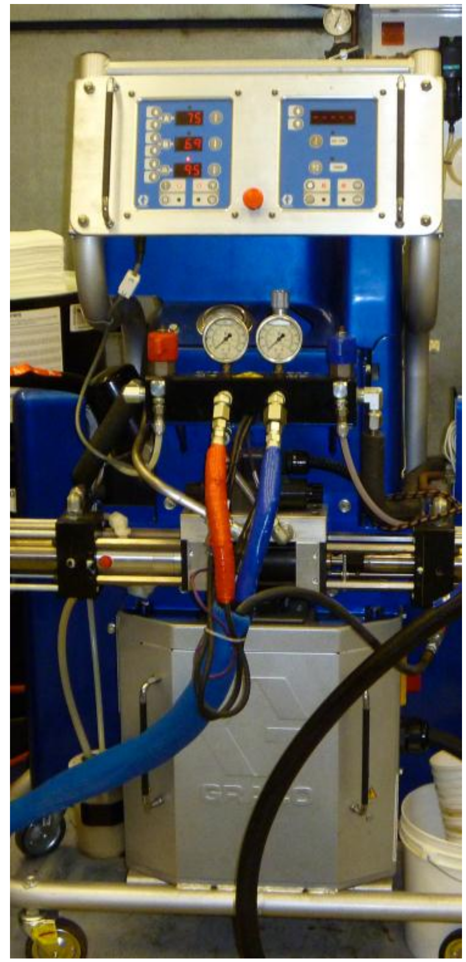
# 2-stage desorption using ‘universal’ TD valve:

**Stage 2: Secondary (trap) desorption with optional (outlet) split**




- Repeat analysis of re-collected samples makes it easy to validate analyte recovery through the TD flow path
- A change to the overall VOC profile indicates any bias

# Spraying Generic Closed-Cell SPF



Applicator is shown on left and spraying equipment shown on right.

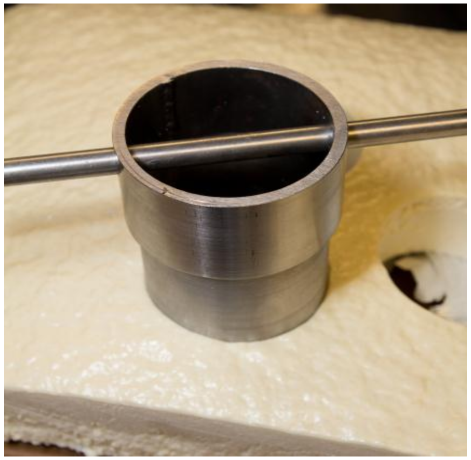
# Sample preparation:
# Sample holding time, packaging and storage studies

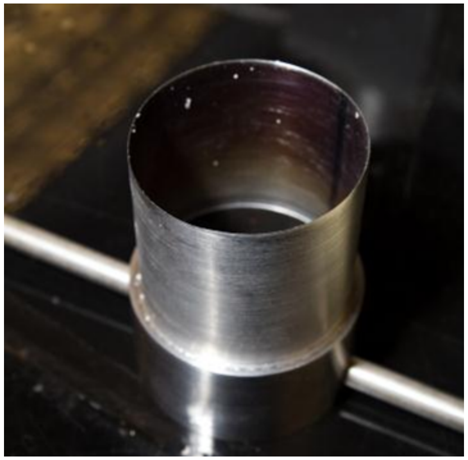
Sample substrate consists of cardboard sheets wrapped with clean aluminum foil.

Five replicate closed-cell SPF samples are shown in the spray booth.

Samples stored in polyethylene terephthalate (PET) layered bags during holding time study

# Microchamber preparation:
# Sample holding time, packaging and storage studies





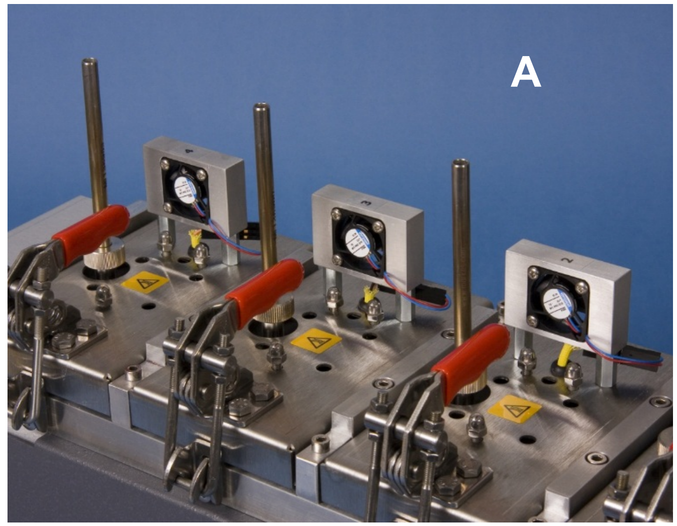
Closed-cell SPF specimen fits tightly into the micro chamber.

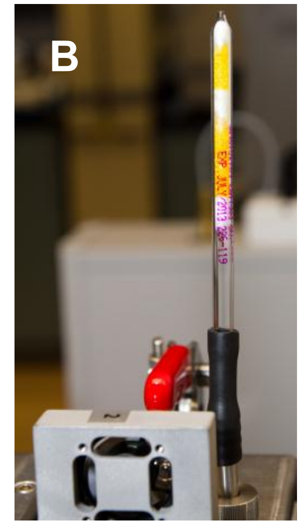
# Sample collection techniques : Sample holding time, packaging and storage studies

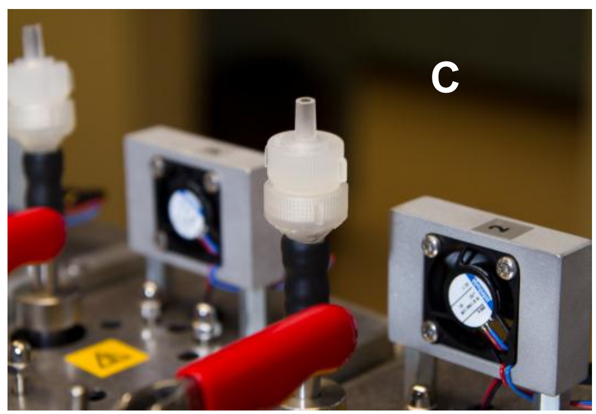
A. Standard TD sorbent tubes

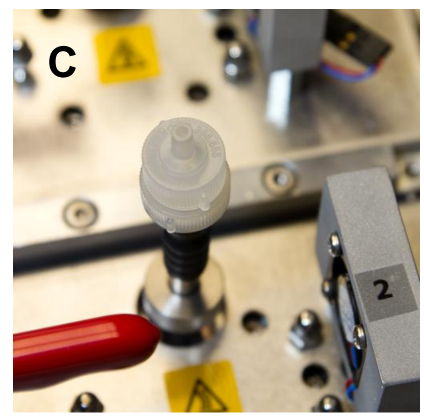
B. Silica gel with DNPH tube for aldehyde analysis

C. Glass-fiber filter with 1-(2-pyridyl)piperazine (PP) and diethyl phthalate.



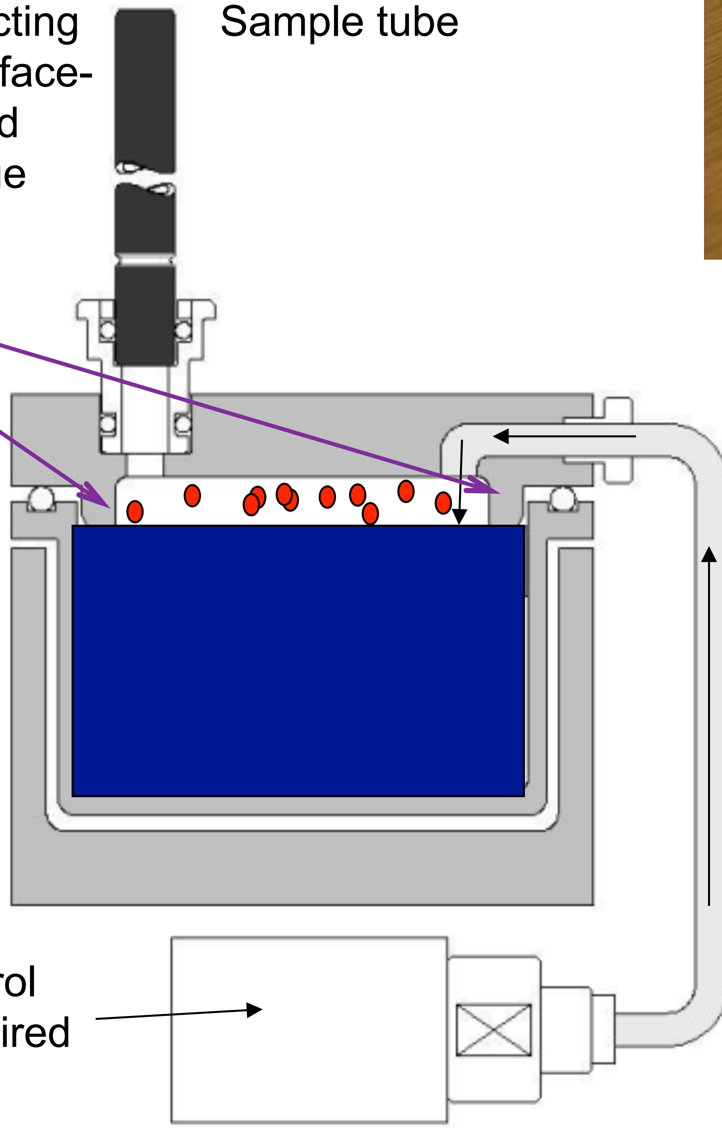



# Microchamber

Heated lid: The collar projecting from lid defines area for surface-only emission testing and minimises ingress of edge emissions

Sample tube



Specific Emission Rate $\mu g/m^2/h$

Heated air stream

Proprietary flow control device – no pump required

***Micro-chamber data has been shown to correlate with results from long term tests using ordinary chambers***

# Determining Wall effects

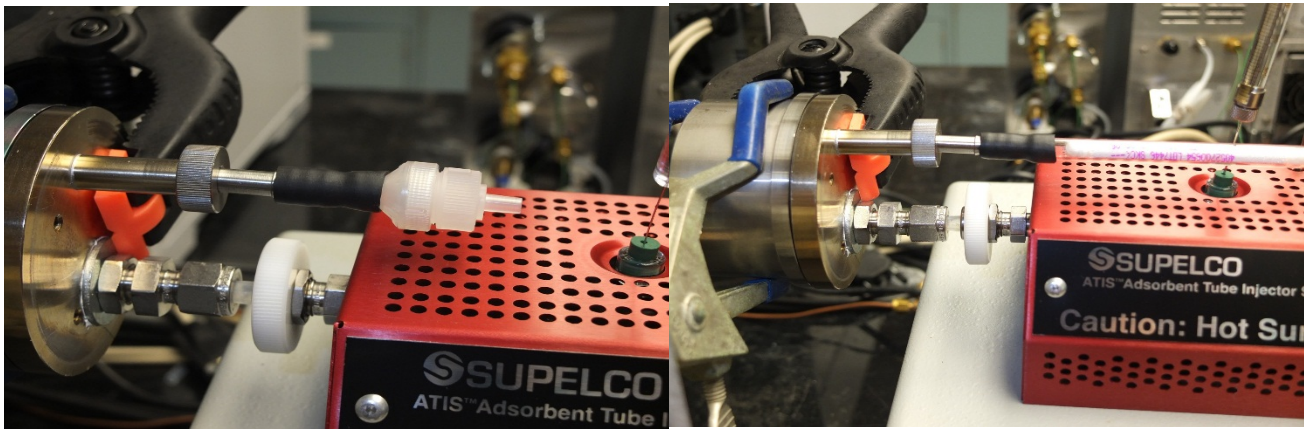
- There is a concern that semi-volatile organic compounds may adhere to the walls of the environmental test chambers, which could significantly bias the emission results.

- The SVOA compounds of interest were spiked into micro chambers and small-scale stainless steel and PTFE lined chambers to evaluate recoveries.

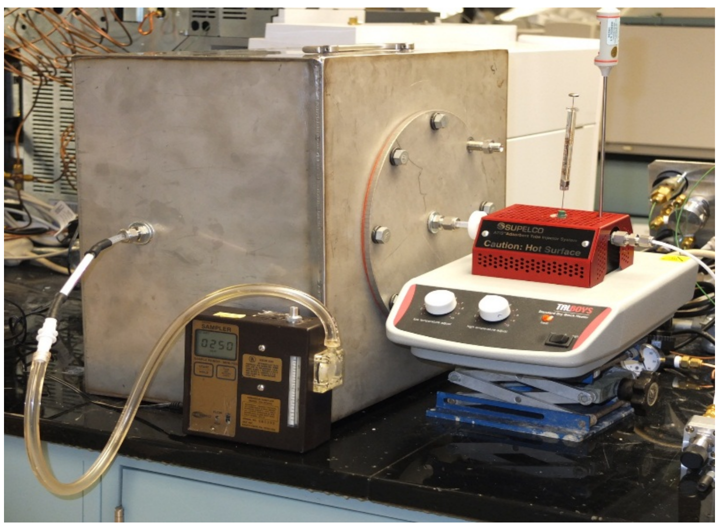
**SVOCs**

- MDI
- Selected amine catalysts
- Flame retardant

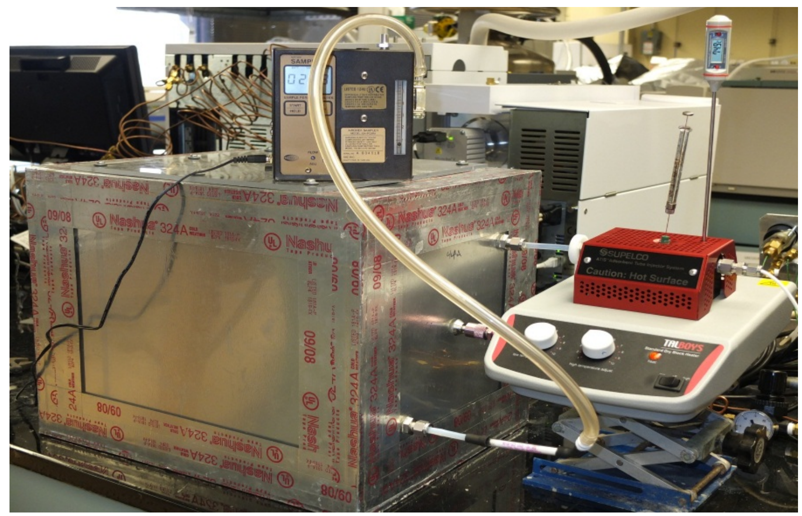
# Spiking of chambers




Microchambers



Stainless Steel Chamber



PTFE Lined Acrylic Chamber

# Spiking of chambers

**MDI**

Spike recoveries were not consistent and a significant percentage of the spiked MDI adhered to the chamber walls, regardless of the material and size of the test chamber.

**Amine Catalysts: RT,**

- Microchamber (stainless steal) 81 to 99% recovery
- PTFE 10-45% recovery
- Stainless steel 4-22% recovery

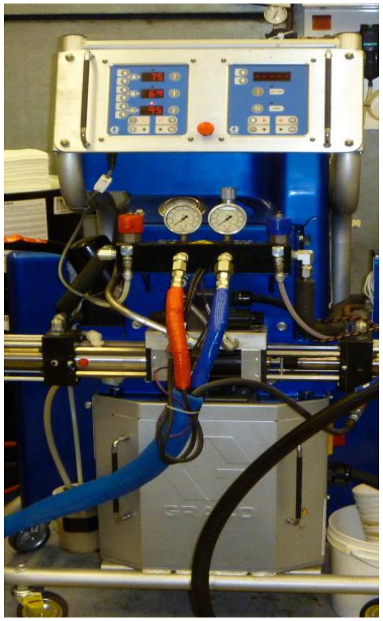
**Flame retardants:**

- RT, 22% RH (except MCTE) Nitrogen gas, minimal recovery from any chamber.
- When the MCTE was increased to ~35%RH excellent recovery was observed.

# ASTM Standards and Work Items

## ASTM D7859-13e1

Standard Practice for Spraying, Sampling, Packaging, and Test Specimen Preparation of Spray Polyurethane Foam (SPF) Insulation for Testing of Emissions Using Environmental Chambers



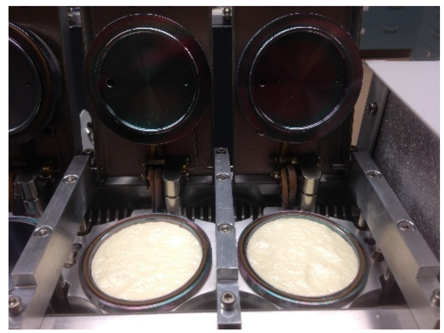
# SPF Objectives

- Compare Chamber size
- Compare temperature
- What time should the samples be collected
- Relative humidity
- Chamber Material
- Flow rate

# Specimens for Chamber Testing

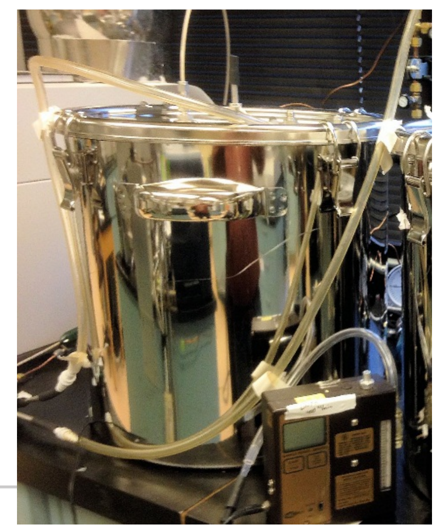
**Micro-Scale Chambers**

- Specimens cut to fit tightly into 114-cc micro-scale chambers



**Small-Scale Chambers**

- Specimens cut to fit tightly into steel sample holders
  - 13x13x6-cm for closed-cell
  - 13x13x9-cm for open-cell
- Placed into 36-L electro-polished small-scale chambers

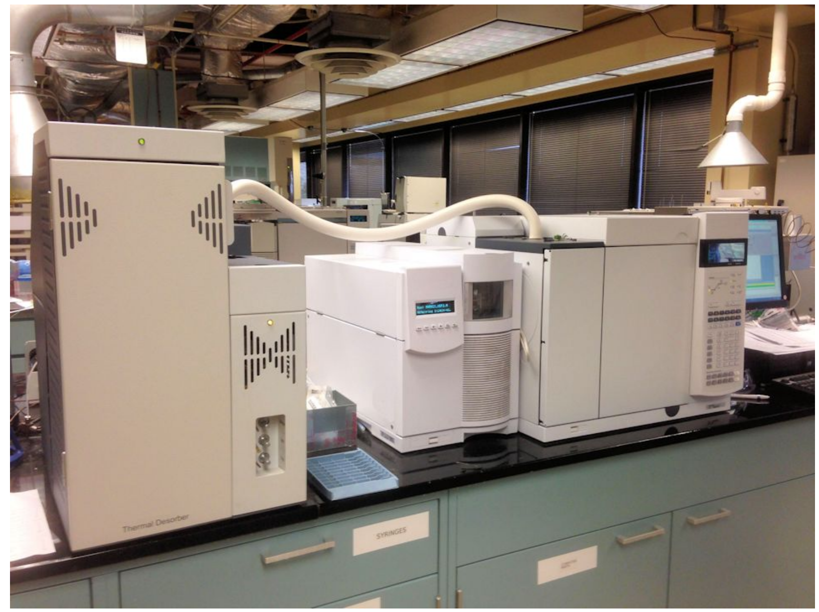


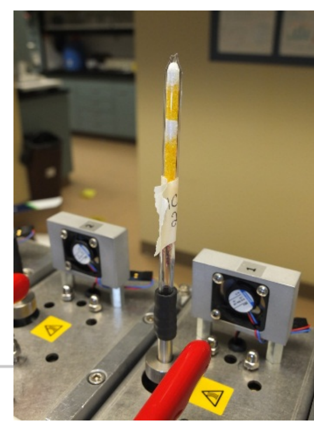
# Chamber Parameters

| Chamber Parameter | Units | Micro-Scale Chamber | Small-Scale Chamber |
|---|---|---|---|
| Flow Rate | mL/min | 50 ±2 | 300 |
| Sampling Rate, cc/min | mL/min | Same as flow rate | 100 |
| Chamber Headspace Volume | $m^3$ | 0.0000161 | 0.0345 |
| Loading Factor (L) | $m^2/m^3$ | 200 | 0.490 |
| Air Change Rate (N) | $h^{-1}$ | 188 | 0.522 |
| Area Specific Flow Rate (N/L) | m/hr | 0.938 | 1.07 |
| Relative Humidity | % | <1 | <1 |
| Sample Area | $m^2$ | 0.00322 | 0.0169 |

# Analytical Determinations

- Emissions samples collected periodically from days 0 to 20.
- Aldehydes
  - ASTM D5197
  - DNPH tubes and HPLC
- VOCs and Flame Retardant
  - EPA TO-17 and ISO 16000 Part 6
  - Thermal Desorption GC/MS





# Target Compounds for this Study

| Target Compound List | Acronym | CAS Number | Description |
|---|---|---|---|
| **HFC-245fa** | - | 460-73-1 | Blowing Agent |
| **Bis (2-Dimethylaminoethyl) ether** | BDMAEE | 3033-62-3 | Catalyst |
| **Tetramethyliminobispropylamine** | TMIBPA | 6711-48-4 | Catalyst |
| **N,N,N-Trimethylaminoethylethanolamine** | TMAEEA | 2212-32-0 | Catalyst |
| **Bis (dimethylaminopropyl) methylamine** | DAPA | 3855-32-1 | Catalyst |
| **Tris-(1-chloro-2-propyl) phosphate** | TCPP | 13674-84-5 | Flame Retardant |
| **Formaldehyde** | - | 50-00-0 | Aldehyde (not in formulation) |
| **Acetaldehyde** | - | 75-07-0 | Aldehyde (not in formulation) |
| **Propionaldehyde** | - | 123-38-6 | Aldehyde (not in formulation) |

Isocyanates (MDI) not evaluated since specialized chambers are necessary.

# Microchamber Parameters

| Parameter | Set Point |
|---|---|
| **Temperature** | 35 C |
| **Gas** | Ultra Zero Air |
| **Flow Rate** | 50 mL/min |
| **Humidity** | 0% |
| **Chamber material** | Deactivated stainless steel |
| **Chamber volume** | 114mL → 1L ? |
| **Depth** | 28 mm |
| **Skin** | Sample submitter specifies if skin is to be left on or not, as described in D7859, must be stated in report |
| **Reporting Units** | µg/m² hr ***AND*** µg/g hr (SPF mass is the initial mass) |
| **Other Reporting Requirements** | If SPF has visual shrunk, note and photograph |
| **Blanks** | Performance Based<br>• Each chamber must be tested once prior to run and have ND for chemicals of interest |
| **Number of foams tested** | Minimum of duplicates<br>• Sample from same foam okay |
| **Sample Location** | • Not with 3 cm of edge of sample<br>• Flattest possible<br>• Similar knit lines in each sample if multiple lifts* |

# Results

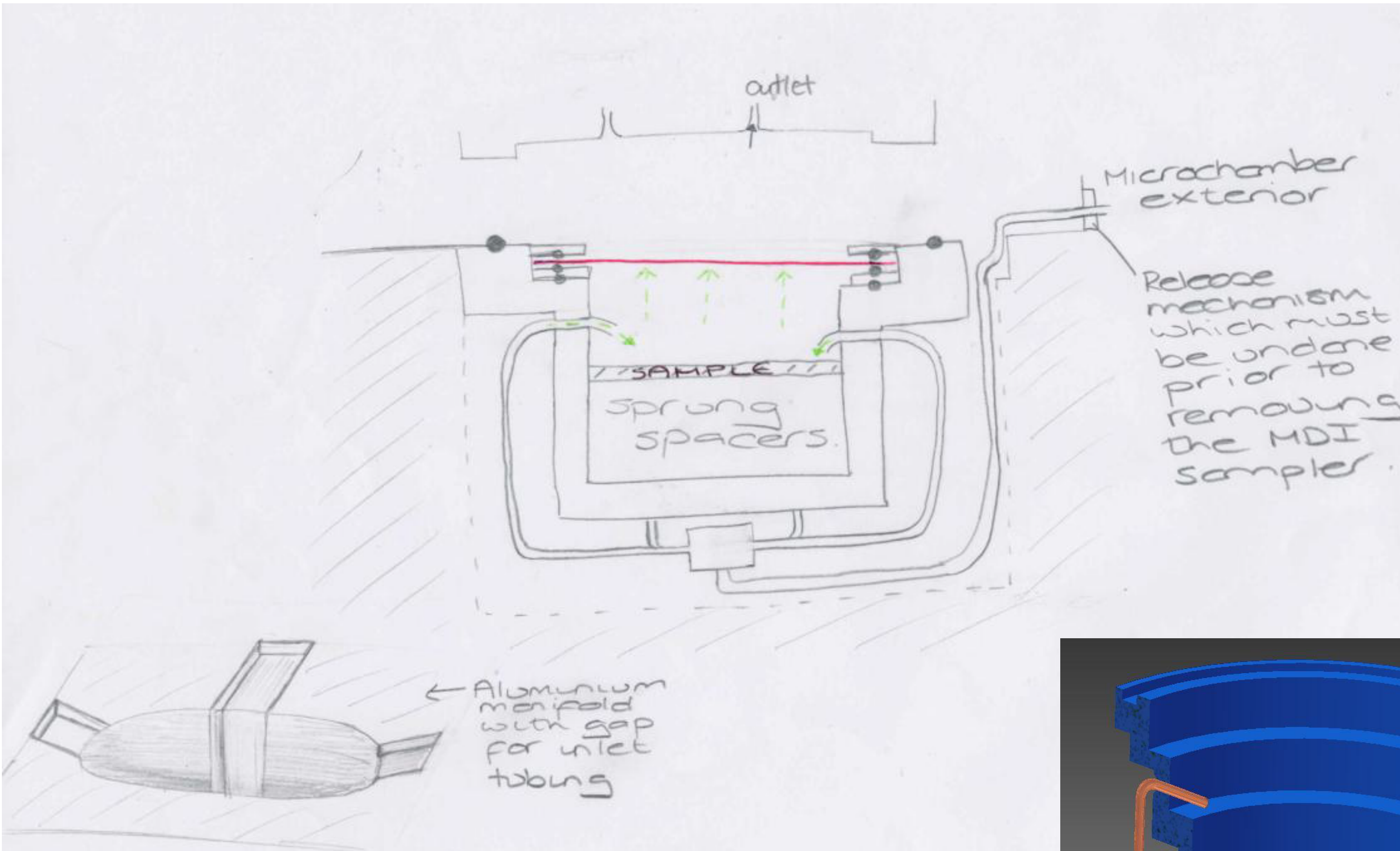
Micro-scale chambers proved to be a useful tool to evaluate SPF insulation for chemical emissions of volatile organic compounds (VOCs).

- After equilibration, the emissions from micro-scale chambers were generally consistent with or slightly higher than small-scale chambers.

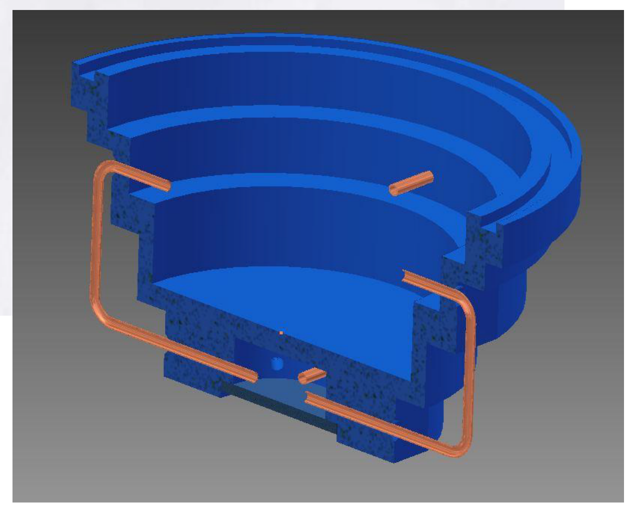
SPF samples can be tested in micro-scale chambers at 23°C to 65°C, but elevated temperatures may not simulate real world environments.

- Careful attention to the sample collection time is necessary at elevated temperatures (initial spikes, baking VOCs out).
- For sample comparisons, emissions can be collected after 2 hours in the chamber; approached near steady state conditions after 7 to 14 days.
- Elevated temperature may be useful to enhance detection of potential aldehyde emissions that are not detected at ambient temperature.

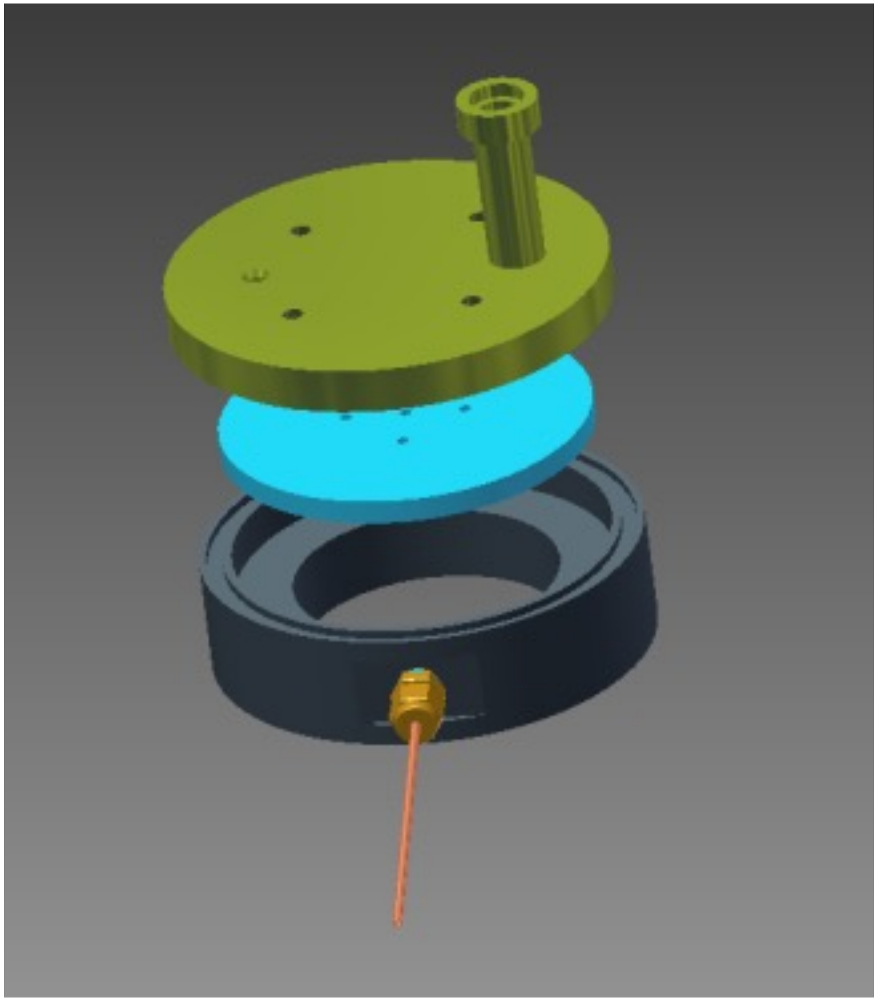
# Future plans





# Methyl Diphenyl Isocyanate



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