Method Development and Research for Measuring Emissions from Spray Polyurethane Foam (SPF) Insulation

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Method Development and Research

Generic Foam Formulations and Compounds of Interest

Evaluation of Thermal Desorption GC/MS for Measuring Potential SPF Emissions

Micro Chamber Parameters and Specimen Preparation

SPF Sample Holding Time and Packaging Evaluation

Evaluation of Wall Effects of Semi-Volatile Compounds in Test Chambers (Adhesion to Chamber Walls)

Generic SPF Formulations

Three generic SPF formulations were developed to evaluate the test methods for measuring emissions.

The formulations represent the following sample types:

- **Open-cell, low density (1/2 pound) high pressure SPF**
- **Closed-cell, medium density (2 pound) high pressure SPF**
- **Kit formulation SPF, 2 components, low-pressure**

Target Compound List for Generic SPF Formulations

Target Compound	Acronym	Description
HFC-245a	-	Blowing Agent
HFC-134a	-	Blowing Agent
Tris-(1-chloro-2-propyl) phosphate	TCPP	Flame Retardant
Bis (2-Dimethylaminoethyl) ether	BDMAEE	Catalyst
Tetramethyliminobispropylamine	TMIBPA	Catalyst
N,N,N-Trimethylaminoethylethanolamine	TMAEEA	Catalyst
Pentamethyldiethylene triamine	PMDTA	Catalyst
Bis (dimethylaminopropyl) methylamine	DAPA	Catalyst
Methylene diphenyl diisocyanate	MDI	Isocyanate

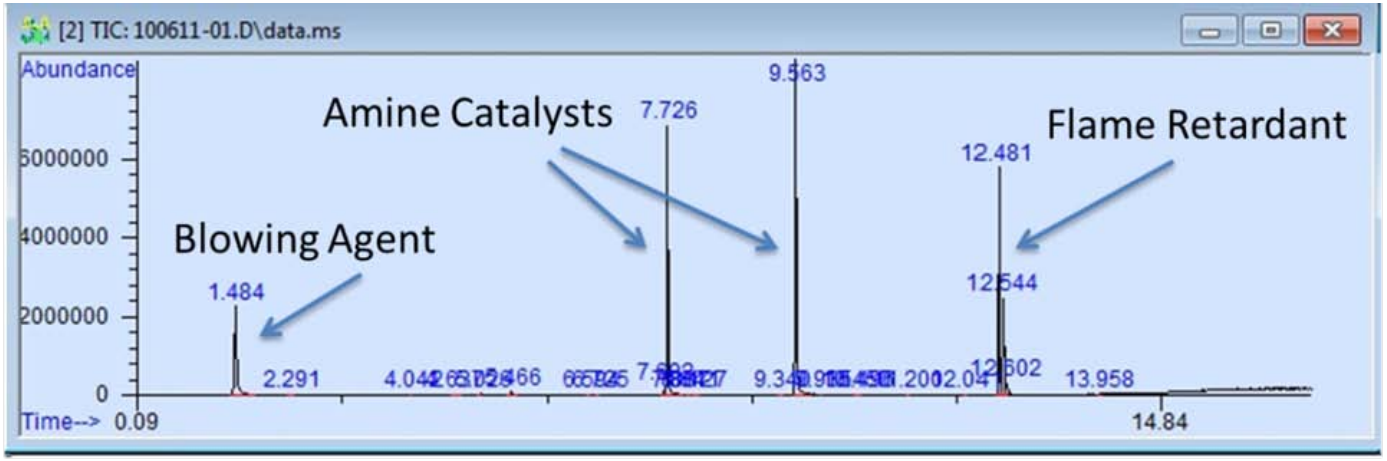
Analytical Method Development Thermal Desorption, GC/MS

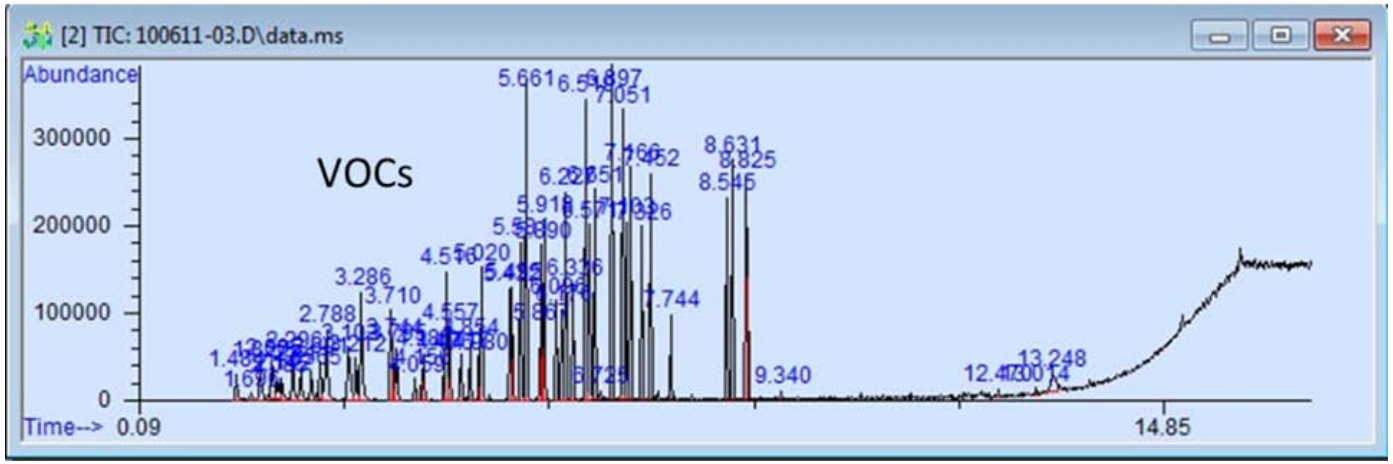
TD:	Markes TD-100
Flow path temperature	160 °C
Sorbent Tube	Tenax TA and Carbopack X sorbent tubes (Stainless Steel)
Split in Standby	10 ml/min
Cold Trap	U-T12ME-2S, Materials Emissions Trap with Tenax and Carbograph 5 TD sorbent
Dry Purge	1 min, 20 ml/min flow to split
Prepurge	0.1 min, default
Primary desorption	270 °C for 8 min, 35 ml/min trap flow, no split flow
Pre-Trap Fire Purge	1 min, 35 ml/min trap flow, 50 ml/min split flow
Cold trap conditions	Trap low: 25 °C, trap high: 300 °C, heating rate: MAX, hold time: 3 min, 50 ml/min split flow
Overall TD split	34.3:1

TD-GC/MS Instrument Conditions

GC/MS:	Agilent 7890 GC and 5975 MSD
Column	Restek Rtx-5 Amine, 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	17.0 min
Carrier gas	He
GC inlet temperature	200 °C
MS source temperature	230 °C
MS quad temperature	150 °C
MS transfer line temperature	250 °C
Mass scan range	m/z = 50-550amu

Example- Total Ion Chromatograms





Target Compounds by TD-GC/MS

Peak Number	Compound Name	MS Quantitation Ion	Retention Time, minutes	Estimated Quantitation Limit, ng
1	HFC-245a	51	1.485	20
2	TMAEEA	58	7.691	200
3	BDMAEE	58	7.727	20
4	PMDTA	72	8.265	50
5	DAPA	58	9.560	100
6	TMIBPA	58	9.654	200
7	TCPP	99	12.477	50

TD-GC/MS Precision and Recovery

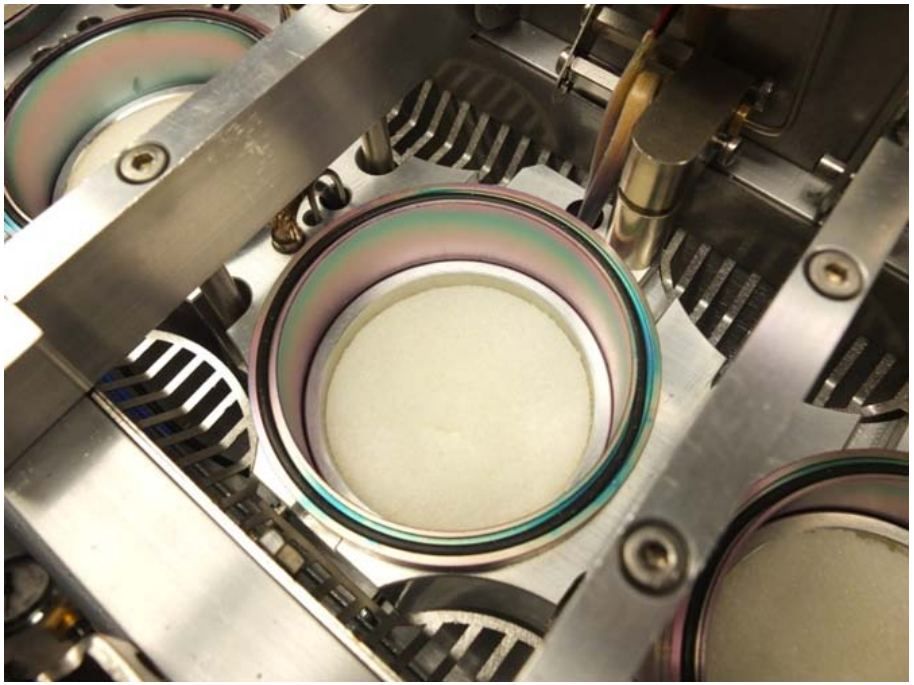
Compound	True Value	Mean	Recovery, %	Standard Deviation	RSD, %
HFC-245a	706	634	89.7	69.1	10.9
TMAEEA	2179	1559	71.5	383	24.6
BDMAEE	1034	977	94.5	40.1	4.10
PMDTA	1114	1035	92.9	36.4	3.52
DAPA	1072	1031	96.2	34.8	3.38
TMIBPA	2397	1631	68.1	217	13.3
TCPP	996	922	92.6	27.1	2.94

Unless otherwise stated, results reported in nanograms (ng) per thermal desorption (TD) tube

Micro Chamber- Specimen Preparation

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

Open-Cell and Kit Formulations



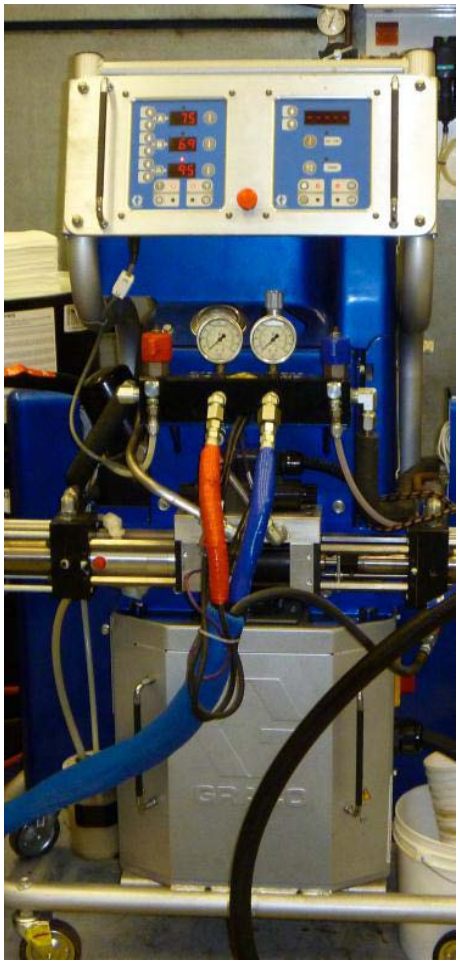
Open-cell SPF with aluminum shim ring fits tightly into the micro chamber.

Low pressure kit formulation loaded into a micro chamber is shown above.

Micro Chamber Test Conditions

Parameter	Value
Sample Diameter, m	0.064
Volume, m^3	5.15E-05
Air Change Rate, h^{-1} (N)	58.2
Loading, m^2/m^3 (L)	62.5
Specific Air Flow Rate (N/L)	0.931
Initial Temperature	23 ^oC

Spraying Generic Closed-Cell SPF for Holding Time Study



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

Holding Time Study
Sample Preparation and Storage

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

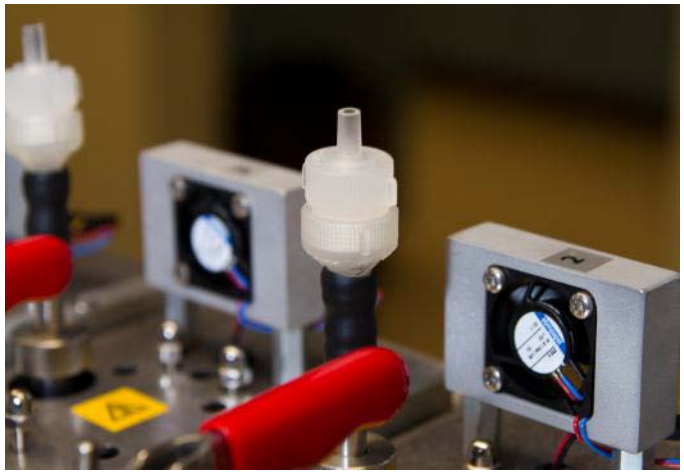
Sample substrate consists of cardboard sheets wrapped with clean aluminum foil.

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

Collecting Emissions from Generic SPF Specimens in Micro Chambers

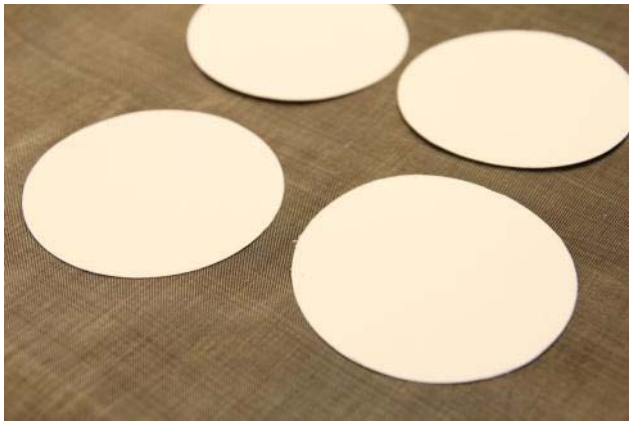
Sample Description	Time, min	Sample Collection and Conditions
Starting Point	0	30 minute equilibration at 23 °C
TD Sample Point 1	30	Thermal Desorption (TD) tubes Sample for 20 minutes (Volume = 1L)
DNPH Sample Point 1	50	Aldehydes with DNPH tubes Sample for 1 hour (Volume = 3L)
TD Sample Point 2	110	Thermal Desorption (TD) tubes Sample for 20 minutes (Volume = 1L)
PP Filter for MDI	130	MDI with 13mm filter with PP Sample for 16 hours
TD Sample Point 3	1090	Thermal Desorption (TD) tubes Sample for 20 minutes (Volume = 1L)
Elevate Temperature	1110	Heat chamber to 40 °C and hold for 10 minutes
TD Sample Point 4	1120	Thermal Desorption (TD) tubes Sample for 10 minutes (Volume = 0.5L)
DNPH Sample Point 2	1130	Aldehydes with DNPH tubes Sample for 1 hour (Volume = 3L)

Sampling from Micro Chamber



13mm Glass-Fiber Filter with
1-(2-pyridyl)piperazine (PP) & diethyl phthalate

BIOS DryCal® Calibrator



90mm Glass-Fiber Filters with PP

Markes TD Tubes

Silica Gel with DNPH Tube

Holding Time Observations

Generic closed-cell and open-cell SPF samples can be stored for up to 48 hours at 23 °C in sealed PET bags without causing a significant change in the emission factor values for target compounds known to be present in the formulation.

The emission factor for the amine catalyst in the low-pressure kit formulation did not appear to be stable in the stored samples. Further research may be necessary for this particular formulation.

MDI Evaluations during Holding Time Study

The MDI was reported as non-detect for all samples collected during the holding time studies:

Component	µg/m³
2,4' MDI	<2
4,4' MDI	<2
Polymeric MDI	<60

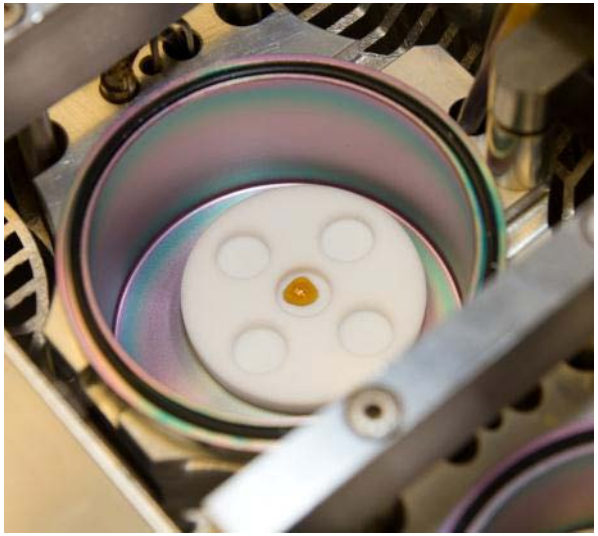
No MDI detected on walls

SVOA Wall Effects Evaluation Spiking Study

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 (MDI, selected amine catalysts and flame retardant) were spiked into micro chambers and small-scale stainless steel and PTFE lined chambers to evaluate recoveries.

MDI Spike Study with Micro Chamber to Evaluate Wall Effects



- MDI (generic formulation) weighed into PTFE coated tray, then placed into micro chamber
  - Flow rate = 100 cc/min
  - Sample temperature and time = 65°C for 2 hours

- MDI emissions collected on 13mm PP filters
- Chamber wall and lid sampled for MDI using 90mm PP filter wipes

MDI (Mixture) Spike Study Results

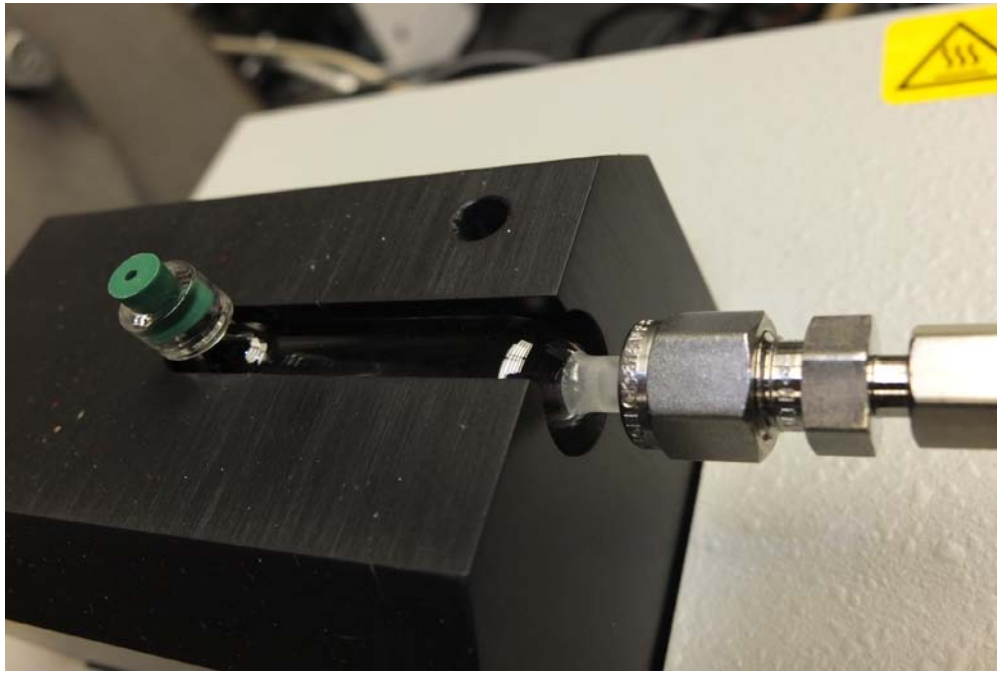
Results reported as % MDI found on chamber walls:

(MDI on Wall) / (MDI on filter + MDI on wall) x 100

Chamber	2,4'-MDI	4,4'-MDI	p-MDI
1	4.6%	8.2%	ND
2	9.4%	37.4%	ND
3	9.7%	28.0%	ND
Blank	ND	ND	ND

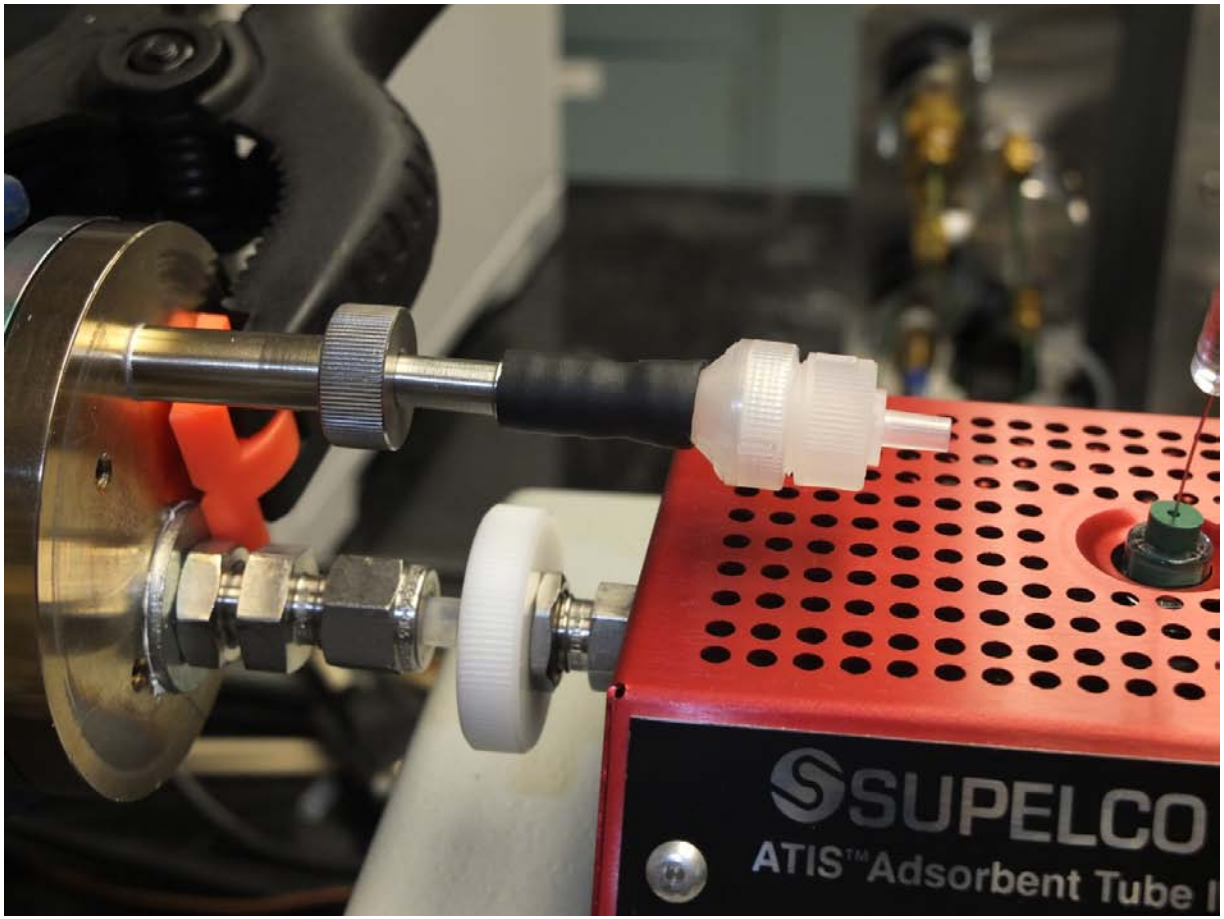
ND = Not detected in chamber wall or PP filter.

Heated Injector System for Spiking Small-Scale and Micro Chambers

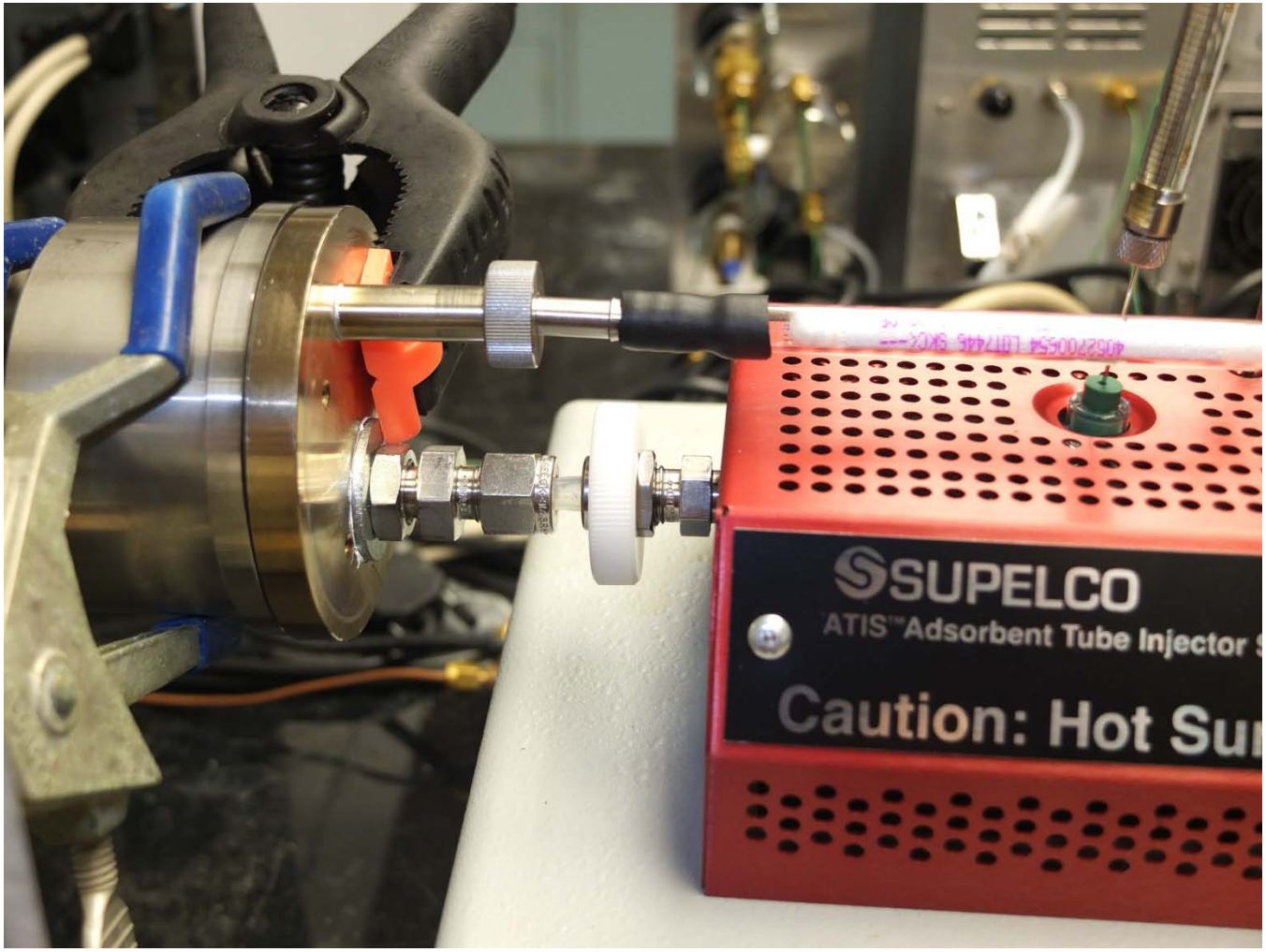


The Supelco Adsorbent Tube Injector System employs the technique of flash vaporization to vaporize the sample into a continuous flow of an inert gas, which carries the sample to the test chamber or sorbent tube.

Micro Chamber with 13mm PP Filter to Evaluate MDI Recovery

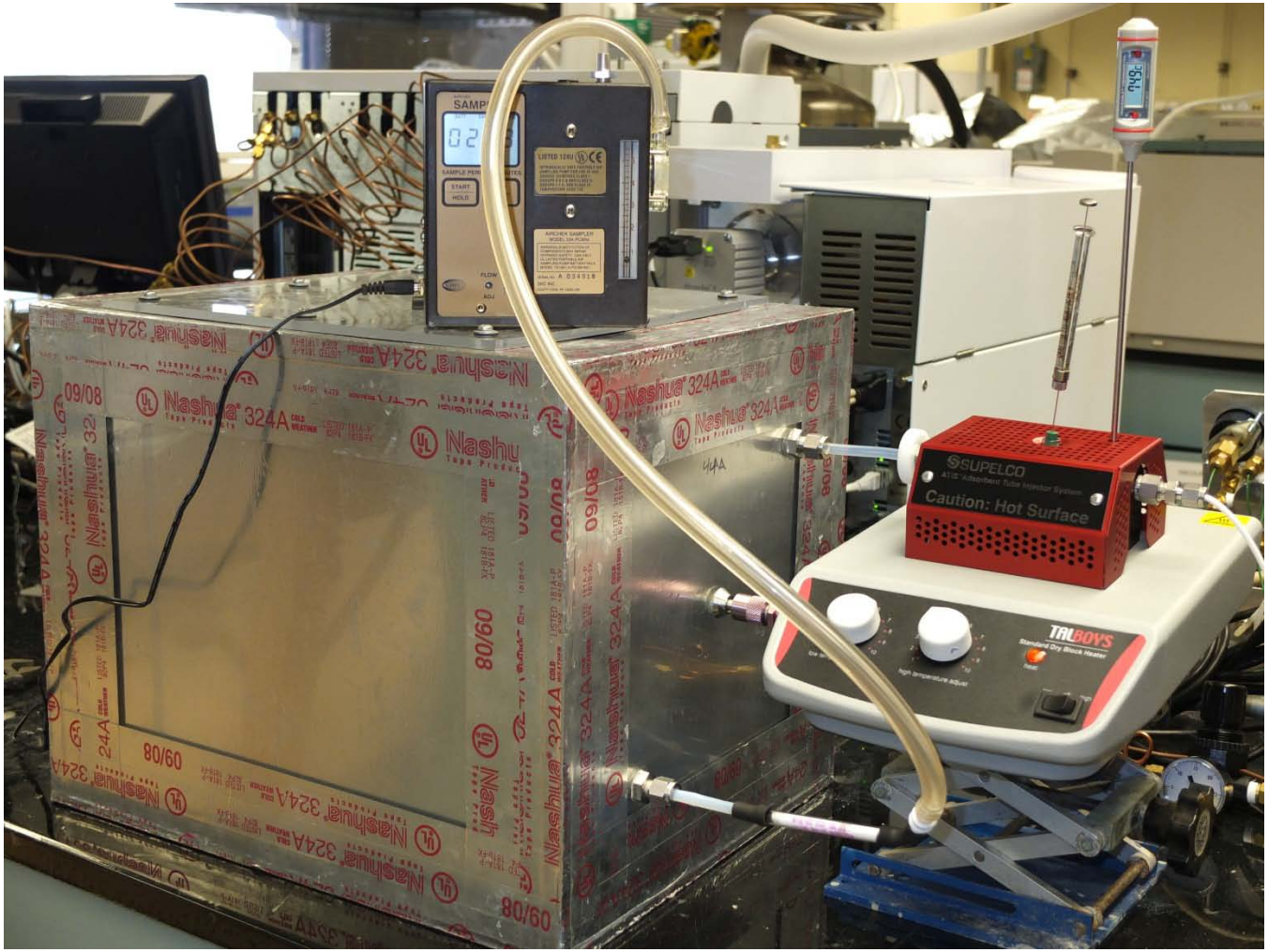


Micro Chamber Spike with XAD-2 Tube



Stainless Steel Chamber Spike

PTFE Lined Acrylic Chamber Spike



Spiking Study Observations

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 catalyst recoveries were acceptable with the micro chamber (ranged from 81 to 99%).

The flame retardant was fully recovered in the micro chamber using air as the carrier gas (containing humidity) with extended sampling time.

Summary of SPF Emissions Research

Developed thermal desorption GC/MS method for measuring potential SPF emissions

Established baseline conditions and sample preparation techniques for measuring SPF emissions with the micro-chamber

Conducted SPF insulation holding time and packaging study using generic SPF formulations; ASTM draft

Evaluated wall effects of semi-volatile compounds in small-scale and micro chambers

Thank you!

Questions