# Research Report for Measuring Emissions from Spray Polyurethane Foam (SPF) Insulation

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# ABSTRACT

This report discusses the status of ongoing analytical method development and research activities to support the development of ASTM standard practices and test methods to measure potential chemical emissions from spray polyurethane foam (SPF) insulation designed for on-site application in buildings. The consensus standards are being developed to evaluate SPF products to establish re-occupancy times for trade workers and residents as well as to assess indoor air quality after installation. Three generic foam formulations including closed-cell, open-cell and a low pressure kit formulation were used to evaluate the test protocols. An analytical method was developed with thermal desorption and GC/MS to measure volatile organic compounds (VOCs), e.g., blowing agents, in addition to semi-volatile organic compounds (SVOCs), e.g., flame retardants and amine catalysts. Sample preparation procedures were developed to test SPF samples in micro-scale chambers to accelerate testing. A holding time study was then conducted with the micro chambers to estimate the maximum time after spraying that SPF samples can be stored in sealed Mylar bags without significant loss of compounds of interest. Semi-volatile organic compounds such as methylenediphenyl diisocyanate (MDI), selected amine catalysts and flame retardant were evaluated for potential losses in the conventional small-scale and micro-scale test chambers due to potential wall effects. The conclusions from this research may be used as the basis to develop several ASTM standards on Committee D22 on Air Quality through Subcommittee D22.05 on Indoor Air.

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# INTRODUCTION

This study was conducted under the direction of the CPI SPF Emissions Workgroup to support the development of ASTM standard(s) at Subcommittee D22.05 on Indoor Air, Work Item WK30960. Specifically, the data will be used towards the development of practices and procedures for measuring the potential air emissions of volatile organic compounds (VOCs) including aldehydes and organic blowing agents, diisocyanates (usually methylene diphenyl diisocyanate or MDI), oligomeric isocyanates, flame retardants and amine catalysts from spray polyurethane foam (SPF) insulation products. SPF insulation is usually applied on-site within the building envelop by trained technicians using specialized equipment; therefore, there is a need to establish allowable re-entry times for building occupants following SPF insulation applications. There is also a need to provide assurance to consumers and building occupants regarding potential longer-term inhalation exposures to potential emissions.

Building products are routinely tested for their emissions of VOCs of concern. For insulation products such as batts and loose-fill insulation, representative samples typically are collected from their manufacturing locations and are laboratory tested for VOC emissions in small-scale environmental chambers at standardized indoor conditions following ASTM Guide D 5116. SPF insulation products are different in that they are formed in place at the building site by chemical reaction rather than produced in a factory setting. SPF insulation application procedures vary among products and the final products potentially are influenced by spray equipment parameters as well as environmental factors at the time of application. These characteristics present special challenges for the creation, collection, and testing of SPF insulation product samples.

A new analytical technique was evaluated and optimized to analyze potential SPF emissions using thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). Procedures were developed for the creation, collection, and handling of test samples representative of both closed-cell and open-cell SPF insulation products and for the preparation of test specimens for environmental chamber testing. The holding time for SPF specimens was evaluated to determine if samples can be preserved and stored in sealed air tight bags to allow time for shipment to the laboratory. SPF samples produced in this manner were tested for their potential emissions using specialized micro-scale environmental test chambers to minimize potential wall effects of semi-volatile organic compounds (amine catalysts, flame retardant, and MDI). The wall effects were then examined by fortifying the chambers with the compounds of interest and measuring recovery in both micro-scale chambers and conventional small-scale test chambers for comparison.

#### APPARATUS AND INSTRUMENTATION

#### Instrumentation

Markes International TD-100 Thermal Desorber connected to Agilent 7890A Gas Chromatrography (GC) and 5975C Inert XL Mass Selective Detector (MSD)

Agilent 6890 GC and 5973N MSD

Agilent 1100 Series Liquid Chromatography (LC) / MSD and Diode Array Detector

Waters 2695 Alliance LC with Fluorescence Detector

Agilent 6890 GC with Nitrogen Phosphorus Detector (NPD)

#### **Environmental Test Chambers**

Markes International M-CTE250 Micro-Chamber/Thermal Extractor, 114-mL capacity

PTFE Lined, Acrylic, Small-Scale Chamber, 37.8-L capacity (approximate)

Stainless Steel Small-Scale Chamber (Grade 304), 37.8-L capacity (approximate)

Sampling Pumps and Flow Controllers

Markes International TC-20 Tube Conditioner

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Markes International Calibration Solution Loading Rig (CSLR<sup>TM</sup>) Supelco ATIS<sup>TM</sup> Adsorbent Tube Injector System BIOS Defender 510 Volumetric Primary Flow Standard, Calibrator SKC Universal Sampling Pump, Model 224-PCXR4 Sorbent Tubes and Media for Sample Collection Markes International Thermal Desorption Tubes: Stainless Steel, Tenax TA 35/60 Stainless Steel, 1cm Quartz Wool, Tenax TA 35/60, Carbopack X 40/60 SKC Xad-2 Sorbent Tubes, Cat. No. 226-30-06 SKC Treated (DNPH) Silica Gel, Cat. No. 226-119 13mm Glass-Fiber Filter with 1-(2-pyridyl)piperazine (PP) & diethyl phthalate in cassette housing 90mm Glass-Fiber Filter with 1-(2-pyridyl)piperazine (PP) **Spraying Equipment and Generic Samples** Graco H-XP2 with T2 2:1 Transfer Pumps A-Side Open-Cell and Closed Cell Generic SPF- Elastospray 800A Iso. 54476251 B-Side Closed Cell Generic SPF- FE 1039624-1B Resin 10955583 B-Side Open-Cell Generic SPF- US B Resin Material 53852123, Lot 7224.563.1 Low Pressure 2 Component Kit SPF Formulation, Handi-Foam **Sample Collection Equipment** Clean cardboard sheets, double wall construction, cut into 30.5 x 30.5-cm pieces Aluminum foil, heavy-gauge roll, approximately 0.024-mm thick Electric knife to scarf and cut SPF samples Circular foam coring tool- constructed of steel to cut SPF insulation samples to fit tightly into micro-scale chambers Mylar bags with aluminum foil layer, light resistant, composite layer approximately 0.127-mm thick. The following sized bags were used-

For closed-cell SPF and the kit formulation, a bag with a zipper seal with dimensions of approximately 46 x 71 cm

For open-cell SPF, a bag size of approximately 51 x 76 cm (zipper seal not available in this size of bag).

#### Packaging tape, clear, approximately 5-cm wide

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# GENERIC SPF FORMULATIONS

In order to evaluate and develop standard test methods for SPF insulation, specific compounds of interest were identified in three generic SPF formulations. These formulations were developed by the CPI ventilation workgroup at the time the emissions research project was initiated. The three generic SPF 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.

All three generic SPF formulations were sprayed on-site according to the CPI ventilation workgroup's specifications. These samples were used to evaluate holding times and sample preparation techniques for micro-scale chamber testing. The diisocyanates, blowing agents, amine catalysts, and flame retardant used in the generic formulations described in Table 1 were treated as the primary compounds to develop and evaluate the analytical and chamber test methods during this study. These compounds were used to show proof of concept for SPF environmental chamber and analytical testing; proprietary formulations that use other compounds may require further research and development.

Table 1- Generic SPF Formulations					
Low Density (1/2 pound) High Pressure SPF Formulation	Medium Density (2 pound) High Pressure SPF Formulation	Low Pressure (2 Component) Kit Formulation			
	A-side				
Polymeric MDI (PMDI) (100%)	PMDI (100%)	PMDI (92.5%)			
		Blowing Agent HFC-134a (7.5% )			
	<b>B-side</b>				
Polyether Polyol (34%)	Aromatic Polyester Polyol (36.39%) Aromatic Amino Polyether Polyol (33.61%)	Polyester Polyol (23%) Polyether Polyol (23%)			
NPE Emulsifier (11.9%)					
<b>Blowing agent</b> Water (20%)	<b>Blowing agent</b> HFC-245fa (6.97%) Water (2.55%)	<b>Blowing Agent</b> HFC-134a (17%)			
Fire Retardant Tris-(1-chloro-2-propyl) phosphate (TCPP) (25.2%) Silicone Surfactant (1.0) Catalyst Bis (2-Dimethylaminoethyl) ether (BDMAEE) (0.9%) Tetramethyliminobispropylamine (TMIBPA) (3.0%) N,N,N-Trimethylaminoethylethanolamine (TMAEEA) (4.0%)	Fire Retardant Tris-(1-chloro-2-propyl) phosphate (TCPP) (15.91%) Silicone Surfactant (1.0) Catalyst Bis (2-Dimethylaminoethyl) ether (BDMAEE) (0.7%) Bis (dimethylaminopropyl) methylamine (DAPA) (2.59%) N,N,N- Trimethylaminoethylethanolamine (TMAEEA) (0.3%)	Fire Retardant Tris-(1-chloro-2-propyl) phosphate (TCPP) (30%) Silicone Surfactant (2%) Catalyst Pentamethyldiethylene triamine (PMDTA) (5%)			

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# EVALUATION OF THERMAL DESORPTION GC/MS FOR MEASURING POTENTIAL SPF EMISSIONS

#### Objective

The objective of this portion of the work was to evaluate thermal desorption and GC/MS for measuring potential emissions from SPF insulation samples. It is preferred to develop a suitable TD-GC/MS methodology for the analysis of all/most target compounds on a single tube, which can be sampled from environmental test chambers. Compounds of interest include, but are not limited to blowing agents, flame retardants, amine catalysts and diisocyanates. The compounds of interest from the generic SPF formulations described in Table 2 were used for evaluation.

Table 2- Compound List for TD-GC/MS Method Evaluation					
Target Compound	Acronym	Description			
HFC-245fa	-	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			

#### **Method Development**

The TD-GC/MS procedure is widely used to measure volatile organic compounds (VOCs) in environmental test chambers; however, it is a novel approach to measure the potential emissions from SPF insulation, specifically the semi-volatile organic compounds. With help from the vendor, a system consisting of a Markes TD-100 Thermal Desorption (TD) unit coupled to an Agilent 7890A Gas Chromatograph (GC) and 5975 Mass Selective Detector (MSD) was evaluated for measuring the compounds of interest in the three generic SPF formulations.

To initially test the system, a purge-and-trap VOC standard, described in US EPA Method 8260B was prepared in methanol at 20-ng/µL from a commercially available stock solution, Spex Certiprep, Cat. 60-BIG-MIX-2000. The standard was injected (1µl) onto a stainless steel thermal desorption tube containing Tenax TA using a Calibration Solution Loading Rig (CSLR<sup>TM</sup>) at approximately 80-cc/min with UHP grade nitrogen as the carrier gas. The samples were analyzed with the TD-GC/MS system using the initial instrument parameters specified in Table 3. The general purpose graphitized carbon cold trap that was installed with the instrument was replaced with a Tenax cold trap. These traps cover similar analyte volatility ranges but the Tenax trap is considered more inert to possible labile (amines/isocyanates) species.

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Table 3- Initial Thermal Desorption, GC/MS Parameters				
Thermal Desorption:				
Flow path temperature	160 °C			
Sorbent Tube	Tenax TA (Stainless Steel)			
Split in Standby	10 ml/min			
Cold Trap	U-T9TNX-2S, Tenax Trap			
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: 3min,			
	50ml/min split flow			
Overall TD split	34.3:1			
GC/MS:				
Column	J&W HP-5MS, 30 m, 0.25 mm x 0.25 µm			
Column flow	1.5 ml/min, constant flow			
Temperature program	40 °C (2 min), 25 °C/min to 320 °C (1 min)			
Total run time	14.2 min			
Carrier gas	He			
GC inlet temperature	250 °C			
MS source temperature	230 °C			
MS quad temperature	150 °C			
MS transfer line temperature	250 °C			
Mass scan range	m/z = 50-550 amu			

One of the advantages of the TD-100 thermal desorber is the ability to recollect samples onto the same or a different TD tube after analysis to allow samples to be reanalyzed. The volatiles on the TD tube were recollected to demonstrate this capability of the TD-100. Chromatograms produced from initial and recollected samples showed that the instrument was working within the manufacturer's specifications with acceptable quantitative recovery. TD tubes were reconditioned for re-use with a Markes tube conditioner as specified by the manufacturer.

To evaluate semi-volatile organic compound performance, individual stock solutions of the amine catalysts and flame retardant were prepared in methanol at approximately 5000-ng/ $\mu$ L then diluted to 500-ng/ $\mu$ L. Similarly, solutions of 4,4'-MDI were prepared in ethyl acetate. 1- $\mu$ l of each solution was spiked onto separate Tenax TA TD tubes and analyzed using the instrument conditions described above. There was a small peak observed for MDI. There was reasonable peak area for each amine (except TMAEEA), and good peak shape for TCPP; however, the amines' peak shapes were not very sharp. The breakdown of TMAEEA to 1,4-dimethylpiperazine was detected; injection of the TMAEEA solution directly onto the split/splitless inlet (without thermal desorption) showed limited conversion indicating the breakdown occurs during thermal desorption.

From instrument installation, the transfer line from the GC to the TD-100 was the head of the GC column, which had the potential to produce poor peak shape. Hence, a 1.5-m deactivated fused silica transfer line was installed, connected via a glass Quick Seal connector to the GC column. In order to extend the volatility range of the analytes retained on the cold trap, a materials emission cold trap was installed and conditioned. Sorbent tubes with Tenax TA and Carbopack X were used for analysis of the same solutions as analyzed earlier. Review of chromatograms from the spiked tubes showed good peak shape for non-basic analytes (e.g. TCPP) but worsened peak shape for the amines.

To improve performance for the amine catalysts, a base-deactivated transfer line and amine optimized GC column (Rtx-5 Amine) was installed and conditioned. The optimized operating conditions for the TD-100 and GC/MS are specified in Table 4. The peak shape for the amine catalysts were much sharper, far superior to those obtained with the original HP-5MS column; however, TMAEEA continued to demonstrate partial conversion to 1,4-dimethylpiperazine during thermal desorption as evidenced by the GC/MS chromatogram and mass spectral match (NIST library) for the breakdown product. This decomposition in the TD contributes to lower response factors for TMAEEA compared to other amine catalysts that were evaluated. The optimized conditions for amine catalysts caused the previously observed small peak for MDI to disappear; therefore, this method would not be suitable for measuring MDI.

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Table 4- Optimized Thermal Desorption GC/MS Parameters				
Thermal Desorption:				
Flow path temperature	160 °C			
Sorbent Tube	Tenax TA and Carbopack X (Stainless Steel)			
Split in Standby	10 ml/min			
Cold Trap	U-T12ME-2S, Materials Emissions Trap (Tenax and Carbograph 5 TD)			
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: 3min,			
	50 ml/min split flow			
Overall TD split	34.3:1			
GC/MS:				
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 = 50-550 amu			

After the instrument was optimized for the recovery of amine catalysts, the VOCs were also evaluated along with the blowing agents. The US EPA Method 8260 purge-and-trap standard continued to show good chromatography as evidenced by GC/MS total ion chromatograms. A stock solution of HFC-245fa was prepared in cold methanol. The HFC-134a standard was purchased from Spex Certiprep, (Custom Solution, Cat. VO-BYRPA-10, Certified as 2000-ug/mL 1,1,1,2-Tetrafluoroethane in methanol). The prepared standards were injected onto the Tenax TA and Carbopack X sorbent tubes using the CSLR loading rig with UHP nitrogen as the carrier gas. The HFC-245fa showed excellent peak shape in the system; however, HFC-134a could not be recovered with the current instrument conditions due to its increased volatility. An example of a total ion chromatograms containing blowing agent (HFC-245fa), amine catalysts (BDMAEE, DAPA), flame retardant (TCPP) and VOCs (EPA Method 8260 compounds) are shown in Figure 1.

#### **Calibration and Method Performance**

The target compounds were calibrated with the optimized instrument parameters by preparing a stock in methanol then preparing calibration solutions from serial dilutions. The calibration ranged from 5000-ng/tube to near the estimated quantitation limit, with the exception of TMAEEA, which was prepared at 10,000-ng/tube since this compound's response factor is significantly lower than the other amine catalyst compounds, presumably from decomposition and breakdown in the TD as described above. Since DAPA and TMIBPA nearly co-elute (very close retention time) with similar mass spectra, these compounds were prepared separately. It should be noted that the same amine catalysts co-elute with other GC methods. For example, these compounds co-elute when analyzed by GC equipped with a Nitrogen Phosphorus Detector (NPD) using a similar capillary column.

The calibration curves, extracted ion chromatogram and mass spectra are shown for each compound in Figures 2 through 8. TMAEEA, BDMAEE and PMDTA showed the best correlation with a quadratic fit; therefore, at least six calibration points were used for these compounds. A linear fit was used for the remaining compounds. As can be seen in Figure 8 in the extracted ion chromatogram, there were two extra peaks immediately following the TCCP, which were assumed to be from impurities: bis (1-chloro-2-propyl)-2-chloropropyl phosphate and bis (2-chloropropyl)-1-chloro-2-propyl phosphate, which are described in the document "OECD SIDS Tris(1-Chloro-2-propyl)phosphate" (UNEP Publications).

The quantitation ions, retention times and quantitation limits are shown in Table 4. The quantitation limits are estimated values based on observations from calibration data and corresponding response factors. Actual reporting limits from

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environmental chambers would be dependent on the volume of air collected at the time of sampling from the chambers onto the sorbent TD tubes (typically 1-L). For example, if 1-L of air is collected onto a TD tube, the estimated quantitation limit for HFC-245fa would be 20-ng/L (equivalent to  $\mu g/m^3$ ).



Figure 1- Example of Total Ion Chromatograms

Mid-level calibration levels were prepared in quadruplicate to determine precision and recovery, which are reported in Table 5. Most compounds showed excellent spike recovery (>85%) and acceptable precision (<15% RSD). However, both TMAEEA and TMIBPA showed lower spike recovery (71% and 68%, respectively); TMIBPA also had relatively poor precision (RSD = 25%). The spike recovery of TMAEE and TMIBPA could possibly improve after recalibration; however, these two compounds appear to be the most challenging to analyze.

# Summary for TD-GC/MS

An optimized TD-GC/MS technique was developed to analyze several volatile organic compounds and semi-volatile organic compounds from the generic SPF formulations using a single sorbent tube and one analytical test per sorbent tube. Other SPF formulations may require monitoring alternative target compounds; therefore, method performance should be assessed for each formulation. Laboratory analysts must be fully aware of the amine catalysts compounds in each formulation to avoid misidentification since some of these compounds are known to co-elute. The thermal desorption (TD) tubes were found suitable to collect samples from both micro-scale and conventional small-scale environmental test chambers since the TD tubes require a relatively small sample volume, usually only 1-L, to produce reasonable detection limits for product emissions testing. The current TD-GC/MS procedure was not found suitable for the analysis of MDI or HFC-134a; therefore, other methods will be required in order to monitor emissions of these compounds.

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	Table 4- Summary of Target Compounds by TD-GC/MS							
Peak Number	Compound Name	MS Quantitation Ion	Retention Time, minutes	Estimated Quantitation Limit, ng				
1	HFC-245fa	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				

	Table 5- Precision and Recovery <sup>1</sup>									
Compound	Tube 1	Tube 2	Tube 3	Tube 4	True Value	Mean	Recovery, %	Standard Deviation	RSD, %	
HFC-245fa	602	551	694	687	706	634	89.7	69.1	10.9	
TMAEEA	1425	2064	1151	1596	2179	1559	71.5	383	24.6	
BDMAEE	923	982	1020	982	1034	977	94.5	40.1	4.10	
PMDTA	1003	1025	1087	1023	1114	1035	92.9	36.4	3.52	
DAPA	1046	1014	1072	993	1072	1031	96.2	34.8	3.38	
TMIBPA	1517	1659	1426	1923	2397	1631	68.1	217	13.3	
ТСРР	960	913	896	919	996	922	92.6	27.1	2.94	

<sup>1</sup>Unless otherwise stated, results reported in nanograms (ng) per thermal desorption (TD) tube

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Linear Regression,  $R^2 = 0.9989$ ; Calibration Levels = 20, 100, 200, 500, 1000, 5000 ng per TD tube



Figure 2- HFC-245fa Calibration, Extracted Ion Chromatogram and Mass Spectrum

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Quadratic Regression,  $R^2 = 0.9996$ ; Calibration Levels = 200, 500, 1000, 2000, 5000, 10000 ng per TD tube



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Quadratic Regression,  $R^2 = 0.9982$ , Calibration Levels = 20, 50, 100, 200, 500, 2000, 5000 ng per TD tube



Figure 4- BDMAEE Calibration, Extracted Ion Chromatogram and Mass Spectrum

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Quadratic Regression,  $R^2 = 0.9982$ , Calibration Levels = 50, 100, 200, 500, 2000, 5000 ng per TD tube





Linear Regression,  $R^2 = 0.9988$ ; Calibration Levels = 100, 200, 500, 2000 and 5000 ng per TD tube





Linear Regression,  $R^2 = 0.9960$ ; Calibration Levels = 200, 500, 1000, 2000, 5000 ng per TD tube



Figure 7- TMBPA Calibration Curve, Extracted Ion Chromatogram and Mass Spectrum



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Linear Regression,  $R^2 = 0.9998$ ; Calibration Levels = 20, 100, 200, 500, 1000, 5000 ng per TD tube



Figure 8- TCPP Calibration Curve, Extracted Ion Chromatogram and Mass Spectrum

#### MICRO-CHAMBER TESTING PARAMETERS AND PREPARATION

#### **Introduction and Objective**

Micro chambers are much smaller than conventional small-scale environmental test chambers that are typically used to measure product emissions. The micro chambers used in this study have a 114-cc capacity and can be operated from ambient to 250 °C. The micro chambers have a flow through design so that emission samples can be collected directly onto sorbent tubes such as the TD tubes described above or with other sorbent tubes (e.g. DNPH treated silica gel to collect aldehydes). The micro chambers were designed to be used as a rapid screening tool for comparing emissions of products in lieu of using larger test chambers; however, micro chambers may also be a better choice for measuring semi-volatile organic compounds due to their lower surface area ratio (chamber wall vs. sample).

The objective was to develop and optimize the operating conditions for testing SPF material in the micro chamber system in order measure potential VOC and SVOC emissions. Several micro chamber test parameters were considered including sample preparation and placement, temperature, loading factor, flow rate and the carrier gas. There was no attempt at this point to correlate or calibrate the micro chamber parameters with conventional small-scale chambers. After the potential wall effects for semi-volatiles are known, correlation between micro chambers and conventional small scale chambers can possibly be made as described in ASTM D7706, Standard Practice for Rapid-Screening of VOC Emissions from Products using Micro-Scale Chambers. Alternatively, micro chamber parameters can also be adjusted to simulate field conditions; for example elevated temperature. The micro chamber parameters were used as the foundation to compare emissions from the generic SPF samples during the holding time study described later in this report.

#### Discussion

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Emphasis was placed on the sample placement in the micro chamber. SPF material tested with conventional small scale chambers have been placed tightly into a rectangular metal box type holder with only one side of the SPF material exposed during the chamber testing to simulate actual field conditions when sprayed into a wall cavity. Micro-scale sample holders were considered, but any additional material placed in the chamber would likely contribute to potential wall effects for semi-volatile compounds. In order to minimize wall effects and maximize the surface area of the sample compared to the chamber walls, the sample was placed directly into the micro chamber using the chamber as the sample holder.

Several attempts were made to cut the SPF insulation samples so that it would fit tightly into the micro chamber. Initially a hole-saw was purchased from a local hardware store; however, this tool cut the SPF material with very jagged and uneven edges. A carbon-tipped saw blade was also tried, without success. Since commercially available saw blades were proven to be unsuccessful, a stainless steel coring tool was fabricated to cut the SPF much like a sharp heavy duty cookie cutter. This tool was able to successfully core all of the generic samples of SPF material at the proper diameter (approximately 2.5 inches or 6.4 cm). Attempts to cut the SPF samples are shown in Figure 9 and the stainless steel coring tool is shown in Figure 10.

Samples were cut on the back side of the foam with an electric carving knife so that the total height was approximately 2cm, and then placed directly into the micro-chamber. For open-cell SPF, aluminum shim rings were used to help seal the edges between the sample and the micro chamber walls. The top surface of the open-cell SPF was also removed with the carving knife to simulate trimming of the insulation along the wall studs. Prepared samples of generic closed-cell, open-cell and low-pressure kit formulations are shown in Figures 11, 12 and 13. As shown in Figure 13, the kit formulation SPF is not as uniform as the other materials making it more difficult to seal around the edges and measure its exposed surface area.

After the samples were placed into the micro-chambers, the remaining headspace of each micro chamber was reduced to approximately 51-cc. The manufacturer recommended a flow rate of 50-cc UHP grade nitrogen/min. With a loaded sample in the chamber, the air exchange rate was 58.2 air exchanges per hour with a loading factor equal to  $62.5 \text{-m}^2/\text{m}^3$ . The temperature was set at 23 °C for initial testing; however, the temperature can be elevated as required to simulate heated wall cavities. Since the carrier gas was UHP grade nitrogen (dry), the relative humidity was not monitored or controlled; however, the manufacturer states this will be a future option. The operating parameters are summarized in Table 6 and the front of the micro chamber system is shown in Figure 14.

#### **Summary of Micro Chamber Parameters for SPF Samples**

A method was developed to collect a sample core, and then to trim and prepare SPF samples for micro chamber testing. Baseline conditions for the micro chamber were developed using vendor recommendations. The micro chamber parameters were used as the basis to compare samples for the holding time study described in the next section.



Figure 9- Attempts to Cutout Closed-Cell SPF for Micro Chamber

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Figure 10- Stainless Steel Coring Tool Fabricated tool made of stainless steel to cut samples for micro chamber testing



**Figure 11- Generic Closed-Cell SPF in Micro Chamber** The generic closed-cell SPF sample fits tightly into the micro chamber.



Figure 12- Generic Open-Cell SPF in Micro Chamber Open-cell SPF with aluminum shim ring fits tightly into the micro chamber



Figure 13- Low-Pressure Kit Formulation SPF in Micro Chamber Generic low pressure kit formulation loaded into a micro chamber

Table 6- Micro Chamber Test Conditions for SPF Testing					
Parameter	Value				
Sample Diameter, m	0.064				
Volume, m <sup>3</sup>	5.15E-05				
Air Change Rate, h <sup>-1</sup> (N)	58.2				
Loading, $m/m^3$ (L)	62.5				
Specific Air Flow Rate (N/L)	0.931				
Initial Temperature	23 °C				



Figure 14- Micro-Chamber Flow / Temperature Control

# SPF SAMPLE HOLDING TIME AND PACKAGING EVALUATION

# **Objectives and Introduction**

The purpose of this research was to determine an appropriate holding time for samples of SPF that are submitted for emissions testing. In order to establish re-occupancy times for SPF products, an adequate holding time will be necessary to prepare and ship samples to laboratories prior to analysis. The holding time(s) from this study may be incorporated into the ASTM standard(s) currently under development. The generic formulations were each sprayed, collected and prepared five times to evaluate the holding times using the micro chamber conditions described in the previous section.

The prepared SPF samples were stored in Mylar bags then placed into micro-chambers at the following times after sample collection:  $\leq 2$  hours, 24 hours, 48 hours, 72 hours and 216 hours (9 days). Air samples were collected periodically for volatile organic compounds (VOCs) and aldehydes using thermal desorption GC/MS and DNPH LC/MS techniques (similar to ASTM D5197), respectively. MDI emissions were sampled using filter media with a derivative followed by LC analysis (Bayer MaterialScience Method 1.7.7, which is based on OSHA Method 47).

The experiment was repeated using all three generic SPF sample types to evaluate the holding time. The generic closedcell SPF samples were analyzed in triplicate; the open-cell and kit formulation samples were tested in duplicate. The maximum holding time was evaluated based on the point in time at which the loss of target compound emissions were not significantly different from the emissions which were identified in the samples with the earliest holding time ( $\leq 2$  hours).

#### Spraying and Packaging Closed-Cell SPF Samples

The closed-cell generic SPF formulation was sprayed in a controlled spray booth on five pieces of 12x12 inch double walled cardboard sheets wrapped in clean aluminum foil as the substrate so that the foam thickness was in the range of 4 to 5-cm using 1 lift. Upon spraying the closed-cell SPF onto the substrate, the foil layer released from the cardboard, which caused a slight mushroom shape to the samples. Therefore, the remaining formulations were sprayed directly to cardboard without the aluminum foil. After spraying, the samples were allowed to cure in the spray booth for 1-hour at 23 °C prior to placing the samples into sealed Mylar bags. The spray applicator and equipment are shown in Figure 15. The sample substrate and closed-cell SPF samples curing in the spray booth are shown in Figures 16 and 17, respectively.

After the SPF samples cured for 1 hour, the samples and substrate were individually placed into Mylar bags equipped with a zipper seal. The air was manually forced out of each bag prior to closing the zipper seal. Each bag was sealed again by creating a 5-cm fold; the fold was repeated several times, and then packaging tape was applied. After the bag was sealed, the time was recorded to begin the holding time for the closed-cell SPF samples. Since the laboratory is on the same campus as the spray booth, shipping was not necessary; the Mylar bags containing the samples were transported to the laboratory within 30-minutes of sealing the bags. The samples were stored in an office environment at room temperature (approximately 23 °C) prior to analysis.

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**Figure 15- Spraying Generic Closed-Cell SPF for Holding Time Study** Applicator is shown on left and spraying equipment shown on right.



Figure 16- SPF Sample Substrate Sample substrate consists of cardboard sheets wrapped with clean aluminum foil



**Figure 17- Closed Cell SPF Samples in Spray Booth** Five replicate closed-cell SPF samples in the spray booth, for holding time study

# **Closed-Cell SPF Sample Preparation and Holding Time Evaluation**

After approximately 1 hour of placing the samples in the Mylar bags, one of the bags was opened in the laboratory then immediately prepared for micro chamber testing in triplicate. Three sample cores were prepared from the sample with a fabricated, circular cutting tool (Figure 10) so that the samples would fit tightly when placed in the micro chambers. Each core sample was then cut on the bottom to a sample height of approximately 2-cm to achieve the desired headspace in the chambers. The samples were quickly inserted into the micro chambers then the chamber lids were closed to initiate testing. A fourth micro chamber was monitored as a control sample or method blank. Operating conditions are specified in Table 6 with an initial temperature of 23 °C.

Upon closing the micro chamber lids, the flow rate was measured and recorded for each chamber (set point = 50-cc/min) using a BIOS Calibrator. Several samples were collected during a 21 hour period. The chambers were allowed to equilibrate for 10 minutes, and then TD tubes (Tenax TA and Carbopack X) were connected directly to the outlet of the micro chambers for 20 minutes to collect potential emissions of amine catalysts, flame retardant, blowing agent and other VOCs. Immediately following the TD tubes, DNPH treated silica gel tubes were connected to the micro chamber for 60 minutes to collect potential emissions of aldehydes. Sampling with both TD and DNPH tubes were repeated. Flow measurements were recorded for each sampling media.

Samples were collected for MDI with 13mm PP filters for 16 hours, followed by another set of TD and DNPH tubes. In order to accelerate the test, the micro chambers were then heated to 40 °C and held for 10 minutes prior to sampling once more with TD tubes (10 minutes). A timeline of sampling events is described in Table 7. After sampling was complete and the micro chambers cooled to room temperature, the SPF samples were removed from the micro chambers and discarded. MDI (if emitted) could adsorb onto the chamber walls during the test; therefore, the micro chamber bodies and lids were wiped with 90mm PP filters moistened with acetone to collect MDI that may have adsorbed onto the chamber walls. The chambers were then cleaned with methanol and heated to 150 °C to bake out any residual materials prior to the next test.

The process of opening Mylar bags, preparing samples for micro chamber testing and collecting samples as described above was repeated four additional times at 24 hours, 48 hours, 72 hours, and 216 hours after sample collection. The results from these tests were compared to the initial test results from the Mylar bag that was opened at 1 hour to evaluate the holding time. The TD tubes were analyzed for VOCs, blowing agent, amine catalysts, and flame retardant with TD-GC/MS as described previously in this report. The DNPH tubes were desorbed with acetone and analyzed for aldehydes with LC and diode array detection (similar to ASTM D5197). The MDI emissions were determined with an LC equipped with a fluorescence detector as described in Bayer MaterialScience Method 1.7.7. The chamber wall wipe samples were analyzed for MDI using LC with mass spectrometry with Conditional Test Method 036 and Bayer MaterialScience Method SA-102.

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Table 7- Sun	Table 7- Summary of Closed-Cell SPF Emissions Collected from Micro Chambers					
Sample Description	Time, min	Sample Collection and Conditions				
Starting Point	0	10 minute equilibration at 23 °C				
TD Sample Point 1	10	Thermal Desorption (TD) tubes Sample for 20 minutes (Volume = 1L)				
DNPH Sample Point 1	30	Aldehydes with DNPH tubes Sample for 1 hour (Volume = $3L$ )				
No Sample	90	No sample collection for 10 minutes				
TD Sample Point 2	100	Thermal Desorption (TD) tubes Sample for 20 minutes (Volume = 1L)				
DNPH Sample Point 2	120	Aldehydes with DNPH tubes Sample for 1 hour (Volume = $3L$ )				
PP Filter for MDI	180	MDI with 13mm filter with PP Sample for 16 hours				
TD Sample Point 3	1140	Thermal Desorption (TD) tubes Sample for 20 minutes (Volume = 1L)				
DNPH Sample Point 3	1160	Aldehydes with DNPH tubes Sample for 1 hour (Volume = $3L$ )				
Elevate Temperature	1220	Heat chamber to 40 °C and hold for 10 minutes				
TD Sample Point 4	1230	Thermal Desorption (TD) tubes Sample for 10 minutes (Volume = $0.5L$ )				
End	1240	Stop Micro-Chamber				

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# Holding Time Results for Generic Closed-Cell SPF

The measured quantities of target compounds captured on the sampling media were converted to individual emission factors as described in ASTM D5116 using the flows and chamber parameters described in Table 6. For replicate chamber tests, a mean emission factor value and the relative standard deviation are reported to assess precision. For the purpose of determining holding time, the first sample's emission factors (Mylar bag opened at 1-hr) were compared against the later samples' emission factors to calculate percent change over the holding time. A negative change indicates that the emission factor decreased over time, while a positive change indicates an increased emission factor over time. The holding time can be examined by determining how long a sample can be stored in a Mylar bag before the emission factor significantly changes. There are no established criteria for the maximum amount of change; however, less than 20 percent change was deemed acceptable for the purpose of this study.

There was no MDI detected in any of the test samples collected during the holding time study for the closed-cell SPF. The calculated emission factors (EF) for the MDI isomers are as follows: both the 2,4'-MDI and 4,4'-MDI emission factors were less than 0.002; the polymeric MDI emission factor was less than 0.060. Additionally, no MDI was observed on the chamber walls during the holding time study for the generic closed-cell SPF. Based on these data, there were no apparent MDI emissions from closed-cell SPF at the operating conditions of the micro chamber test. Because there were no emissions or change in emissions, the holding time could not be determined based on MDI values.

The emission factors for the blowing agent, HFC-245fa, used in the generic closed-cell SPF are shown in Table 8. The emission factors for the equivalent sample collection time did not significantly change over the 216-hour holding time study. Additionally, the emission factors all showed excellent precision (RSD values less than 5%). For example, the TD sample point 1 had initial emission factor of 3.59 and dropped to 3.08 after 216 hours storage, resulting in a -14% change. Similarly, TD time point 2 had an initial emission factor 3.06, which dropped to 2.72 over 216 hour's storage, resulting in a -11% change. Based on the observed emission factors, samples can be stored for at least 216 hours when measuring HFC-245fa emissions. This compound is a good indicator for monitoring VOCs during storage since HFC-245fa is the most volatile target compound detected with the TD-GC/MS method.

Amine catalysts were not detected in any of the samples at 23 °C; however, BDMAEE and DAPA were detected after the micro chambers were heated to 40 °C. The observed emission factors are shown in Table 9. There was a 44 % change in the emission factor for BDMAEE at 216 hours storage time; however, the emission factor only dropped 18 % during 72 hours of storage. The emission factors for DAPA did not significantly change over the entire 216 hour storage time. Based on these observations, the closed-cell SPF can be stored up to 72 hours before the emission factor for BDMAEE significantly changes.

The only aldehyde compound that was detected at levels significantly greater than the method blank was acetaldehyde during the first two DNPH sampling points. Based on these data, the emission factor change was -26 % after 72 hours storage; while the sample stored for 48 hours only changed -10 %. Based on these data, the acetaldehyde emission factor appears to be stable for at least 48 hours of storage. The acetaldehyde data are shown in Table 10.

Two other volatile organic compounds with much lower emission factors were also monitored to evaluate the effect of their emissions with increased sample storage time. Since these compounds are not target compounds, they were identified with the NIST Mass Spectral Library, and then compared against a single US EPA Method 8260 reference standard (20-ng each) to estimate their emission factors. The compounds were identified as 1,2-dichloropropane and chlorobenzene, and their estimated emission factors are shown in Table 11. Both compounds appeared to demonstrate that the closed-cell SPF sample can be stored for up to 48 hours in Mylar bags before the emission factors significantly change.

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Table 8- Blowin	Table 8- Blowing Agent Holding Time Evaluation in Closed-Cell SPF							
Storage Time, Hours	1	24	48	72	216			
HFC-245fa								
TD Sample Point 1 at 23 °C								
Mean Emission Factor, n=3	3.59	3.54	3.46	3.39	3.08			
Precision, RSD, %	1.63	2.29	2.80	2.30	2.82			
% Change from 1 hr. Storage		-1.24	-3.45	-5.53	-14.2			
TD Sample Point 2 at 23 °C								
Mean Emission Factor, n=3	3.06	3.14	3.08	2.95	2.72			
Precision, RSD, %	2.90	3.91	4.59	3.35	1.96			
% Change from 1 hr. Storage		2.63	0.75	-3.81	-11.2			
TD Sample Point 3 at 23 °C								
Mean Emission Factor, n=3	2.19	2.16	2.27	2.13	1.77			
Precision, RSD, %	0.69	3.22	3.69	3.36	1.38			
% Change from 1 hr. Storage		-1.46	3.83	-2.55	-19.0			
TD Sample Point 4 at 40 °C								
Mean Emission Factor, n=3	6.25	6.18	6.18	5.98	5.63			
Precision, RSD, %	1.08	2.93	0.80	4.09	4.24			
% Change from 1 hr. Storage		-1.17	-1.11	-4.36	-9.97			

n = number of chamber replicate samples; RSD = relative standard deviation.

Table 9- Amine Catalysts Holding Time Evaluation in Closed-Cell SPF						
Storage Time, Hours	1	24	48	72	216	
BDMAEE						
TD Sample Point 4 at 40 °C						
Mean Emission Factor, n=3	0.127	0.117	0.129	0.105	0.071	
Precision, RSD, %	12.6	20.5	22.8	20.3	8.6	
% Change from 1 hr. Storage		-7.96	1.76	-17.6	-43.8	
DAPA						
TD Sample Point 4 at 40 °C						
Mean Emission Factor, n=3	0.113	0.128	0.121	0.124	0.111	
Precision, RSD, %	0.4	9.4	7.6	6.8	4.4	
% Change from 1 hr. Storage		13.1	6.95	9.37	-1.72	

# n = number of chamber replicate samples; RSD = relative standard deviation.

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Table 10- Aldehydes Holding Time Evaluation in Closed-Cell SPF						
Storage Time, Hours	1	24	48	72	216	
Acetaldehyde						
DNPH Sample Point 1 at 23 °C						
Mean Emission Factor, n=3	0.355	0.288	0.321	0.263	0.196	
Precision, RSD, %	10.2	12.6	18.6	11.0	17.2	
% Change from 1 hr. Storage		-18.8	-9.57	-25.7	-44.7	
DNPH Sample Point 2 at 23 °C						
Mean Emission Factor, n=3	0.191	0.222	0.212	0.207	0.152	
Precision, RSD, %	37.5	11.7	13.1	30.4	12.4	
% Change from 1 hr. Storage		15.8	10.8	8.2	-20.4	

n = number of chamber replicate samples; RSD = relative standard deviation.

Table 11	Table 11- VOC Holding Time Evaluation in Closed-Cell SPF						
Storage Time, Hours	1	24	48	72	216		
1,2-Dichloropropane							
TD Sample Point 1 at 23 °C							
Mean Emission Factor, n=3	0.0998	0.0813	0.0836	0.0552	0.0225		
Precision, RSD, %	16.6	9.8	26.3	2.2	16.5		
% Change from 1 hr. Storage		-18.5	-16.3	-44.7	-77.4		
TD Sample Point 2 at 23 °C							
Mean Emission Factor, n=3	0.0443	0.0432	0.0370	0.0255	0.0124		
Precision, RSD, %	7.1	13.5	17.9	15.9	16.8		
% Change from 1 hr. Storage		-2.44	-16.5	-42.4	-72.0		
Chlonohongono							
TD Sample Point 1 at 23 °C							
Mean Emission Factor, n=3	0.00418	0.00391	0.00359	0.00287	0.00167		
Precision, RSD, %	23.8	11.7	32.0	17.1	14.9		
% Change from 1 hr. Storage		-6.58	-14.2	-31.4	-60.1		
TD Sample Point 2 at 23 °C							
Mean Emission Factor, n=3	0.00307	0.00269	0.00288	0.00211	0		
Precision, RSD, %	0.6	8.9	17.5	18.0	-		
% Change from 1 hr. Storage		-12.3	-6.06	-31.2	-100		

# Emission factors are estimated values compared against response factors of 20-ng VOC standard. n = number of chamber replicate samples; RSD = relative standard deviation.

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# Spraying and Packaging Open-Cell and Kit Formulation SPF Samples

The generic open-cell and kit SPF formulations were each sprayed on the same day in a controlled spray booth. Both formulations were sprayed directly onto five pieces of 12x12 inch double walled cardboard sheets as the substrate so that the foam thickness was in the range of 9 to 10-cm using 1 lift (open-cell) or 4 to 5-cm using 1 lift (kit formulation). The kit formulation did not require high pressure spray equipment; rather this SPF was prepared from a self-contained kit that contains both the A and B sides of material, transfer line and spray nozzle. After spraying, the samples were allowed to cure in the spray booth for 1-hour at 23 °C prior to placing the samples into sealed Mylar bags.

After the SPF samples cured for 1 hour, the samples including their substrate were individually placed into Mylar bags. Since the open-cell samples were thicker, they required a larger Mylar bag, which was not available with a zipper seal; therefore, only the kit formulation samples were stored in bags with a zipper seal. The air was manually forced out of each bag prior to closing the zipper seal (if equipped). Each bag was sealed by creating a 5-cm fold; the fold was repeated several times, and then packaging tape was applied. After the bag was sealed, the time was recorded to begin the holding time for the open-cell and kit formulation SPF samples. Since the laboratory is on the same campus as the spray booth, shipping was not necessary; the Mylar bags containing the samples were transported to the laboratory within approximately 1 hour of sealing the bags. The samples were stored in an office environment at room temperature (approximately 23 °C) prior to analysis.

#### **Open-Cell SPF Sample Preparation for Micro Chamber Testing**

After approximately 2 hours of placing the samples in the Mylar bags, one of the bags was opened in the laboratory then immediately prepared for micro chamber testing in duplicate. Two sample cores were prepared from the sample with a fabricated, circular cutting tool (Figure 10) so that the samples would fit tightly when placed in the micro chambers. The top surface of the material was trimmed to simulate field conditions for this material, then each core sample was cut on the bottom to a sample height of approximately 2-cm to achieve the desired headspace in the chambers. Aluminum shims were used to help seal the outer edges of the sample along the chamber walls (see Figure 12). The samples were quickly inserted into the micro chambers then the chamber lids were closed to initiate testing. Operating conditions are specified in Table 6 with an initial temperature of 23 °C.

#### **Kit Formulation Sample Preparation**

After approximately 2 hours of placing the samples in the Mylar bags, one of the bags was opened in the laboratory then immediately prepared for micro chamber testing in duplicate. Two sample cores were prepared from the sample with a fabricated, circular cutting tool (Figure 10) so that the samples would fit tightly when placed in the micro chambers. This material tended to stick to the cardboard surface so it was somewhat difficult to remove from the substrate. Each core sample was cut on the bottom to a sample height of approximately 2-cm to achieve the desired headspace in the chambers; although the surface of the kit formulation was somewhat uneven making it more difficult to seal in the chamber (Figure 13). The samples were quickly inserted into the micro chambers then the chamber lids were closed to initiate testing. Operating conditions are specified in Table 6 with an initial temperature of 23 °C.

#### Holding Time Evaluation for Open-Cell and Kit Formulations

Upon closing the micro chamber lids, the flow rate was measured and recorded for each chamber (set point = 50-cc/min) using a BIOS Calibrator. Several samples were collected during a 20 hour period. The chambers were allowed to equilibrate for 30 minutes, and then TD tubes (Tenax TA and Carbopack X) were connected directly to the outlet of the micro chambers for 20 minutes to collect potential emissions of amine catalysts, flame retardant, blowing agent and other VOCs. Immediately following the TD tubes, DNPH treated silica gel tubes were connected to the micro chamber for 60 minutes to collect potential emissions of aldehydes. Sampling with the TD tubes was then repeated. Flow measurements were recorded for each sampling media.

Samples were collected for MDI with 13mm PP filters for 16 hours, followed by another set of TD tubes. In order to accelerate the test, the micro chambers were then heated to 40 °C and held for 10 minutes prior to sampling once more with TD tubes (10 minutes) and with DNPH tubes (60 minutes). A timeline of sampling events is described in Table 12. After sampling was complete and the micro chambers cooled to room temperature, the SPF samples were removed from the micro chambers and discarded. MDI (if emitted) could adsorb onto the chamber walls during the test; therefore, the micro chamber bodies and lids were wiped with 90mm PP filters moistened with acetone to collect MDI that may have adsorbed onto the chamber walls. The chambers were then cleaned with methanol and heated to 150 °C to bake out any residual materials prior to the next test.

The process of opening Mylar bags, preparing samples for micro chamber testing and collecting samples as described above was repeated four additional times at 24 hours, 48 hours, 72 hours, and 216 hours after sample collection. The results from

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these tests were compared to the initial test results from the Mylar bag that was opened at 2 hours to evaluate the holding time. The TD tubes were analyzed for VOCs, blowing agent, amine catalysts, and flame retardant with TD-GC/MS as described previously in this report. The DNPH tubes were desorbed with acetone and analyzed for aldehydes with LC and diode array detection (similar to ASTM D5197). The MDI emissions were determined with an LC equipped with a fluorescence detector. The chamber wall wipe samples were analyzed for MDI using LC with mass spectrometry (Conditional Test Method 036 and Bayer MaterialScience SA-102).

The masses of target compounds captured on the sampling media were converted to individual emission factors as described in ASTM D5116 using the flows and chamber parameters described in Table 6. For duplicate chamber tests, a mean emission factor value and the relative percent difference are reported to assess precision. For the purpose of determining holding time, the first sample's emission factors (Mylar bag opened at 2-hrs) were compared against the later samples' emission factors to calculate percent change over the holding time. A negative change indicates that the emission factor decreased over time, while a positive change indicates an increased emission factor over time. The holding time can be examined by determining how long a sample can be stored in a Mylar bag before the emission factor significantly changes. There are no established criteria for the maximum amount of change; however, less than 20 percent change was deemed acceptable for the purpose of this study.

There was no MDI detected in any of the test samples collected during the holding time study for both the open-cell and kit formulations of SPF. The calculated emission factors (EF) for the MDI isomers are as follows: both the 2,4'-MDI and 4,4'-MDI emission factors were less than 0.002; the polymeric MDI emission factor was less than 0.060. Additionally, no MDI was observed on the chamber walls during the holding time study. Based on these data, there were no apparent MDI emissions from either open-cell or kit SPF formulations at the operating conditions of the micro chamber test. Because there were no emissions or change in emissions, the holding time could not be determined based on MDI values.

There were no aldehydes detected at concentrations that were significantly greater than their corresponding method blanks in either the open-cell or kit formulations; however, the observed method control samples and sorbent tubes showed possible contamination. Because of this, the holding time study was repeated with the generic open-cell formulation. The sampling time was extended to 16 hours with a new lot of DNPH sorbent tubes. The control samples improved and once again, there were no aldehydes detected that were significantly greater than their corresponding control samples. Because of this, the holding time for aldehydes was not further evaluated.

#### Holding Time Evaluation for Open-Cell SPF

Emission factors for target compounds in the open-cell SPF with micro chambers were calculated as described previously. The emission factors for BDMAEE, TMIBPA (amine catalysts) and TCPP (flame retardant) are summarized in Table 13. The TMIBPA and TCCP were only observed when the chambers were heated to 40 °C (TD Sample Point 4). With the exception of BDMAEE in TD Sample Point 1, all of the emission factors appear to have less than 20 % change during 48-hours of storage in Mylar bags. The higher variability observed during TD Sample Point 1 may indicate that the samples had not yet reached a state of equilibrium in the test chamber.

As done previously, two selected VOC compounds with relatively low emission factors (near the detection limit) were also evaluated. Emission factors for 1,2-dichloropropane and chlorobenzene were estimated by comparison to a reference standard prepared at 20-ng of each compound per TD tube. The estimated emission factors are shown in Table 14. The observed emissions factors appear to increase with storage time in Mylar bags as compared to the original 2-hour sample. VOC compounds at this level would not likely impact the re-occupancy times; however, it may not be appropriate to monitor low-level VOC compounds to assess indoor air quality until samples have reached equilibrium. For example, CA Specification 01350 specifies a 10-day conditioning time in the chamber prior to taking emission measurements to evaluate VOC emissions from indoor sources. Further research may be necessary to optimize the conditioning time in micro chambers for IAQ studies.

#### Holding Time Evaluation for Kit Formulation SPF

Emission factors for the observed target compounds in the kit formulation are shown in Table 15. PMDTA (amine catalyst) was observed in all four TD sample points collected during each chamber test. The emission factor increased during storage up to 72 hours, and then dropped to a negative change by 216 hours of storage time. This trend was observed for all for TD sampling points. TCPP (flame retardant) was only observed in the TD sample point with the chambers heated to 40 °C; although there was a fairly large amount of variability between duplicate test measurements for TCPP under these conditions.

Two selected VOC compounds with emission factors near the detection limit were also compared to the emission factors from the sample stored for 2-hours. Data are shown in Tables 16 and 17 for 1,2-dichloropropane and chlorobenzene, respectively. Similar to the PMDTA results, the emission factors increased during storage time for up to 72 hours then dropped to a negative change by 216 hours storage time. As described above, these compounds may not be reaching equilibrium in the test chamber and

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may require a longer conditioning time. Further research may be necessary to optimize the conditioning time in the micro chambers for this formulation.

# **Summary of Holding Time Study Conclusions**

Generic closed-cell and open-cell SPF samples can be stored for up to 48 hours at 23 °C in sealed Mylar 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 kit formulation did not appear to be stable in the stored samples. Further research may be required to assess holding time in this formulation. VOC compound measurements near the detection limit were not stable in the stored open-cell and kit formulations. However, these measurements would not likely impact the ability to assess re-occupancy times. Furthermore, IAQ monitoring (e.g. CA 01350) for the VOC compounds would be subjected to much longer conditioning times than used in this study.

Table 12- Summary of Open-Cell and Kit SPF Emissions Collected from 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)				
End	1190	Stop Micro-Chamber				

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Table 13- Amine Catalysts & TCPP Holding Time Evaluation in Open-Cell SPF					
Storage Time, Hours	2	24	48	72	216
BDMAEE					
TD Sample Point 1 at 23 °C					
Mean Emission Factor, n=2	3.63	4.59	4.78	4.47	4.16
Precision, RPD	6.13	15.2	2.83	13.9	3.20
% Change from 2 hr. Storage		26.5	31.6	23.0	14.7
TD Sample Point 2 at 23 °C					
Mean Emission Factor, n=2	5.34	5.04	4.92	4.65	4.42
Precision, RPD	2.93	1.11	1.90	4.44	5.51
% Change from 2 hr. Storage		-5.69	-7.87	-13.0	-17.3
TD Sample Point 3 at 23 °C					
Mean Emission Factor, n=2	3.51	3.69	3.88	3.41	3.17
Precision, RPD	2.70	4.46	7.61	8.17	0.85
% Change from 2 hr. Storage		5.20	10.5	-2.75	-9.57
TD Sample Point 4 at 40 °C					
Mean Emission Factor, n=2	14.9	15.1	15.5	15.4	15.3
Precision, RPD	2.71	0.25	4.57	1.93	2.11
% Change from 2 hr. Storage		1.02	3.70	3.51	2.75
TMIBPA					
TD Sample Point 4 at 40 °C					
Mean Emission Factor, n=2	0.818	0.797	0.797	0.809	0.826
Precision, RPD	4.1	1.0	1.1	2.9	0.5
% Change from 2 hr. Storage		-2.55	-2.54	-1.05	1.01
ТСРР					
TD Sample Point 4 at 40 °C					
Mean Emission Factor, n=2	0.461	0.378	0.475	0.356	0.420
Precision, RPD	7.4	37.0	1.1	24.7	20.4
% Change from 2 hr. Storage		-18.1	2.94	-22.9	-8.97

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Table 14- VOC Holding Time Evaluation in Open-Cell SPF					
Storage Time, Hours	2	24	48	72	216
1,2-Dichloropropane					
TD Sample Point 1 at 23 °C					
Mean Emission Factor, n=2	0.0114	0.0204	0.0313	0.0184	0.0185
Precision, RPD	3.61	23.1	3.43	1.98	27.7
% Change from 2 hr. Storage		78.0	174	60.5	62.0
TD Sample Point 2 at 23 °C					
Mean Emission Factor, n=2	0.00632	0.00973	0.01451	0.00889	0.00926
Precision, RPD	8.02	16.6	6.68	3.50	25.7
% Change from 2 hr. Storage		53.9	129	40.6	46.5
Chlorobenzene					
TD Sample Point 1 at 23 °C					
Mean Emission Factor, n=2	0.0295	0.0463	0.0569	0.0418	0.0411
Precision, RPD	5.9	13.4	4.7	1.0	21.6
% Change from 2 hr. Storage		57.1	92.9	41.9	39.5
TD Sample Point 2 at 23 °C					
Mean Emission Factor, n=2	0.0256	0.0357	0.0400	0.0300	0.0279
Precision, RPD	1.2	12.0	1.3	2.0	21.6
% Change from 2 hr. Storage		39.4	56.0	17.2	8.8
TD Sample Point 3 at 23 °C					
Mean Emission Factor, n=2	0.00253	0.00309	0.00409	0.00280	0.00301
Precision, RPD	2.1	-	4.0	1.9	19.4
% Change from 2 hr. Storage		22.0	61.6	10.7	18.8
TD Sample Point 4 at 40 °C					
Mean Emission Factor, n=2	0.0123	0.0180	0.0206	0.0166	0.0171
Precision, RPD	10.2	7.7	5.7	3.3	12.5
% Change from 2 hr. Storage		46.4	68.4	34.9	39.3

Emission factors are estimated values compared against response factors of 20-ng VOC standard. n = number of chamber replicate samples; RPD = relative percent difference.

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Table 15- PMDTA and TO	<b>CPP Holding Tim</b>	ne Evaluation	in Kit Formu	lation SPF	
Storage Time, Hours	2	24	48	72	216
PMDTA					
TD Sample Point 1 at 23 °C					
Mean Emission Factor, n=2	2.21	2.69	5.64	7.00	0.669
Precision, RPD	33.3	0.53	8.29	24.9	25.6
% Change from 2 hr. Storage		21.8	155	217	-69.7
TD Sample Point 2 at 23 °C					
Mean Emission Factor, n=2	1.77	2.22	6.15	7.53	0.548
Precision, RPD	33.6	16.0	10.8	20.7	23.3
% Change from 2 hr. Storage		25.5	248	325	-69.0
TD Sample Point 3 at 23 °C					
Mean Emission Factor, n=2	0.276	0.509	2.27	2.49	0.0661
Precision, RPD	42.2	1.47	5.31	27.9	56.4
% Change from 2 hr. Storage		84.8	723	804	-76.0
TD Sample Point 4 at 40 °C					
Mean Emission Factor, n=2	13.0	16.8	18.9	21.5	8.33
Precision, RPD	11.5	19.1	17.4	32.3	31.1
% Change from 2 hr. Storage		28.9	45.3	65.4	-35.9
ТСРР					
TD Sample Point 4 at 40 °C					
Mean Emission Factor, n=2	1.06	1.36	1.45	1.39	0.877
Precision, RPD	33.6	46.6	32.9	34.2	30.2
% Change from 2 hr. Storage		28.7	37.4	31.5	-16.9

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Table 16- VOC Holdin	Table 16- VOC Holding Time Evaluation in Kit Formulation SPF					
Storage Time, Hours	2	24	48	72	216	
1,2-Dichloropropane						
TD Sample Point 1 at 23 °C						
Mean Emission Factor, n=2	0.0174	0.0353	0.0316	0.0384	0.00847	
Precision, RPD	12.2	2.8	12.7	38.9	10.9	
% Change from 2 hr. Storage		60.9	48.6	71.5	-30.2	
TD Sample Point 2 at 23 °C						
Mean Emission Factor, n=2	0.00999	0.0196	0.0172	0.0223	0.00506	
Precision, RPD	8.9	3.6	22.9	28.0	0.6	
% Change from 2 hr. Storage		96.1	72.4	122.9	-49.3	
TD Sample Point 3 at 23 °C						
Mean Emission Factor, n=2	0.00238	0.00488	0.00413	0.00537	0.00131	
Precision, RPD	13.1	8.2	5.0	25.9	-	
% Change from 2 hr. Storage		105	73.4	125	-44.9	
TD Sample Point 4 at 40 °C						
Mean Emission Factor, n=2	0.0294	0.0888	0.0697	0.0962	0.0209	
Precision, RPD	16.7	23.3	27.3	49.8	27.5	
% Change from 2 hr. Storage		202	137	227	-29.1	

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Table 17- VOC Holding Time Evaluation in Kit Formulation SPF					
Storage Time, hours	2	24	48	72	216
Chlorobenzene					
TD Sample Point 1 at 23 °C					
Mean Emission Factor, n=2	0.0197	0.0311	0.0295	0.0350	0.0105
Precision, RPD	8.1	7.9	6.2	31.3	0.8
% Change from 2 hr. Storage		57.9	49.8	77.5	-46.6
TD Sample Point 2 at 23 °C					
Mean Emission Factor, n=2	0.0138	0.0218	0.0201	0.0240	0.00788
Precision, RPD	6.8	5.6	9.3	28.7	2.4
% Change from 2 hr. Storage		57.3	45.5	73.6	-43.0
TD Sample Point 3 at 23 °C					
Mean Emission Factor, n=2	0.00502	0.00816	0.00716	0.00851	0.00306
Precision, RPD	4.9	7.8	9.3	20.6	8.1
% Change from 2 hr. Storage		62.7	42.7	69.7	-39.0
TD Sample Point 4 at 40 °C					
Mean Emission Factor, n=2	0.0600	0.1241	0.1023	0.1251	0.0441
Precision, RPD	16.3	22.5	23.6	41.4	25.4
% Change from 2 hr. Storage		107	70.4	108	-26.6

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# EVALUATION OF WALL EFFECTS OF SEMI-VOLATILE COMPOUNDS IN TEST CHAMBERS

# **Introduction and Objectives**

The purpose of this research was to conduct chemical substance spike and recovery studies in typical small scale environmental chambers and micro-chambers to identify the degree of adsorption onto chamber surfaces/components that could possibly occur for airborne semi-volatile compounds that may potentially be released from newly-installed SPF insulation. For this particular study, the chemicals of interest are 1) methylene diphenyl diisocyanate (MDI), 2) selected amine catalysts, and 3) a flame retardant (TCPP).

The small-scale environmental chambers (~38-L) that were evaluated were constructed of 1) PTFE-lined acrylic, and 2) stainless steel. The micro-chamber (~114-mL) is made with polished and deactivated stainless steel; the unit is available commercially from Markes International. A known quantity of each chemical substance was introduced into the air of each chamber type. Duplicates or triplicates were prepared in several cases. The application of heat was needed to volatilize the chemical substances, either by directly heating the micro chamber or using a heated injection port to introduce the spiked compounds.

Appropriate air sampling and analytical techniques were then used to capture the airborne chemicals inside the chambers. In addition, the chamber surfaces were wiped with appropriate sampling media/solvent, and then analyzed for MDI using relevant analytical techniques to attempt to quantify how much of the MDI adsorbed to the chamber surfaces. The airborne and adsorbed chemicals were compared against the original mass that was released into the chamber. These data will permit an evaluation of the appropriateness of each chamber type for each chemical substance.

## MDI Spike into Micro Chamber with PTFE Tray

Polymeric MDI used in both the generic open-cell and closed-cell SPF formulations was weighed into a PTFE tray shown in Figure 18. Approximately 40-mg of MDI was placed in three PTFE trays, and then placed directly in three micro chambers. A fourth tray and chamber were treated as a method blank and quality control sample. Potential MDI emissions were collected on 13-mm glass-fiber filters with 1-(2-pyridyl)piperazine (PP) & diethyl phthalate in cassette housings at 23 °C (chamber temperature) for 4 hours at 100-cc/min with UHP grade nitrogen as the carrier gas.

After the test, the chamber walls were wiped with 90-mm glass-fiber filters with 1-(2-pyridyl)piperazine (PP), moistened with acetone. The 13-mm filters were tested for 2,4'-MDI, 4,4'-MDI, and p-MDI with a Waters 2695 Alliance LC with Fluorescence Detector as described in Bayer Method 1.7.7. The wipe samples were analyzed with an Agilent 1100 Series Liquid Chromatography (LC) / MSD as described in US EPA Conditional Test Method 036 and Bayer MaterialScience Method SA-102. The 13-mm and 90-mm PP filters are shown in Figure 19.

There was no MDI detected in any of the test samples (air emissions and chamber walls) collected at 23 °C. The procedure was repeated at 40 °C for 2 hours; however, no MDI was detected in any of the test samples at 40 °C. In order to volatilize a fraction of the MDI in the test chamber, the procedure was repeated a third time, but at 65 °C (chamber temperature) for 2 hours. No p-MDI was detected in any of the test samples. Results for 2,4'-MDI and 4,4'-MDI collected at 65 °C are shown in Table 18. The observed values were not very consistent, but the data show that up to 37% of the volatilized 4,4'-MDI adhered to the micro chamber walls.

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**Figure 18- MDI Spike in PTFE Spiking Tray** MDI weighed into PTFE spiking tray and placed into micro chamber



**Figure 19- Media for Capturing MDI from Chambers** 13mm PP filter shown on left and 90mm PP filters shown on right

Table 18- Summary of MDI Spikes in Micro Chambers at 65 °C						
Micro Chamber	Total Measured 2,4'-MDI, μg	% of 2,4'-MDI on Walls	Total Measured 4,4'-MDI, μg	% of 4,4'-MDI on Walls	Total Measured p-MDI, µg	% of p-MDI on Walls
1	0.378	4.64	0.839	8.17	<3	-
2	0.144	9.41	0.304	37.4	<3	-
3	0.222	9.71	0.347	28.0	<3	-
Blank	<0.1	-	< 0.1	-	<3	-

Spike = approximately 40-mg of MDI (generic SPF formulation) into PTFE spiking tray.

Micro chambers heated to 65 °C for 2 hrs.

Samples collected on 13mm PP filters at 100-cc/min for 2 hours.

Chambers were cooled to 23 °C, and then walls wiped with 90mm PP filters moistened with acetone.

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#### **MDI Spikes into Environmental Test Chambers**

To avoid heating the test chamber and to evaluate other chamber types, a heated injection port was used to spike the MDI so that vapor could be introduced directly into the environmental test chamber. A spike solution of polymeric MDI was prepared at approximately 5000  $\mu$ g/mL in methylene chloride. This solution was introduced into the injection port with a gas tight syringe (5  $\mu$ L = ~25  $\mu$ g p-MDI).

A Supelco ATIS was used as the injection port system and is shown in Figure 20. The MDI solution was injected into the ATIS at 100 °C using UHP grade nitrogen as the carrier gas at 100-cc/min. The MDI was collected for 20 minutes onto 13-mm PP filters (ATIS only, chambers disconnected) to measure the actual amount of 2,4'-MDI, 4,4'-MDI, and p-MDI exiting the ATIS, or the amount expected to enter the test chambers in order to calculate recoveries.

The ATIS was connected directly to a micro chamber as shown in Figure 21. After injection, the MDI was sampled with 13-mm PP filters for 20 minutes at 100-cc/min (approximately 20 air exchanges). The walls were then wiped with 90-mm PP filters that were moistened with acetone. The micro chamber test was repeated five times (3 runs with stainless steel micro chamber and 2 runs with deactivated stainless steel micro chamber).

In order to compare the data to conventional small-scale test chambers, the heated injection port system was connected directly to the PTFE lined and stainless steel 38-L test chambers. The MDI was injected into the ATIS system at 100-cc/min for 20-minutes connected to the chamber inlet, but the emission samples were collected on 13-mm PP filters for 20 hours at 600-cc/min (approximately 20 air exchanges). The small-scale test chambers tests were both conducted in duplicate. The walls of each chamber were then wiped with two 90-mm PP filters that were moistened with acetone.

MDI testing was performed as described above. As shown in Table 19, recoveries were very inconsistent, and a significant amount of the measured MDI was found to be on the chamber walls, regardless of the chamber size and material. Some of the differences in measurements may be due to the inlet gas, which was room air in the case of the PTFE and stainless steel chambers since MDI can adhere to particles, which could have possibly affected the recovery measurements. The data do show that further research is necessary to minimize wall effects when measuring MDI emissions from environmental test chambers.

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# Figure 20- ATIS Heated Injection Port Chamber

The Supelco ATIS is a sample preparation device for adsorbent tubes. The 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. The sample pathway is constructed of glass and stainless steel. The calibration standard is injected by a syringe through a replaceable septum in the center of the injection glassware, which is heated.

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# Figure 21- Micro Chamber and 13mm PP Filter

ATIS injection port (right) connected to micro chamber (left) using short PTFE transfer line. A 13-mm PP filter is connected to the exit port to capture MDI.

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Table 19- MDI Chamber Spike Recovery Summary						
Chamber Type	Measured in Air, µg	Measured on Walls, µg	Total Measured, µg	% on Walls	% Recovered	
4,4'-MDI						
PTFE Lined Acrylic Chamber, 38-L	0.025	0.021	0.046	45.8	2.12	
Duplicate	0.454	0.345	0.799	43.1	37.0	
Stainless Steel Chamber, 38-L	0.024	0.958	0.982	97.5	45.5	
Duplicate	0.710	0.503	1.213	41.4	56.1	
Micro Chamber, 114-mL	0.093	0.071	0.164	43.3	7.61	
Duplicate	0.044	0.355	0.399	89.1	18.5	
Triplicate	0.024	0.287	0.310	92.3	14.4	
Micro Chamber, Deactivated, 114-mL	0.015	0.302	0.317	95.2	14.7	
Duplicate	< 0.01	1.47	1.47	100	68.1	

Measured Spike =  $2.16 \mu g 4,4$ '-MDI; based on 2 replicate injections into ATIS, RPD = 3.48 %

Injection port (ATIS) temperature = 100 °C at 100-cc UHP Nitrogen/min.

Recovery measured after approximately 20 air exchanges from the chamber.

Micro Chamber carrier gas = 100-cc/min UHP grade Nitrogen, Outlet Temperature = ~25 °C.

Stainless Steel and PTFE Chamber carrier gas = room air, 600-cc/min; RH = 23 to 33 %, Temperature = 22 °C.

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#### Amine Catalysts Spikes into Environmental Test Chambers

Similar to the MDI spike study, selected amine catalyst used in the generic SPF formulations were spiked into micro chambers and conventional small-scale PTFE and stainless steel chambers. A solution of three amine catalysts (BDMAEE, PMDTA, and DAPA) was prepared at approximately 5000  $\mu$ g/mL each in methanol. This solution was introduced into the injection port of the ATIS with a gas tight syringe (20  $\mu$ L = ~100  $\mu$ g of each catalyst).

The solution of amine catalysts was injected into the ATIS at 75 °C using UHP grade nitrogen as the carrier gas at 100cc/min. The emissions of amine catalysts were collected for 20 minutes onto XAD-2 tubes (ATIS only, chambers disconnected) to measure the actual amount of BDMAEE, PMDTA and DAPA exiting the ATIS, or the amount expected to enter the test chambers. The amine catalysts were determined with GC/MS after desorbing the sorbent in the tubes with 2-mL of acetone (Bayer MaterialScience Method 2.10.3, modified, Rtx-5 MS column with mass spectrophotometry detection). The XAD-2 tubes were preferable to using TD tubes so that longer term samples could be collected to measure total recoveries.

The ATIS injection port was connected and spiked into the micro chamber and small-scale stainless steel and PTFE 38-L chambers for comparison. The environmental test chambers connected to the ATIS system are shown in Figures 22-24. Each chamber was spiked in duplicate to assess precision of each chamber test. The micro chambers were sampled for 20 minutes at 100-cc/min (~20 air exchanges) and the 38-L chambers were sampled for 20 hours at 600-cc/min (~20 air exchanges). The results and calculated spike recoveries are shown in Table 20.

The micro chambers showed acceptable recoveries (81 to 99%). The recoveries with micro chambers were much better than the 38-L stainless steel chambers (5 to 22%) and 38-L PTFE lined chambers (13 to 46%). Based on these observations, the micro chamber appears to be the best choice for testing emissions of amine catalysts; however, each catalyst should be evaluated to confirm recovery (no loss to chamber walls) prior to testing. Furthermore, improvements to the conventional chambers may also improve spike recoveries (e.g. electro polishing the stainless steel).

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# **Figure 22- Micro Chamber Spike with XAD-2 Tube** ATIS injection port (right) connected to micro chamber (left) using short PTFE transfer line. An XAD-2 sorbent tube is connected to the exit port to capture amine catalysts or flame retardant.

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# Figure 23- Stainless Steel Chamber Spike

ATIS injection port (right) connected to small-scale stainless steel chamber (left) using short PTFE transfer line. A small personal sampling pump is used to pull chamber effluent through an XAD-2 sorbent tube to capture amine catalysts or flame retardant.

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# Figure 24- PTFE Lined Acrylic Chamber Spike

ATIS injection port (right) connected to small-scale PTFE lined acrylic chamber (left) using short PTFE transfer line. A small personal sampling pump is used to pull chamber effluent through an XAD-2 sorbent tube to capture amine catalysts or flame retardant.

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Table 20- Amine Catalysts Chamber Spike Summary						
	Determined	Measured in	Chamber, µg		Precision,	
Chamber Type and Material	Spike Amount	Run 1	Run 2	% Recovery	RPD	
BDMAEE						
Micro Chamber, 114-mL	85.8 μg	86.5	83.1	98.8	3.93	
PTFE Lined Chamber, 38-L	RPD = 4.78	38.3	39.7	45.5	3.66	
Stainless Steel Chamber, 38-L	2 replicates	17.1	20.6	22.0	20.5	
PMDTA						
Micro Chamber, 114-mL	93.7 μg	80.8	81.6	86.7	0.99	
PTFE Lined Acrylic Chamber, 38-L	RPD = 7.79	18.9	22.1	21.9	16.9	
Stainless Steel Chamber, 38-L	2 replicates	3.62	3.96	4.04	9.39	
DAPA						
Micro Chamber, 114-mL	92.5 μg	76.0	73.6	80.9	3.16	
PTFE Lined Acrylic Chamber, 38-L	RPD = 11.0	11.1	12.9	13.0	16.2	
Stainless Steel Chamber, 38-L	2 replicates	3.78	4.70	4.58	24.3	

Injection port (ATIS) temperature = 75 °C at 100-cc UHP Nitrogen/min.

Recovery measured after approximately 20 air exchanges from the chamber.

Micro Chamber carrier gas = 100-cc/min. UHP grade Nitrogen, Outlet Temperature =  $\sim 25$  °C.

Stainless Steel and PTFE Chamber carrier gas = room air, 600-cc/min; RH = 23 to 33 %, Temperature = 22 °C.

#### Flame Retardant Spike into Test Chambers

The flame retardant used in the generic SPF formulations were spiked into micro chambers and conventional small-scale PTFE and stainless steel chambers. A solution of TCPP was prepared at approximately 5000  $\mu$ g/mL each in methylene chloride. This solution was introduced into the injection port of the ATIS with a gas tight syringe (20  $\mu$ L = ~100  $\mu$ g of each catalyst).

The solution containing TCPP was injected into the ATIS at 100 °C using UHP grade nitrogen as the carrier gas at 100cc/min. The emission samples were collected for 20 minutes onto XAD-2 tubes (ATIS only, chambers disconnected) to measure the actual amount of TCPP exiting the ATIS, or the amount expected to enter the test chambers. The TCPP was then determined by GC/MS after desorbing the sorbent in the tubes with 2-mL of methylene chloride. The XAD-2 tubes were preferable to using TD tubes so that longer term samples could be collected to measure total recoveries.

In order to spike the flame retardant, the ATIS injection port was connected to the micro chamber, small-scale stainless steel and PTFE 38-L chambers as shown in Figures 22-24. Three micro chambers were spiked: stainless steel, deactivated stainless steel, and a stainless steel chamber wrapped in heat tape at 40 °C. The micro chambers were sampled for 20 minutes at 100-cc/min (~20 air exchanges) and the 38-L chambers were sampled for 20 hours at 600-cc/min (~20 air exchanges). The results and calculated spike recoveries are shown in Table 21.

The recoveries with micro chambers (2%) were initially much less than the 38-L stainless steel chambers (25%) and 38-L PTFE lined chambers (38%). Heating the micro chamber to 40 °C increased the recovery but still unacceptably low (4%). One explanation for higher recoveries in the larger chambers would be the longer residence and sampling time (20 hours for the 38-L chambers vs. 20 minutes for the micro chambers). Another possibility might be that the inlet gas was room air for the 38-L chambers instead of only using UHP nitrogen in the micro chambers. The room air contained humidity and possibly particulate that could have affected the recovery.

In order to evaluate air as the carrier gas and residence time, TCCP was spiked into a micro chamber using room air as the carrier gas with a personal sampling pump set to 200-cc/min. A sample was collected for 10 minutes on XAD-2 to achieve

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approximately 20 air exchanges. The TCPP spike study was repeated two additional times in the micro chamber; a sample was collected onto XAD-2 for 4 hours and another collected for 16 hours to evaluate the impact of increasing the residence / sampling time. As shown in Table 22, the recoveries were significantly higher using air as the carrier gas with the micro chamber, and after 16 hours, complete recovery was achieved (>100%).

The observed results demonstrate that all of the TCPP can be recovered from the micro chamber using air as the carrier gas and extending the sampling time to 16 hours. For comparison, the conventional small-scale chambers constructed of stainless steel and lined with PTFE that were sampled for 20 hours showed incomplete recovery of only 25% and 38%, respectively. According to the vendor, introducing relative humidity into the micro chamber can improve the recovery of some semi-volatile organic compounds, such as TCPP. Because of this, the use of high purity compressed air with a humidity controlled system may be necessary to achieve complete recovery of the flame retardant.

Table 21- TCPP Chamber Spiking Study Results						
Chamber Type and Material	Determined Spike Amount	Measured in Chamber, µg	% Recovery			
ТСРР						
PTFE Lined Acrylic Chamber, 38-L		14.3	38.2			
Stainless Steel Chamber, 38-L	37.4 ug	9.42	25.2			
Micro Chamber, Deactivated, 114-mLRSD = 3.89 %Micro Chamber, Stainless Steel, 114-mL3 replicates		0.70	1.9			
		0.82	2.2			
Micro Chamber, Heated to 40°C, 114-mL		1.62	4.3			

Injection port (ATIS) temperature = 100 °C at 100-cc UHP Nitrogen/min.

Recovery measured after approximately 20 air exchanges from the chamber.

Micro Chamber carrier gas = UHP grade Nitrogen, Temperature = 22 °C.

Stainless Steel and PTFE Chamber carrier gas = room air; RH = 22 %, Temperature = 22C.

Table 22- Spike Recovery of TCPP in Micro Chamber with Room Air						
Sampling Time	Relative Humidity, %	Temperature	TCPP Spike	Measured TCPP in Chamber, µg	% Recovery	
10 minutes	22	22		5.32	10.4	
1 hour	35	21	51.0 μg	10.1	19.8	
4 hours	35	21	RSD = 1.39 3 replicates	23.5	46.1	
16 hours	35 to 53	21	5 Tepheutes	59	116	

Injection port (ATIS) temperature = 100 °C.

Air exchange rate = 2 exchanges/min; flow rate = 224 cc/min; RH = 35-53%

# SUMMARY OF SPIKING STUDY CONCLUSIONS

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. MDI spike recoveries were

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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 significantly higher in the micro chamber; recoveries were poor with conventional small scale chambers. The flame retardant was fully recovered in the micro chamber using air as the carrier gas (containing humidity) with extended sampling time.

#### Summary of Recommendations for Future Work

This study showed proof of concept for using TD-GC/MS to analyze emissions from SPF samples. Further validation will be required to standardize this procedure at ASTM and to assess the precision and bias of the method.

Spike recovery for amine catalysts and flame retardant were greatly improved using the micro chamber; however, further optimization of the parameters will be required. For example, controlling relative humidity should be investigated. There should also be an attempt to correlate the emissions observed with conventional small-scale chambers and micro-scale chambers. Small scale chamber surfaces should also be evaluated to determine if spike recoveries can be improved (e.g. electro-polished surfaces).

MDI seems to "stick" to the surface of the chamber walls; therefore, a modified environmental test chamber may be required to recover MDI emissions. There is currently research being planned by Markes International and the International Isocyanate institute (III) to modify the micro chamber design to optimize MDI recovery. CPI may want to partner with them to support this effort.

Environmental storage and shipping conditions may need to be investigated for SPF samples (e.g. temperature, relative humidity, atmospheric pressure etc.). Further research will be necessary to evaluate the holding time of the low pressure kit formulation since the observed emissions were not constant throughout the study. Conditioning samples for measuring low concentrations of VOC compounds should be investigated for IAQ measurements.

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# **REFERENCED METHODS AND DOCUMENTS**

# ASTM, US EPA and Other Standards

ASTM D5116 - 10 Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products, 2010 ASTM International

ASTM D5197 - 09e1 Standard Test Method for Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)

Method 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), SW-846, US EPA 1996

Organization for Economic Co-operation and Development (OECD) SIDS Tris(1-Chloro-2-propyl)phosphate, UNEP Publications

ASTM D7706 - 11 Standard Practice for Rapid Screening of VOC Emissions from Products Using Micro-Scale Chambers, 2011, ASTM International

California Specification 01350, Standard Method for the Testing and Evaluation of Volatile Organic Chemical Emissions from Indoor Sources Using Environmental Chambers, Version 1.1, February 2010

Conditional Test Method 036, Method for Measurement of Isocyanate Compounds in Stack Emissions, Technology Transfer Network Emission Measurement Center, US EPA

Methylene bis(phenylisocyanate) (MDI), Method 47, Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah, March 1983

# Bayer MaterialScience Methods<sup>1</sup>

Method SA-102 Analysis of Isocyanates (Liquid Chromatography, Diode Array/MSD/FLD)

Method 2.10.3 - Determination of Aliphatic Amine Catalysts in Air by Sampling with a XAD-2 Sorbent Tube and Analysis by Capillary Gas Chromatography

Method No: 1.7.7 Determination of Airborne Methylene bis(phenylisocyanate) by Sampling on a 1-(2-pyridyl)piperazine/Diethylphthalate-Coated Glass-Fiber Filter and Analysis by High Performance Liquid Chromatography

<sup>&</sup>lt;sup>1</sup> Bayer MaterialScience methods are internal documents, which are proprietary. Similar methods are referenced when applicable.

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