

Topic B 1: Sources of indoor air pollutants

Development of Test Systems for Characterizing Emissions from Spray Polyurethane Foam Insulation (SPFI) Products

Mark A MASON^{1,*}, Ken KREBS¹, Mark BARNES¹, Dale GREENWELL¹, Charles BEVINGTON², Carol HETFIELD², Katherine SLEASMAN², Nancy ROACHE³, Gary FOLK³, Gunnar SKARPING⁴, Marianne DALENE⁴, and Daniel KARLSSON⁴

¹United States Environmental Protection Agency, National Risk Management Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, North Carolina, USA

²United States Environmental Protection Agency, Office of Pollution Prevention and Toxic Substances, Washington, DC., USA

³ARCADIS, Durham, NC, USA

⁴IFKAN, Hässleholm, Sweden

*Corresponding email: mason.mark@epa.gov

Keywords: SPFI, flame retardant, amine catalyst, VOC, diisocyanate emissions

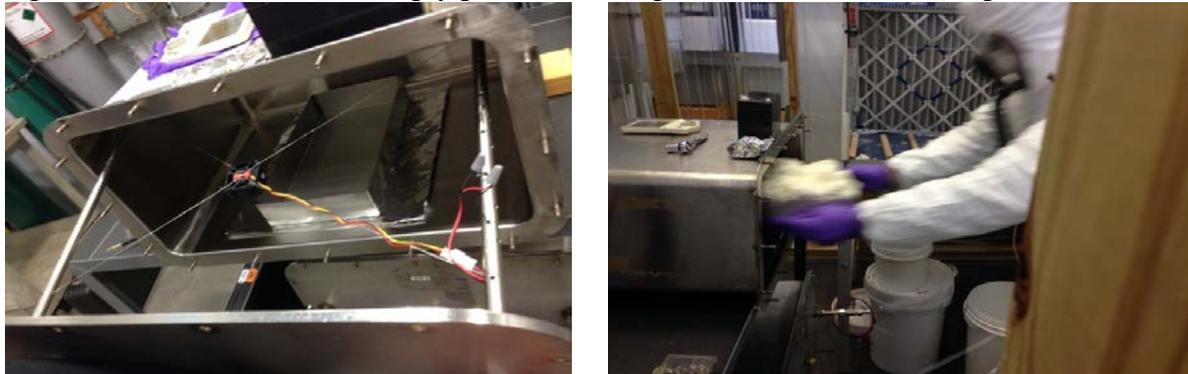
INTRODUCTION: The relationship between onsite manufacture of spray polyurethane foam insulation (SPFI) and potential exposures to diisocyanates, amines, flame retardants (FRs), blowing agents, aldehydes and other organic compounds that may be emitted from SPFI is not well understood. EPA is developing methods to characterize emissions from SPFI products to support development of ASTM consensus standards for use by stakeholders to evaluate and improve products and to support a broader strategy to develop assessment tools and models that relate polyurethane foam product usage to potential exposures. Our approach is to develop emissions test systems specific to the challenges posed by a potentially wide range of reactive and semivolatile emissions, conduct scale-up experiments in full-scale chambers to inform interpretation of emissions data, and investigate emissions from products in assemblies and environments that simulate actual usage. We are currently in the first phase; development of emissions test systems and protocols specific to SPFI emissions.

This paper presents methods employed in a pilot emissions test conducted in 53 liter (L) test chamber (ASTM D5116-10) using elements of Canadian National Standard S744-09 with a low pressure two component spray foam system. Specific objectives of this pilot experiment were to obtain insight into utility of small stainless steel chambers to characterize emissions from freshly prepared SPFI samples using a variety of sampling and analysis approaches.

METHODS: Samples were prepared in a hood in a ventilated tented enclosure in a high bay building. Foam was applied to a stainless steel tray sized to create a nominal sample surface area to chamber volume ratio of 1 m²/m³ with target sample depth of 5.1 cm. Foam was also applied to surrogate wood and stainless steel substrates fitted with thermocouples to investigate curing temperatures in different substrates. Foam was applied in two lifts with fifteen minutes between lifts to allow for dissipation of heat. Following the second application, the sample was quickly placed into a chamber and sampling for isocyanates was initiated. The test chamber was transported to the laboratory and placed into an incubator at 40 °C. The isocyanate sampler was removed and the chamber was connected to clean air supplied at 0.935 L/min and humidified to 50% relative humidity (RH) at 23 °C. Air samples were collected at various times over the 1200+ hour test period by pulling chamber air

through sampling media using calibrated mass flow controllers and vacuum pumps. Wipe samples were collected from interior chamber surfaces at the end of the test to assess sorption on the chamber walls.

Figure 1. Test chamber with empty pan and loading chamber with SPFI sample.



Sampling and analysis: Isocyanates were collected and derivatized to stable di-n-butylamine (DBA) derivatives by pulling chamber air through samplers (Sigma Aldrich, 2014) consisting of a denuder lined with glass fiber filter (GFF) treated with DBA and a filter cassette which also holds a DBA-treated GFF. DBA derivatives are extracted, concentrated, identified and quantified using a high performance liquid chromatograph equipped with triple quadrupole mass spectrometer (HPLC-MSMS) (Gylstram, 2014). Aldehydes were collected on DNPH cartridges and determined by HPLC-DAD per ASTM D-5197-09. A blowing agent 1,1,1,2, tetrafluoroethane, (HFC-134a) flame retardant (FR) tris (1-chloro-2-propyl) phosphate (TCPP), amine catalyst pentamethyldiethylenetriamine (PMDTA) and other volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) were collected on stainless steel tubes containing Tenax or combination Tenax and carbon molecular sieve (MARKES C3) for analysis by thermal desorption gas chromatography and mass spectral detection (TD-GC/MSD). Flame retardants were also collected on cartridges containing polyurethane foam (PUF) for solvent extraction and analysis by GC-MSD (Liu, 2014).

Four isocyanate samples were collected through the face plate of the chamber over the first 14 hours of the test. DNPH, PUF, Tenax, and Tenax C3 samples were collected periodically for over 1200 hours from ports on the faceplate of the chamber and/or from ports in a sampling manifold located outside of the incubator in the chamber exhaust. Background samples were collected and analyzed for all media prior to the start of the experiment.

RESULTS and DISCUSSION: The temperature characterization experiments revealed similar patterns for stainless steel and wood substrates with internal foam temperatures reaching just over 100 °C in the stainless steel sample holder and 95 °C in the wood substrate following application of the first lift. Temperatures in the stainless steel tray rose to 90 °C with application of the second lift versus 65 °C in the wooden substrate. The time-temperature profiles for the test temperature characterization samples suggest that the temperatures of the sample in the emissions test chamber would have reached near ambient temperature by the time the chamber was placed in the incubator at 40 °C. Mono and diisocyanates were identified in three samples collected through the first 2.4 hours. Because the chamber was loaded in the area where the samples were prepared, laboratory air may have contributed to the isocyanates observed in the chamber air. Tenax samples collected during or shortly after isocyanate sampling contained DBA. Side studies confirmed that DBA diffuses from the sampler into the chamber with the sampler protruding through the faceplate. TCPP, acetaldehyde, acetone, and formaldehyde were quantifiable through 1200 hours. Due to

instrument problems, 1200 hour sample data is not yet available for the amine catalyst PMDTA or HFC-134a. TCPP was recovered from the wipe samples of the chamber walls at the end of the test.

CONCLUSIONS: This small chamber test provided insight into the types of compounds potentially emitted from SPFI and insight into time frame for emissions. Based upon results of this test, we have made modifications to the chamber faceplate, mixing fan, and outlet sampling manifold and we are investigating several approaches to prevent DBA diffusion into the chamber during isocyanate sampling. Future tests will evaluate the impact of sample loading in the foam production area. Sorption and desorption parameters for the FRs are needed to enable interpretation of the chamber concentration data. Experiments that capture emissions during application will be needed to sort out differences in emissions between application and curing phases. Observations of TCPP and HCHO emissions for 1200 plus hours indicate potential for long term emissions, and indicate a need for emissions data over the ranges of temperatures of the environments where the products are used.

The material in this document has been subject to Agency technical and policy review, and approved for publication. The views expressed by individual authors, however, are their own, and do not necessarily reflect those of the U.S. Environmental Protection Agency.

Acknowledgements: The authors thank Matt Barnes for extraction and analysis of the PUF and the wipe samples.

REFERENCES:

ASTM D5116-10, 2010. Standard guide for small-scale environmental chamber determinations of organic emissions from indoor materials/products. ASTM International, West Conshohocken, PA.

ASTM D5197-09e1, 2009. Standard test method for determination of formaldehyde and other carbonyl compounds in air (Active Sampler Methodology). ASTM International, West Conshohocken, PA.

ASSET™ EZ4-NCO Dry Sampler for Isocyanates, Downloaded 3/3/2014 from:

<http://www.sigmaldrich.com/analytical-chromatography/air-monitoring/asset-ncsampler.html>.

CAN/ULC-744-09, Standard Laboratory Guide for the Determination of Volatile Organic Compound Emissions from Polyurethane Foam. Underwriters Laboratory of Canada, Ottawa, Canada. April 1, 2009.

Gylestam D, Riddar J, Karelsson D, Dahlin J, Dalene M, and Skarping G (2014) Dry sampling of gas-phase isocyanates and isocyanate aerosols from thermal degradation of polyurethane, Ann. Occup Hyg. 58 (1) 28-49.

Liu X, Roache N, Allen M (2014) Development of a small chamber method for SVOC sink effect study, Manuscript HA0315 accepted for presentation at “Indoor Air 2014, The 13th International Conference on Indoor Air Quality and Climate” July 7-12, 2014 Hong Kong