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An experimental study of spray foam insulation products- evidence of 1,2-dichloropropane and 1,4-dioxane emissions

Dzhordzhio Naldzhiev^{1,2,*}, Dejan Mumovic¹, Matija Strlic²

¹ Institute for Environmental Design and Engineering (IEDE), University College London (UCL), London, United Kingdom

² Institute for Sustainable Heritage (ISH), University College London (UCL), London, United Kingdom

*Dzhordzhio.naldzhiev.16@ucl.ac.uk

Abstract. An experimental study was conducted using SPME-GC-MS and TD-GC-MS to analyse VOC emissions from three spray foam insulation products. Two closed cell and one open cell materials were tested using SPME-GC-MS passive sampling and a range of VOCs were found with 1,2-dichloropropane (1,2-DCP) found in all products. TD-GC-MS analysis of Product 1 (a closed cell foam) and the raw material used for its production (B-side) showed that 1,4-dioxane and 1,2-DCP were both present in the raw material and emitted from the cured foam product. Our findings are currently limited and preliminary, but do seem to indicate that industrial contamination of raw chemicals could be the likely source of these compounds. This could raise the issue of Class 1 and 2B carcinogen VOCs being present in raw polyurethane spray foam insulation (SPF) materials should systematic evidence is provided. As per WHO guidance, it would be a better strategy to remove pollutants at the source. Further research will aim to quantify emission concentrations during application and examine the impact of application strategies.

1. Introduction

The polyurethane market is a growing industry. In the U.S. alone polyurethane products generated \$2.2 billion in revenue in 2015 with the highest proportion (35.9%) of them being used in the building and construction industry (1). The use of polyurethane building insulation products is expected to increase further taking into account the current global climate of ambitious energy efficiency targets (EU: 30% energy savings by 2030 (2) UK: 20% improvement in energy efficiency by 2030 (3), US: reduce greenhouse gas (GHG) emissions by 26-28% and China: reduce GHG intensity by 60-65% by 2030 (4). Although the potential for energy savings is significant, an important potential unintended consequence on the indoor environment is the potential release of volatile organic compounds (VOCs) from these insulation products (5). The research on VOCs from polyurethane spray foam materials (SPF) is fairly limited considering the scale of the industry and the wide application range of such products (6). Some possible and confirmed carcinogens have been found off-gassing from spray foam insulation products, such as 1,2-dichloropropane (1,2-DCP) and 1,4-dioxane (7), although their exact origin has remained unknown. The objective of this paper is to provide further clarity on the possible sources of these emissions.

2. Methods

Two separate methods were used in order to determine the presence of 1,2-dichloropropane (1,2-DCP) and 1,4-dioxane in SPF samples: passive diffusion sampling using solid phase microextraction (SPME) coupled with gas chromatography-mass spectrometry (GC-MS) and desorption tubes, which



were analysed using automated thermal desorption (TD) coupled with GC-MS. TD was used for both headspace analysis and spiking directly on tubes.

2.1. SPME-GC-MS (Passive sampling)

In the first set of experiments, three different SPF products were prepared and analysed. Product 1 was a two-component (A-side and B-side) closed cell spray foam used for insulation of buildings. Product 2 was a commercially available DIY two-component (A-side and B-side) closed cell spray foam used for insulation of buildings, gaps, cracks and expansion joints. Product 3 was a commercially available DIY one-component spray foam used for general gap filling, bonding and insulation purposes.

2.1.1. Spray foam production. The products were made in a shaded area outdoors at 8-11 °C and relative humidity (RH) 68-82% according to a Met Office weather station. Prior to samples being cut, the foams were left to cure outdoors for 48 h in a shaded area with no direct sunlight. The cured foams were kept in a storage bag in a laboratory (18-23 °C) for a period of 27 days before samples for SPME analysis were cut out.

2.1.2. Sampling and storage conditions. The sampling methodology followed the ASTM D7859-19 standard (8). Small samples (2-5 mm) were cut out of the surface and core, with a different blade for each product, and placed in 20-ml glass vials. Once the samples were placed in vials, they were stored for 5 days before testing with SPME-GC-MS. The sample sizes had a cured weight between 88-102mg.

2.1.3. Instruments and analytical conditions. Sample headspace was analysed using a CTC Analytics CombiPAL Headspace Autosampler with a SPME fibre coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS). The autosampler was connected to a Perkins Elmer 500 gas chromatograph coupled with a Perkin Elmer Clarus 560D mass spectrometer. The column used was a 60 m x 0.25 mm x 1.5 µm VOCOL fused silica capillary. For each run, the SPME fibre was inserted into the vial, piercing the septum and the emissions were sampled for 60 min. Between two analyses, the SPME fibre was heated to 250 °C and conditioned for 30 min under a flow of nitrogen (50 mL/min). The analytical parameters were set to detect a wide range of VOCs and are summarized in Table 1.

Table 1. SPME-GC-MS analysis operational parameters

SPME		Setup
Headspace sampling duration		60 min
GC		Setup
Helium flow		1 mL/min
Temperature gradient		50 °C (hold 5 min), 10 °C/min to 100 °C, 5 °C/min to 200 °C, 2 °C/min to 220 °C (hold)
Run time		60 min
MS		Setup
MS Ionization Mode; MS Scan range		E+; 45-300 (TIC Mode)
MS Inlet; MS Source		200 °C; 180 °C

2.2. TD-GC-MS (Active sampling)

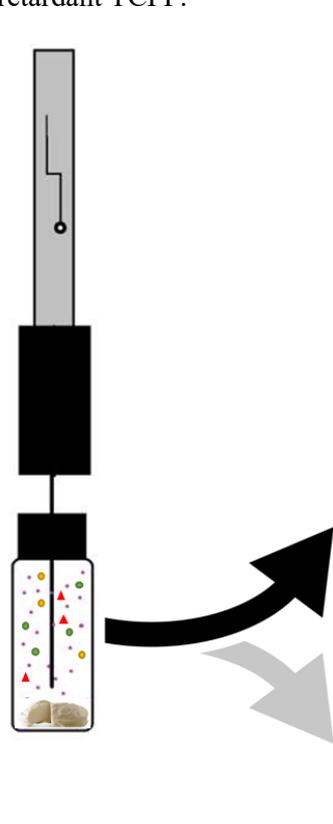
In the second experiment only Product 1 was analysed. After it was stored for 6 months in a sealed bag, pieces were cut out of the surface and core of the product and placed in a 1000-ml Duran glass bottle, which was then closed with a cap. The weight of the sample was 2241 mg. The VOC analysis was undertaken 7 days after the foam was cut and placed into the bottle, thus providing sufficient time for most VOCs to reach a significant concentration, if not the steady state, within the glass bottle. Air

was extracted through two Carbopack-B tubes connected in a series. The sampling duration was 30 min and the flow rate 35 mL/min ($\pm 5\%$). A third conditioned Carbopack-B tube was used to filter the incoming air as per the Naldzhiev et al. (2017) sampling procedure. In a separate experiment, four Carbopack-B and four Tenax TA tubes were spiked directly with 5 μ l B-side of Product 1 (which is a liquid). All tubes were analysed as per Table 1 in Naldzhiev et al. (2017) TD-GC-MS analytical conditions.

3. Results

3.1. SPME-GC-MS

The chromatograms were repeatable for the same sample and exhibited consistently similar peaks for different samples. Figure 1 summarises compounds identified using SPME-GC-MS. The only chemical constituents that were present in all spray foams according to the manufacturer-provided safety data sheets (SDS) are the isocyanates (MDI) and/or polymeric MDI (pMDI) and the flame retardant TCPP.



Compounds found (listed on material safety data sheet)	CAS	Bp (°C)	
4,4-MDI	101-68-8	314	
Polymeric MDI (pMDI)	9016-87-9	392	
Dibutyltin dilaurate (DBTDL)	77-58-7	204	
Tris(chloropropyl)phosphate (TCPP)	13674-84-5	235-248	
BDMAEE	3033-62-3	189	
<i>N,N</i> -bis[3-(dimethylamino)propyl]- <i>N',N'</i> -dimethylpropane-1,3-	33329-35-0	298	
Isobutane	75-28-5	-12	
Propane	74-98-6	-42	
Halogenated aliphatic polyether polyol	68441-62-3	238	
Dimethylbis[(1-oxoneodecl)oxy]stannane	68928-76-7	266	
Alkanes, C14-17, chloro	85535-85-9	>200	
Triethyl phosphate (TEP)	78-40-0	216	
HFC-365mfc	406-58-6	40	
Norflurane (HFC-134a)	811-97-2	-26	
<i>trans</i> -1,2-dichloroethylene	156-60-5	48-60	
Dimethyl ether	115-10-6	-25	
Additional compounds found (not listed on material safety data sheets)	CAS	Bp (°C)	Product
1,2-DCP	78-87-5	95.5	1,2 and 3
1,4-dioxane	123-91-1	101	1
Chlorobenzene	108-90-7	132	1,2 and 3
Dimethyl methylphosphonate	756-79-6	181	3

Figure 1. SPME-GC-MS results. Compounds highlighted in red- not in NIST library, yellow- not detected using SPME-GC-MS method, green- successfully detected emissions

1,2-DCP was present in all of the samples, whilst 1,4-dioxane was present only in Product 1 (Figure 1). The peak heights of all compounds in Figure 1 had a signal-to-noise (S/N) ratio of more than 10, which means they are present beyond doubt and could be quantified once calibration curves are developed (9). Neither of the chemicals were found in either Blank 1 or Blank 2. The compounds that have not been detected using SPME-GC-MS, highlighted in red or yellow in Figure 1, could still be present in the headspace of the vials, but the method as used in this research may not be appropriate for their analysis and identification. BDMAEE and TCPP have been successfully identified and quantified using TD-GC-MS (10,11). A possible explanation of their absence in the chromatograms could be the unsuitability of SPME sampling, the analytical conditions or the fact that the boiling points of some compounds are higher than the oven temperature (220 °C).

3.2. TD-GC-MS method

1,2-DCP was recorded as the second largest peak, following triethyl phosphate. We used single ion monitoring (SIM) to isolate the chromatogram peaks associated with the highest m/z ions for the compounds: 63 for 1,2-DCP and 88 for 1,4-dioxane. Figure 1 demonstrates the 1,2-DCP and 1,4-dioxane found in Product 1 using both SPME and TD.

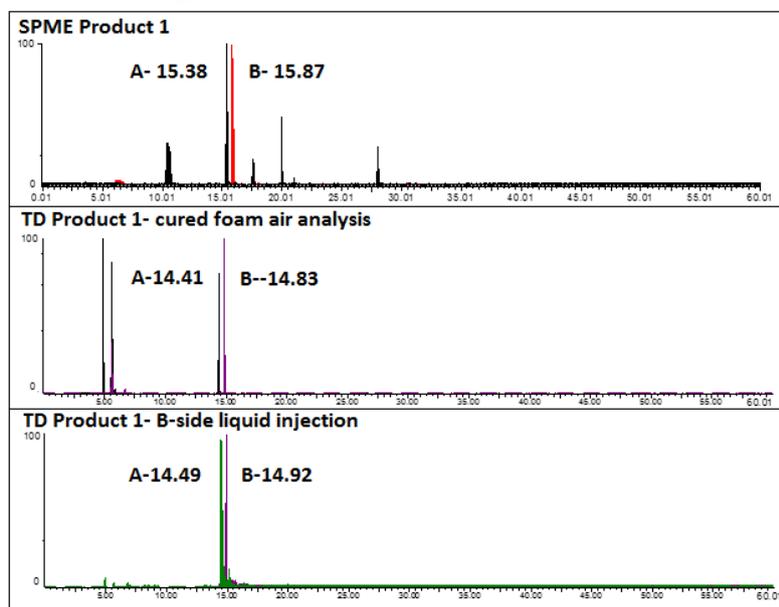


Figure 2. Single ion chromatograms for 1,2-DCP and 1,4-dioxane, obtained from SPME-GC-MS and TD-GC-MS headspace analysis of cured Product 1 foam and direct injection TD-GC-MS analysis of raw material (5 μ l of B-side from Product 1). “A” represents 1,2 DCP and “B” represents 1,4-dioxane.

4. Discussion

Figure 1 lists the known chemicals present in the liquid form of the spray foam materials as per the safety data sheets. The only chemicals that are used in all three products are the pMDI/4,4-MDI (isocyanates) and TCPP (flame retardant). Our findings confirm that 1,2-DCP and 1,4-dioxane are present in the liquid B-side of the spray foam and may thus contribute to VOC emissions from the cured product. The different storage conditions of the foams during the curing process could have impacted the emissions quantitatively, but the aim of this research is qualitative, hence this was not considered essential for the purpose of the study. On the basis of this study, it is unknown if the concentrations of chemicals in the foam reach detectable levels indoors and may vary depending on the application. It may be that the isocyanate reaction during or after the production of foam represents an additional source of these compounds. In order to confirm the source of possible emissions and quantify 1,2-DCP and 1,4-dioxane in the liquid and the cured product, a mass balance should be established in the future. Salthammer (12) found 1,2-DCP to be a breakdown product of tris(1,3-dichloroisopropyl)phosphate (TDCPP), but not of TCPP. Thus, degradation of the TCPP emitted from the foam during curing does not present itself as a likely explanation for the presence of 1,2-DCP in the finished product. Based on our findings, it is possible to hypothesise the reasons for the presence of 1,2-DCP and 1,4-dioxane (Figures 1 and 2) in spray foam insulation products:

- 1,2-DCP may be used as a processing solvent in the production of one-component foams, and of the B-side of the two-component foam. It is known that 1,2-DCP has been used in the production of toluene diisocyanate (13)
- 1,4-dioxane may be used as a processing solvent during production of the B-side of the two-component foam. It is known that 1,4-dioxane has been used in chemical processing (14)

- A chemical reaction within the B-side liquid of the two-component foam and/or the finished one- and two-component products leads to the formation of 1,2-DCP and/or 1,4-dioxane
- A combination of the above

The third hypothesis explains our findings less well, as the chemical composition of the three products was different and in addition, 1,2-DCP and 1,4-dioxane were present in the liquid of the B-side (Figures 1 and 2) as well as off-gassed by a cured spray foam product (7). The findings of Sleasman et al. (7) demonstrate that 1,2-DCP and 1,4-dioxane emissions are emitted from other SPF products as well. It was previously hypothesised that these two chemicals are by-products or residual products (7,10,11,15), but our spiking experiments with the B-side demonstrate that at least some emissions from Product 1 are due to the compounds already being present in the B-side (Figures 1 and 2). As 1,2-DCP has been classified as a Group 1 human carcinogen (16) and 1,4-dioxane as a Group 2B possible carcinogen (17) by the World Health Organisation (WHO), it could be argued that eliminating them at the source would be the optimal strategy as it follows WHO air quality guidelines for pollutants (18). Although removing the two compounds at the source would not eliminate the need for having robust application procedures and ventilation strategies for spray foam installation based on other compounds (isocyanates, flame retardants, catalyst amines, etc.). A further point to mention is that as 1,2-DCP and 1,4-dioxane are Group 1 and 2B human carcinogens (IARC), they must be disclosed in the safety data sheets as per Regulation (EC) No 1907/2006 (REACH) of the European Union (EU) if their concentration is higher than 0.1% of the raw mixture. As per OSHA Hazard Communication Standard (HCS) (29 CFR 1910.1200(g)) in the United States, carcinogenic compounds must be disclosed in the safety data sheets if they are known constituents of the raw product (no information about the minimum concentration requiring disclosure could be found in the OSHA document). 1,2 DCP was used as a solvent for producing some building materials, such as paint strippers and varnishes but its use in their production has been discontinued in the 1980s (19)(13). Although this study is only preliminary, it is important to raise awareness that if further evidence is presented for the presence of Group 1 and 2B human carcinogens in spray foam products, then issues with contamination should be resolved. This would remove the risk of human exposure to these two compounds entirely as it follows WHO guidelines of using source control as best practice (18).

5. Conclusion

Samples from three different spray foam insulation products (two closed cell and one open cell) were analysed with SPME-GC-MS and TD-GC-MS. Five of the SPF constituents disclosed in the safety data sheets were identified and in addition 1,2-DCP (Group 1 carcinogen) emissions were detected in all samples and 1,4-dioxane (Group 2B carcinogen) in one of the closed cell spray foams.

1,2-DCP and 1,4-dioxane have been found to be constituent chemicals of the raw liquid of the closed cell spray foam insulation product. Our findings hypothesise on the source of these emissions and the data suggest that contamination could have occurred during the process of production of SPF raw materials. We are hoping that our findings will stimulate further research into these emissions in order to minimise any potential unintended consequences on building users' health. The optimal strategy of reducing exposure for commercially available products could be to eliminate the compounds at the source. Our future work will consist of systematic quantification of 1,2-DCP and 1,4-dioxane emissions during application from a range of commercially available SPF materials and further testing of possible reaction or degradation processes.

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