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Measurement of Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation Using an Automated Micro-Scale Chamber Coupled Directly with the Analysis System

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Keywords

LabWorks Platform, material emission, dynamic headspace, micro-scale emission chamber, spray polyurethane foam, thermal extraction, VDA 278

Abstract

The GERSTEL LabWorks Platform, complemented by an dynamic headspace (DHS) system and coupled with Gas Chromatography/ Mass Spectrometry (GC/MS) was used for fully automated micro-scale chamber material emission analysis of Spray Polyurethane Foam (SPF). Closed-cell and open-cell SPF samples were analyzed for emissions of TVOCs and high boiling compounds such as, for example, flame retardants and amine catalyst. Foam samples were analyzed qualitatively, and 15 hour emission tests subsequently carried out to investigate off-gassing mechanisms of the foams. The effect of sample temperature was examined using an automated sequence in which the sample temperature was changed at defined times to simulate the heating of foam insulation in attics or roofs. The experiments provided unattended operation with precise control and documentation of the principal variables in micro-scale chamber experiments: Time, gas flow, and temperature. Samples were subsequently analyzed using the VDA 278 method with direct thermal desorption at 90 °C to determine VOC emissions. Good correlation was obtained between the two methods from a qualitative point of view. Semi-quantitative results were obtained using toluene equivalents.

Introduction

Sprayed Polyurethane foam (SPF) insulation is widely used in construction and for renovation and thermal insulation of existing buildings. Potentially harmful effects from emitted chemical components such as amine catalysts [1] and flame retardants [2] are a focus of current research. Besides documenting exposure to building occupants, determination of emission behavior of SPF insulation can be used by SPF manufacturers to establish safe re-entry times for workers and re-occupancy times for residents [3].

Emission test chamber methods are widely used for determination of the emission of compounds from building products [4]: air is sampled through tubes (typically) containing a sorbent, and the tubes are analyzed using thermal desorption and gas chromatography/mass spectrometry (TD-GC/MS) [5]. However, poor analytical recovery due to significant sink effects for high boiling-point compounds (flame retardants, amine catalysts) has been observed when using conventional test chambers [3, 6]. For this reason, further development of consensus standards for measuring chemical emissions from SPF samples in smaller micro-scale chambers is required, as sink effects are greatly diminished in the much smaller chambers [6].

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Like conventional environmental chambers, the micro-scale chambers used to date for SPF emission measurements are off-line devices, i.e. separate from the analytical instrumentation used. Consequently, the amount of manual interactions required impose limitations to their usefulness for experiments that require multiple changes to analysis conditions. An analyst or technician must be available to manually set temperatures and flows as well as to remove and replace the thermal desorption tubes, effectively controlling the sampling times.

In this work, a large volume dynamic headspace autosampler (DHS L) was added to the GERSTEL LabWorks Platform and combined with GC/MS as shown in Figure 1. It was used as a fully automated on-line micro-scale chamber system for the analysis of SPF samples. The system used enables fully automated sampling of SPF emissions with software control of flows, temperatures, and sampling duration/time. In this way, emission behavior versus time is easily, accurately and reliably obtained, and experiments at different flows or temperatures (to simulate different installation conditions, for example) are also greatly simplified.



Figure 1: 11-Position on-line micro-scale chamber system combined with GERSTEL LabWorks Platform and coupled with GC/MS.

Another widely used method to determine VOC and FOG emissions from Polyurethane foam used as interior material in automobile industry is the VDA 278 method [7] using a Thermal Desorption System (TDS 3) and Autosampler (Figure 2). This method is used to determine VOCs and SVOCs in small samples by direct thermal extraction. The samples are placed in thermal desorption tubes and total emission values per sample mass ($\mu\text{g/g}$) are de-

termined rather than the surface emission rate ($\mu\text{g/m}^2\text{h}$). Analysis based on the VDA 278 method is quicker, easier and substantially less costly to perform than emission chamber methods and only a small amount of sample is needed. The values determined using the VDA 278 method are described in the method as follows: "In this method two semi-quantitative cumulative values are determined which allow the emission of volatile organic compounds (VOC value) and the portion of condensable substances (FOG value) to be estimated. Furthermore, single substance emissions are determined." Even though the determined values are not directly comparable with the results from emission chamber analysis, these are well known and established as a means of qualifying whether materials are acceptable for use in vehicle interiors.



Figure 2: Thermal Desorption System (TDS 3) with autosampler (TDS A).

Experimental

Chemicals

Target compounds are listed in Table 1 with names, acronyms, CAS numbers and boiling points. TMIBPA, BDMAEE, PMDTA, TMAEEA and toluene were GC/MS grade and purchased from Sigma Aldrich (Germany). DAPA and TCPP were purchased from abcr GmbH (Germany) in GC/MS grade.

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Table 1: Target compound with acronym, CAS-number, and boiling point at 1 atm.

Target Compound	Acronym	CAS-Number	Bp [°C @ 1atm]
1,1,1,3,3-Pentafluoropropane	HFC-245fa	460-73-1	15
Bis(dimethylaminopropyl)methylamine	DAPA	3855-32-1	102
Tetramethyliminobispropylamine	TMIBPA	6711-48-4	128 -131
Bis(2-Dimethylaminoethyl)ether	BDMAEE	3033-62-3	189
Pentamethyldiethylenetriamine	PMDTA	3030-47-5	198
N,N,N-Trimethylaminoethylethanolamine	TMAEEA	2212-32-0	207
Tris-(1-chloro-2-propyl)phosphate	TCPP	13674-84-5	244
Toluene	-	108-88-3	111

Generic SPF insulation samples. Two SPF insulation samples were obtained from the Center for the Polyurethanes Industry (CPI), a part of the American Chemistry Council. One sample type was an open-cell foam and the other was a closed-cell foam. Both samples were packaged and shipped according to ASTM practice D7859-13e1 [8]. The foams were about 50 x 50 cm and about 10 cm thick. They were wrapped in two sheets of clean aluminum foil and sealed in Mylar bags with a zipper seal. Prior to testing, the samples were stored in unopened Mylar bags in the laboratory shielded from exposure to light. The laboratory temperature was controlled at 23 °C. The samples were opened directly before a sample was taken, wrapped and sealed in Mylar bags again directly thereafter. Using a custom-made coring tool (Figure 3, left), SPF

samples, 92 mm in diameter and of varying thicknesses (3, 5 and 8 cm) were prepared. All samples were cored from the surface to the bottom and cut at the bottom to get the required thickness (i.e., the top outer surfaces were left on the samples). Coring was started from the top side to make sure the top surface of samples did not crack during the process. After coring, the samples were pushed out of the tool, cut to the desired thickness, reversed and re-inserted into the coring tool. The coring tool has an adjustable, tightly fitting sliding bottom plate, which allows samples of different heights to be positioned with the upper surface at the same height flush with the top of the tool. The sample together with the coring tool was placed in a one liter DHS container (Figure 3, right).



Figure 3: Custom-made coring tool and sample of the SPF open-cell foam (left) and the coring tool together with the sample, the surface at the top, placed into the one Liter container (right).

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Instrumentation

DHS Large Autosampler used for the Micro-scale Chamber Method.

A Dynamic Headspace System – Large (DHS L) autosampler together with DHS L containers were used as an automated micro-scale chamber system (Figure 1). The containers (micro-scale chambers) are made of electro-polished stainless steel with an inert coating (Figure 3). Three chamber sizes are available: 250, 500, and 1000 mL. All have the same diameter and the same lids, and vary only in height. The chambers are air tight and have very low blank values and greatly diminished sink effects (detailed information below). Gas flow into the chamber is controlled via a

mass flow controller (5 -100 mL/min, accuracy $\pm 2\%$). The outlet gas flow is also recorded to verify chamber integrity and measure the actual sampling volume. Different purge gases can be used, for example, synthetic air, nitrogen or helium. Dry synthetic air was used for this work. The temperature in the micro-scale chambers can be set from just over room temperature to 200 °C with an accuracy of ± 1.0 °C. The DHS L system is automated using the GERSTEL LabWork Platform, automating the purging and sampling process. Analytes are purged from the micro-scale chambers onto sorbent tubes at user-selected time intervals, followed by thermal desorption-GC/MS analysis. The different steps in the automated micro-scale chamber method are shown in Figure 4.

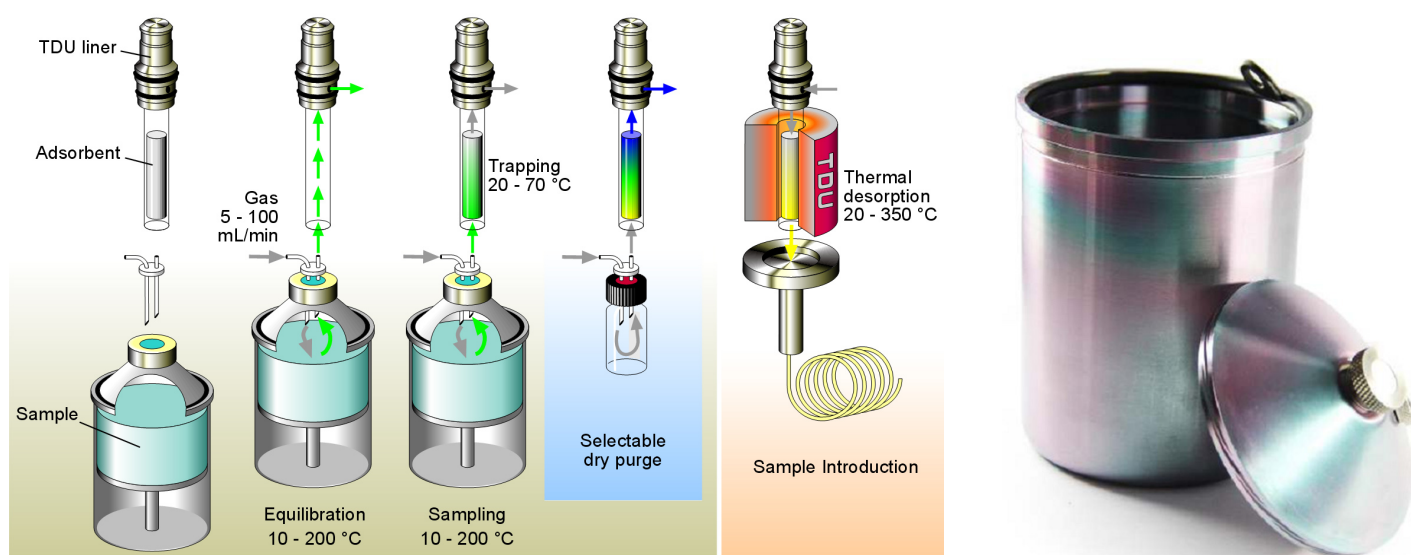


Figure 4: Automated micro-scale chamber method steps for a surface emission sample (left) with one liter DHS containers, made of electro-polished stainless steel and an inert surface coating (right).

Micro-scale chamber parameter	Value
Sample surface area A [m ²]	6.65 E ⁻³
Chamber volume above the sample [m ³]	1.05E ⁻⁴
Air exchange rate N [h ⁻¹]	28.6
Surface specific air flow q [m ³ m ⁻² h ⁻¹]	0.45
Temperature [°C]	23, 40, 65 (± 1)
Relative humidity [%]	0
Sampling Volume [L]	1 (closed-cell SPF) / 0.2 (open-cell SPF)

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Analysis Conditions LabWorks Platform

TDU splitless, desorption flow 51.5 mL/min
 20 °C (0.2 min); 720 °C/min to 270 °C (8 min)
 280 °C transfer heater

CIS split 34:1
 -40 °C (1.5 min); 12 °C/s to 280 °C (5 min)

Analysis Conditions Agilent 7890B GC

Column 30 m Rtx-5 Amine (Restek)
 $d_i = 0.25$ mm $d_f = 0.5$ μ m

Pneumatics He, constant flow = 1.5 mL/min

Oven 40 °C (2 min); 20 °C/min to 280 °C (4 min)

Analysis Conditions Agilent 5977 MS

MSD Scan, 40 - 550 amu

Calculation of Emission Factors (EF)

Emission factors of target compounds were quantitatively determined using calibration curves and emission equations below. Emission factors for TVOC and the blowing agent HFC-245fa were estimated using toluene equivalents according DIN EN ISO 16000-6 [5] and emission equations below.

The results of micro-chamber tests are reported as specific emission factors (EF) normalized to the specimen's exposed surface area according to ISO standards using Equation 1 below, the emission factor is also referred to as surface specific emission rate (SER):

$$EF = c \times \frac{N}{L} = c \times \frac{N \cdot V}{A} = c \times q$$

c: concentration of air sample [μ g m⁻³]

N: air exchange rate [h⁻¹]

V: Sampling Volume [m³]

A: Sample Surface Area [m²]

q: Surface specific air flow rate [m³ m⁻² h⁻¹]

Quantitation and Semi-quantitation

Target compounds detected following thermal desorption from the Tenax TA sorbent were identified and quantified with standard calibration methods as available in Agilent MassHunter Qualitative Analysis (B.07.02). Calibration solutions with different concentration levels were spiked into tubes containing Tenax TA® sorbent and then thermally desorbed into the GC/MS system. Due

to chromatographic co-elution between BDMAEE and TMAEEA and between DAPA and TMIPBA, two sets of calibration standards were prepared: standard 1 (BDMAEE, PMDTA, DAPA and TCPP) and standard 2 (TMIBPA and TMAEEA). Each calibration level was run in triplicate. Quantifier/qualifier MS ions, linearity, and calibration range were listed (Table 2). Good linearity was shown for all target compounds within the calibration range, with correlation coefficients ranging from 0.986 to 0.997.

Table 2: MS quantifier and qualifier ions, linearity, and calibration ranges for target compounds. Quantifier ions are the first of the set of three.

Target Compound (Acronym)	MS Ions	Linear Regression [R ²]	Calibration range [ng]
BDMAEE	58/71/42	0.997	25 - 1000
PMDTA	72/58/115	0.996	25 - 500
DAPA	58/85/70	0.989	25 - 500
TCPP	125/99/157	0.986	25 - 1000
TMIBPA	58/85/70	0.992	200 - 2500
TMAEEA	88/58/44	0.997	200 - 5000

For non-targeted VOC compounds, an 80% or better match was necessary for tentative identification using the NIST spectral library (Version 2.2, 2014, NIST, Gaithersburg, MD). Only peaks that met the library match minimum percentage were reported.

Background and Sink Effects

DHS Large containers with the coring tool inserted were conditioned at 150 °C for 2 hours in an oven before use. Following the analysis, the containers were washed with a diluted commercial cleaning solution and thermally conditioned. Common standard methods require that either background levels for VOCs of interest should be 10% or less of the lowest levels of interest for actual samples, or TVOC values should be smaller than 20 ng/L and individual VOCs concentrations be smaller than 2 ng/L. Both requirements were met with the performed cleaning and conditioning steps.

In this application, the lowest level standard tube is loaded with 25 ng of each compound. Compared to this level, the combined background of the DHS L vessel and coring tool was very low, with no direct target compound interference (Figure 5). The toluene equivalent TVOC value of the background was 9.5 ng/L, significantly below the 20 ng/L limit. The background peaks observed correspond to low molecular weight siloxanes, some of which could originate from column and/or septum bleed.

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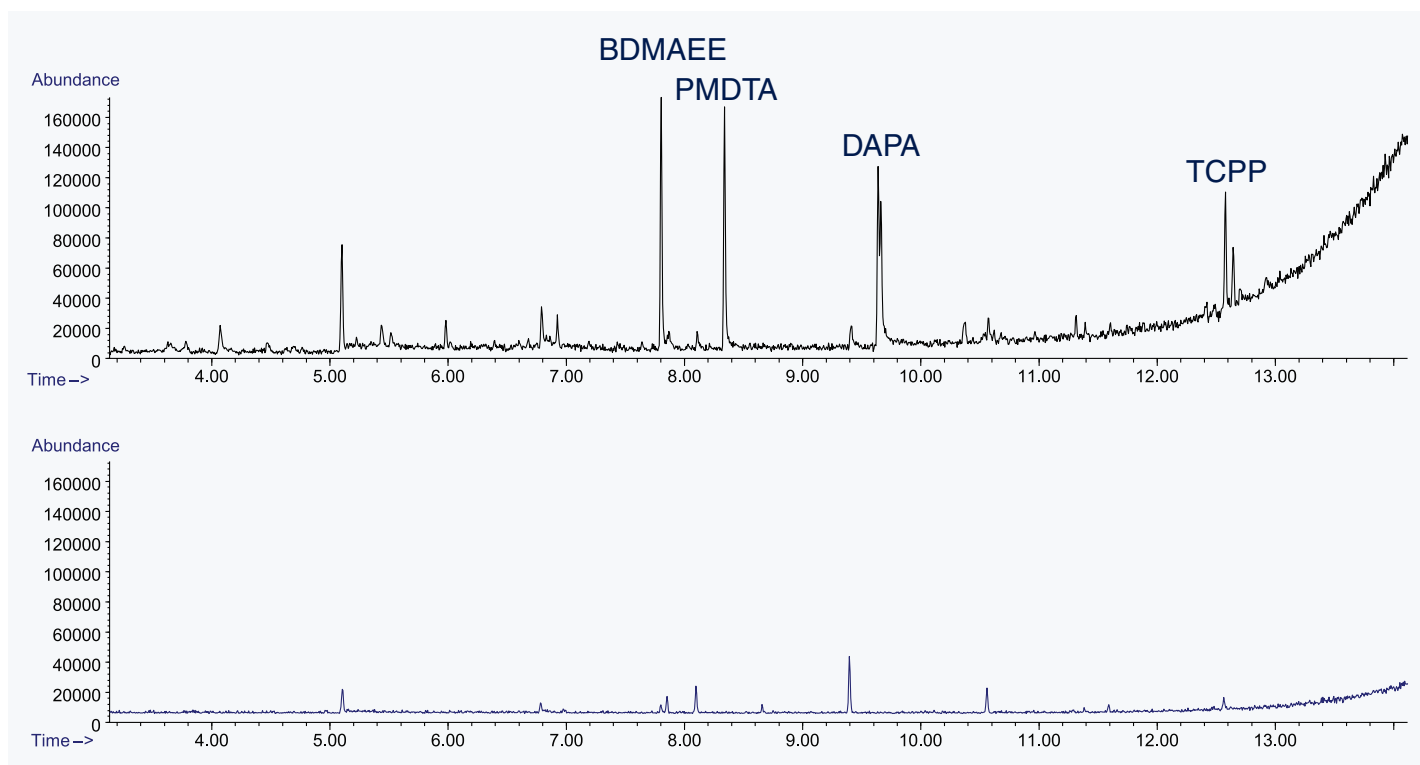


Figure 5: Lowest level SPF standard (25 ng per TD tube, top) compared with the background of the DHS Large one liter container the coring tool inserted (65°C, 1 liter sampling volume, bottom chromatogram).

“Sink Effect” is a term that describes the adsorption/desorption characteristics of a test chamber system during use. Sink effects can lead to changes in analyte concentrations inside the chamber and therefore to incorrect results being reported. The sink effect can be related to the materials used to construct the chamber and is also related to the boiling point and vapor pressure of substances measured [6]. This means very volatile compounds have no/very low sink effects while less volatile compounds show more sink effects that might be also affected by the chamber’s construction.

DHS L vessels are made of stainless steel, electro-polished, and coated with either a commercial (Sulfinert®) coating or a proprietary inert coating; the former was used for the data presented here. Because of the commonality of these steps with sink effect counter measures employed by others, sink effects here were assumed to be minimized.

Direct Thermal Extraction based on the VDA 278 Method

Thermal extraction analysis performed using the VDA 278 method is widely used for material testing in the automobile industry to estimate the emissions of volatile organic compounds (VOC value) and condensable substances (FOG value). In our study, the meth-

od was adjusted for SPF samples. Small amounts of SPF Insulation were heated in a thermal desorption tube at a defined temperature and purge flow for a defined period of time. The volatile and semi-volatile compounds emitted during the process were cryofocused in a cold trap before being transferred to a GC column for analysis by GC-MS. A TDS A2 autosampler with a TDS 3 thermal desorption system were used for thermal desorption analysis and a CIS 4 was used as cold (concentrator) trap. All the apparatus parameter settings followed VDA 278 except desorption temperature and time, which were adjusted for SPF samples.

Thermal Extraction Parameters

Extraction temperature	23, 40, 65, 90, 120 °C (± 1.5 °C)
Transfer line temperature	280 °C
Extraction flow	82 ml/min
Cryofocusing temperature	-120 °C
Split ratio	60:1

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Results and Discussion

Micro-scale Chamber Method. Effect of Sample Thickness

The combined coring tool and sample holder used for this work can be adjusted to different sample heights, ranging from 1 to 9 cm. Samples were prepared in different heights, 3, 5, and 8 cm respectively, the exposed sample surface area was constant regardless of volume. The top surface "skin" of the SPF samples taken for the work reported here was always kept intact and was positioned at the top (sampling end) of the micro-scale chamber. Open-cell foam was chosen for this experiment because closed cell foam is known to have a stronger barrier at the surface that should make the effect of sample thickness less observable (see discussion below regarding emissions vs. time for both types of foam). The results are shown in Figure 6. Increased sample thickness provides more signal and more analysis sensitivity. This observation indicates that the emission for open cell foam is controlled by source-phase mass transfer (internal diffusion), meaning that the source-phase mass transfer coefficient is much bigger than gas-phase mass transfer coefficient [9]. Thus, the mass of analyte emitted through the top surface of the open foam sample increases with sample thickness, and consequently the specific emission rate also increases with the sample thickness (i.e., the emission rate grows with increasing sample mass and volume).

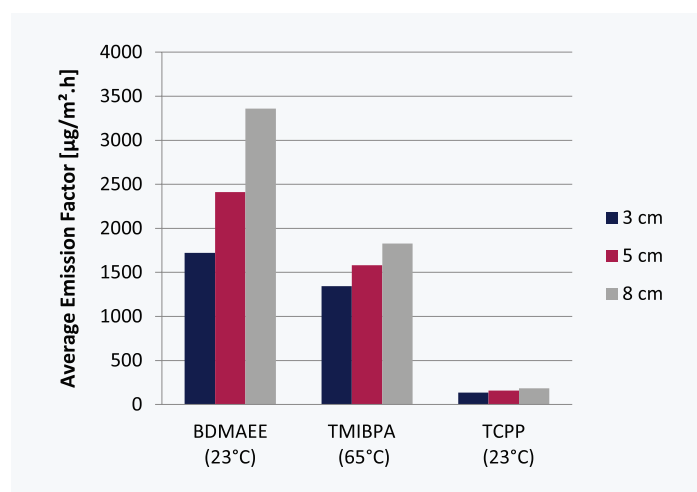


Figure 6: Emission factors [$\mu\text{g m}^{-2} \text{h}^{-1}$] of three open-cell samples with three different thicknesses but the same surface area at 23 °C or 65 °C. VOC's and SVOC's emitted from open- versus closed-cell SPF foam.

The primary VOC's and SVOC's emitted by the open-cell SPF samples at 23 °C were BDMAEE, tetramethylpropanediamine and 2,2,4,6,6-pentamethylheptane. The flame retardant TCP and amine catalyst TMIBPA were also detected at 23 °C. No TMIBPA or TCP were detected at 23 °C in previous work perhaps due to the smaller sample volumes used.

The primary VOCs emitted by closed-cell SPF samples at 23°C were trans-1,2-dichloroethylene and similar chlorinated alkenes or alkanes, such as 1-chloro-1-propene, 3-chloro-1-propene and 1,2-dichloropropane. Other VOCs as well as SVOC amine catalysts BDMAEE, DAPA and flame retardants were emitted in much smaller amounts. The blowing agent HFC-245fa was detected in the closed-cell sample, presumably because it is not readily released from closed-cell foams. Low molecular weight siloxanes were found, indicating the presence of silicone stabilizers [10]. Overall, the closed-cell SPF samples delivered lower emissions than the open-cell samples at the same temperature.

The VOCs identified in the closed cell foam differ substantially from those in the open cell foam, although compounds found in both foam types can be emitted into indoor air. Chlorinated VOCs (e.g. 1,2-dichloropropane) are thought to originate from flame retardants and their impurities [11]. N,N'-dimethylpiperazine is a thermal degradation product of TMAEEA. This amine catalyst was not detected in either sample, possibly because it is thermally labile. Detecting these target compounds at low levels is important because amine catalysts used to produce SPF insulation may have harmful effects [1], and chlorinated alkanes and alcohols are known hazards [10] (1,2-dichloropropane is classified as possible carcinogen). Tertiary amine catalysts have unique odors with typically parts per billion (ppb) odor thresholds [12], so low-level emissions of amines may lead to complaints about unpleasant odors.

Emission Factors Versus Time

Up to this point the focus of this discussion has been on looking at the performance of the chambers and not aspects of the overall automated system; repeated measurements over time are one use of such a system. Both open and closed cell SPF samples were measured repeatedly over time to observe changes in emission factors. The results can be found in Figure 7.

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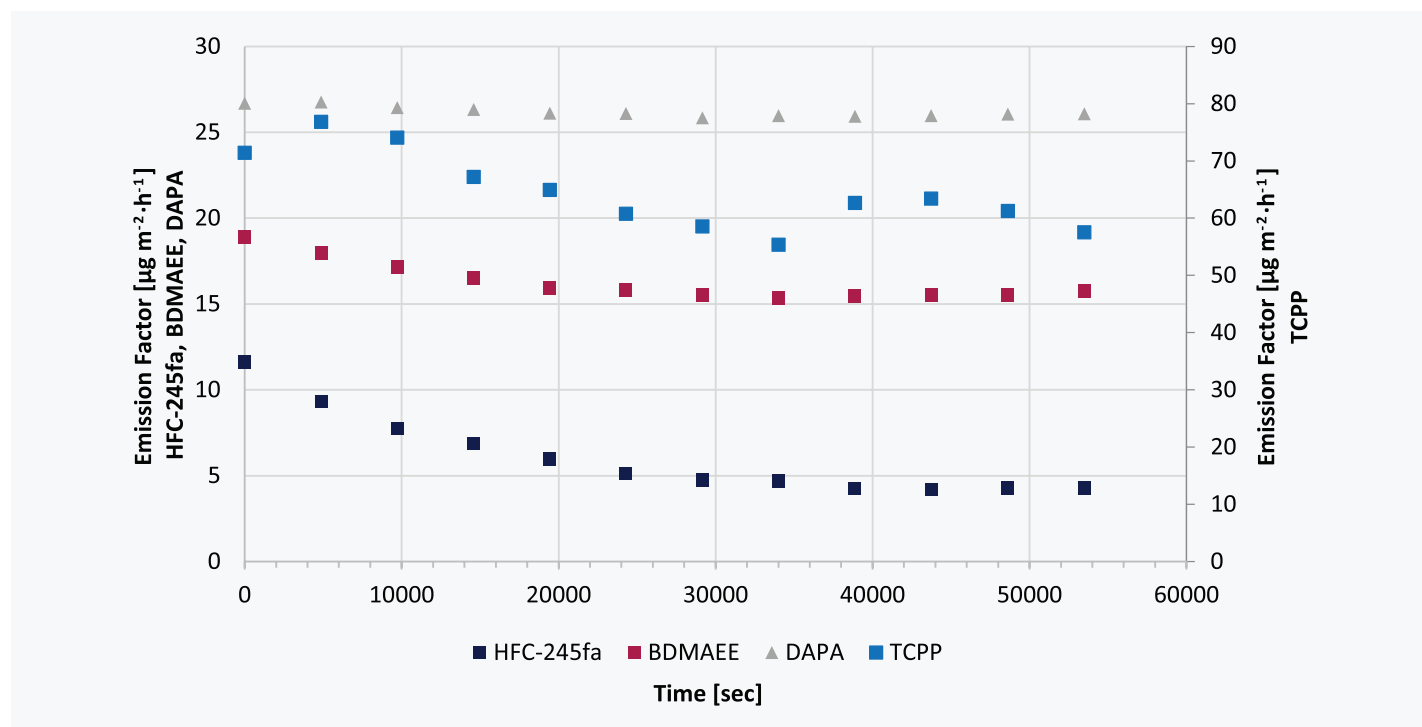


Figure 7: Emission factors as a function of time for HFC-245fa, BDMAEE, DAPA, and TCPP in closed-cell SPF.

The open-cell SPF sample showed relatively constant emissions over 12 hours, with a 3.0% percent RSD for BDMAEE and a 2.5% RSD for TCPP. For closed-cell samples, the emission factors of HFC-245fa and TCPP fell over time. After about eight hours the emissions of HFC-245fa reached approximately stable values. However, the flame retardant TCPP still did not reach a constant emission value within 12 hours, possibly due to a lower diffusion coefficient and higher molecular weight/higher boiling point. BDMAEE and DAPA had more or less constant emission factors over 12 hours, similar to open-cell SPF. For closed-cell samples, the relatively low emissions determined for amines and other target compounds might be improved with a higher sampling volume such as, for example, two liters.

Because these measurements were performed by an automated system, there was no need for an analyst to insert and remove TD tubes every hour over a period of more than 12 hours, as normally required. Additionally, the analyses were performed by the system with precise control of time, flows and temperatures. All data were logged by the system for documentation and traceability.

Emission Factors at Elevated Temperatures

The emission factors of the amine catalysts, flame retardant and blowing agent (closed-cell sample only) increased dramatically at

elevated temperatures. In the open-cell sample, TMIBPA could only be quantitatively determined at 65 °C. At each temperature, replicate measurements were stable over the measurement period (3 hours). This constant emission suggests emission controlled by source-phase mass transfer (internal diffusion) in the open-cell sample, as was also observed in the previous emission vs. time work above.

In the closed-cell sample, emissions of all target compounds also increased at elevated temperatures. Replicate measurements were constant at 40 °C during three measurements (3 hours), which also suggest internal diffusion controlled emission. Replicate measurements over three hours at elevated temperature (65 °C) showed a decreasing trend. This trend may indicate that target compound concentrations in the sample are depleted over the course of the emission tests. If this were true, heating a closed-cell sample to 65 °C for several hours may reduce emissions below observable levels.

Direct Thermal Extraction Method based on VDA 278

Method development was carried out for SPF insulation samples based on the VDA 278 method, and the resulting data was qualitatively compared with micro-scale chamber data. The aim was to establish an easy and quick test method to complement mi-

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cro-scale chamber measurements for quality control and product development of SPF insulation. Edge and surface effects were also studied using this direct thermal desorption method.

Qualitative Comparison of Results obtained using VDA Method 278 and Micro-scale Chambers

Pieces of SPF insulation were cut using a customized tool and placed in TDS tubes. Samples were analyzed at 23 °C, 40 °C and 65 °C (like the micro-scale chamber experiments) and two additional temperatures at 90 °C and 120 °C as specified in the VDA 278 method for VOC and FOG analysis, respectively. Each temperature was held for 30 min. Helium was used as carrier gas and thermal extraction was performed at a flow rate of 80 ml/min. During the extraction, VOCs and SVOCs were transferred from the sample and cryofocused on a deactivated glass wool substrate in the CIS liner. After extraction, the CIS liner was heated very quickly and the cryofocused analytes transferred onto the GC column for

GC-MS analysis.

As seen in the micro-scale chamber (DHS L) results, open-cell samples exhibited higher emission levels for VOCs than closed-cell samples when analyzed by direct thermal extraction. The analytes BDMAEE, TMIBPA and TCPP) were determined at 23 °C in the DHS Large micro-scale chamber. When using direct thermal extraction, the temperature must be at least 40 °C in order to determine TMIBPA in the much smaller sample used. At 90 °C, the amine catalyst TMAEEA was also found, this compound was not detected even at 65 °C using the micro-chamber method. Finally, thermal extraction at 90 °C and 120 °C resulted in the column being overloaded with TCPP. Moreover, at 120 °C no BDMAEE was detected, most likely due to thermal degradation. In order to qualitatively compare results with the micro-scale chamber method, a direct thermal extraction temperature of 40 °C was deemed the most suitable for open cell samples (See Fig. 8).

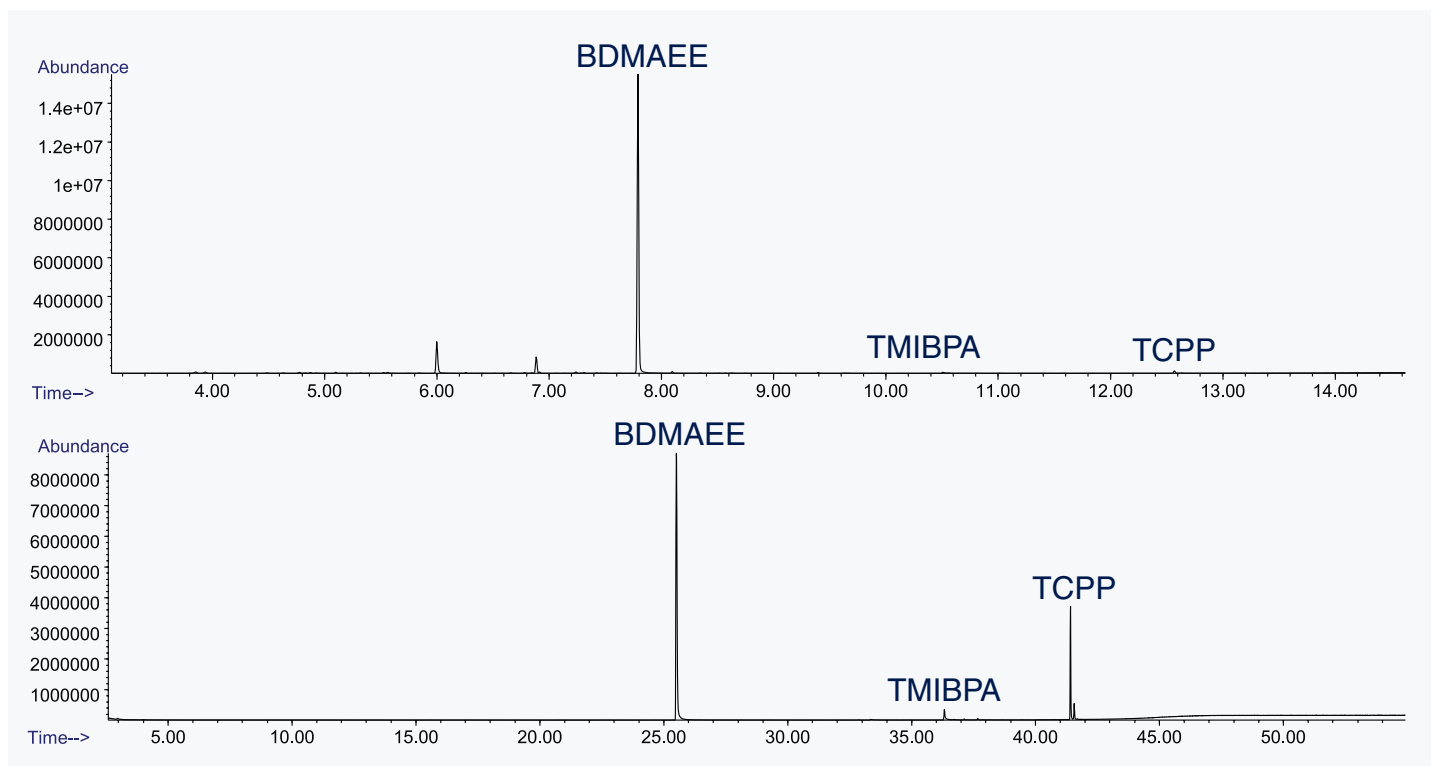


Figure 8: Chromatograms obtained from open-cell SPF insulation with micro-scale chamber method using DHS L at 23 °C (top) and direct thermal desorption using TDS3 at 40 °C (bottom).

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For closed-cell samples, at 23 °C and 40 °C, only the blowing agent HFC-245fa and small TCPP peaks were found. At 65 °C, BDMAEE and DAPA were also clearly detected. At 120 °C, the column is overloaded with TCPP. Consequently, the temperature chosen for direct thermal extraction of closed-cell samples was 65 °C.

Water Issue in Foam Samples

Open cell SPF samples can contain large amounts of water, which can in turn lead to ice blockage in the PTV inlet at the low temperatures used for cryofocusing. Also, water can negatively impact GC-MS system stability. In such a case, it is recommended to use the "Solvent Vent" function in the TDS to purge water out of the system at 20 °C for one minute before thermal extraction.

Conclusions

An automated micro-scale chamber system was used to determine chemical emissions from spray polyurethane foam insulation using a dynamic headspace autosampler for large samples (DHS Large). Blowing agents, amine catalysts and flame retardants used in open-cell and closed-cell SPF samples were clearly detected at 23 °C and with higher emission factors at elevated temperatures of 40 °C and 65 °C. A lower sampling volume was needed for higher-emitting open-cell samples than for lower-emitting closed-cell samples. Emission behavior and emission factors over time were easily obtained over 15 hour periods using the automated micro-scale chamber sampling system. The observed emission behavior indicates a source-phase mass transfer process (internal diffusion) happens in foam samples (particularly open-cell SPF insulation) and is the controlling factor for emission values. Closed-cell samples undergo two emission processes: At first a gas-phase mass transfer (external diffusion) process at the surface followed by a source-phase mass transfer process from the bulk.

Automation of these experiments has the obvious advantage of less involvement of the analyst and better reliability due to elimination or reduction of operator error. In addition, the major variables in a micro-scale chamber experiment – flow, temperature, and time – are all under computer control in the system presented here. Sampling times, temperatures, and volumes are determined with a very high degree of precision, which can be important for mathematical modelling of air concentration decay [5]. Computer control can also be used for transmission of method parameters between systems.

Direct thermal extraction using a Thermal Desorption System (TDS) was also used successfully to qualitatively and quantitatively evaluate SPF and other polyurethane foam samples, and in general the same compounds are observed in both methods (although for the samples analyzed in this work, the VDA 278 method had to be adapted and the system operated at temperatures lower than specified in the method to avoid over-loading the GCMS. The advantage of the modified VDA 278 method is the reduced sample size and faster overall analysis time. A drawback of direct thermal extraction might be higher RSD values, which is related to the reduced sample size.

To specify results as surface emission factors, micro scale chamber methods can better simulate real application conditions. Direct thermal extraction might be the right tool to estimate an emission potential of a given material, due to higher method temperatures and the more efficient extraction process. Therefore VDA 278 related methods could be especially useful for building material emission data bases to help identify sources of an observed indoor air pollution.

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