APPNOTE

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Determination of Volatile Organic Compound Emissions from Building Materials using Automated Micro-scale Chamber Dynamic Headspace Sampling

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Keywords

Dynamic Headspace Large (DHS L), Gas Chromatography-Mass Spectrometry (GC-MS), Material Emissions, Volatile Organic Compounds (VOCs)

Abstract

There is growing concern that VOC emissions from materials used indoors in buildings should be monitored to ensure that building occupants are not exposed to potentially harmful chemicals. Monitoring can be absolute (determining, for example, emission rates in micrograms per square meter-hour), or relative (e.g., does one building product emit more or less than others). Automating the sampling process removes efficiency barriers associated with these types of studies when using environmental test chambers or even micro-scale chambers to monitor the potential impact of VOC emissions on indoor air quality.

In this study, the Dynamic Headspace (DHS Large) system with a 1 L sampling vessel was used to monitor volatile organic compound (VOC) emissions from building materials. The DHS large can be set up to perform a single dynamic headspace sampling under set conditions or to sample multiple times from the same vessel, providing near real time monitoring of the sample's volatile emission profile.

Introduction

Widely diffused indoor air pollutants include VOCs emitted from building materials, furniture, and other household products. These VOCs include numerous compounds, such as alcohols, for example 2-ethyl-1-hexanol, aldehydes, for example formaldehyde, ketones, for example methyl isobutyl ketone, hydrocarbons, for example toluene, and halogenated hydrocarbons, such as, for example chloroform. These pollutants migrate into indoor air and can accumulate in occupants over time leading to adverse health effects that may include headaches, dizziness, nausea, fatigue, and more. In addition, some VOCs are known to have carcinogenic, mutagenic, and teratogenic properties [1,2]. Efficient monitoring of building materials for VOC emissions can help prevent use of materials that may lead to inferior indoor air quality and associated risk to occupants.

Environmental test chambers and micro-scale chambers are commonly used to measure the emissions of building materials into indoor air. The use of these chambers is outlined in many standard methods, such as ASTM D7706, D6670, D5116, and ISO methods 16000-28 and 12219-1. A barrier to more widespread adoption of these sampling vessels is the lack of automation as these types of chambers usually require off-line operation where a sorbent tube or DNPH cartridge (for formaldehyde) is manually placed at the outlet of the chamber to collect a specified volume of air pumped through the system. Afterwards the tube/cartridge must be manually removed and stored for later analysis.

The GERSTEL DHS Large provides the only automated sampling chamber solution for efficient determination of material emissions. DHS L enables analysis of heterogenous or bulk samples of up to 1 L in volume without the need for cutting, grinding or other means of homogenization, normally required when taking smaller representative samples. Absolute emission rate measurements

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can be determined as well as sample-to-sample variations in emissions, with the latter being of great value for QC and related applications. Both approaches are discussed in the above-mentioned standards.

Experimental

Instrumentation

GERSTEL MPS robotic sampler, GERSTEL Thermal Desorption Unit (TDU 2), GERSTEL Cooled Inlet System (CIS 4) with LN_2 option, GERSTEL Dynamic Headspace Large (DHS L), Agilent 8890/5977B GC-MSD

Analysis Conditions

TDU	splitless
	40 °C; 720 °C/min to 280 °C (3 min)
CIS	glass bead liner
	solvent vent (50 mL/min), split 20:1
	-120 °C; 12 °C/sec to 280 °C (3 min)
Pneumatics	He, P_i = 7.07 psi
	constant flow 1 mL/min
Column	30 m Rxi 5-MS (Restek)
	d_i=0.25 mm, d_f=0.25 µm
Oven	40 °C (2 min), 15 °C/min to 280 °C (2 min)
MSD	full scan, 40 – 350 amu

Analysis Conditions DHS

Trap	Tenax TA
Incubation	40 °C (5 min)
Sampling	sample 40 °C
	trap 25 °C
	volume 1200 mL (20 mL/min)

Analysis Conditions DHS Off-gassing Series

Trap	Tenax TA
Incubation	30, 40, and 50 °C (5 min)
Sampling	sample 30, 40, and 50 °C
	trap 25 °C
	volume 600 mL (20 mL/min)

Sample Description

Carpet, wallpaper, floor tiles, and contact paper purchased from a local store. All materials had self-adhesive backing.

Sample Preparation

A 75 x 110 mm rectangle was cut from each sample. The backing was removed, and the material was adhered to a metal coupon with the same dimensions to simulate adhering the material to a surface. The coupon was placed in the 1 L DHS L vessel for extraction. Figure 1 shows a sample of the coupon with the 1 L DHS L vessel.

Figure 1: Contact paper sample on the coupon with 1 L DHS L vessel.

Standard Preparation

Standards of methyl isobutyl ketone (MIBK) and toluene were prepared in methanol. One microliter of standard was spiked onto the glass frit of a TDU tube filled with Tenax TA®. Dry nitrogen was passed through the tube for 3 minutes at a flow rate of 50 mL/min to purge the solvent.

Results and Discussion

Figure 2 shows a picture of the system used for this study. Figure 3 shows the automated microscale chamber method steps.

Figure 2: DHS L system coupled with TD-GC/MS.

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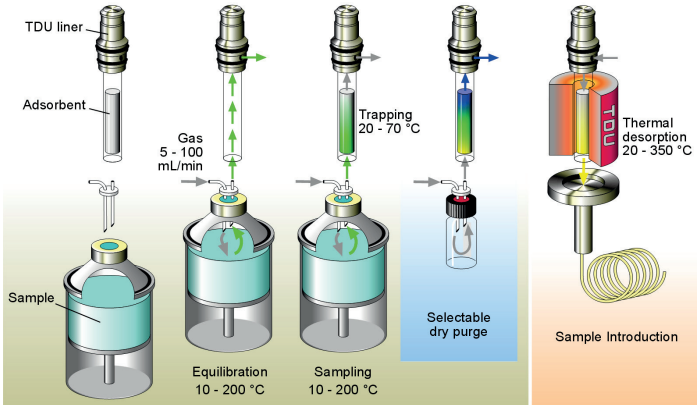

Figure 3: Automated microscale chamber method steps.

Figures 4-7 show the total ion current (TIC) chromatograms for the carpet, wallpaper, floor tile, and contact paper samples, respectively. The carpet and floor tile samples emitted lower amounts of VOCs than the wallpaper and contact paper samples. A wide variety of VOCs are seen across the samples including alcohols, aldehydes, esters, hydrocarbons, halogenated species, and ketones. All four samples emit compounds associated with adverse health effects. These include 1,2-dichlorobenzene and 4-phenylcyclohexene (carpet), phenol and 1,2-dichloropropane (wallpaper), 2-ethyl-1-hexanol and biphenyl (floor tile), and toluene and methyl isobutyl ketone (contact paper).

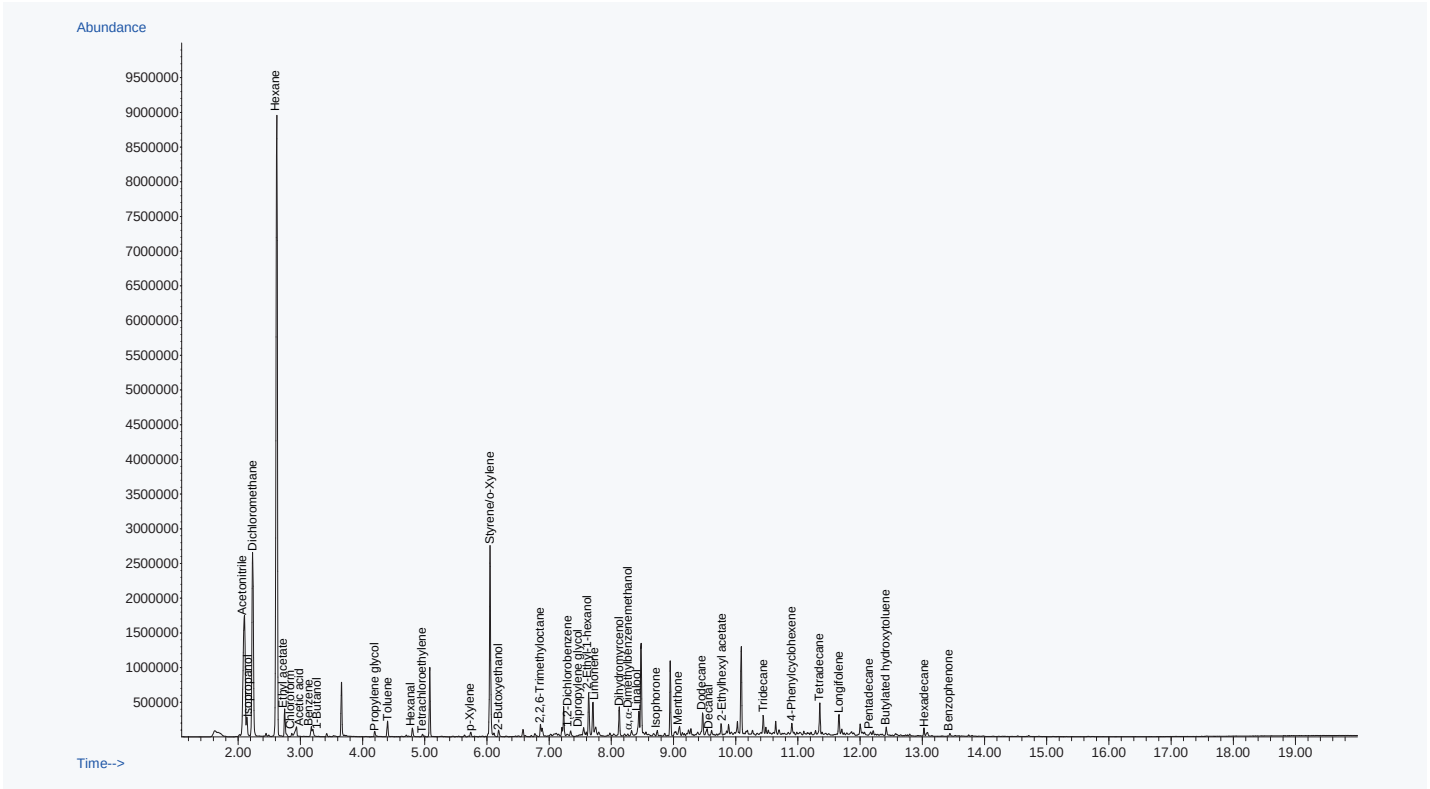

Figure 4: Total ion chromatogram for carpet sample.

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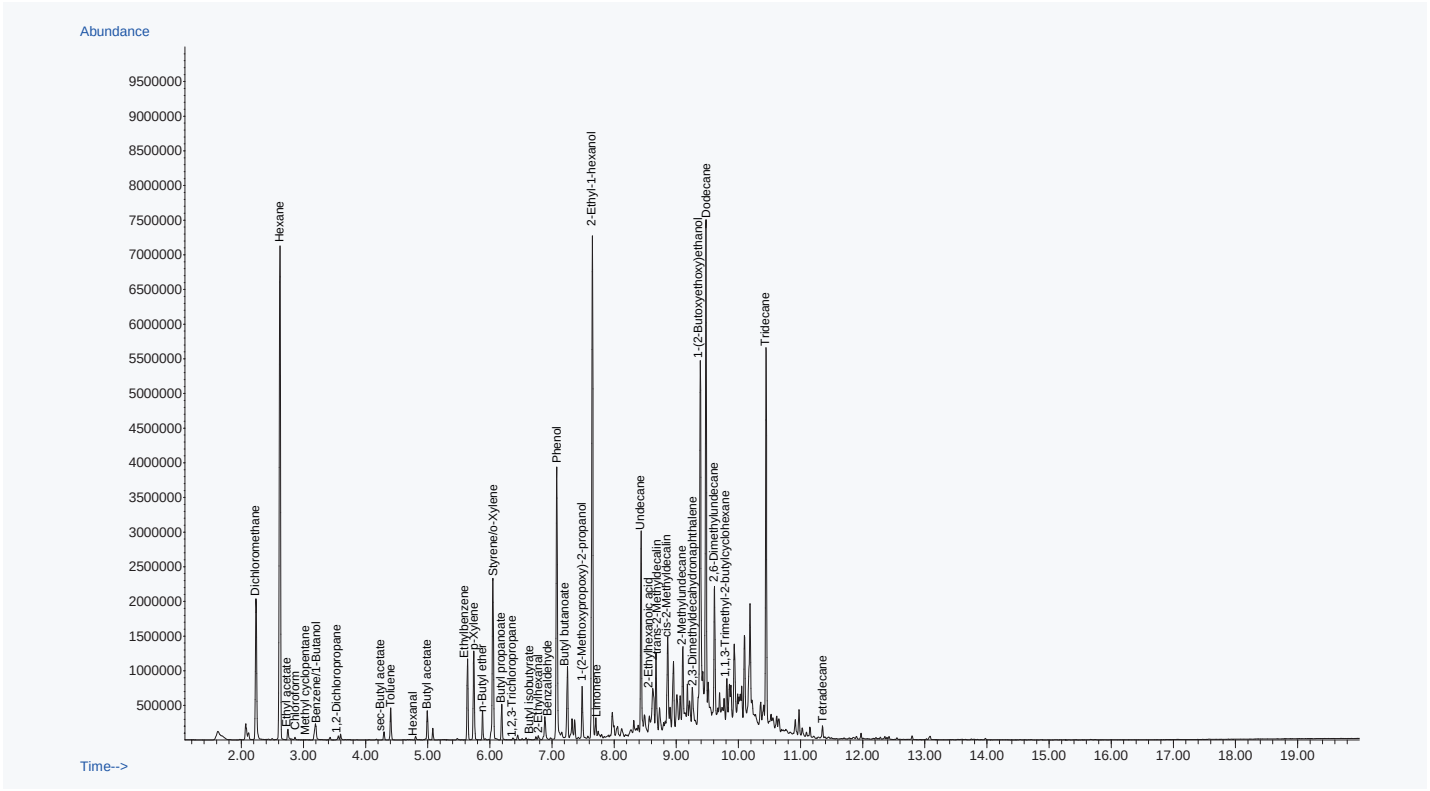

Figure 5: Total ion chromatogram for wallpaper sample.

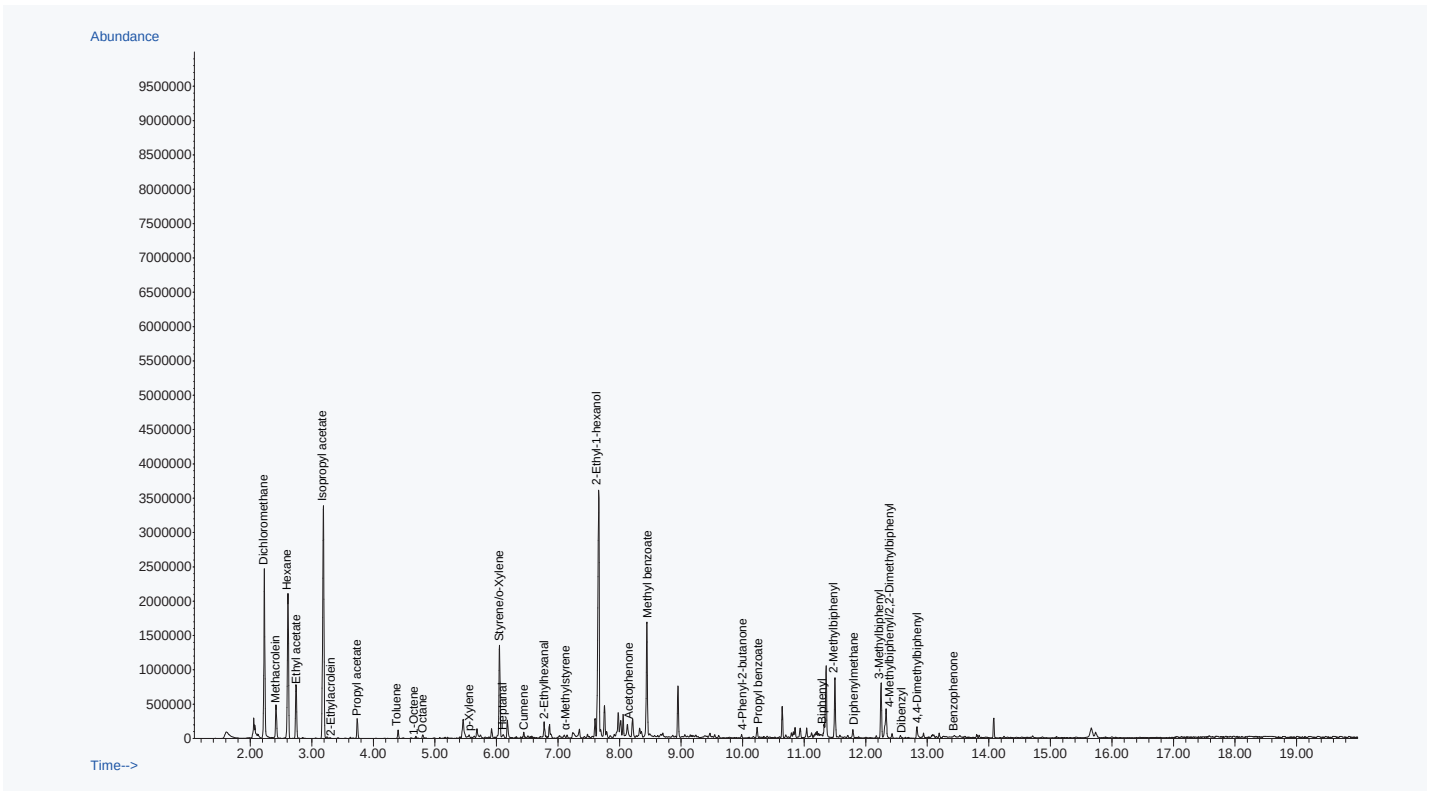

Figure 6: Total ion chromatogram for floor tile sample.

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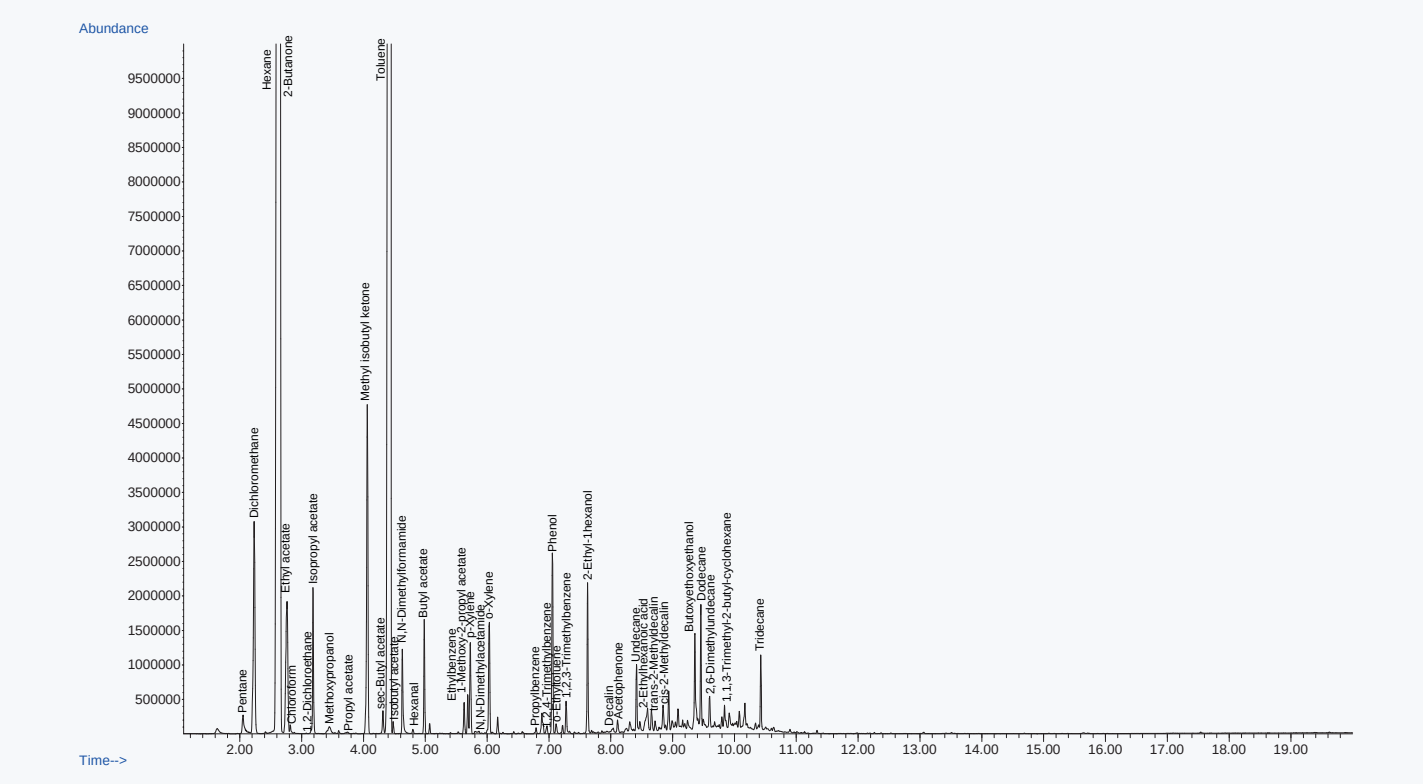

Figure 7: Total ion chromatogram for contact paper sample.

To further understand the VOC emissions, a set of experiments were performed to examine off-gassing from the contact paper sample over an extended period of time at different temperatures. The Maestro software enables near real time monitoring of the sample's emissions over a set period by allowing samples to be extracted by dynamic headspace using a different desorption tube for each extraction. Samples were extracted at 30, 40, and 50 °C over a period of two hours. A different Tenax TA® filled tube was used at each time-point, collecting a volume of 600 mL over 30 minutes each time. When the extraction series was complete, the tubes were thermally desorbed followed by GC-MS analysis.

Tables 1 and 2 show quantitative results for toluene and methyl isobutyl ketone off-gassing, respectively. At temperatures above 30 °C toluene and methyl isobutyl ketone levels are elevated. For both compounds, the amounts steadily increase in the first 90 minutes, but level off after about 2 hours. Over the two-hour period, a total of 84 - 1,796 ng/g of toluene and 14 - 201 ng/g of methyl isobutyl ketone was emitted per liter of gas for the temperature range studied.

Table 1: Quantitative results for toluene off-gassing from the contact paper in ng/g.

Time [min]	30 °C	40 °C	50 °C
30	13.6	262	146
60	48.2	881	937
90	65.6	1,411	1,521
120	73.5	1,756	1,692
Total over 2 hrs	201	4,310	4,298
Total per liter	83.7	1,796	1,791

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Table 2: Quantitative results for methyl isobutyl ketone off-gassing from the contact paper in ng/g.

Time [min]	30 °C	40 °C	50 °C
30	4.02	14.4	13.4
60	8.20	49.5	87.5
90	10.1	85.3	170
120	10.4	115	212
Total over 3 hrs	32.7	265	483
Total per liter	13.6	110	201

In micro-chamber testing, emission factors are sometimes used to express the VOC amount emitted as a function of the test item surface area. The emission factor (EF), sometimes referred to as specific emission rate, is calculated using the equation below:

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

c: concentration of air sample [µg/m^{-3}]
N: air exchange rate [h^{-1}]
V: sampling volume [m^3]
A: sample surface area [m^2]
q: surface specific air flow rate [m^3 m^{-2} h^{-1}]

Figure 8 shows the emission factor for toluene in the contact paper as a function of time at temperatures of 30, 40 and 50 °C. At 30 °C, the toluene level is fairly constant with an average EF value of 117 µg/m^2 h. At 40 and 50 °C, the toluene EF reaches a maximum at 120 minutes.

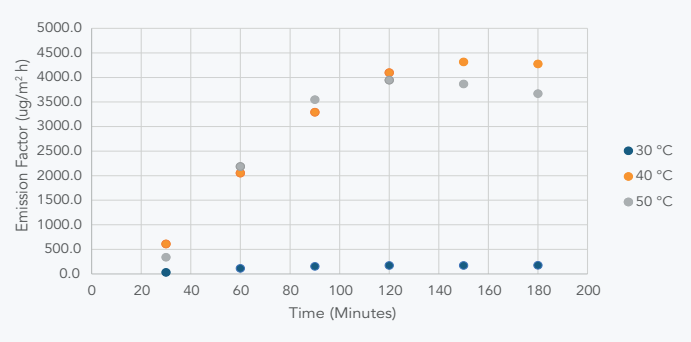

Figure 8: Emission factor for toluene in contact paper as a function of time at 30, 40 and 50 °C.

Figure 9 shows the emission factor for methyl isobutyl ketone in the contact paper as a function of time at temperatures of 30, 40 and 50 °C. At 30 °C, the methyl isobutyl ketone level is fairly constant with an average EF value of 19.1 µg/m^2 h. At 40 and 50 °C, the methyl isobutyl ketone EF reaches a maximum at 120 minutes.

The average emission factors for toluene are 6-15 times higher than for methyl isobutyl ketone, depending on the temperature.

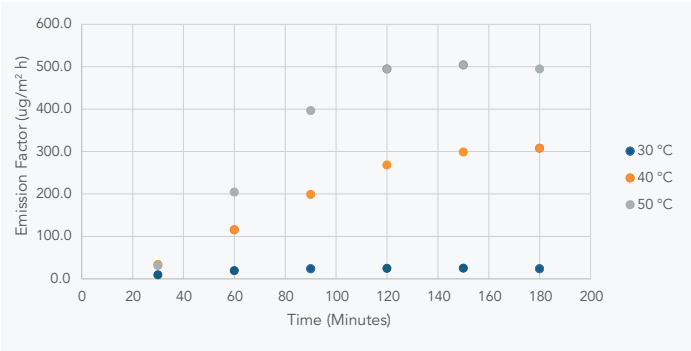

Figure 9: Emission factor for methyl isobutyl ketone in contact paper as a function of time at 30, 40 and 50 °C.

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Conclusions

The DHS L is the only system that allows for automated, efficient, and reliable monitoring of VOC emissions from building materials. The Maestro software allows for multiple extractions from the same vessel which can be used to monitor off-gassing of materials over time. Several classes of VOCs were identified including some with associated health risks. The off-gassing experiment showed that the amounts of toluene and methyl isobutyl ketone increased in the first 90 minutes and then reached a steady state. The system provides an easy means of obtaining time related volatile emission profiles from building materials, while eliminating the manual trap swapping required when using environmental test chambers or micro-chambers. If multiple samples need to be analyzed, the GERSTEL DHS Large autosampler can accommodate up to 11 sample vessels.

References

[1] US EPA; OAR. Introduction to Indoor Air Quality; EPA United States Environmental Protection Agency: Washington, DC, USA, **2016**.

[2] WHO Regional Office for Europe. WHO Guidelines for Indoor Air Quality: Selected Pollutants; WHO: Copenhagen, Denmark, **2010**; Volume 35.