

# Assessing the shelf-life of a prototype reference material for product emissions testing

Cynthia Howard-Reed<sup>1,\*</sup>, Zhe Liu<sup>2</sup>, Steve Cox<sup>2</sup>, Dan Samarov<sup>1</sup>, Dennis Leber<sup>1</sup>, and John Little<sup>2</sup>

<sup>1</sup>National Institute of Standards and Technology, Gaithersburg, MD USA

<sup>2</sup>Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA USA

\* *Corresponding email: chreed@nist.gov*

## SUMMARY

The National Institute of Standards and Technology (NIST) and Virginia Tech (VT) are developing a volatile organic compound (VOC) reference material to validate product emissions chamber testing. To verify the storage method of the material and determine its potential shelf-life, a series of tests was completed to measure the film's emission rates after storage times of up to 6 months. The emission rate of toluene was measured from each film in a 50 L stainless steel chamber after storage times of 1 day, 13 days, 23 days, 41 days, 62 days, 104 days, 139 days, and 181 days. Although an inverse relationship between material sample age and toluene emission rate was observed at 2 h and 24 h, the difference in the amount of toluene emitted from each of the different aged samples becomes less evident and eventually statistically indistinguishable at 48 h and beyond.

## IMPLICATIONS

As demand increases for low-emitting materials and labeling programs proliferate, a material with a known emission rate will improve the measurement process for laboratories to independently validate the performance of their test chambers. Before such a reference material can be used in practice, many challenges need to be resolved including the stability of its emission rates during shelf-life.

## KEYWORDS

Volatile organic compounds, test method validation, product certification

## INTRODUCTION

Currently, there is no commercially-available reference material that laboratories can use to validate their emissions testing chambers. The National Institute of Standards and Technology (NIST) is collaborating with Virginia Tech (VT) to develop a homogeneous material with a known emission rate that mimics a real building material. The prototype material consists of a polymer film that is loaded with a specific VOC (currently toluene) through a sorption/diffusion process. The loaded polymer has an emission profile similar to a typical "dry" building material (e.g., sheet flooring) that can be measured in small chambers commonly used for emissions testing. After loading, the film is sealed in aluminum foil and maintained at temperatures less than  $-20$  °C to mitigate the loss of toluene. The material has undergone extensive testing with promising results that demonstrate acceptable within and between laboratory consistency (Cox et al., 2010; Howard-Reed et al., 2011). However, earlier tests have indicated a possible sample age effect. The objective of this study was to determine the change in emission profile of a toluene sample over a shelf-life of 6 months.

## METHOD

For this study, a single batch of eight polymethyl pentene films (6 cm x 6 cm) were loaded with toluene as described by Cox et al. (2010) and by Howard-Reed et al. (2011). The mass of toluene added to each film in this batch at equilibrium was  $720 \mu\text{g} \pm 0.04 \%$  as measured using a microbalance. The initial toluene concentration in the film was determined to be  $7.89 \times 10^5 \text{ mg/m}^3 \pm 0.04 \%$ .

Once the films reached equilibrium (after approximately 10 days of toluene loading), they were individually removed from the loading vessel and double-wrapped in aluminium foil. The wrapped samples were sealed in a plastic bag and placed in a cooler with dry ice ( $\approx -78 \text{ }^\circ\text{C}$ ). The film at this stage is defined to be 0 days old. Preparing each sample for storage takes approximately 0.5 min to 1 min to complete. Samples were shipped overnight in the dry ice cooler to NIST, where they were placed in a freezer at  $-20 \text{ }^\circ\text{C}$ .

The emission rate of toluene from each film was measured in the same stainless steel chamber (volume of  $0.051 \text{ m}^3$ ) for each test. The chamber was operated with a mixing fan at a temperature of  $23 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$ , relative humidity of  $50 \text{ } \% \pm 0.1 \text{ } \%$ , and an airflow rate of  $0.065 \text{ m}^3/\text{h} \pm 0.002 \text{ m}^3/\text{h}$ . Five minutes prior to starting the test, the sample film in its packaging was removed from the freezer. The experimental time zero for the chamber test was the time the sample was removed from the packaging and placed in the chamber. The film was positioned in the center of the chamber using an aluminum frame that allowed both sides of the film to be exposed ( $2 \text{ surfaces} \times 6 \text{ cm} \times 6 \text{ cm} = 72 \text{ cm}^2$  total area exposed).

Chamber air samples were collected on sorbent tubes at various time intervals between 0.5 h and 240 h. A minimum of 10 duplicate samples were collected during each test. All sample tubes were analyzed using thermal desorption gas chromatography/mass spectrometry (GC/MS). The measurement uncertainty for the toluene concentration was determined at each chamber sample time.

On the first day after manufacture (sample age of 1 day), one of the eight films was randomly selected and subjected to the described chamber testing. This process was repeated for the remaining seven films such that the second sample was tested at 13 days, the third sample at 23 days, the fourth sample at 41 days, the fifth sample at 62 days, the sixth sample at 104 days, the seventh sample at 139 days, and the eighth sample at 181 days. In addition to measuring the chamber toluene concentration at specific times, total mass emitted was also determined by estimating the area under the emissions curve. Mass emission rates can be estimated assuming a quasi-steady-state concentration and the chamber airflow rate in the following mass balance equation:

$$E_{\text{ss},t} = QC_t \tag{1}$$

where  $E_{\text{ss},t}$  is the approximate emission rate at time  $t$  ( $\mu\text{g}/\text{h}$ ),  $Q$  is the chamber airflow rate ( $\text{m}^3/\text{h}$ ), and  $C_t$  is the chamber toluene concentration at time  $t$  ( $\mu\text{g}/\text{m}^3$ ).

## RESULTS

The toluene concentrations for sample 1 measured at 1 day and sample 8 measured at 181 days are shown in Figure 1. All samples followed a similar emission profile with most concentrations falling between these two limits. Uncertainties associated with each data point in Figure 1 were calculated based on propagation of errors associated with the air sample volume and analytical calibration parameters required to determine the chamber concentration

of toluene. The resulting expanded uncertainties for each measured concentration ranged from 6.0 % to 15 %.

As shown in Figure 1, the concentrations of toluene measured in the first few hours dropped by 35 % between the 1 day old sample and 181 day old sample. However, as sampling time further increased, the measured differences between the two samples reduced such that they were within the measurement uncertainty.

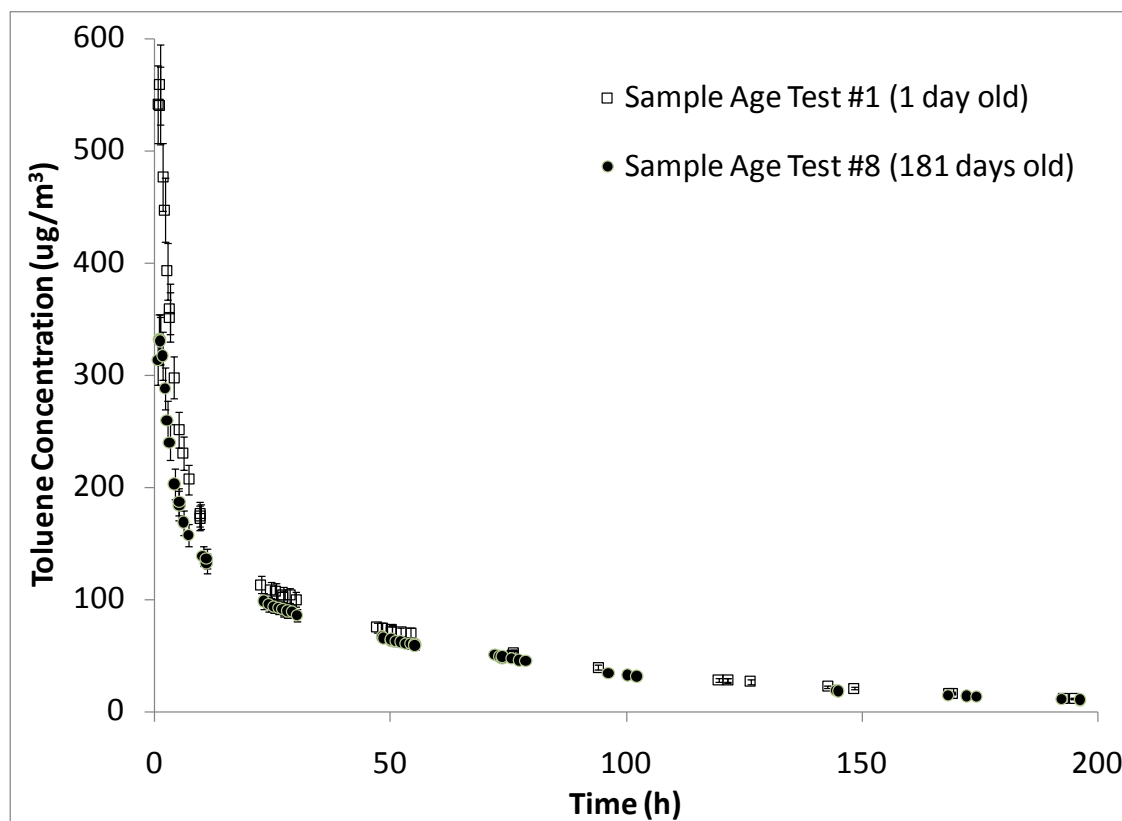


Figure 1. Toluene concentrations measured for a 1 day old and 181 day old reference film.

Figure 2 compares the concentrations measured at specific sampling times during the first 2 days of a chamber test for all 8 films. As shown in Figure 2, the toluene concentration measured at 2 h for the 1 day old sample and 13 day old sample are similar (within 0.1 %), but there is a consistent decrease in concentration at this sampling time for samples older than 23 days. As indicated above, this trend is less clear for the remaining sampling points. For example, the relative standard deviation (RSD) between all 8 films is 16 % at a sampling time of 2 h, and is 7.9 % and 7.7 % for sampling times of 24 h and 48 h, respectively. Later sampling points from 72 h to 192 h are shown in Figure 3. The RSD between all 8 films at these sample points range from 6.2 % to 9.0 %.

A linear regression model was fit to determine the presence of a sample age effect for toluene concentrations measured at different sampling time points. Based on this analysis, a significant ( $p$ -value  $< 0.05$ ) inverse relationship between material sample age and toluene concentration was only identified for chamber air samples measured at 2 h and 24 h. The degree of significance decreased as chamber sampling times increased beyond 24 h to the point the difference in toluene concentrations amongst the various sample ages became statistically indistinguishable. Further work is necessary to obtain an accurate estimate of the

chamber sample time for which the difference in toluene concentrations is no longer significant.

In addition to comparing toluene concentrations at specific sampling time points, the total mass emitted between 0 h and 192 h for each test is provided in Table 1. These estimates are based on area under the toluene emissions curve when the curve was fit using a model similar to that described in Howard-Reed et al. (2011). The expanded uncertainties in Table 1 are based on the uncertainty associated with the measured toluene concentration and chamber airflow rate. The mass emission estimates for the first six samples are within the measurement error of the estimate of the total mass loaded on each film (720  $\mu\text{g}$ ). Since this estimate includes the initial sample points, there is an expected marked decrease in mass emitted from the one day old to 6 month old sample. However, if the mass emitted excludes the initial 48 h data, the range of mass emitted is  $250 \mu\text{g} \pm 30 \mu\text{g}$  to  $306 \mu\text{g} \pm 38 \mu\text{g}$  with a relative standard deviation of 7.1 %.

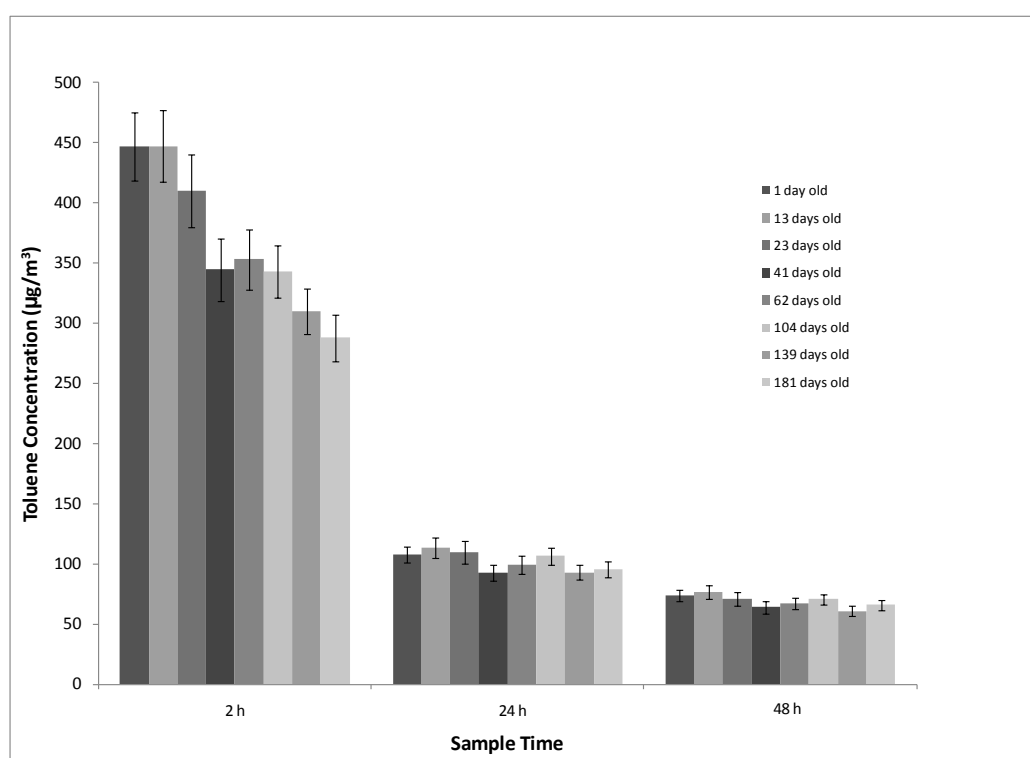


Figure 2. Toluene concentrations for eight different aged films during first two days of chamber test.

Table 1. Total mass emitted through first 192 h of each test.

Sample Age (days)	Mass Emitted ( $\mu\text{g}$ )
1	$748 \pm 90$
13	$764 \pm 95$
23	$724 \pm 93$
41	$640 \pm 83$
62	$666 \pm 83$
104	$674 \pm 84$
139	$588 \pm 71$
181	$625 \pm 75$

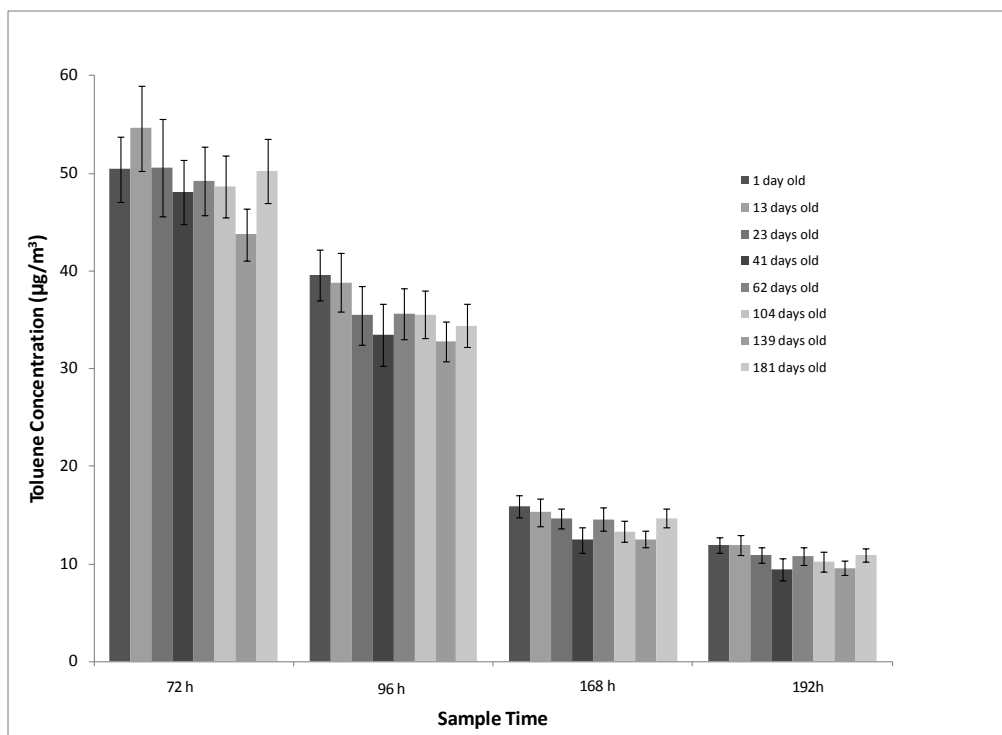


Figure 3. Toluene concentrations for eight different aged films during later sampling times during chamber test.

## DISCUSSION/CONCLUSIONS

The results from this study provide important information about the impact of shelf-life on the emission characteristics of the prototype reference film. Clearly the amount of toluene emitted in the first 24 h of a chamber test decreases with sample age. However, this effect diminishes at later sampling points. In fact, previous tests showed similar relative standard deviations between chamber concentrations for films within two weeks of sample age as were measured in this study for films tested over six months (Howard-Reed et al., 2011). To allow for shelf-life effects, the current form of the reference material would be better suited to assess laboratory chamber performance at sampling times later than 48 h during a chamber test. It should be noted that the earliest sample time for most standard test methods is 24 h after the specimen is loaded in the chamber, and is often not until 72 h (CDPH, 2010; ECA, 2005).

It is not clear what causes the initial toluene emission rate to change with time. One possibility is that the toluene is escaping the packaging during storage, despite maintaining the samples at  $-20\text{ }^{\circ}\text{C}$ . The subzero storage temperature could also be affecting the polymer structure properties such that the film behaves differently during the initial period of the chamber test. Another possibility is that the toluene is diffusing into sterically-hindered regions of the polymer material over time. This may have caused the older samples to have more mass remaining at 192 h than the newer samples. Future work is planned to investigate the “missing mass” using an alternative approach. For example, the microbalance used during sample loading could be used to measure the loaded film mass at different sample ages after storage.

## ACKNOWLEDGEMENT

The authors would like to thank John Mathew, Michelle Neese, and Steven Nabinger for their laboratory assistance during this project. The contributions of Virginia Tech to this work were

funded under Measurement Science and Engineering Research Grant No. NANB9D9154 from the National Institute of Standards and Technology.

## REFERENCES

- CDPH. 2010. Standard method for the testing and evaluation of volatile organic chemical emissions from indoor sources using environmental chambers, Version 1.1. California Department of Public Health.
- Cox, S.S, Liu, Z, Little, J.C, Howard-Reed, C, Nabinger, S.J, and Persily, A. 2010. Diffusion-controlled reference material for VOC emissions testing: proof of concept. *Indoor Air*, 20, 424-433.
- ECA. 2005. European collaborative action indoor air quality and its impact on man, harmonisation of indoor material emissions labeling systems in the EU, inventory of existing schemes. Report No. 24, EUR 21891 EN.
- Howard-Reed, C, Liu, Z, Benning, J, Cox, S, Samarov, D, Leber, D, Hodgson, A.T, Mason, S, Won, D, and Little, J.C. 2011. Diffusion-controlled reference material for volatile organic compound emissions testing: pilot inter-laboratory study. Submitted to *Building and Environment*.