

VOC Emissions from a LIFE Reference: Small Chamber Tests and Factorial Studies

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Content submitted to and published by:
Building and Environment
2012; Volume 57; 282-289

U.S. Department of Commerce
Dr. Rebecca M. Blank, Acting Secretary



National Institute of Standards and Technology
Patrick D. Gallagher, Director

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VOC Emissions from a LIFE Reference: Small Chamber Tests and Factorial Studies

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Abstract

A liquid-inner tube diffusion-film-emission (LIFE) reference was developed to quickly evaluate the performance of a chamber system for furniture/building material VOC emission tests. The reference has a constant emission rate determined by an analytical balance at typical temperature and relative humidity conditions, and is able to provide predictable concentrations in a chamber testing system. A 51 L stainless steel chamber was used to test the LIFE reference's performance at an air temperature of 23 °C with 50 % RH. Factorial studies of the LIFE reference's emission under various temperatures (10 °C, 23 °C and 30 °C) and relative humidities (33 %, 50 % and 70 %) showed that the emission rate is sensitive to the chamber environment. A numerical regression equation was developed to describe the impact of chamber temperature, relative humidity and their interaction on the reference's emission, with the difference between prediction and testing results of less than 6 % at 23 °C and 30 °C.

Keywords: VOC emission; reference material; chamber; furniture; indoor air quality (IAQ)

1. Introduction

The ability to accurately evaluate volatile organic compound (VOC) emissions from furniture and building materials requires reliable and consistent chamber emission tests. However, previous chamber comparisons show significant variations among laboratory testing results [1-6]. One means of addressing these inconsistencies is by using a reference material with an

independently known emission rate to evaluate the performance of a laboratory emission chamber. According to the Committee on Reference Materials of the International Organization for Standardization, a reference material is one that is “sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.” [7]. Once the reference material has been sufficiently tested and accepted, it could then be distributed to several different laboratories for testing in target chambers. If each laboratory follows the same chamber operation protocols, the resulting reference material emission rates can be compared. It is also possible to compare an individual laboratory’s emission rate to an independently determined value for the reference material. Recently, Virginia Tech (VT) and the National Institute of Standards and Technology (NIST) developed a prototype reference material that simulates the emission of a VOC from a building material [8]. The VT/NIST reference material consists of a polymethyl pentene (PMP) film loaded to equilibrium with toluene. The emission profile of the PMP reference in a ventilated chamber is similar to a real building material’s emission, which increases initially to a peak concentration followed by decay. The test procedures used for the PMP reference specify that chamber air samples are collected at 24 h, 48 h and 72 h. These sampling times are similar to those required by common material labeling tests. In the first 24 h, the peak emission rate is characterized by a transient profile that is apparently less repeatable, followed by the stabilization of the chamber air concentration. After 24 h, the emission profile and resulting chamber concentration are changing at a much slower rate, thereby reducing the uncertainty between the measured data and the predictions by a mass transfer model. Although the PMP reference has performed well in laboratory testing [8-10], it currently must be shipped and stored below a temperature of 0 °C to maintain the toluene in the film after loading. Currently, the

material is shipped on dry ice and stored in a freezer until ready for use, which complicates its handling.

To complement the PMP reference material and address some of the issues associated with shipping and storage, another reference, LIFE (liquid-inner tube diffusion-film-emission), was developed [11]. The LIFE reference consists of a Teflon tube that contains pure toluene liquid and an overlying headspace. There is a thin film (aluminum oxide melamine-impregnated paper) on top of the tube as a diffusion layer through which the toluene gas is emitted from the headspace. As long as there is liquid toluene in the tube, the LIFE reference can maintain a constant chamber toluene concentration after 6 h conditioning in the chamber. This design also simplifies shipping and storage, as the liquid toluene can be loaded into the bottle on site. The emission rate of the reference is measured with an analytical balance at the environmental conditions of interest, typically an air temperature of 23 °C and 50 % relative humidity. Originally, the LIFE reference was designed to evaluate the performance of a full-scale chamber. In order to better complement the current PMP film design for small chamber testing, the LIFE reference was scaled down.

Previous tests have shown that a chamber's environmental conditions of temperature and relative humidity have the potential to influence the emission of certain VOCs from furniture and other building materials. Thus, if a chamber is not operating at the specified environmental set-points for a test, the emission rate results could vary. For example, previous research shows emissions of most VOC species from building materials to increase with increasing temperature, while some of them are less influenced by temperature for long term emissions (after about 4 weeks) [12-15]. The potential impact of relative humidity on VOC emissions from building materials is less clear and appears to depend on the chemical species and type of material

[12,14,16-18]. To better understand the influence of these factors on the emission rate of the LIFE reference source, and use this information to better assess chamber performance, factorial studies of temperature and relative humidity were conducted.

2. Scaling LIFE Source for Small Scale Chambers

The original LIFE reference source was designed to evaluate the performance of a large scale chamber (e.g., 30 m³). For this study, a smaller 51 L chamber was used with an air change rate of 1 h⁻¹ (see Figure 1), requiring the emissions source strength to be reduced by using a small diameter emission opening in the LIFE source.

Figure 1. LIFE reference in a stainless steel chamber.

A dimensionless mass transfer model was developed previously to investigate the design principles of a toluene LIFE reference [11]. Several key assumptions were supported by the dimensionless modeling analysis: (1) the convective mass transfer resistance on the surface of the film can be ignored, compared to the diffusion resistance in the film, if the airflow speed of the chamber is > 0.014 m/s; and, (2) the emission of a LIFE reference becomes stable after a new reference is made once the inner-tube gas-phase VOC penetrates the film (about 0.4 h for toluene), thus, the film is under steady state emission conditions during the regular emission usage.

Based on these assumptions, a simplified emission model for the LIFE reference at steady state emission condition can be used. The mass balance equation describing the chamber toluene concentration is:

$$V \frac{dC_a}{dt} = \dot{m} - QC_a \quad (1)$$

where, \dot{m} is the reference's emission rate ($\mu\text{g/s}$); C_a is the toluene concentrations in the chamber ($\mu\text{g/m}^3$); V is the volume of the chamber (m^3); Q is the air flow rate in the chamber (m^3/s); and, t is testing time (s).

Results of previous dimensionless analysis of an unsteady-state mass transfer model [11] show that the influence of changes in the chamber toluene concentration on the emission rate through the film can be ignored. Thus, mass transfer of toluene molecules in the film can be treated as steady state diffusion during the testing period. The diffusion equation of toluene in the film can be simplified as a steady-state equation:

$$\frac{d^2C}{dx^2} = 0 \quad (2)$$

where, C is the toluene concentrations in the film ($\mu\text{g/m}^3$); and, x is the dimension of the diffusion direction (m).

The boundary conditions and initial condition of equations (1) and (2) are:

$$C|_{x=0} = K \cdot C_{\text{sat}} \quad (3)$$

$$C|_{x=L} = K \cdot C_a \quad (4)$$

$$C_a|_{t=0} = 0 \quad (5)$$

where, K is solid/gas phase partition coefficient of toluene in the film; L is the thickness of the film (m); and, C_{sat} is the toluene saturation concentration in the inner-tube gas-phase ($\mu\text{g/m}^3$).

Based on Fick's Law, emission rate of the reference is written as:

$$\dot{m} = -AD_m \left. \frac{dC}{dx} \right|_{x=L} \quad (6)$$

where, A is the emission area of the film (m^2); and, D_m is the diffusion coefficient of toluene in the film (m^2/s).

The analytical solution of the emission rate is derived as:

$$\dot{m} = \frac{-AD_m KC_{\text{sat}}}{\frac{AD_m K}{Q} (\exp(-\frac{Q}{V}t) - 1) - L} \quad (7)$$

The LIFE reference source was originally designed for full-scale chamber applications. The emission parameters, D_m and K , of the full-size film used in Equation (7) were previously determined to be $8.5 \times 10^{-12} \text{ m}^2/\text{s}$ and 704, respectively [11]. The predicted emission rate is shown in Figure 2. The predicted emission rate of the reference designed for the full-scale chamber is $5.76 \mu\text{g}/\text{s}$, while the measured emission rate is $5.56 \pm 0.01 \mu\text{g}/\text{s}$. These two values are within 3 % of each other. According to the calculation of equation (7), the rescaled film diameter is 1 mm with an expected emission rate of $0.004 \mu\text{g}/\text{s}$.

Figure 2. Model prediction of reference's emission rate.

The value of chamber airflow rate (Q) in equation (7) is a variable that might impact the emission rate of the reference. Applicable conditions of chamber airflow rate need to be analyzed to ensure the influence of the airflow rate on the emission rate can be ignored. This requirement can be written as $\frac{AD_m K}{Q} \ll L$ to determine the limitation of airflow rate in the small-scale

chamber. An air change factor (f) is introduced as $f = \frac{L}{AD_m K} Q$. The relationship between air

change factor and normalized emission rate for 1000 h of emission simulation ($\frac{\dot{m}|_{t=1000\text{h}}}{\dot{m}|_{t=0}}$) based

on equation (7) is shown in Figure 3, with the film diameter for small chamber reference of 1 mm. Figure 3 indicates that a higher f value reduces the emission rate difference between $t = 0$ h and $t = 1000$ h, but only by a maximum value of 0.2 % at the chamber airflow rate condition of 0.092 mL/min. Thus, the influence of chamber airflow rate on the re-scaled reference's emission can be ignored.

Figure 3. Relationship between air change factor and normalized emission rate.

3. Experimental method

3.1 Emission profile prediction

The LIFE reference applied for small-scale chambers consists of a 20 mm diameter Teflon tube with a height of 34 mm. 5 mL of liquid toluene with a purity of 99.8 % is injected into the tube. A 1.0 mm diameter aluminum oxide melamine-impregnated paper with a thickness of 0.15 mm is used on top of the tube as the diffusion film.

It is also possible to determine the LIFE source's emission rate using gravimetric measurements. Based on 94.5 h monitoring using an analytical balance having an accuracy of 10 μg at the environmental conditions of 23 $^{\circ}\text{C}$ and 50 % relative humidity, the reference's mass decrease is linear with time and its mass-time relationship can be described as:

$$m = m_0 - \dot{m}t \quad (8)$$

where, m and m_0 are the reference's mass and initial mass (μg), respectively.

The emission rate of toluene (\dot{m}) is the absolute value of the slope of mass-time relationship of the reference. The gravimetrically-determined emission rate of toluene is relatively constant with a value of 0.0412 ± 0.0001 $\mu\text{g/s}$. However, the emission rate is higher than the value predicted by equation (7) of 0.004 $\mu\text{g/s}$. It is possible that the emission parameters (diffusion and

partition coefficients) of the film at the millimeter scale are not the same as that of the original film size of centimeters, for which the emission parameters are measured. Because of the film's potential non-uniformity on the millimeter scale, the film's self-similarity criteria is needed to be investigated to address the minimum predictable size of the reference. Future work includes measuring the diffusion and partition coefficients at the millimeter scale. Due to this discrepancy, the emission rate is determined only by the mass weighing method and is used to predict the chamber toluene concentration.

The emission profile of the reference in a chamber can be described from equation (1) and (5), for which the solution is:

$$C_a = \frac{\dot{m}}{Q} (1 - \exp(-\frac{Q}{V}t)) \quad (9)$$

51 L stainless steel ventilated chambers were used to test the reference with an air change rate of 1 h^{-1} . The chamber toluene concentration increases from zero towards a steady state concentration ($C_{a,\text{steady}} = \frac{\dot{m}}{Q}$) as indicated by equation (9). At least four hours are needed for the chamber toluene concentration to approach steady state, which is $(2694 \pm 7) \mu\text{g}/\text{m}^3$.

Laboratories are measuring chamber concentrations, which are determined based on the mass balance equation (Equation 1). As this equation shows, the chamber concentration (and resulting measurement uncertainty) is directly dependent on the emission rate of the reference source (\dot{m}), air flow rate in the chamber (Q), volume of the chamber (V) and the duration of testing time (t). So called influence factors can also contribute to the uncertainties associated with real chamber testing in different laboratories. For example, the variation of temperature and relative humidity could affect the toluene saturation concentration (C_{sat}) and emission parameters in the film (D_m , K), which could impact the source's emission rate. In addition, uncertainties associated with the

sampling volume of air from the chambers as well as in the VOC analytical instruments and their calibrations are additional sources of error that could result in inconsistent measurements among different laboratory tests.

3.2 Chamber tests

To evaluate the performance of the re-scaled LIFE reference, two well-characterized 51 L stainless steel chambers are used. The mixing performance of both chambers have been verified using the procedure in ASTM D5116 [19] through tracer gas (sulfur hexafluoride, SF₆) testing. Following the ASTM D5116 procedure, the difference between the measured and predicted SF₆ concentration during a tracer gas decay was less than 5 %. The two chambers are located in an incubator for temperature control. Humidity was controlled by mixing wet and dry airstreams using mass flow controllers. For the performance evaluation tests, the temperature, relative humidity and chamber air change rate were set at 23 °C, 50 %, and 1 h⁻¹, respectively. The air supply and relative humidity control system are shown in Figure 4. The actual chamber control points are listed in Table 1.

Figure 4. Chamber environment control system.
Table 1. Actual chamber control points.

Both chambers were flushed with clean air prior to testing in order to make sure the chamber toluene background concentrations were less than 2 µg/m³ [10]. Mixing fans in both chambers were operated to maintain a uniform toluene concentration in the chambers.

Chamber 1 was used to compare the chamber testing results with those predicted by the mass weighing method. A stopwatch was used to measure the elapsed time of the experiment and was

started when the LIFE reference was put into the chamber. After loading, the chamber was sealed within 1 min to minimize the variation in the chamber environmental conditions and the toluene losses from the chamber during this loading period. To determine the chamber toluene concentration profile, duplicate samples were collected every 15 min to 30 min by pumping chamber exhaust air through Tenax TA tubes. All of the samples were analyzed by thermal desorption (TD) and gas chromatography with mass spectrometer (GC/MS). Standard deviations of the chamber testing results were calculated and the measured chamber toluene concentrations were compared with those predicted by equation (9). Repeatability of the test was validated by the same method at the same chamber environment.

In previous inter-laboratory studies, a PMP reference was tested in chamber 2. Therefore, a LIFE reference comparison was also operated in chamber 2 to investigate the consistency of the two different references. Chamber 2 was run at the same environmental set-points as chamber 1 which are the same as those used for the PMP reference tests. Duplicate samples were collected when the chamber was at steady state (4 h after the start of the tests).

3.3 Factorial studies of LIFE reference's emission

Temperature and relative humidity are two key parameters affecting a building product's emission rate. ISO 16000-9 Standard [20] specifies a temperature of $23\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ and relative humidity of $50\% \pm 3\%$. If a chamber is not operated within these set-points, the emission rate results may be compromised. Thus it is important to understand the sensitivity of the emission rate of the LIFE reference to these parameters.

Chamber 1 was used for the temperature and relative humidity factorial studies. Temperatures were set in the chamber at three levels $10\text{ }^{\circ}\text{C}$, $23\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$. For temperatures

of 10 °C and 23 °C, relative humidities of 33 %, 50 % and 70 % were used. For a temperature of 30 °C, the chamber tests were only operated at the relative humidities of 33 % and 50 %, because a relative humidity of 70 % at 30 °C is out of the range of the environmental control system. The design of the reference's factorial studies is listed in Table 2. For each temperature and relative humidity combination, the LIFE reference's emission rate was determined by mass weighing and also calculated based on steady state chamber concentration data by using the inverse of equation (9). The emission rate at each environmental set-point was calculated by the reference's mass decrease before and after the period when the reference was in the chamber. The steady state chamber toluene concentration was measured 6 hours after the chamber was loaded with the reference and sealed using the same sampling and analysis method previously described. The measured concentration was then compared with the value predicted by the emission rate weighed using the analytical balance. When the chamber environment was changed to a new set-point, the temperature and relative humidity were allowed to stabilize for at least 1 hour before starting a new test. All of the experiments were repeated at least once.

Table 2. Experimental design for reference's factorial studies.

Two-factor analysis of variance (ANOVA) method [21] was used for the analysis of the experimental data. SS_{RH} (sum of squares for factor RH), SS_T (sum of squares for factor T), $SS_{RH,T}$ (interaction between factor RH and T) and SS_E (error sum of squares) are the four parameters used to indicate the variability of the experimental data.

Mean squares (MS) are obtained by dividing the sums of squares (SS) by their associated degrees of freedom (df).

$$MS = \frac{SS}{df} \quad (10)$$

The F^* test statistics based on the appropriate mean squares follow the F distribution, which is written as:

$$F^* = \frac{MS}{MS_E} \quad (11)$$

The F^* values of factor RH main effects (α_i), factor T main effects (β_j), and interactions between factor RH and T ($(\alpha\beta)_{ij}$) are compared with the critical values of the F distribution at 95 % confidence level. For each factor, if its F^* value is larger than its critical value, the factor is identified having effect on the analyzed experimental data.

4. Results and discussion

4.1 Chamber evaluation results

The toluene concentration profile in Chamber 1 for normal testing under the temperature of 23 °C and relative humidity of 50 % is shown in Figure 5. The chamber testing results match the predictions using equation (9), which are based on the reference's mass measurement. Duplicate sample analysis shows the standard deviation for each data point. The maximum value of the standard deviation for this test was 3.6 %. Repeatability of the experiment is also confirmed in the figure. Steady state chamber toluene concentration (4 h results) differences between chamber testing results and mass predictions are 2.3 % for experiment 1 and 3.7 % for the replicate test.

Figure 5. Toluene concentration profile in Chamber 1.

A comparison of the LIFE reference and the PMP reference is presented in Table 3. The LIFE reference's chamber test was sampled at 6 h after the test started, when the chamber

toluene concentration was at steady state, while PMP reference chamber test was sampled at 24 h, 48 h and 72 h. The differences between the chamber toluene concentrations tested and those predicted for both references are less than 15 %, which supports the reliability of the chamber testing results for both reference material.

Table 3. Predictive accuracy for LIFE and PMP references.

4.2 Influence of temperature and relative humidity on reference's emission

The reference's emission rates under different combinations of chamber temperature and relative humidity are listed in Table 4.

Table 4. Experiment results for factorial studies on reference's emission.

The correlation of the reference's emission rate and temperature is shown in Figure 6. For each temperature set-point, different data points present the reference's emission rates under different relative humidities. Standard deviation for each data point (less than 5.81 %) shows the repeatability of the emission rate tests. Generally, a linear relationship between the emission rate and temperature is observed, with an R^2 value of 0.97 for the linear regression without taking relative humidity into consideration. Temperature affects the reference's emission rate due to the change in toluene saturation vapor pressure in the reference tube air and the diffusion coefficient of toluene in the film and solid/gas phase partition coefficient of toluene in the film. For a temperature range of $(23 \pm 1) ^\circ\text{C}$, the emission rate variation is less than 6.1 %, which is the uncertainty associated with the standard chamber testing method itself.

Figure 6. Correlation of the reference's emission rate and temperature.

Relative humidity has an apparently smaller effect on the reference's emission rate than temperature. The correlation of the reference's emission rate and relative humidity is shown in Figure 7. Standard deviation for each data point (less than 5.8 %) shows the repeatability of the emission rate tests. The increase of relative humidity from 33 % to 50 % reduces the reference's emission rate, while increasing the relative humidity from 50 % to 70 % reveals an interaction with temperature. For a temperature of 10 °C, the emission rate increases with increasing relative humidity from 50 % to 70 %, while at a temperature of 23 °C, an opposite trend is observed. The maximum emission rate variations in the relative humidity range of (50 ± 3) % are 2.8 % at 10 °C, 1.5 % at 23 °C and 1.4 % at 30 °C.

Figure 8 shows the results with absolute humidity on the x-axis, which ranges from 3.1×10^{-3} (kg water)/(m³ air) to 15.16×10^{-3} (kg water)/(m³ air). Because of the limitation of the environmental control system for the chamber, a larger relative humidity range is not achievable.

However, the emission rate difference ($\frac{\dot{m}_{\max} - \dot{m}_{\min}}{\dot{m}_{\text{RH}=50\%}} \times 100\%$) caused by relative humidity change is 182 % with the absolute value difference of 8.14 ng/s at 10 °C, but only 13 % at 23 °C and 8 % at 30 °C as shown in Figure 7. Because of the small variation in the emission rate over the relative humidity range from 33 % to 70 %, more testing set-points in this range are not considered necessary. Those data are analyzed in ANOVA model for detailed factorial studies and are addressed below.

Figure 7. Correlation of the reference's emission rate and relative humidity.
Figure 8. Correlation of the reference's emission rate and absolute humidity.

Since experimental data at 30 °C and 70 % RH is not available, the reference's emission rate data determined by the mass weighing have to be separated into two parts to conduct a partial study of factor RH (relative humidity) and factor T (temperature) main effects and interactions between RH and T for unequal sample sizes. Experimental data under the chamber temperature set-point of 10 °C, 23 °C and 30 °C with the relative humidity of 33 % and 50 % are collected as part I, while chamber temperature set-point of 10 °C and 23 °C with the relative humidity of 33 %, 50 % and 70 % are collected as part II. ANOVA analysis results for both parts are shown in Table 5 and Table 6.

Table 5. Factorial studies: part I.
Table 6. Factorial studies: part II.

All the factor RH and factor T main effects and interactions between RH and T are significant, with coefficients $F^*/F > 1$. Temperature is the dominant parameter, having a greater impact on the reference's emission than relative humidity.

The regression model describing the relationship between the LIFE emission rate and impacting parameters (factor RH, factor T and RH - T interactions) is fitted by a least-square method as follows:

$$\dot{m} = -2.72 \times 10^{-2} + 3.40 \times 10^{-3} T + 2.23 \times 10^{-4} RH - 1.77 \times 10^{-5} T \cdot RH \quad (12)$$

A comparison between regression and experimental results is shown in Table 7. The differences between regression and experimental results are less than 6 % for temperature conditions of 23 °C and 30 °C. However, at 10 °C, the differences between the regression model prediction and test results are greater than 26 %.

Table 7. Comparison between regression and test.

Figure 9 shows the chamber testing results for the factorial studies. For each temperature set-point, different data points represent tests at different relative humidity conditions. The measured chamber toluene concentrations match the weighing predictions for all the designed chamber temperature and relative humidity combination conditions. The horizontal and vertical error bars for each data present the standard deviation of predicted chamber concentration based on the average of measured emission rate (less than 9 %) and chamber concentration measurement (less than 32 %). Thus, for future application of the reference, a laboratory's ability to accurately control the chamber temperature and relative humidity can be revealed by comparing the measured concentration data and that predicted for the same environmental conditions.

Figure 9. Chamber tests in different environments.

4.3 Potential Confounding Factors

To investigate issues related to the stability of the Tenax TA sorbent that might influence the chamber testing results during the sampling and analyzing process, additional checks were made. For the experiments at the chamber environment of 10 °C, 33 % and 23 °C, 50 %, samples were taken with the sample flow rate of 100 mL/min, 200 mL/min, 300 mL/min, 400 mL/min and 50 mL/min, 100 mL/min, 150 mL/min, 200 mL/min, respectively. All the samples were analyzed by GC/MS to determine if the sample flow rate influences the toluene adsorption performance of the Tenax TA tubes. Idris et al. [22] reported that with the sample flow rate increasing from 50 mL/min to 200 mL/min, toluene adsorption performance on Tenax TA decreases at 25 % relative humidity and increases at 80 % relative humidity. Figure 10 shows the results at 10 °C,

33 % and 23 °C, 50 %. At each temperature, data are normalized by their average value. Duplicate sample analysis shows the standard deviation for each data point. However, there is no obvious impact of sample flow rate on the total adsorbed mass of toluene. For the sample flow rate between 50 mL/min and 400 mL/min, the analyzed results are on average within 5.1 %. For the reference's chamber evaluation tests and factorial studies, all the data are sampled in the flow rate range of 100 mL/min to 150 mL/min to standardize the procedure.

Figure 10. Tube analysis in different sample flow rate.

In addition, a direct injection experiment was run in the chamber and repeated to determine if the difference of relative humidity in the sampled air influences the toluene adsorption performance in Tenax TA tubes. A toluene permeation tube was used to generate a constant toluene flow into chamber 1. The temperature in the chamber was controlled at 23 °C, with the relative humidity at 33 %, 50 % and 70 %. Samples of steady state toluene concentrations in the chamber were taken 24 h after each change in the chamber relative humidity. Figure 11 shows the results of these tests, which reveals no dependence on relative humidity at 23 °C. The results match a previous report that showed Tenax TA to be a stable toluene sorbent that is unaffected by humidity [23]. This independent experiment also proved that the observed concentration differences in the chamber under different temperature conditions are due to the sensitivity of the reference to relative humidity and not to the measurement procedure.

Figure 11. Toluene injection experiment in the chamber.

5. Conclusion

A toluene LIFE reference originally designed for full-scale size chambers was scaled down for use in small-scale chambers. Emission tests were completed in 51 L stainless steel chambers to test the reference's performance. The difference between the chamber toluene concentration from the chamber testing and the model prediction is similar to that seen for a PMP toluene reference in the same chambers. However, the chamber testing time using LIFE reference is less than 6 h, which is much shorter than the PMP reference. Therefore, the LIFE reference might be useful for a quick evaluation of a chamber testing system before doing a longer test, while the PMP reference can provide more realistic tests in comparison to existing material emission testing protocols. Factorial studies of the LIFE reference investigated the impact of temperature and relative humidity on the emission rate of the reference. A numerical regression equation was developed to describe the influence of temperature, relative humidity and their interaction, with the difference between prediction and testing results less than 6 % at air temperatures of 23 °C and 30 °C. The LIFE reference is shown to be sensitive to the chamber environment, which may be useful in checking the environmental control accuracy of the chambers. The reference's emission variation under constant chamber testing conditions is less than 6.1 %. Also, chamber tests show the stability of the Tenax TA absorbent, which provides uniform results under different relative humidity (33 %, 50 %, 70 %) and sample flow rate (50 mL/min to 400 mL/min) conditions.

Although, Equation (7) was not valid with the previously determined diffusion and partition coefficients, the LIFE reference can still be useful for validating the performance of small-scale chambers. Some apparent advantages of the LIFE source include: (1) the reference is tested in an environmental chamber with a specific set of environment conditions (temperature and relative

humidity) following the same kind of measurement protocol as that for furniture or building material. No additional heating or air supply system is required to generate emissions, as is the case with traditional permeation tubes; (2) the emission rate of the reference can be measured by balance and predicted by model in a limited circumstances when the film is at its self-similarity scale; (3) the emission rate of the reference is constant under certain environment conditions which allows a smooth concentration increase to steady state in 6 h.

In conclusion, the LIFE reference is a reliable, fast, and easily-used reference material for the evaluation of chamber performance for both full-scale and small-scale chambers. It has been accepted as a Chinese standard material [24] and might be useful in other labeling program test method validation protocols. Next steps in its development and application include evaluating the performance of the LIFE reference in an inter-laboratory study, as well as expanding its use to other chemicals of concern (e.g., formaldehyde).

Acknowledgements

The participation of Wenjuan Wei and Jinping Zhang in this research was supported in part by the National Natural Science Foundation of China (no. 50725620, no. 51106011) and by the Beijing Municipal Science and Technology Commission (BMSTC) (no. D09050603750802) projects.

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Table 1.

Chamber parameter	Actual control points	
	Chamber 1	Chamber 2
Temperature (°C)	23 ± 1	23 ± 1
Relative humidity (%)	50 ± 1	50 ± 1
Air change rate (h ⁻¹)	0.913 ± 0.001	0.944 ± 0.006

Table 2.

Relative humidity (%)	Temperature (°C)		
	10	23	30
33	Y	Y	Y
50	Y	Y	Y
70	Y	Y	N

Table 3.

LIFE reference*		PMP reference	
Test time (h)	Diff** %	Test time (h)	Diff** %
6	10.9	24	-10.1
6	14.1	48	2.69
		72	12.4

*The same reference was tested twice in chamber 2.

**Diff is the difference between chamber testing results and model prediction,

$$\text{Diff} = \frac{C_{a,\text{test}} - C_{a,\text{predict}}}{C_{a,\text{predict}}} \times 100$$

Table 4.

Relative humidity (%)	Temperature (°C)		
	10	23	30
	Emission rate ($\mu\text{g/s}$)		
33	1.21×10^{-2}	4.29×10^{-2}	6.60×10^{-2}
33	1.76×10^{-2}	4.19×10^{-2}	6.52×10^{-2}
Average	1.14×10^{-2}	4.24×10^{-2}	6.56×10^{-2}
50	4.35×10^{-3}	4.11×10^{-2}	6.13×10^{-2}
50	4.61×10^{-3}	4.12×10^{-2}	6.04×10^{-2}
Average	4.48×10^{-3}	4.12×10^{-2}	6.09×10^{-2}
70	1.27×10^{-2}	3.86×10^{-2}	
70	1.26×10^{-2}	3.55×10^{-2}	
Average	1.26×10^{-2}	3.71×10^{-3}	

Table 5.

Source of variation	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i> *	<i>F</i>	<i>F</i> */ <i>F</i>
Factor RH	5.54×10^{-5}	1	5.54×10^{-5}	142	5.99	23.8
Factor T	6.22×10^{-3}	2	3.11×10^{-3}	7980	5.14	1550
RH - T interactions	1.65×10^{-5}	2	8.24×10^{-6}	21.2	5.14	4.11
Error	2.34×10^{-6}	6	3.90×10^{-7}			

Table 6.

Source of variation	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i> *	<i>F</i>	<i>F</i> */ <i>F</i>
Factor RH	3.33×10^{-5}	2	1.66×10^{-5}	16.1	5.14	3.14
Factor T	2.83×10^{-3}	1	2.83×10^{-3}	2740	5.99	458
RH - T interactions	7.51×10^{-5}	2	3.75×10^{-5}	36.4	5.14	7.08
Error	6.19×10^{-6}	6	1.03×10^{-6}			

Table 7.

Item	Temperature (°C)		
	10	23	30
	Emission rate (µg/s)		
RH = 33 %, regression	8.28×10^{-3}	4.49×10^{-2}	6.45×10^{-2}
RH = 33 %, test	1.14×10^{-2}	4.24×10^{-2}	6.56×10^{-2}
Diff* %	37.7	-5.48	1.64
RH = 50 %, regression	9.06×10^{-3}	4.17×10^{-2}	5.93×10^{-2}
RH = 50 %, test	4.48×10^{-3}	4.12×10^{-2}	6.09×10^{-2}
Diff* %	-50.6	-1.32	2.56
RH = 70 %, regression	9.98×10^{-3}	3.80×10^{-2}	
RH = 70 %, test	1.26×10^{-2}	3.71×10^{-2}	
Diff* %	26.5	-2.52	

*Diff is the difference between chamber testing results and prediction by the regression model,

$$\text{Diff} = \frac{\dot{m}_{\text{test}} - \dot{m}_{\text{regression}}}{\dot{m}_{\text{regression}}} \times 100$$

Figures

Figure 1.



Figure 2.

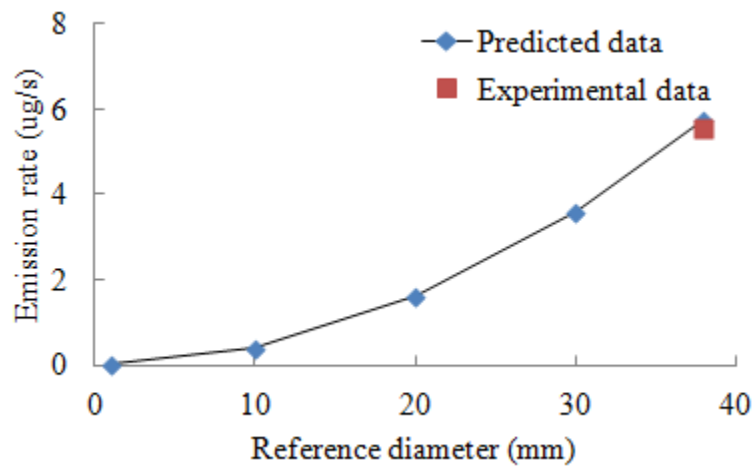


Figure 3.

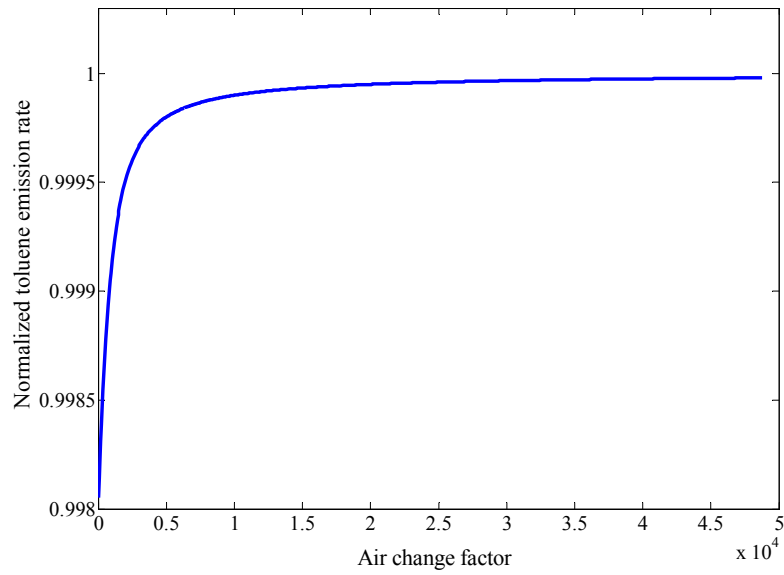


Figure 4.

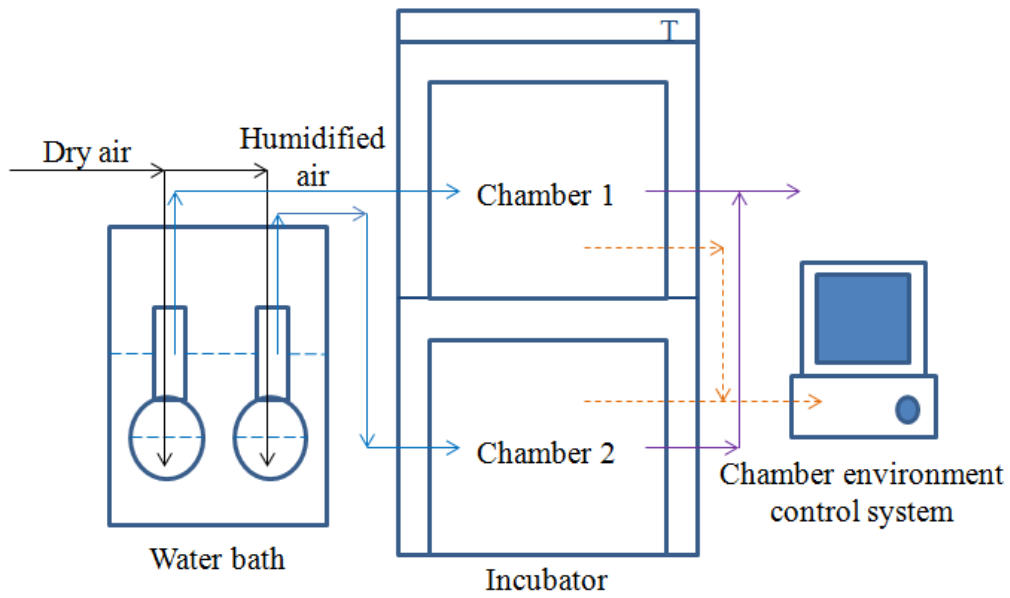


Figure 5.

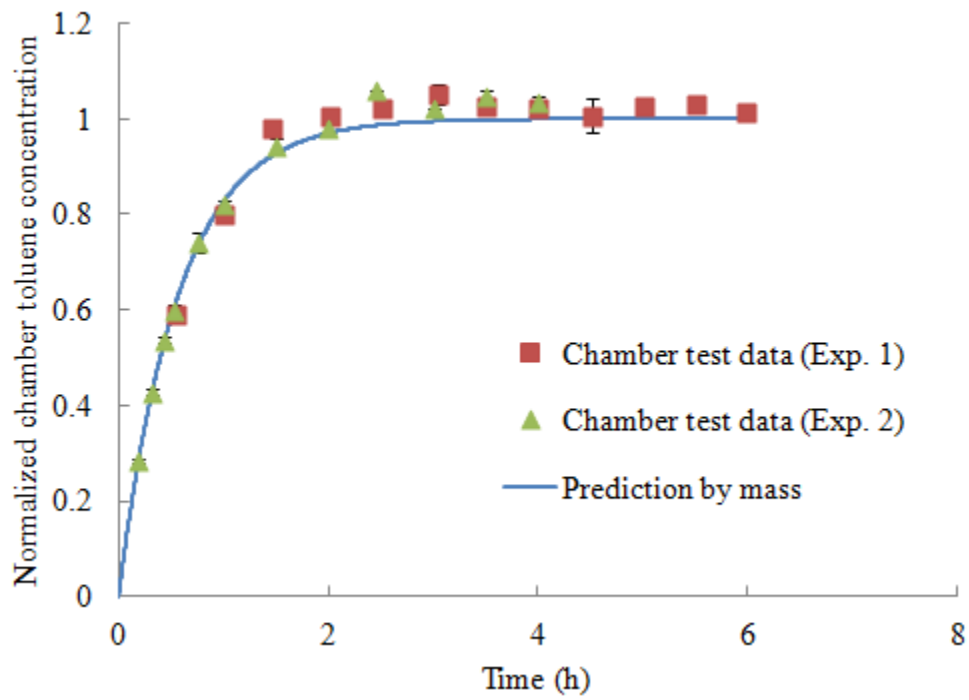


Figure 6.

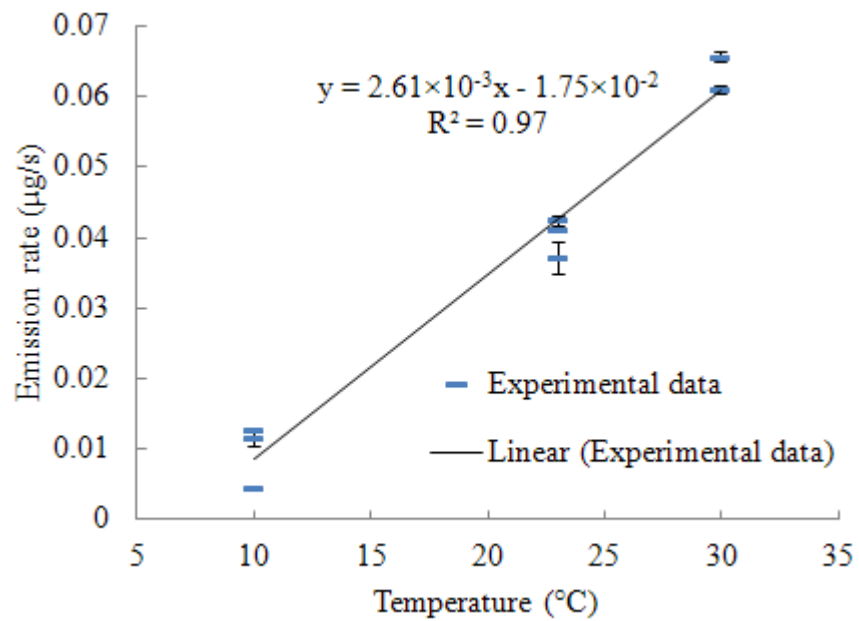


Figure 7.

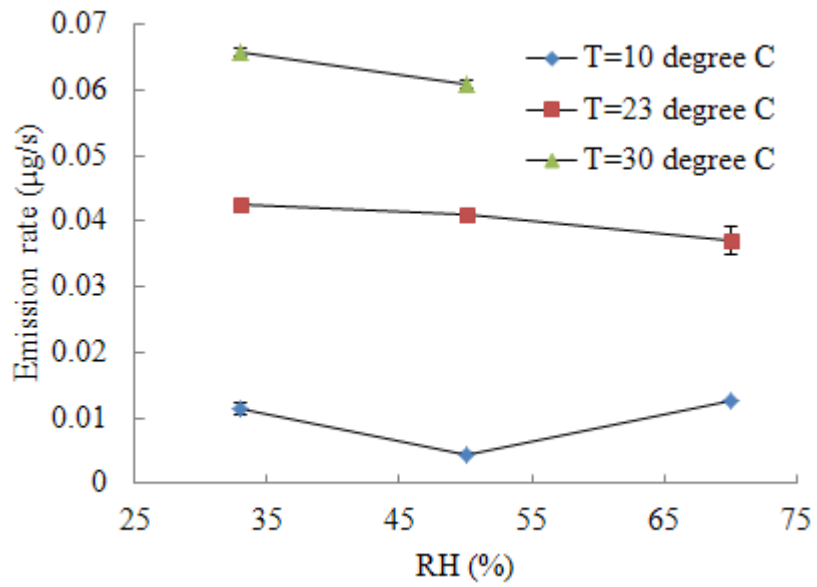


Figure 8.

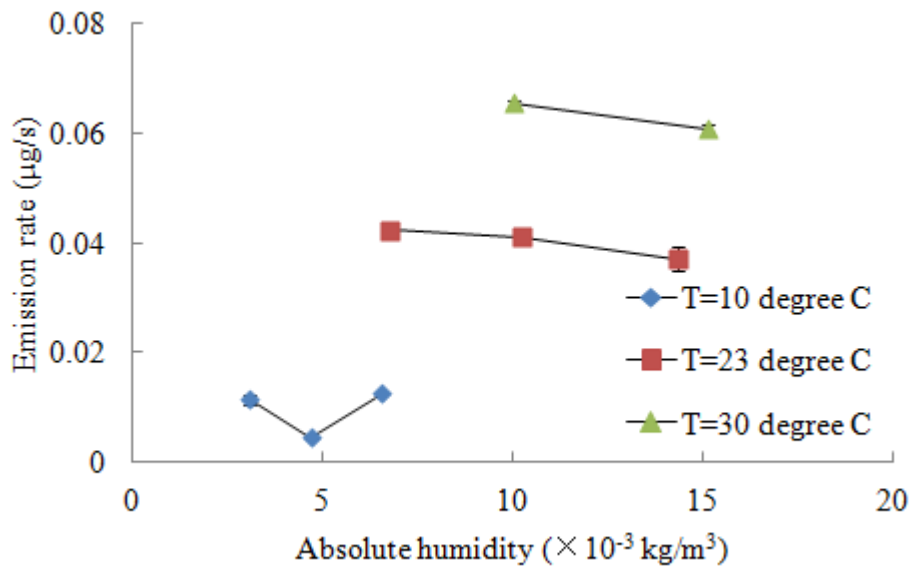


Figure 9.

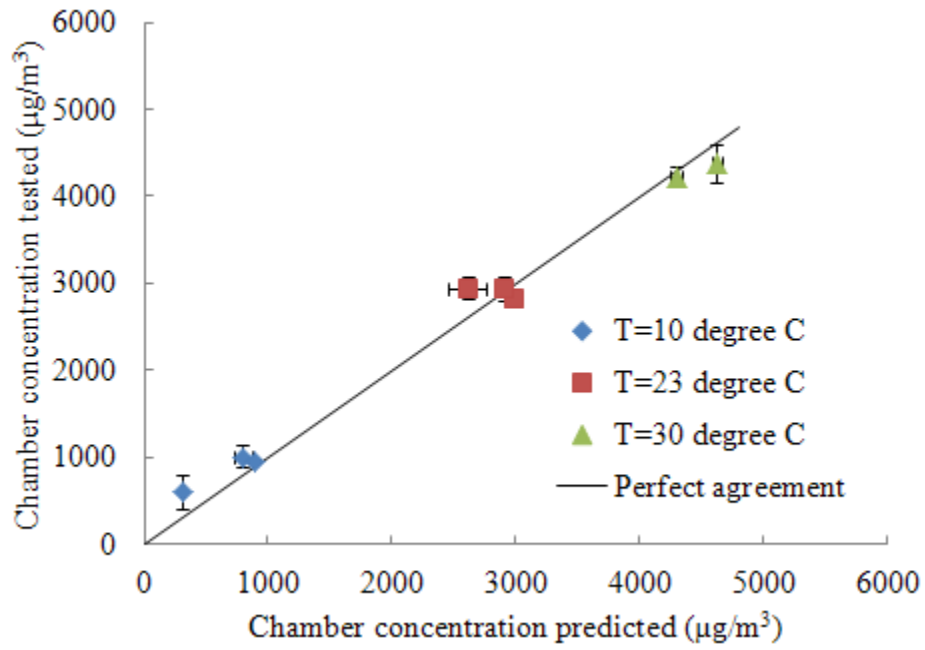


Figure 10.

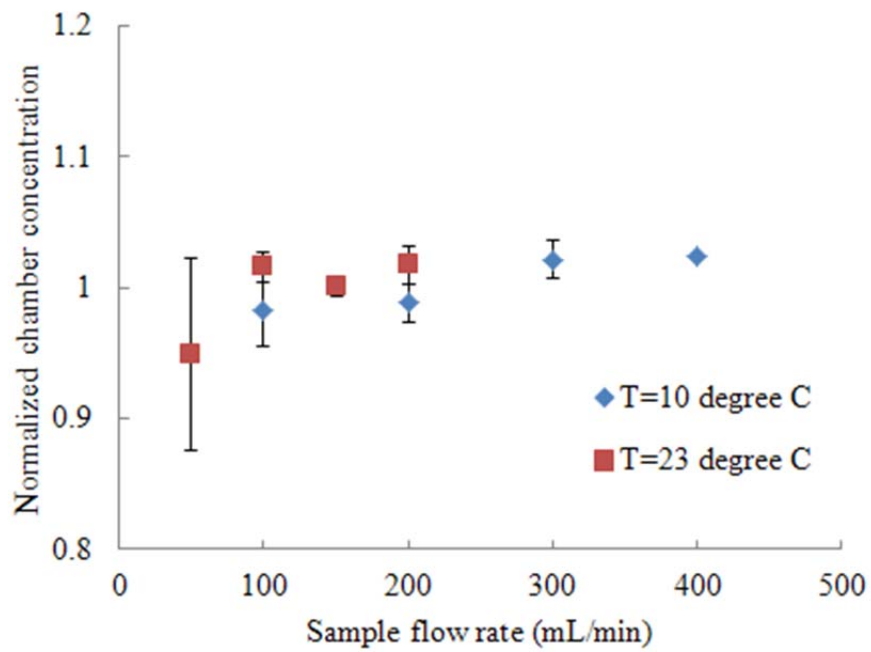


Figure 11.

