

Diffusion-controlled Reference Material for VOC Emission Testing: Effect of Temperature and Humidity

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Diffusion-controlled Reference Material for VOC Emissions Testing: Impact of Temperature and Humidity

Abstract

To improve the reliability and accuracy of chamber tests for measuring emissions of volatile organic compounds (VOCs) from interior materials, Virginia Tech (VT) and the National Institute of Standards and Technology (NIST) have pursued a program to develop reference materials for VOC emissions testing. As part of this program, a prototype reference material has been developed by loading toluene into a polymethylpentene (PMP) film. Its emission characteristic parameters, including material-phase diffusion coefficient (D) and material/air partition coefficient (K), have been measured at 23 °C. A fundamental mass-transfer model can then be used to predict the toluene emission rate from the reference material at 23 °C, which can serve as a reference value for validating emission profiles measured by different laboratories. In this paper, the impact of temperature and humidity on the performance of the reference material was investigated. Emissions from the reference material were measured in chambers at 10 °C, 23 °C and 30 °C and at different relative humidity levels (RH). D and K values at different temperature and RH were also determined using a completely independent microbalance method. It was found that RH does not significantly affect D and K and has no impact on emission chamber test results. However, D and K depend strongly on temperature and emissions are increased substantially at elevated temperatures. A statistical analysis shows acceptable agreement between model-predicted and measured concentrations, suggesting that the model can indeed predict measured emission profiles at different temperatures. The reference material can therefore be applied to a wider range of emission chamber testing conditions.

Keywords: Volatile organic compounds, Emission testing, Temperature, Relative humidity, Polymethylpentene

Practical Implications:

A reference material was previously developed as a validation tool for emission testing in chambers at specified temperature and relative humidity conditions. A follow-up study has investigated the effect of temperature and humidity on the performance of the reference material.

The results indicate that the reference material can be applied to a wider range of emission chamber testing conditions and can be suitable for different testing purposes in different laboratories.

1 Introduction

It has been well-recognized that a variety of building materials and consumer products such as carpets, flooring, composite wood and paints are important sources of volatile organic compounds (VOCs) in indoor air (Weschler, 2009). Due to their large surface area and permanent presence in the indoor environment, indoor VOC concentrations typically exceed outdoor levels. Because people spend over 80 % of their time indoors (Adgate et al., 2004), indoor VOC exposure can significantly affect occupants' comfort, health and productivity (Dorgan et al., 1998; EPA, 1991; WHO, 1983).

Variations of indoor air temperature and humidity are common in buildings. For example, Raja et al. (2001) measured a mean temperature of 24 °C and a maximum of 33 °C in 15 naturally ventilated buildings in UK in 1996-1997; Zhang and Yoshino (2010) measured relative humidity levels (RH) in residential houses across nine cities of China and observed very large variations among cities, from below 20 % to above 80 %; Dili et al. (2010) measured 100 households in India and reported a temperature range of 28 °C to 32 °C and a RH range of 28 % to 100 %; Kim et al. (2011) measured over 1000 air-conditioned buildings in Korea, Japan and the United States and reported a temperature range of 20.1 °C to 26 °C and a RH range of 20.4 % to 54.6 %. These temperature and humidity variations are important because they can affect VOC emission rates from interior materials and thus indoor VOC concentrations. For example, formaldehyde emission rate from chipboard was found to double for every 7 °C rise in temperature within the range of 14 °C to 31 °C (Andersen et al., 1975). Similarly, Myers (1985) reported that formaldehyde emission rate from particleboard increased by a factor of 5.2 when temperature increased from 23 °C to 40 °C. Positive correlations between emission rates and temperature were also obtained for other VOCs from some building materials (Crawford and Lungu, 2011; Lin et al., 2009). However, little or negligible impact of temperature on VOC emissions from some materials has also been observed (Sollinger et al., 1994; Wiglusz et al., 2002; Wolkoff, 1998) as well as an opposite trend (Haghighat and Bellis, 1998).

The impact of RH on VOC emissions is also not always clear. Andersen et al. (1975) reported a doubling in formaldehyde emission rate from chipboard when RH increased from 30 % to 70 %. Lin et al. (2009) reported emissions of several VOCs from wood flooring were increased at higher RH. However, the impact of humidity was negligible in some other cases and a decreasing trend has also been observed (Wolkoff, 1998). The complicated impact of temperature and humidity on VOC emissions may be explained by interactions between different types of materials, VOCs and the environment (Wolkoff, 1998), and further experimental and theoretical research is required.

Currently, the primary method to characterize VOC emissions from various materials in support of developing low-emitting products is to perform emission chamber tests, measuring VOC emissions from test materials in chambers at specified temperature and RH. To improve the reliability and accuracy of emission chamber tests, Virginia Tech (VT) and the National Institute of Standards and Technology (NIST) have developed a prototype reference material that mimics a real building material and has a known emission rate (Cox et al., 2010). A polymethylpentene (PMP) film was selected as the substrate that can be loaded with toluene through a diffusion process. The loaded film has an emission profile similar to a typical “dry” material (e.g., flooring) that can be measured in small emissions testing chambers. A unique advantage of this reference material is that its emission profile can be predicted accurately by a fundamental mass-transfer model with independently measured material parameters (diffusion coefficient D , partition coefficient K , and initial material-phase concentration C_0). The predicted emission profile therefore serves as a reference value and can be compared to measured results by individual laboratories. The feasibility and capability of the reference material in validating emissions testing results and calibrating testing procedures have been demonstrated in a series of inter-laboratory studies (Howard-Reed et al., 2011a; Howard-Reed et al., 2011b). However, the prototype reference material has only been validated at 23 °C and employed in inter-laboratory studies at this temperature. Furthermore, the impact of humidity on its emissions has not been studied.

In the present work, the impact of temperature and humidity on reference material emissions was investigated. Emission chamber tests were performed at 10 °C, 23 °C and 30 °C and at different

RH levels. The characteristic parameters (D and K) of the reference material were also determined at various temperature and RH. It was found that RH, in the range tested, does not affect D and K and has no significant impact on the emission chamber test results. However, D and K are temperature dependent and emission rates increase significantly at elevated temperatures. When the appropriate parameters are used, the model predictions match the chamber test results very well, suggesting that it can indeed predict the true emission profiles at different temperatures. This work enables the reference material to be applied over a wider range of environmental conditions and provides a theoretical basis for assessing uncertainties of emissions testing results stemming from variations of temperature and humidity.

2 Methods

2.1 Producing reference materials for emissions testing

The reference materials were created by loading gas-phase toluene into clean PMP films through a diffusion process (Cox et al., 2010; Howard-Reed et al., 2011a). A diffusion vial containing pure liquid toluene was placed in a calibration gas generator (Dynacalibrator 190, VICI Metronics Inc., Santa Clara, CA). Clean, dry air from a compressed gas cylinder was passed through the calibration gas generator to create a continuous dry gas stream with a constant toluene concentration. The gas-phase toluene concentration in the gas stream was determined by weighing the diffusion vial at intervals to obtain the toluene release rate and then dividing by the dry gas stream flow rate. As shown in Figure 1(a), the toluene-containing dry air was then passed through a stainless steel loading vessel containing several PMP films ($6.0\text{ cm} \times 6.0\text{ cm} \times 0.025\text{ cm}$) supported on aluminum screens. The effluent gas stream from the loading vessel was then passed across an additional film ($3.6\text{ cm} \times 3.6\text{ cm} \times 0.025\text{ cm}$) mounted on a high-resolution ($0.1\text{ }\mu\text{g}$) dynamic microbalance (Thermo Cahn D-200, Thermo Fisher Scientific, Waltham, MA). During the loading process (about 10 days), gas-phase toluene diffused into the films until sorption equilibrium was reached between the material-phase and gas-phase. Because the film on the microbalance was subject to the same mass transfer process as the films in the loading vessel, its transient mass gain recorded by the microbalance, as shown in Figure 1(b), could be used to monitor the loading process and to determine when sorption equilibrium was reached. The material-phase concentration of toluene in the loaded films (C_0) can also be derived from the microbalance data by dividing the total toluene mass gain of the microbalance-mounted film by

its volume. Results reported throughout this manuscript are expressed as the measurement mean \pm one standard deviation. All reference material samples tested in this study were produced in a single loading batch and C_0 was determined to be $780 \text{ g/m}^3 \pm 30 \text{ g/m}^3$.

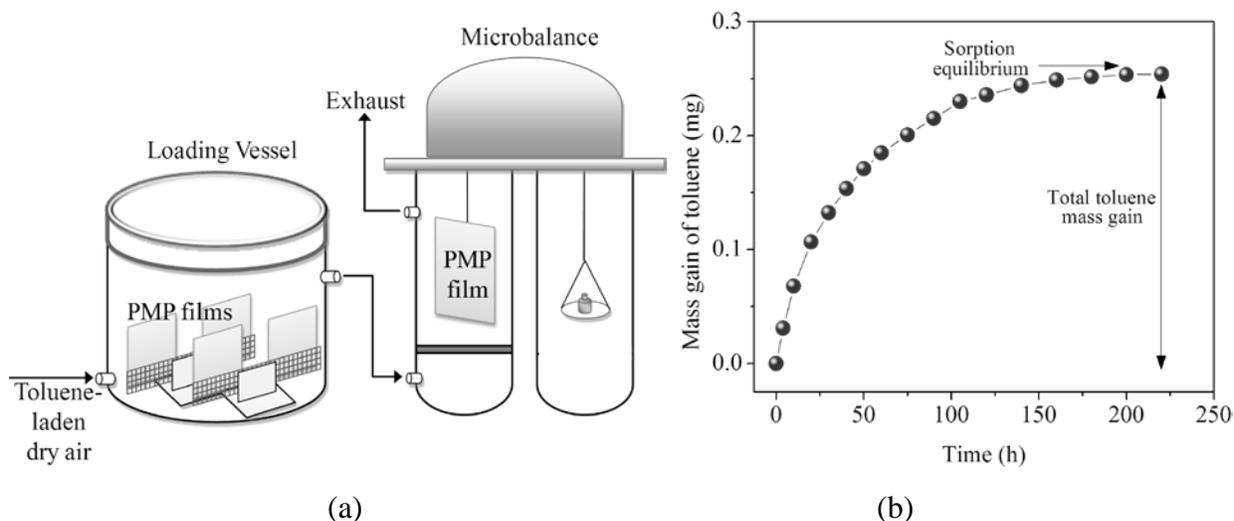


Figure 1 Loading process to produce reference materials: (a) schematic diagram of the loading system; (b) transient toluene mass gain recorded by the microbalance during the loading process.

2.2 Measuring emissions at different temperature/RH

When the microbalance data indicated that sorption equilibrium had been reached, the loading process was considered complete. The films were removed from the loading vessel and packaged to minimize exposure to ambient air. The packaging procedure included wrapping each film in heavy-duty aluminum foil, placing it in a small sealable plastic bag, and carefully evacuating air at each step. The bags were then coded, placed in coolers containing dry ice, and sent by overnight delivery to NIST. After arriving at NIST, the reference materials were retained in the original packages and stored in a freezer at $-20 \text{ }^\circ\text{C}$ until tested. The reference material samples were tested at NIST in a 51-L chamber with an air change rate of 1 h^{-1} following ASTM Standard D5116-2010 (ASTM, 2010). Testing protocols have been discussed in detail in the literature (Cox et al., 2010; Howard-Reed et al., 2011a) and are summarized here. Before being tested, each sample was removed from the freezer and maintained in the package at room temperature for 5 minutes. Then it was removed from the package and placed in a sample holder in the emissions testing chamber with both sides exposed to the chamber air. Temperature and

humidity set point values in each chamber test are summarized in Table 1. Temperature variations in all the tests were less than 0.2 °C and RH variations were less 0.2 %. During each chamber test period, chamber air samples were collected on sorbent tubes at periodic time intervals, and toluene concentrations in the samples were quantified by thermal desorption and gas chromatography/mass spectrometry (TD-GC/MS).

Table 1 Emission chamber test conditions.

Test	1	2	3	4	5
Chamber volume (m ³)	0.051				
Air flow rate (m ³ /h)	0.051				
^a Film surface area (m ²)	7.2×10 ⁻³				
^b Film thickness (m)	1.27×10 ⁻⁴				
Temperature (°C)	23	23	23	10	30
Humidity (% RH)	15	70	50	50	47

^a *A* is the total surface area of both sides of the reference material (two-sided source)

^b *L* is the half thickness of the reference material (two-sided source)

2.3 Determining *D* and *K* at different temperature/RH

The key material parameters affecting emissions include diffusion coefficient (*D*), partition coefficient (*K*) and initial material-phase concentration (*C*₀). *C*₀ is determined during the loading process and is independent of temperature and RH. However, *D* and *K* can be affected by temperature and RH, as suggested for some VOC/material combinations (Deng et al., 2009; Xu and Zhang, 2011; Zhang et al., 2007), resulting in different emission profiles during chamber testing. Therefore, the impact of temperature on *D* and *K* of the reference material was investigated by determining their values at 10 °C, 23 °C and 30 °C with the RH fixed at 0 %. To evaluate the humidity impact on *D* and *K*, their values were measured at 0 % and 50 % RH at 23 °C.

The microbalance sorption/desorption method was employed to determine *D* and *K* of the reference material (Cox et al., 2010). A clean PMP sample (3.6 cm × 3.6 cm × 0.0254 cm) was placed into the small glass chamber of the microbalance and sample mass was monitored during

toluene sorption/desorption cycles. During each sorption period, a gas stream with a constant toluene concentration (y) was passed through the microbalance sample chamber until sorption equilibrium was reached, generating a sorption curve. Clean air was then passed through the sample chamber, and the transient mass loss due to desorption was recorded, generating a desorption curve.

The microbalance was contained in a temperature-controlled cabinet so that the temperature of each sorption/desorption cycle was accurately regulated. The temperature variations within all the sorption/desorption tests were less than 0.2 °C. The RH of each sorption/desorption test was adjusted by controlling the ratio of a 100 % RH gas stream and a dry gas stream that were combined before passing through the microbalance sample chamber.

K can be determined from the sorption curve by

$$K = C_{\infty}/y \quad (1)$$

where C_{∞} is the material-phase concentration in equilibrium with y , which can be calculated by dividing the total mass gain when equilibrium is reached (M_{∞}) by the sample volume. D is determined by fitting a Fickian diffusion model for a thin slab to the sorption and desorption curve, which is given by (Crank, 1975):

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \cdot \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{4H^2}\right] \quad (2)$$

where M_t is the total mass of the VOC that has entered or left the sample in time t , M_{∞} is the total mass gain when equilibrium is reached, and $2H$ is the sample thickness.

2.4 Predicting emission profiles

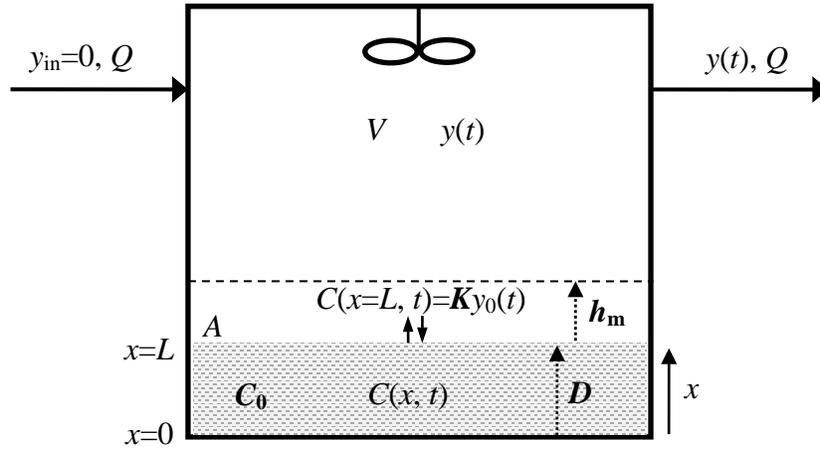


Figure 2 Schematic representation of the reference material in an emission chamber showing mechanisms governing VOC emission rate.

It has been shown that the emission profile of the reference material at 23 °C can be accurately predicted by a fundamental mass-transfer model (Howard-Reed et al., 2011a; Liu et al., 2011). Figure 2 shows the mechanisms governing the VOC emission from the reference material in an emission chamber. These mechanisms include internal diffusion of the VOC within the material (characterized by the diffusion coefficient, D), partition between the material and air at the material/air interface (characterized by the partition coefficient between the material and air, K), and external convective mass transfer near the emission surface (characterized by the convective mass-transfer coefficient, h_m). The external convective mass transfer is shown to be negligible compared to the internal diffusion for the reference material because the emission is diffusion controlled (Cox et al., 2010). Therefore, the boundary layer adjacent to the emission surface can be ignored and an instantaneous partition equilibrium can be assumed between the bulk chamber air and the material surface, or

$$K = \frac{C(x,t)|_{x=L}}{y(t)} \quad (3)$$

where $C(x, t)$ is the material-phase concentration as a function of the distance from the bottom of the material x and time t , $y(t)$ is the VOC concentration in the well-mixed chamber air as a

function of time, and L is the material thickness. When a uniform initial VOC concentration in the material (C_0) is assumed, $C(x, t)$ is given by (Little et al., 1994):

$$C(x, t) = 2C_0 \sum_{n=1}^{\infty} \left\{ \frac{\exp(-Dq_n^2 t)(h - kq_n^2) \cos(q_n x)}{\left[L(h - kq_n^2)^2 + q_n^2(L + k) + h \right] \cos(q_n L)} \right\} \quad (4)$$

where

$$h = \frac{Q/A}{D \cdot K} \quad (5)$$

$$k = \frac{V/A}{K} \quad (6)$$

and the q_n s are the positive roots of

$$q_n \tan(q_n L) = h - kq_n^2 \quad (7)$$

In Equation (4), A is the exposed surface area of the material, Q is the chamber flow rate, and V is the chamber volume. When C is obtained by Equation (4), y can be derived from Equation (3). In the present work, C_0 was determined from the microbalance measured toluene mass gain in the loading process and is independent of temperature and RH. To predict emission profiles of the reference material at various temperature and RH conditions, D and K values measured at the corresponding conditions should be used while other parameters, including L , A , Q , and V , were obtained from the geometry of the reference material and the chamber configuration. Although the present model is constructed to predict emissions from a single-sided source, it is also applicable to emissions when both sides of the material are exposed to the chamber air, with A indicating the total surface area of both sides and L indicating half of the material thickness.

3 Results and discussion

3.1 Emission chamber test results

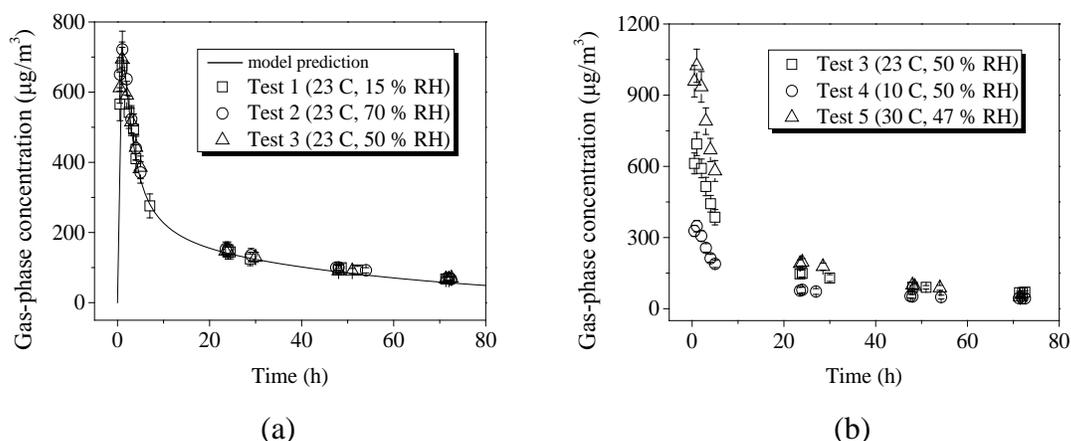


Figure 3 Measured gas-phase toluene concentration profiles in emission chamber tests: (a) tests conducted at 23 °C with different RH ; (b) tests conducted at different temperatures and roughly 50 % RH.

Figure 3 shows the measured chamber concentration profiles in all the five emission chamber tests, with Figure 3(a) comparing the results of the three tests (test 1, 2 and 3) carried out at the same temperature (23 °C) and Figure 3(b) comparing the results of the three tests (test 3, 4, and 5) performed at roughly the same RH level (~50 %). Figure 3(a) illustrates that test 1, 2 and 3 resulted in very similar emission profiles, although RH varied from 15 % to 70 %, demonstrating humidity does not affect the emission of the reference material significantly at 23 °C. Figure 3(b) shows, however, that the emission profiles measured at different temperatures were significantly different, with higher temperature accelerating emissions substantially. During the first 10 hours, chamber concentrations in test 5 (30 °C) were about 1.5 times higher than concentrations in test 3 (23 °C) and about 3 times higher than concentrations in test 4 (10 °C). However, the differences became smaller with time because faster emissions at elevated temperatures also lead to faster depletion of the material-phase concentration and thus faster decay of the chamber concentration. The results suggest that when using this reference material in chamber studies, temperature should be carefully controlled.

3.2 Diffusion and partition coefficients at different temperature/RH

To evaluate the temperature effect on D and K , microbalance sorption/desorption tests were carried out at 10 °C, 23 °C and 30 °C with a fixed 0 % RH. Figures 4(a), 5(a) and 6(a) display the microbalance measured mass gain/loss data of the PMP film during the sorption/desorption cycles at the three temperatures, respectively. It is found that the sorption and desorption curves at the three temperatures were all symmetrical, implying that the sorption and desorption of toluene in the reference material is completely reversible. Furthermore, with the gas-phase concentrations (y) roughly the same for the three sorption tests shown in the figures, more toluene mass was absorbed by the film at lower temperatures but it also took longer for the film and the gas to reach partition equilibrium. This is expected because at lower temperatures, the vapor pressure of toluene is reduced so that more molecules tend to be present in the material phase and the random motion of toluene molecules is less intense so that diffusion occurs more slowly. Figures 4(b), 5(b) and 6(b) show that D was obtained by fitting the Fickian diffusion model (Equation (2)) to the normalized sorption and desorption data for 10 °C, 23 °C and 30 °C, respectively. D was determined to be $(1.0 \pm 0.2) \times 10^{-14}$ m²/s, $(3.3 \pm 0.3) \times 10^{-14}$ m²/s and $(6.4 \pm 0.3) \times 10^{-14}$ m²/s for 10 °C, 23 °C and 30 °C, respectively, increasing substantially with rising temperature. As shown by Equation (1), K can be calculated from the total toluene mass gain of the PMP film (M_∞) in each sorption test and the gas-phase concentration in equilibrium (y). K was determined to be 1200 ± 80 , 500 ± 30 , and 370 ± 20 for 10 °C, 23 °C and 30 °C, respectively, decreasing with rising temperature. The dependence of D and K on temperature explains the difference among the measured emission profiles of the reference material at different temperatures (Figure 3(b)). At elevated temperatures, D increases and K decreases, thereby enhancing emissions and increasing the chamber concentration during the early period. However, because the toluene mass in the film is finite, the faster emission also leads to a faster decay of the chamber concentration during the later period.

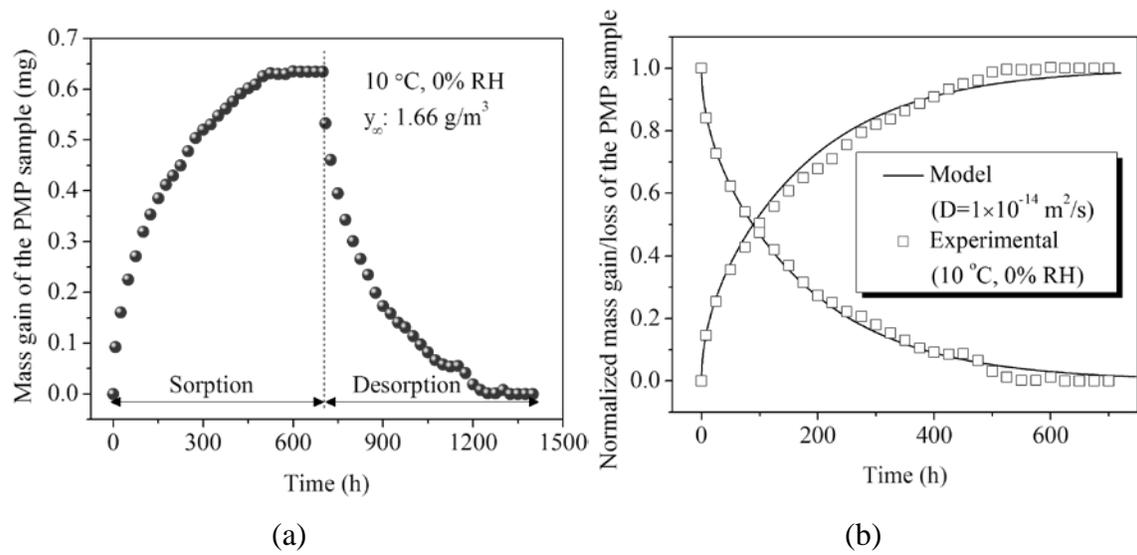


Figure 4 (a) Transient mass gain/loss during the sorption/desorption test at 10 °C and 0 % RH; (b) fitting the Fickian diffusion model (Equation (2)) to the normalized sorption and desorption data to determine D at 10 °C and 0 % RH.

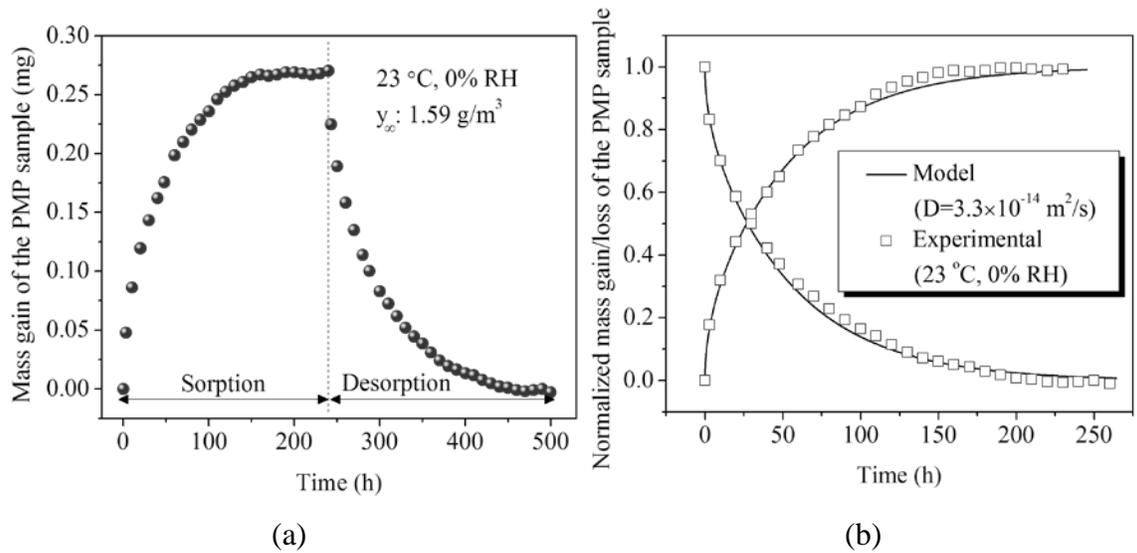


Figure 5 (a) Transient mass gain/loss during the sorption/desorption test at 23 °C and 0 % RH; (b) fitting the Fickian diffusion model (Equation (2)) to the normalized sorption and desorption data to determine D at 23 °C and 0 % RH.

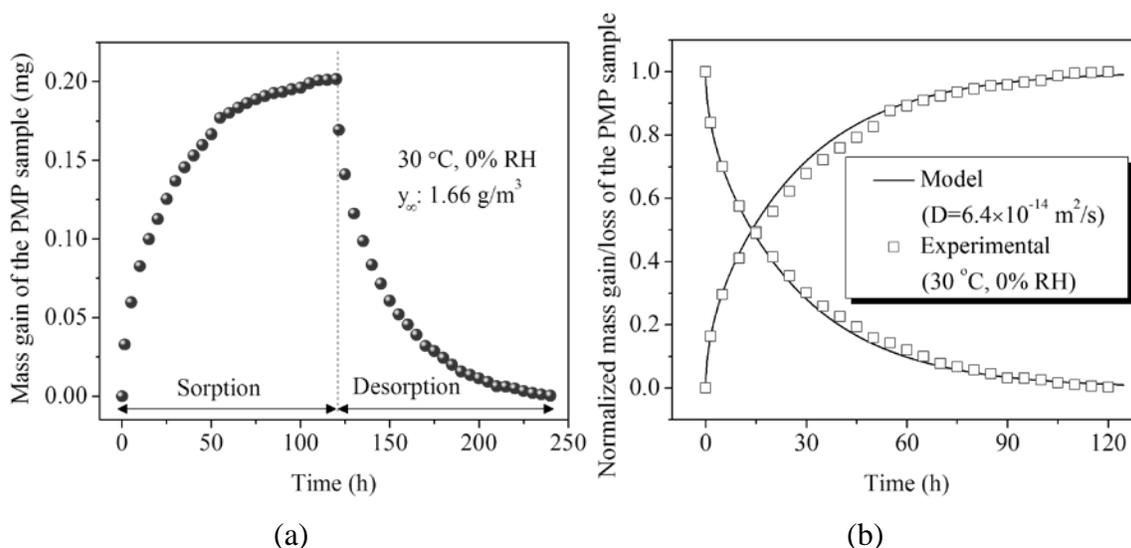


Figure 6 (a) Transient mass gain/loss during the sorption/desorption test at 30 °C and 0 % RH; (b) fitting the Fickian diffusion model (Equation (2)) to the normalized sorption and desorption data to determine D at 30 °C and 0 % RH.

To evaluate the impact of humidity on D and K , a sorption/desorption test was performed at 50 % RH and 23 °C, with the transient mass gain/loss of the PMP sample shown in Figure 7. During the test, dry clean air was passed across the film and then humidified to 50 % RH at ~70 h. Only a small amount of water was absorbed by the PMP film. Maintaining 50 % RH, the sorption and subsequent desorption test was run to completion (~660 h). The airflow was then switched to dry air in order to examine desorption of water vapor from the film. Comparing the 50 % RH test results (red squares and lines in Figure 7) with the test carried out with dry air (blue squares and lines), it appears the absorption of water vapor does not significantly affect the mass change profiles due to sorption and desorption of toluene and therefore does not change D and K . This further implies that D and K determined at 0 % RH are also applicable to humid conditions and that humidity in chamber tests should have no measurable impact on toluene emissions from the reference material, which is consistent with the observations in the emission chamber tests at different RH (Figure 3(a)).

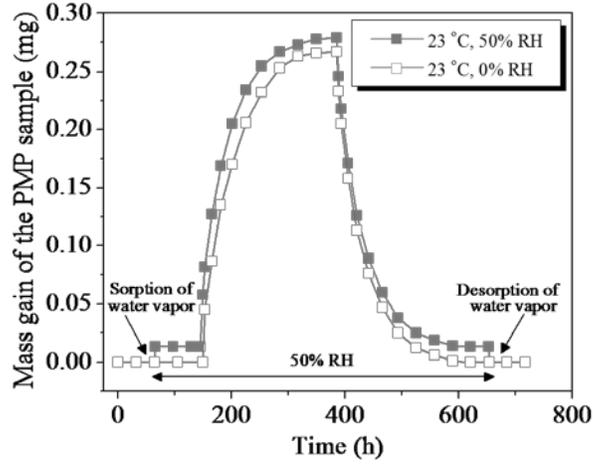


Figure 7 Microbalance measured mass gain/loss of the PMP sample during sorption/desorption tests at 0 % and 50 % RH, at 23 °C.

Therefore, D and K of toluene in the reference material are exclusively dependent on temperature, for which we can develop simple correlations. The dependence of diffusion coefficient in polymers on temperature is frequently assumed to follow an Arrhenius-type equation (Chandak et al., 1997; Yang et al., 2001; Zhang and Niu, 2003; Zhao et al., 2006), or:

$$D = D_0 \exp(-E_d / RT) \quad (8)$$

where E_d is the activation energy for diffusion, R is the ideal gas constant, T is temperature and D_0 is a prefactor. Assuming E_d is constant, Equation (8) can be expressed as

$$D = B_1 \cdot \exp(-B_2 / T) \quad (9)$$

where B_1 and B_2 are both constant for a given VOC/material combination. Therefore, it can be fitted to the measured D to obtain B_1 and B_2 for toluene in the reference material. Figure 8(a) shows the experimental data obey the correlation very well and the obtained correlation can be used to estimate D values at different temperatures. Zhang et al. (2007) found that the relationship between K of dry building materials and temperature follows

$$K = P_1 \cdot T^{1/2} \exp(-P_2 / T) \quad (10)$$

where P_1 and P_2 are constant for a given VOC/material combination. Fitting the formula to the measured K , Figure 8(b) shows that K of the reference material follows this correlation well, which can be used to predict K values at different temperatures.

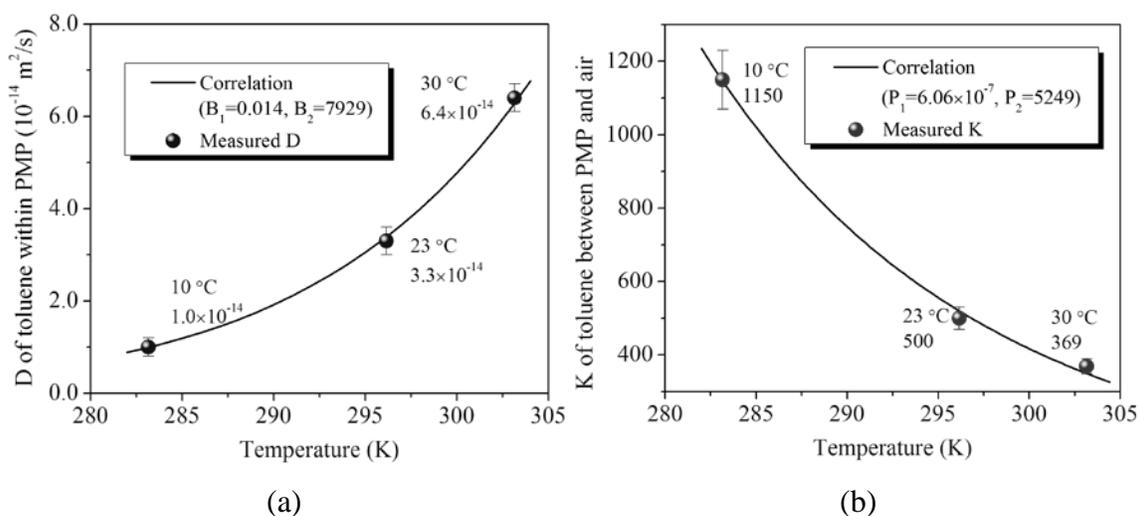


Figure 8 Correlations for temperature dependence of (a) D ($D = 0.014 \cdot \exp(-7929/T)$) and (b) K ($K = 6.06 \times 10^{-7} \cdot T^{1/2} \cdot \exp(5249/T)$).

3.3 Model predicted emission profiles

The model parameters required to predict the emission profiles of the reference material (Equations 3 through 7) are D , K , C_0 and other directly measurable parameters, including L , A , Q , and V . The variability of V , Q , A , and L are ignored given they were precisely controlled and were subject to little variation. To estimate the uncertainties of model predicted chamber concentrations associated with the uncertainties of D , K and C_0 , the Monte Carlo method (Cox et al., 2010) was employed. Approximately 10,000 repeated model simulations were carried out with D , K and C_0 randomly sampled from their distributions and the other parameters (L , A , Q , and V) fixed for each individual run. The results of the 10,000 model predictions were then pooled to assess the expected average value and variation of y as a function of time. Figure 9 shows the model predictions at the three temperatures, with the black solid line indicating the mean of the transient gas-phase toluene concentration in the chamber air and the shaded area indicating the range of mean transient gas-phase concentration \pm one standard deviation. For each temperature, the model predicted emission profile is consistent with the experimental measurements, validating its predictive capability under different environmental conditions. It has been shown that at 23 °C, the toluene emission from the reference material is controlled by internal diffusion and that the external convective mass transfer can be ignored (Cox et al., 2010). A measure of the relative significance of internal mass-transfer resistance versus external

convective mass-transfer resistance can be given by Bi_m/K , where Bi_m (Biot number) is equal to $h_m \times L/D$. When Bi_m/K is much greater than one, internal diffusion controls the emission rate and external convective mass-transfer is negligible. It should be noted that given h_m is roughly 3×10^{-3} m/s (Cox et al., 2010), Bi_m/K values at all three temperatures are on the order of 10^4 . Therefore, the diffusion-based emission model is indeed applicable for the reference material.

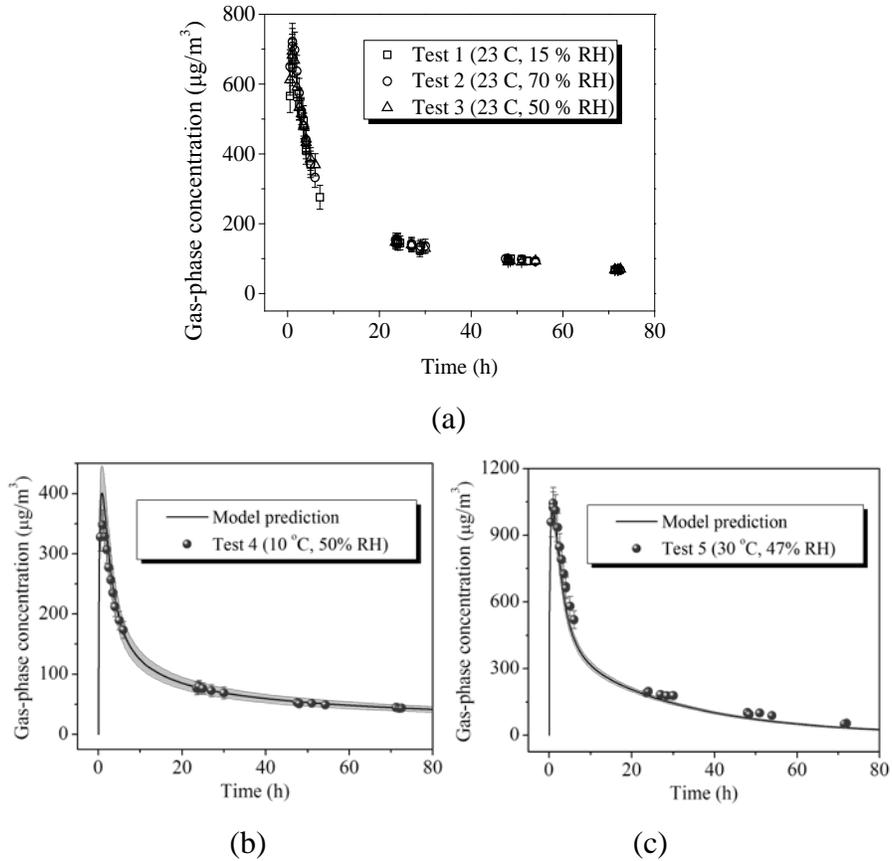


Figure 9 Comparison of measured and predicted emission profiles in emission chamber tests: (a) test 1, 2 and 3 (23 °C); (b) test 4 (10 °C); (c) test 5 (30 °C).

3.4 Assessment of agreement between model-predicted and measured concentrations

Differences between chamber-measured and model-predicted gas-phase toluene concentrations can result from 1) errors associated with the measurement procedure, 2) model assumptions, and 3) inaccuracies in model parameters. Two statistical analyses were used to assess the degree of agreement between model predictions and chamber measurements. In the first analysis, the correlation coefficient, r , was calculated for each data set. The correlation coefficient is a

measure of the strength of the relationship between measured and predicted concentrations. The second analysis, normalized mean square error (NMSE), is a measure of the magnitude of the prediction error relative to measured and predicted concentrations. ASTM D5157-97 (ASTM 2008) advises that an r value of 0.9 or greater and a NMSE of 0.25 or lower indicates acceptable agreement between model-predicted and chamber-measured concentrations. The results of the analysis are summarized in Table 2.

Table 2 Statistical analysis summary.

Test	Temp. (°C)	RH (%)	r	NMSE
1	23	15	0.990	0.017
2	23	70	0.998	0.005
3	23	50	0.994	0.009
4	10	47	0.998	0.018
5	30	47	0.996	0.019

The analysis shows that the agreement between the model and measured concentrations represented by r and NSME is relatively strong for all tests indicating that model predictions compare well to experimental observations.

4 Conclusions

In this paper, toluene emissions from the reference material were measured in chamber tests at different temperature and RH, and the mass transfer parameters, D , K , and C_0 , were measured independently using the microbalance method. Both experiments show that humidity has no significant impact on diffusion and partition coefficients at the experimental temperatures and thus does not affect the emission profiles in chamber tests. However, elevated temperature significantly increases the diffusion coefficient and reduces the partition coefficient and thus substantially accelerates the emission rate. Therefore, when attempting to validate emissions testing results through interlaboratory comparison, chamber operating temperature must be rigorously synchronized and controlled to ensure that measurements are fundamentally comparable. However, because toluene emissions from reference materials are controlled by

internal diffusion, the diffusion-based emission model is able to accurately predict emission rates at different temperatures when diffusion and partition coefficients are known. Furthermore, the proposed correlations between D and K and temperature can be used to estimate D and K for various temperatures. Therefore, when the reference material is tested in chambers under different environmental conditions, the model can still adequately predict emission rates for validating the experimental measurements, allowing the application of the reference material over a broader range of environmental conditions.

5 Acknowledgements

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6 Disclaimer

The full description of the procedures used in this paper requires the identification of certain commercial products and their suppliers. The inclusion of such information should in no way be construed as indicating that such products or suppliers are endorsed by NIST or are recommended by NIST, or that they are necessarily the best materials, instruments, software, or suppliers for the purposes described.

7 References

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