

DIFFUSION-CONTROLLED REFERENCE MATERIAL FOR VOC EMISSIONS TESTING

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ABSTRACT

To improve the reliability and accuracy of tests used to measure emissions of volatile organic compounds (VOCs) from samples of interior building products, the National Institute of Standards and Technology (NIST) and Virginia Tech (VT) have created a program to develop reference materials for volatile organic compounds emissions testing. A diffusion-controlled reference material and associated mechanistic model for predicting the emission profiles under various testing conditions have been developed. The feasibility of the reference material has been extensively evaluated and its capability in assessing emission testing performance has been demonstrated in a series of inter-laboratories studies. Reference materials have the potential to build consensus and confidence in emissions testing as well as to “level the playing field” for product testing laboratories and manufacturers.

KEYWORDS

Reference material, VOCs, Emissions testing, Emission model, Inter-laboratory study

INTRODUCTION

To reduce indoor exposure to harmful volatile organic compounds (VOCs), low VOC-emitting products are increasingly in demand. They are usually tested in emission chambers by independent laboratories, but very different emission profiles are often obtained for the same product tested in different laboratories (Cox et al. 2010). There is a compelling need for a reference emission source that can be used to evaluate and calibrate the testing procedures. The National Institute of Standards and Technology (NIST) and Virginia Tech (VT) have developed a polymer that mimics a real building material and has a known emission rate. A polymer film was selected as a substrate that can be loaded with a representative VOC through a diffusion process. The loaded film has an emission profile similar to a typical “dry” building material (e.g., particle board) that can be measured in small emissions testing chambers. A unique advantage of this emission source is that its emission profiles can be predicted accurately by a fundamental mass transfer model. The predicted emission profile therefore serves as a reference value for validating the measured results by different laboratories, evaluating the test performance, and identifying the root cause of variability.

The objective of this paper is to review the approach of developing the reference material for VOC emissions testing over four phases in the project. In Phase I, a prototype reference material was developed whose emission profile in emissions testing chambers could be predicted by the model with reasonable accuracy (Cox et al. 2010; Liu et al., 2011). Phase II, a pilot inter-laboratory study (ILS 1) was conducted with four laboratories in North America to assess the prototype reference material’s potential as a reference source (Howard-Reed et al. 2011a). Phase III further characterized the reference material’s properties, including the

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effects of a fan, humidity, and shelf-life (Howard-Reed et al. 2011b) on emissions. Phase IV includes a pilot international inter-laboratory study (ILS 2) with two laboratories (Howard-Reed et al. 2011c), and an expanded international inter-laboratory study involving fourteen laboratories (ILS 3), which is currently undergoing.

RESEARCH METHODS

Producing reference materials

An ideal reference material will emit VOCs at a predictable rate and in quantities similar to those generated by typical building products. Critical material properties include purity, thickness, and mass-transfer parameters such as diffusion coefficient and partition coefficient. Considering all these factors, a commercially available pure polymer, polymethyl pentene (PMP) was selected as the substrate. According to a microbalance test measuring the mass change of a PMP film in the presence of clean air, its mass stabilized after a few hours, suggesting the material does not contain significant amount of volatile additives or contaminants (Cox et al. 2010).

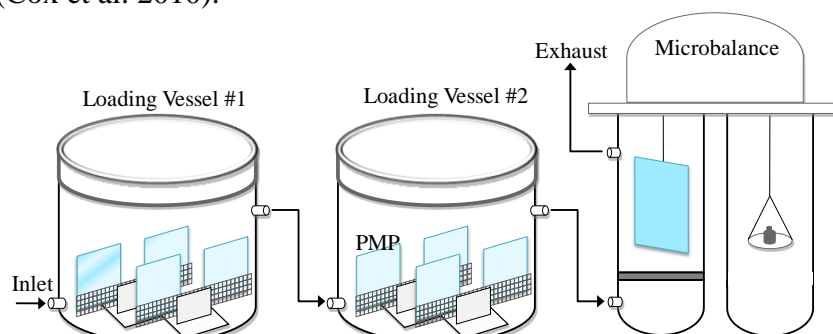


Figure 1. Loading process to produce reference materials

Toluene is chosen as the first representative VOC for the reference material. To load the PMP films with a specific amount of toluene, a gas calibrator with a mass flow controller is used to generate a continuous air stream with a constant toluene concentration. As shown in Figure 1, the toluene-laden dry air is passed through one or more stainless steel vessels connected in series (depending on the number of films required), each with several polymer films (6 cm×6 cm×0.0254 cm) secured on aluminium screen fixtures. The effluent air from the last vessel is passed through a high-resolution dynamic microbalance which holds an extra film and monitors its mass throughout the loading process. During the loading process (about 2-3 weeks), toluene molecules diffuse from the air into the films until sorption equilibrium is reached between the material-phase and gas-phase. The mass change data recorded by the microbalance is used to monitor the loading process and determine the material-phase concentration of toluene in the films when loading is complete (C_0).

Distributing reference materials for emissions testing

When the microbalance data indicates that sorption equilibrium has been reached, the loading process is considered complete. The films are removed from loading vessels one at a time for packaging to minimize exposure to ambient air. The packaging procedure includes wrapping each film in heavy-duty aluminium foil and placing it in a small sealable plastic bag, carefully evacuating air at each step. The bags are then coded, placed in coolers with dry ice, and sent by express mail to emissions testing laboratories. After arriving at the laboratories, the reference materials are retained in the original packaging and stored in a freezer at -20 °C. The laboratories, including NIST and other laboratories participating in the three ILS, generally measure the emission profiles of each film in small emission chambers following the

guidelines of ASTM International (ASTM 2010) with detailed testing protocols provided in the literature (Cox et al. 2010; Howard-Reed et al. 2011a, b, c).

Emission profile prediction

The emission of toluene from the reference material under various chamber configurations can be predicted using a mechanistic mass-transfer model (Cox et al. 2010; Liu et al. 2011). The principle of the model and method used to obtain the model parameters are briefly summarized here. The emission of a VOC from a homogeneous dry material to a well-mixed chamber includes internal diffusion within the material, characterized by the diffusion coefficient (D), partition between the air and the material at their interface, characterized by the partition coefficient (K), and the convective mass transfer near the material surface, which can be neglected for our diffusion-controlled reference material (Cox et al. 2010). When surface area (A), thickness of the material (L), volume (V) and airflow rate (Q) of the chamber are known, and assuming a uniform initial VOC concentration in the material (C_0), the chamber air concentration, y , can be predicted over time.

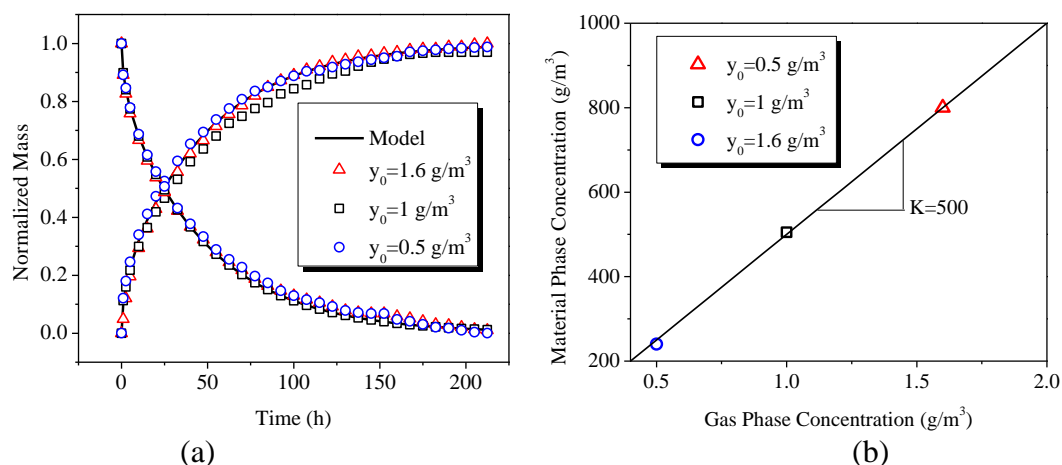


Figure 2. Determine D and K from microbalance tests (a) fitting a Fickian diffusion model to the sorption and desorption data to get D (b) determining K by linear regression

The model parameters include D , K , C_0 and other directly measurable parameters (A , L , V and Q). C_0 depends on the loading and should be derived from the total mass increase of the film monitored by the microbalance during loading. D and K are determined via independent microbalance sorption and desorption tests: recording the mass change when passing dry air with toluene through a clean PMP sample until partition equilibrium (sorption) is reached and then passing dry clean air through the sample (desorption) (Cox et al. 2010). As shown in Figure 2a, the microbalance tests were performed under three different gas concentrations. By fitting a Fickian diffusion model to the sorption and desorption data, D of toluene in PMP was found to be $(3.6 \pm 0.7) \times 10^{-14} \text{ m}^2/\text{s}$ at $23 \text{ }^\circ\text{C}$ and independent of concentration. Also from the sorption data, the material-phase concentrations in equilibrium with the corresponding gas concentrations were obtained and K was found to be 500 ± 30 from the linear correlation between the gas-phase and material-phase concentrations in equilibrium (Figure 2b).

RESULTS AND DISCUSSION

Phase I – Validation of the emission model

Figure 3a shows the concentrations of two identical tests conducted by NIST, except that one was performed with the chamber fan off and the other with the fan on (Howard-Reed et al. 2011a). Both sides of the reference material were exposed to the chamber air. The black line is the model prediction using mean values of D , K and C_0 . The shaded band indicates the

model uncertainty due to uncertainties in D , K and C_0 , which is assessed by a Monte Carlo simulation (Cox et al. 2010). As shown, the two tests are very close to each other, indicating the chamber air was well mixed in both cases. The model prediction with independently measured parameters matches the chamber test results very well, validating the model for predicting emission profiles and providing proof-of-concept for the reference material.

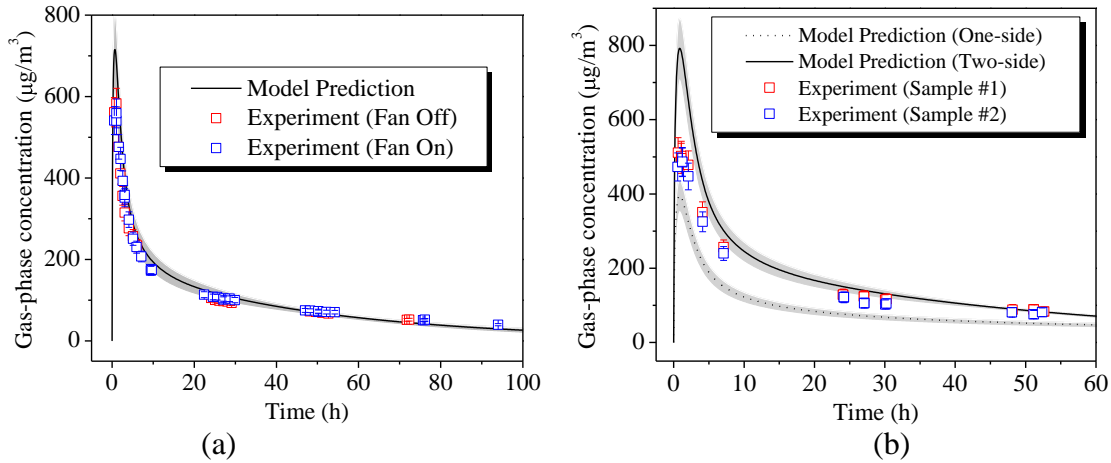


Figure 3. Comparisons between model predictions and chamber data in ILS 1 (a) validating the model (b) diagnosing problems in chamber tests

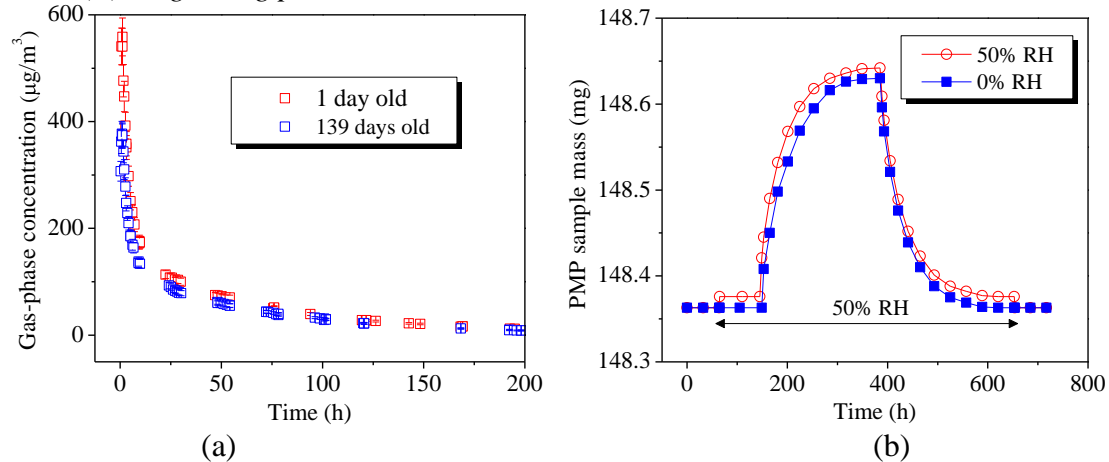


Figure 4. Further characterizing emission properties (a) emission profiles of 1-day-old and 139-day-old reference materials (b) humidity impacts on sorption/desorption test results

Phase II – Pilot inter-laboratory study (ILS 1)

In ILS 1, the reference material was held flat against an aluminium platform in the chambers with toluene expected to emit from one side of the material only (Howard-Reed et al. 2011a). Figure 3b shows the measured emission profiles for two replicate tests by one participating laboratory. However, the model assuming that one side of the material was exposed underestimated the measured results, while the model considering both sides as emission surfaces overestimated the results substantially. It was thus hypothesized that toluene escaped from the material surface in contact with the base so that the emission profiles fall between the ideal one-sided and two-sided cases. It was later confirmed that the samples were not held perfectly flat on the platform and that some air gaps existed beneath the samples, thus illustrating the value of the predictive model. The same problem occurred to other participant laboratories in ILS 1. The fact that the source is standardized and well-characterized by the mechanistic model greatly facilitated the identification and resolution of the problem.

Phase III – Impacts of shelf-life and humidity on emissions

Reference materials may lose noticeable amounts of toluene during storage, causing additional uncertainties in emissions testing. To assess the shelf-life effects, eight films were produced in a single batch, delivered to NIST, and stored in freezers (Howard-Reed et al. 2011b). They were randomly tested on day 1 (sample age of 1 day), days 13, 23, 41, 62, 104, 139, and 181, following the standard test method. Figure 4a shows the emission profiles of the 1-day-old and 139-day-old reference materials while other films followed similar emission profiles with most concentrations falling between the two limits. As shown by Figure 4a as well as the results for the other six films (Howard-Reed et al. 2011b), the amount of toluene emitted in the first 24 h of a chamber test decreases with sample age. However, this effect diminished as sampling time increased. Therefore, it is necessary to minimize the storage time before chamber testing to examine emissions during early stage while shelf-life impact is not critical if long-term emissions (>48 h) are the focus of the emissions testing.

Figure 4b shows the microbalance sorption/desorption tests at 0 and 50% RH. At about 80 h, dry air was switched to 50% RH air and very small amount of water was absorbed by the PMP film on microbalance (3.6 cm×3.6 cm×0.0254 cm) (red circles and lines). Maintaining 50% RH, sorption/desorption test was then carried out and when the desorption cycle was finished, air flow was switched to dry air again to examine desorption of water vapour. Compared with an identical test carried out with 0% RH air throughout (blue squares and lines), the presence of water vapour has very low impact on the sorption/desorption behaviour of PMP. Therefore, humidity in chambers should have no impacts on the emissions of the reference material and D and K determined under 0% RH are applicable to other humidity levels.

Phase IV – Pilot international inter-laboratory study

Figure 5 shows the chamber testing results of the two laboratories participating in ILS 2 (Howard-Reed et al. 2011c). In general, there was good agreement between the emission profiles measured for each reference material in both laboratories, and the measured emission profiles agree well with model predictions, with deviations of less than 10%. Although it is hard to directly compare chamber concentrations measured by each laboratory when different chamber configurations (V and Q) were employed, the model predictions can still be used as reference values to validate the emissions testing method in individual laboratories.

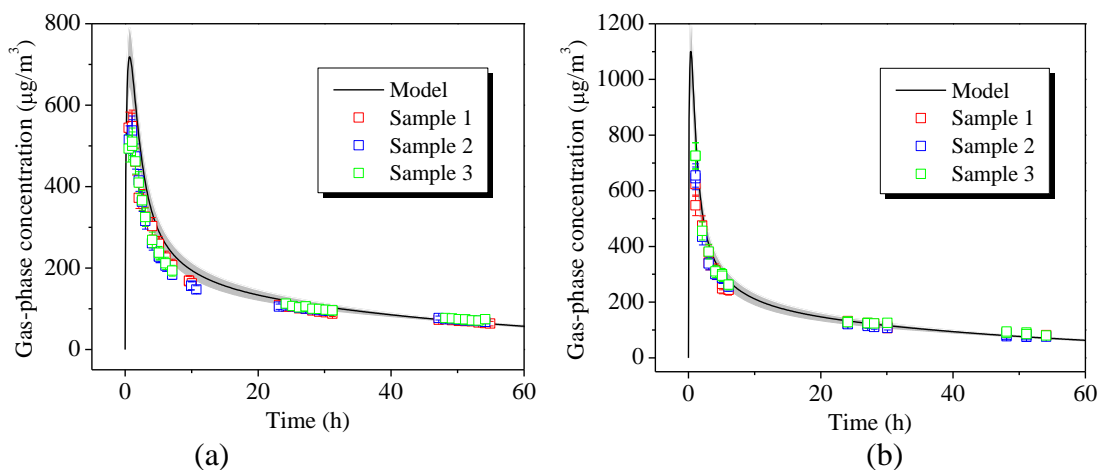


Figure 5. Results of ILS 2 (a) laboratory A (b) laboratory B

CONCLUSION AND IMPLICATIONS

The proof-of-concept test and inter-laboratory studies have demonstrated that the reference material mimics a real building material and can be used as a reference VOC emission source

to validate emissions testing procedures by different laboratories. Since the emission profiles under various chamber settings can be predicted accurately with a mass-transfer model, the reference material possesses a unique advantage and will allow laboratories to independently check their small-scale chamber measurements without the need for an organized inter-laboratory study. Furthermore, because the emission profiles are predicted based on a mechanistic understanding, knowledge of the mass transfer properties can be used to create representative materials with different ranges of emissions profiles by selecting materials with different D , K and C_0 .

As illustrated by the proof-of-concept test, reliable values of D , K and C_0 can also be obtained. Therefore, in addition to validating VOC emission testing, the reference material can also be used to validate techniques for measuring the mass-transfer parameters themselves (such as D , K and C_0) which are general requirements in applying emission modelling and also substantial challenges in material emission research. Finally, the reference material concept is currently being expanded to other VOCs such as n-butanol and dodecane.

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