Diffusion-controlled reference material for VOC emissions testing: validation and application of a mass transfer model

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1 Introduction

To reduce indoor exposure to harmful volatile organic compounds (VOCs), low VOC-emitting products are increasingly in demand. These are usually tested in emission chambers by independent laboratories, but very different profiles are often obtained for the same product tested in different laboratories. There is a compelling need for a reference emission source that can be used to evaluate and calibrate the testing procedures. We have developed a reference material by loading toluene into a polymethyl pentene (PMP) film, which mimics real building products and can be tested in typical emissions chambers (Cox et al., 2010). A unique advantage of this reference material is that the emission profile can be predicted accurately by a fundamental mass transfer model. The predicted emission profile therefore serves as a standard value for validating the measured results by different laboratories and evaluating the test performance. This paper presents the validation of the model and an example application of the model for diagnosing problems of emission testing procedures in a recent pilot inter-laboratory study (ILS).

2 Materials/Methods

Figure 1 shows the configuration of the model predicting gas-phase concentration of VOC (y) emitted from the reference material (thickness is L and exposed area is A) in a chamber with volume of V and ventilation rate of Q. The transient diffusion of the VOC within the slab is

$$\partial C(x,t)/\partial t = D\cdot \partial C^2(x,t)/\partial x^2 \, , \qquad (1)$$

where C is the material-phase concentration in the slab and D is the diffusion coefficient of the VOC within the material. The bottom boundary condition assumes a zero mass flux through the base. The upper boundary condition is given by a mass balance on the VOC in the air, or

$$\frac{dy(t)}{dt}V = -A\cdot D\left.\frac{\partial C(x,t)}{\partial x}\right|_{x=L} - Q\cdot y(t), \qquad (2)$$

where y is assumed to be always in equilibrium with the material surface via a partition coefficient (K). This assumption is valid when convective mass transfer is fast compared to internal diffusion (Cox et al., 2010). Given a uniform initial concentration (C_0) in the material, there is an analytical solution of the equation set for calculating y (Cox et al., 2010). D and K are determined by microbalance sorption and desorption tests to be $(3.6\pm 0.7)\times 10^{-14}$ m^2/s and 500 ± 30, respectively (Howard-Reed et al., 2011; Cox et al., 2010). When loading the material with toluene, an airstream with a known concentration of toluene is introduced, and the absorbed mass at the end of the loading process is divided by sample volume to get C_0.

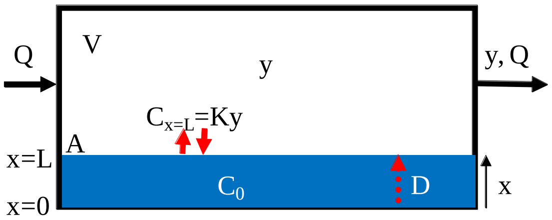

Figure 1. Schematic representation of the model

Each loaded reference material film is wrapped in aluminum foil, placed in a sealed plastic bag, and shipped in a cooler on dry ice to the testing laboratories. Arriving at the laboratory, the reference material is retained in the original packaging and stored in a freezer at -20 °C. Then it is tested in a stainless steel chamber following the guidelines of ASTM D5116-2010 (ASTM, 2010) to measure the toluene concentration profile in the chamber.

3 Results

Figure 2 shows the measured emission profiles of two identical tests, except one was performed with the chamber fan off and the other with the fan on. Each reference material was placed in a specially-designed fixture in the chamber so that both sides were fully exposed to the chamber air. The black line is the model prediction using the measured C_0 for the reference material and mean values of D and K. The shaded band indicates the model prediction uncertainty due to uncertainties in D, K and C_0, which is assessed by a Monte Carlo simulation. As shown, the two tests are very close to each other, indicating that emissions are unaffected by mixing. The model prediction with independently measured parameters matches the measured concentrations extremely well, validating the model for predicting emission profiles.

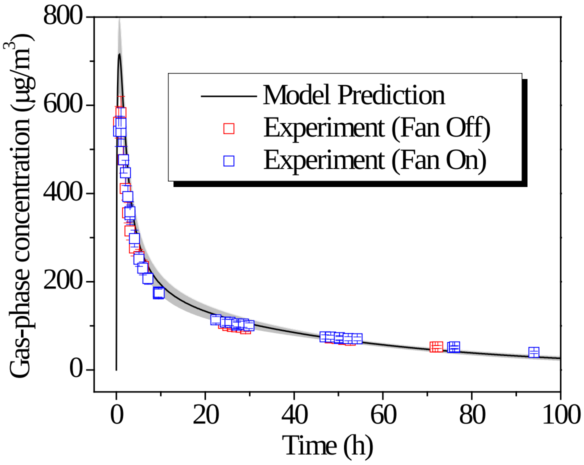

Figure 2. Model validation

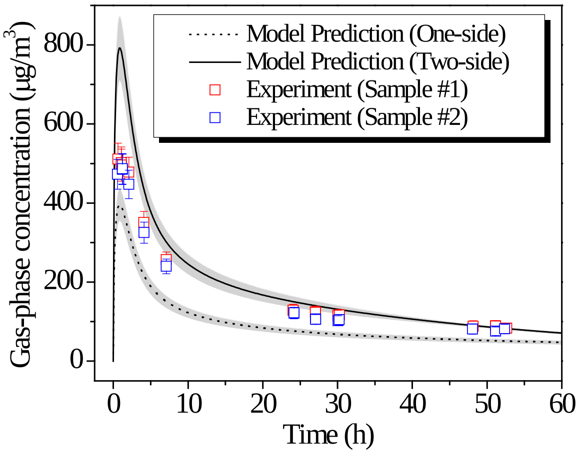

Figure 3. Comparison between emission test results and model predictions

After being validated, the model was applied to analyze recent pilot ILS results (Howard-Reed et al., 2010). In the ILS, 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. Figure 3 shows the measured emission profiles for two replicate tests. 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 a portion of the material surface in contact with the base so that the emission profiles fall between the ideal one-side case and two-side case. It was later confirmed that the samples were not held perfectly flat on the aluminium platform and that some air gaps existed between the sample and platform, thus illustrating the value of the predictive model.

4 Conclusions

The mass-transfer model which predicts emissions from the reference material has been validated using emission chamber results and is expected to predict the true emission profiles under a range of experimental conditions. Based on the discrepancies between recent ILS results and the model prediction, it was found that the tested samples were inappropriately secured in the chamber, showing the usefulness of the model when evaluating emission test procedures and chamber performance. A reference material with an independently known emission rate gives testing laboratories a valuable tool to assess their chamber, air sampling, and analytical performance.

5 References

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