Diffusion-controlled reference material for VOC emissions testing: The effect of temperature and humidity

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1 Introduction

To improve the reliability of chamber tests for measuring emissions of volatile organic compounds (VOCs) from interior products, the National Institute of Standards and Technology (NIST) and Virginia Tech (VT) have created a prototype reference material by loading toluene into a polymethylpentene (PMP) film (Cox et al. 2010). The emission parameters of the reference material, including toluene concentration in preloaded films (C₀), material-phase diffusion coefficient (D), and material/air partition coefficient (K), have been measured at 23 °C and 0% relative humidity (RH). A fundamental mass-transfer model is able to predict the true toluene emission profile from the reference material at 23 °C, which serves as the reference value to validate the measured chamber concentration by different laboratories and to evaluate the test performance. The feasibility and usefulness of the reference material has been demonstrated in several inter-laboratory studies (Howard-Reed et al. 2011).

In the present work, the effect of temperature and humidity on the emission parameters was determined and the model was validated for a range of temperatures and RH. The reference material can therefore be applied over a wider range of emissions testing conditions.

2 Materials/Methods

Producing reference materials

To infuse toluene into PMP films, an air stream with a constant toluene concentration was passed into a loading vessel containing several PMP films so that toluene diffused into the films until sorption equilibrium was reached between the air stream and the films. To determine C_0 , which is independent of temperature and humidity, the outlet flow from the loading vessel was further passed across an extra film whose mass gain was monitored by a microbalance.

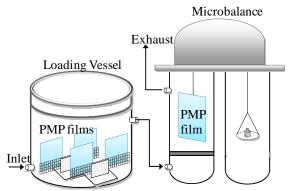


Figure 1: Loading vessel and microbalance.

Measuring emissions in chambers

Pre-loaded films were wrapped tightly in aluminum foil and sent to NIST in a cooler with dry ice. When received by NIST, the films were stored at -20 °C until being tested. The emission profile of each film was measured in a small chamber following ASTM Standard D5116-2010. Chamber tests were carried out at 10, 23, and 30 °C with different RH levels.

Determining D and K for different conditions

A microbalance sorption/desorption method was used to determine D and K (Cox et al. 2010). The mass gain when passing an air stream with toluene across a clean PMP sample was recorded until partition equilibrium was reached (sorption). Then clean air was passed across the film and its mass decrease was also monitored (desorption). The sorption/desorption tests were carried out at 10, 23, and 30 °C. At 23 °C, 0% and 50% RH were tested by adjusting the humidity of the incoming air stream.

Predicting emission profiles

With independently measured D and K at different temperature and RH levels, as well as

the known values of C_0 , toluene emissions from the reference material under various chamber configurations can be predicted using a masstransfer model (Cox et al. 2010). The model predictions can then be compared to the chamber test results to validate the model for a range of temperature and humidity.

3 Results and Discussion

Figure 2 shows the mass gain of a PMP film during the sorption/desorption tests at the three temperatures and 0% RH, with an incoming gasphase concentration of ~1.6 g/m³. At lower temperature, more toluene mass was absorbed but it took longer to reach equilibrium. By fitting a Fickian diffusion model to the normalized sorption/desorption data, D was found to be $(1.0\pm0.2)\times10^{-14}$, $(3.3\pm0.3)\times10^{-14}$ and $(6.4\pm0.3)\times10^{-14}$ m²/s at 10, 23 and 30 °C. From the total mass gain in each sorption cycle, the material-phase concentration in equilibrium with the incoming gas-phase concentration can be obtained and K can be determined from their ratio. K was found to be 1150±80, 500±30, and 370±20 at 10, 23 and 30 °C.

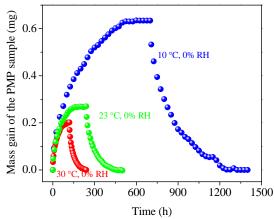


Figure 2: Sorption and desorption mass gain.

Figure 3 compares the sorption/desorption test results at 0% and 50% RH. It is shown that only a small amount of water vapor was absorbed by the PMP sample. The absorption of water vapor however did not change the sorption/desorption curves and thus has no impact on D and K. Humidity should therefore have no impact on emissions of toluene from the PMP film in chamber tests. Figure 4 shows the measured emission profiles at different temperature and RH levels. The emission profiles at 23 °C with different RH are indeed identical. Overall, the measured chamber concentrations agree with the model predictions well at all temperatures.

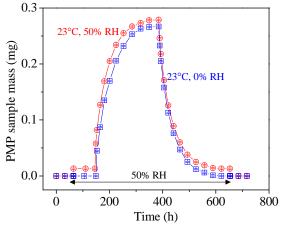


Figure 3: Humidity effect on microbalance test.

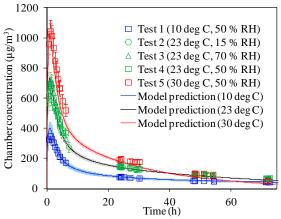


Figure 4: Measured and predicted emissions.

4 Conclusions

In the present work, D and K of the reference material were shown to be independent of humidity. However, D increases while K decreases with temperature and therefore the emission rate is enhanced at higher temperature. The emission model was validated for a range of temperature and RH. The reference material and emission model can therefore be applied to a broader range of chamber tests.

5 References

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