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Development of a Reference Material for Building Product Emissions Testing

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ABSTRACT

The business of measuring volatile organic compound (VOC) emissions from building products and materials has grown to include more than 100 laboratories, many with unique testing equipment and analytical techniques. For the purposes of labeling building products as "acceptable" for indoor air quality as part of sustainable building programs, it is important for participating laboratories to demonstrate that its chosen methods can measure product emission rates within an acceptable uncertainty. Currently, equivalence between emissions testing laboratories is established with inter-laboratory studies. These studies can be time consuming, expensive, and do not provide a "true" emission value for comparison. To reduce the need for inter-laboratory studies and improve the reliability of emissions measurements, the National Institute of Standards and Technology (NIST) and Virginia Tech (VT) have collaborated to develop a reference material that has an independently known emission rate. The prototype material consists of a thin polymethyl pentene (PMP) film that is loaded to equilibrium with a VOC. Extensive testing at NIST and other measurement laboratories have shown the film to behave as a homogenous and consistent emissions source. Current research efforts include evaluating the film performance at different environmental conditions and expanding the approach to include other chemicals. The use of reference materials in product emissions testing has the potential to provide an independent test method validation approach that can instill more confidence in product labeling programs.

INTRODUCTION

The most common way to determine the volatile organic compound (VOC) emissions from a building product or material is to place the product, or portion of a product, in an inert chamber under controlled environmental conditions (e.g., temperature, relative humidity and air change rate) similar to what is seen in a typical building and measure the resulting chamber concentrations at specific time points (e.g., 24 h, 48 h, etc.). Most emissions test protocols include the following six steps: 1) selection, packaging, transport and storage of material/product samples; 2) preparation and conditioning of sample specimens; 3) operation of emission test equipment; 4) gas-phase sampling; 5) sample analysis; and 6) data analysis and interpretation. A more detailed description of the emissions process and most of these steps can be found in the

ASTM standard guide for small chamber testing[1] and the ASTM standard practice for large chamber testing.[2]

For a chamber test, the product emission rate is not measured directly, but, rather calculated using a mass balance on the chamber air.[1] The resulting measurement uncertainty is based on the mass balance parameters of airflow rate and chamber air concentration, as well as several factors that affect a product's emission rate such as chamber temperature, relative humidity, extent of mixing, etc. These sources of uncertainty may contribute to significant variability within and between laboratories that do chamber testing. In fact, previous interlaboratory studies have shown typical variability between labs to be around 40 % and as high as 240 %.[3]

To reduce the measurement variability and better understand the associated uncertainty, validation of a laboratory's procedures is required. Currently the only approach used to verify the performance of laboratory chambers is with an inter-laboratory study (ILS). Such studies can be expensive and time-consuming. An independent way to check a laboratory's chamber performance, and reduce the need for inter-laboratory studies, is with a reference material that has a known emission rate. A reference material is defined as "a material, 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."[4] The National Institute of Standards and Technology (NIST) and Virginia Tech (VT) have collaborated to develop such a reference source that mimics a real building material and has a known emission rate. The objective of this paper is to review the multi-phase process to develop a prototype reference material for emissions testing.

REFERENCE MATERIAL DEVELOPMENT

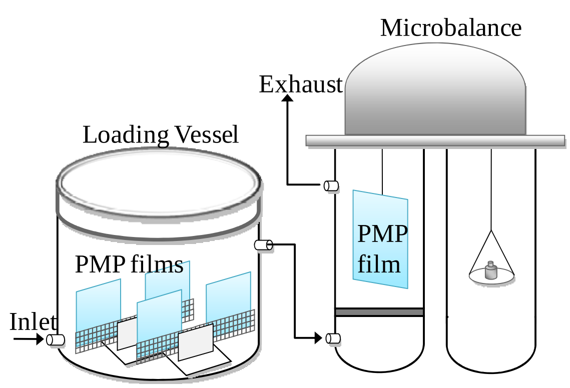
An ideal reference material will emit VOCs at a predictable rate and in quantities sufficient for detection and quantification over the required period of time. Other desirable criteria include the ability to produce the material in large batches, consistent performance in different laboratory chambers and chemical stability with a known shelf-life. Finally, it would be preferable that the reference source emits VOCs in a manner similar to "real" building materials and products.

The development of an appropriate reference material has followed a multi-phase approach including the following steps: 1) select a suitable substrate material that can be loaded with a typical VOC(s); 2) use a small-scale environmental chamber to measure the emissions profile of the reference VOC material; 3) characterize material performance in different laboratory chambers and at different environmental conditions; 4) assess material packaging and shelf-life; and 5) establish reference emission rate value for the source. These steps have been described in significant detail in several other publications[5-8] and will be summarized briefly here. The development of the prototype emissions reference material has also included the development of a fundamental mass transfer model that can predict the material's emission rate in any laboratory chamber using values for basic material properties of the film. More information regarding this model can be found elsewhere.[5]

Loading Reference Films

A commercially available polymer film, polymethyl pentene (PMP), was selected as an acceptable substrate material based on its purity, 0.254 mm thickness, and fundamental mass transfer parameters that mimic the mass transfer properties of vinyl flooring. The next step was to load a VOC into the film. Toluene was selected as the initial VOC to try since it is a representative indoor air quality contaminant and is relatively easy to work with and measure. To load the polymer films with a specific amount of toluene, a gas calibrator with a mass flow controller was used to generate a continuous air stream with a constant toluene concentration. As shown in Figure 1, the toluene-laden air was passed through a stainless steel vessel holding several polymer films that were approximately 4 cm x 4 cm. To date, as many as 48 films have been loaded in the same batch. The effluent air from the second vessel was passed through a high-resolution (0.1 µg) dynamic microbalance and then exhausted to a fume hood. One extra film was suspended in the microbalance and its mass was monitored throughout the loading process. During the loading process, toluene molecules were absorbed into the films until sorption equilibrium was reached between the material-phase and air-phase. It typically took 2 to 3 weeks to reach equilibrium. Simultaneously, the film on the microbalance underwent the same mass transfer process and was representative of all of the film samples. Therefore, the mass change data recorded by the microbalance was used to assess the loading process and determine when equilibrium was reached. The total mass increase of the film at the end of the loading process was divided by its volume to determine the material-phase concentration of toluene, which was assumed to be equal to the material-phase concentration of the films in the loading vessel.

Figure 1: Loading Toluene Films



Once loaded to equilibrium, the polymer films were wrapped tightly in aluminum foil and sealed in a plastic specimen bag. The packaged films were immediately placed in a cooler containing dry ice. Dry ice was found to be necessary to keep the toluene from escaping the loaded film. Packaged films were distributed to test laboratories using coolers and dry ice. Upon receipt, laboratories were instructed to place packaged films in a laboratory freezer (-20 °C) until ready for testing.

Chamber Tests

The reference film is designed to emit toluene at a sufficient concentration that can be measured in an environmental chamber. A test method to measure the film's emission rate was developed based on ASTM's D5116 Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products.[1] The reference material chamber method setpoints include a temperature of 23 °C, relative humidity of 50 %, and chamber airflow rate on the order of 0.05 m^3/h. The method also includes specific instructions for sample preparation, chamber loading of specimen, and air sample collection times.[6] In general, the method allows laboratories to collect and analyze chamber air samples in the manner of their choice. As a result, emission measurements reflect potential sources of variability of the chemical analysis as well as chamber operation.

A summary of the chamber tests completed to date is provided in Table 1. As shown in Table 1, most of the chamber studies have been conducted at NIST in a 51 L stainless steel chamber. However, the prototype material has been evaluated in 13 other laboratories as well. Over 80 films have been tested in a chamber to date.

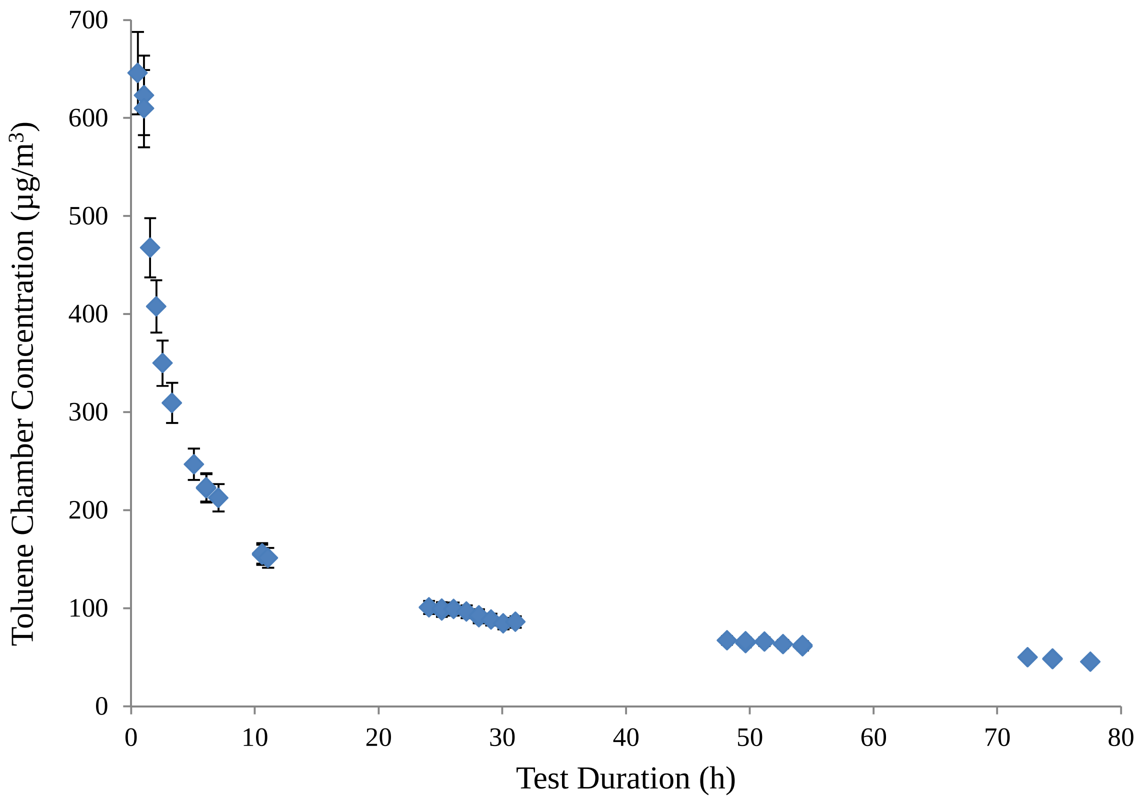
Table 1. Prototype reference material chamber studies completed to date.

Test Description	Participating Laboratories	# Tests per Lab	Reference
Proof of Concept	NIST	10	5
Pilot ILS	3 + NIST	4	6
Sample Holder Refinement	NIST	4	6
Chamber Mixing	NIST	4	6
Shelf Life	NIST	8	7
Pilot International ILS	1 + NIST	3	8
International ILS	13 + NIST	2	Paper under development
Temperature (10 C, 23 C, 30 C) and Relative Humidity (15 %, 50 %, 70 %)	NIST	7	Paper under development
Improved Packaging	1 + NIST	5	Paper under development

RESULTS

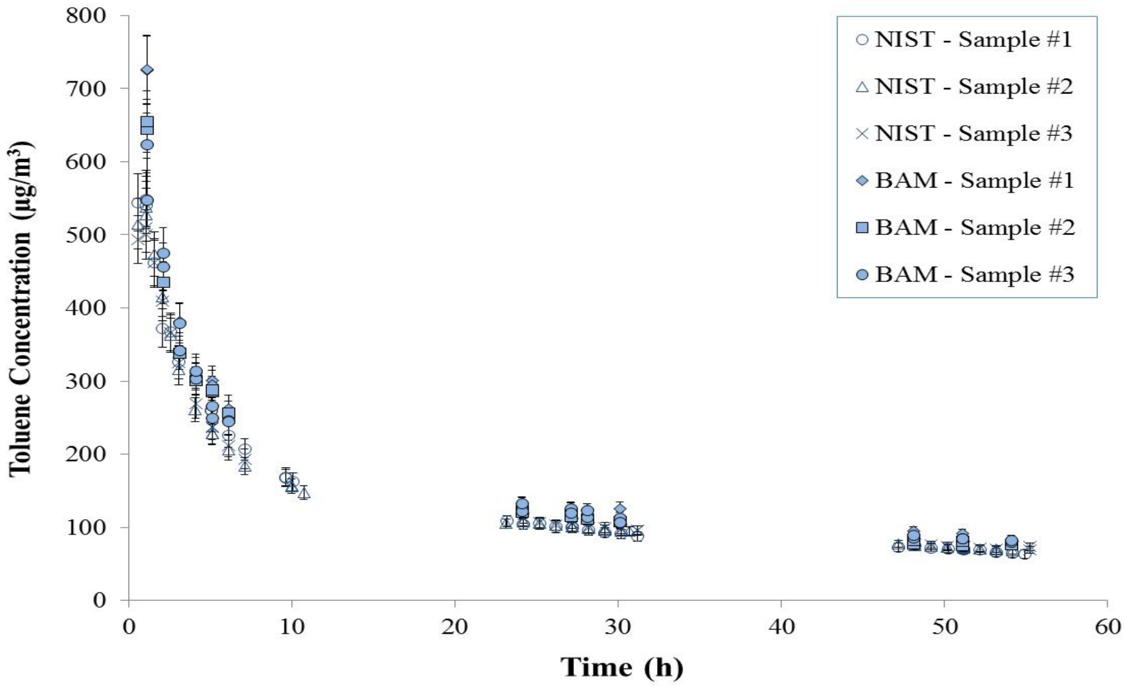
The prototype reference has an emission profile similar to a "real" building material. As shown in Figure 2, the chamber air concentration of toluene reaches a maximum value within the first 1 h to 2 h the film is in the chamber and then decays exponentially as a function of time. The error bars for each data point in Figure 2 represent an expanded uncertainty. The general shape of the emission profile has been consistent between tests, however, the peak concentration was reduced for lower temperature tests and older sample films (> 23 days at time of test).[7] Factors such as relative humidity and use of a mixing fan have not been shown to impact the chamber concentrations.[6]

Figure 2. Reference Material Example Emission Profile



A next step in the reference material development is to establish its reference emission value. Since there is not a primary measurement method available to measure the emission rate, the reference emission value for a batch of reference films may be established by chamber measurements at a single laboratory and/or multiple laboratories. Several pilot inter-laboratory studies have been conducted to compare NIST measurements to other laboratories. Figure 3 shows a comparison with The Federal Institute for Material Research and Testing in Germany (BAM). As shown in Figure 3, the reference film behaved similarly in the different chambers. The higher peak concentration in the BAM chamber can be attributed to its size being half that of the chamber at NIST. At the later sampling points, the relative standard deviation between the two laboratories is less than 10 %. A second pilot ILS with four laboratories was conducted where again the mean emission rate for all four laboratories were similar with a relative standard deviation between the laboratories of 9.4 % at a sampling time of 48 h. This level of consistency between laboratories indicates that it will be possible to establish the source's reference emission value based on measurements in multiple laboratories.

Figure 3: Results of Pilot International ILS



CONCLUSIONS

A prototype reference emissions source has been developed that provides a valuable tool for validating and even improving the performance of product emissions testing chambers. Proof-of-concept tests 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. With improved laboratory accreditation in place, there is the potential for substantial growth in the sustainable building products market. To date, the prototype material has been successfully evaluated in multiple laboratory chambers and at several different operating conditions. Current work includes improving the material packaging for shipping and storage and developing a process to manufacture hundreds of films in a single batch.

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