Evaluation of a Formaldehyde Reference Material for Small Chamber Emission Testing

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SUMMARY
Formaldehyde reference materials are being developed by the National Institute of Standards and Technology (NIST) for use in regulatory emission testing certification programs. Emission rates for a prototype formaldehyde reference material were determined using small-scale chamber experiments. The uncertainty associated with the average emission rate was determined using a set of six reference material prototypes and measurement traceability to the International System of Units (Kg, m, s). Overall, the 95 % confidence interval on the random (Type A) error plus the quantified systematic (Type B) error represents 4.9 % of the average emission rate. A four lab inter-comparison study was performed using the prototype reference material. Three of the labs measured similar emission rates, with a relative standard deviation of 3.2 %. The fourth lab measured higher emission rates; the cause was not investigated.

KEYWORDS
Uncertainty, Building Materials, Composite Wood Products, ASTM D6007

1 INTRODUCTION
The development and use of building materials and products with low air emissions of volatile organic compounds (VOCs) is a key part of a sustainability strategy to reduce energy use in buildings while preserving indoor air quality. Reference materials are needed to help ensure the accuracy and repeatability of measured VOC emission rates associated with the labelling and certification of low-emitting products (e.g. the Untied States Environmental Protection Agency Formaldehyde Emission Standards for Composite Wood Products rule and the California Air Resources Board Airborne Toxic Control Measure to Reduce Formaldehyde Emissions Form Composite Wood Products). The goal of this effort is to produce a formaldehyde reference material prototype with small, stable levels of uncertainty that can be used for emission chamber system evaluation and trouble-shooting.


Figure 1: The prototype standard consists of a formalin ampule, a stainless-steel cap, a stainless-steel insert, two stainless steel frits with 2-μm pore size, a polydimethylsiloxane (PDMS) membrane, eight stainless steel screws, a PTFE base with 3 mL formalin well, and four o-rings.

2 METHODS
The NIST prototype formaldehyde reference material (Figure 1) consists of a polytetrafluoroethylene (PTFE) bottle with a stainless-steel cap. The bottle is loaded with formalin solution (formaldehyde in water). Diffusion of formaldehyde from the bottle is limited by a replaceable thin polydimethylsiloxane membrane in the cap. Small-scale chamber experiments following ASTM D6007 (Standard Test Method for De-

termining Formaldehyde Concentrations in Air from Wood Products Using a Small-Scale Chamber) were used to test the performance of the formaldehyde reference standard. The emission rate was calculated using a mass balance approach. The emission rate for the system, although not yet certified, has been determined in NIST environmental chambers under a range of temperatures, relative humidity (RH) and air change rates to quantify uncertainty.

Formaldehyde reference materials were sent to four laboratories for an inter-comparison study. Each lab prepared the bottle per video instructions and placed it in a chamber (20 L to 88 L) operated under the following target conditions: 25 ºC, 50% relative humidity, 1 air change per hour. The chambers were sampled in triplicate between 16-24 hours after the start of the experiment using 2,4-Dinitrophenylhydrazine (DNPH) samplers. Extracted DNPH samples were analyzed by high performance liquid chromatography (HPLC).

3 RESULTS AND DISCUSSION

Uncertainty. Using uncertainty propagation, the Type A (random) uncertainty of emission rate, E, was evaluated based on the measurements of the variables (flow rate, temperature and concentration) in sixteen different experiments using five bottles. The 95 % coverage interval (k=2) for the Type A error for experiments was 1.9 % of the average emission rate. The sum of the Type B error (systematic) was 3.0 % of the average emission rate when accounting for the flow rate, temperature and relative humidity. Overall, the 95 % confidence interval on the Type A error plus the quantified Type B error represents 4.9 % of the average emission rate.

Inter-laboratory Comparison. Results from the inter-laboratory study are shown in Table 1. The average emission rate for the four labs was 2.3 μg h^{-1} (relative standard deviation, RSD, 14 %). The uncertainty analysis showed that the emission rate should increase 0.12 μg h^{-1} $°C^{-1}$ and decrease 0.0021 μg h^{-1} $\%RH^{-1}$. Correcting for the slightly different parameters for each lab, using these relationships does not change the average emission rate value (RSD 13%).

Table 1. Results of inter-laboratory comparison. Values in parenthesis are relative standard deviations.

Lab	Average Emission Rate (μg h^{-1})	Relative Standard Deviation (%)	Chamber Volume (L)	Temperature (°C)	Relative Humidity (%)	Air change Rate (h^{-1})
1	2.1	1.8	67	24.9 (0.4)	50.7 (0.5)	1.00 (0.00)
2	2.2	1.0	20	25.0 (0.3)	47.5 (1.5)	1.01 (0.00)
3	2.2	0.2	67	25.0 (0.0)	50.3 (0.0)	1.00 (0.0)
4	2.8	3.9	88	25.3 (0.1)	47.9 (0.3)	1.00 (N/A)

The relative standard deviation for the emission rate for the first three labs was 3.2%. This is inline with the total quantified error for the bottle, 4.9%. Possible sources of the fourth lab's higher emission rates were not investigated.

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