

Characterizing Uncertainty of a Formaldehyde Reference Standard

Dustin Poppendieck

Engineering Laboratory, National Institute of Standards and Technology
100 Bureau Drive Gaithersburg, MD 20899

Content submitted to and published by:
Healthy Building 2015 Conference

U.S. Department of Commerce
Penny Pritzker, Secretary of Commerce



National Institute of Standards and Technology
Willie E May, Director

DISCLAIMERS

Certain commercial entities, equipment, or materials may be identified in this document in order to describe an experimental procedure or concept adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the entities, materials, or equipment are necessarily the best available for the purpose.

Any link(s) to website(s) in this document have been provided because they may have information of interest to our readers. NIST does not necessarily endorse the views expressed or the facts presented on these sites. Further, NIST does not endorse any commercial products that may be advertised or available on these sites.

CHARACTERIZING UNCERTAINTY OF A FORMALDEHYDE REFERENCE STANDARD

Dustin POPPENDIECK^{1,*}

¹Indoor Air Quality and Ventilation Group, Engineering Laboratory, 100 Bureau Drive, Mail Stop 8633, Gaithersburg, MD 20899-8633

*Corresponding email: dustin.poppendieck@nist.gov

Keywords: Chamber testing, formaldehyde, reference standard

SUMMARY

High performance buildings need to be energy efficient and provide adequate ventilation for indoor air quality, which can be made easier with low emitting building materials. Based in part on these motivations, the United States Environmental Protection Agency (EPA) issued a proposed rule to implement statutory formaldehyde emission standards for hardwood plywood, medium density fiberboard, and particle board products. A Formaldehyde Reference Standard (FRS) is being developed by the National Institute of Standards and Technology (NIST) to assist the implementation of this rule. The goal of this effort is to produce a FRS with small, stable level of uncertainty that can be used in emission chamber system evaluation and troubleshooting. This presentation will highlight uncertainty quantification from preliminary testing of the proposed NIST FRS to begin in February 2015.

INTRODUCTION

High performance buildings need to balance energy efficiency and providing adequate ventilation for indoor air quality. The level of required ventilation can potentially be reduced when low emitting building materials are used. The United States Environmental Protection Agency (EPA) issued a proposed rule to implement statutory formaldehyde emission standards for hardwood plywood, medium density fiberboard, and particle board products. The proposed rule requires formaldehyde emission chamber testing of various wood products and third-party certification of emission testing. A Formaldehyde Reference Standard (FRS) is being developed by the National Institute of Standards and Technology (NIST) to assist implementation of this rule. The intent of the FRS is to assist in evaluating chamber testing performance and support the small chamber/large chamber equivalency requirements in the proposed EPA rule and the existing California Air Resources Board (CARB) Airborne Toxic Control Measure (ATCM) to Reduce Formaldehyde Emissions from Composite Wood Products. Previous interlaboratory testing of standard wood products has shown large variability (e.g. 20 % standard deviations, Yrieix 2010). The goal of this effort is to produce a FRS with small, stable level of uncertainty that can be used in emission chamber system evaluation and troubleshooting.

This presentation will highlight uncertainty quantification from preliminary testing of the proposed NIST FRS. All measurements related to chamber testing (formaldehyde concentration, temperature, relative humidity, flow and pressure) will be traceable to NIST primary standards. The experiments will be conducted in the spring of 2015; this abstract reviews the methods to be used.

METHODOLOGIES

Experiments will be conducted following ASTM D6007-02 (2008) (Standard Test Method for Determining Formaldehyde Concentrations in Air from Wood Products Using a Small-Scale Chamber) as closely as possible. In this method, small samples of wood are introduced into a climate-controlled chamber (0.02 m³ to 1 m³ volume, 0.5/h air change rate, 25 °C ± 1 °C temperature and 50 % ± 4 % relative humidity) at a standard loading ratio. Formaldehyde concentrations are measured once the chamber has reached equilibrium and emission rates are calculated. This work will deviate from ASTM D6007 in the following ways:

- The tested material is a formaldehyde-water solution contained in a small bottle (as described below) instead of a wood sample.
- The samples will be analyzed using a quantum cascade laser trace gas monitor. This instrument provides real time data with standard uncertainties of the measurements less than 0.1 ppb_v (0.13 µg/m³), making it advantageous compared to the chromotropic acid test procedure described in D6007.

Experiments to test the formaldehyde reference standard will be conducted in the NIST small chamber system. Only one 50 L chamber will be used in this research. A zero air generator will supply formaldehyde free air to the chamber. To achieve the desired relative humidity (50 %), humidified and dry air streams will be mixed in a controlled fashion using two mass flow controllers (MFC).

Each experiment will consist of placing a formalin-containing Teflon and stainless steel bottle in the chamber (Figure 1). This design is based on work done by Wei et. al. (2013). The 1 mL ampules of 16 % formalin solution (mass of formaldehyde/volume of distilled deionized water) will be acquired from an outside manufacturer.



Figure 1: NIST formaldehyde reference standard (FRS). The FRS consists of a formalin ampule, a stainless steel lid, a compression set screw, a polydimethylsiloxane (PDMS) membrane, four stainless steel screws, a Teflon base with 3 mL formalin well, and an O-ring. The lid is sealed to the bottle with the screws.

Formaldehyde from the FRS will diffuse through a thin polydimethylsiloxane (PDMS, 1.0 mm) membrane, eventually reaching a steady state formaldehyde concentration in the chamber. The target steady state formaldehyde concentration is between 20 and 50 ppb_v (25 µg/m³ and 63 µg/m³). The key component of the FRS is the replaceable membrane. Each time the FRS is used a new membrane and new formalin solution will be placed in the bottle. Formaldehyde concentrations will be measured using a quantum cascade laser trace gas monitor. Given the known absorption spectra for each of the known constituents, the

measured spectra can be deconvoluted to determine the concentration of the formaldehyde, formic acid and water in the sample. Currently experiments are planned to be run until the formaldehyde concentration reaches a value that does not change more than 2 % over six hours. Ten bottles have been manufactured in this first phase of the project. Initially a random selection of five of these bottles will be tested twice. Each replicate experiment of each bottle will use a new membrane and new formalin ampule. These initial data will be used to confirm that the uncertainty of the emission rate is within acceptable bounds.

Measurement Equation

The chamber system's small mixing fan produces a uniform contaminant concentration. Hence, the emission rate of the FRS will be determined using a single-zone mass balance approach. The formalin concentration in the bottle should remain relatively constant for the duration of the experiment, resulting a steady-state diffusion across the membrane. This constant emission rate will result in the chamber reaching a steady state formaldehyde concentration. The emission rate can be determined as follows:

$$E = Q(C - C_{in}) \quad (1)$$

Where E is the emission rate ($\mu\text{g/h}$), Q is the total flow rate (m^3/h), C is the formaldehyde concentration in the chamber ($\mu\text{g}/\text{m}^3$) and C_{in} is the formaldehyde concentration entering the chamber from sources other than the formaldehyde diffusing out of the bottle ($\mu\text{g}/\text{m}^3$, which should be zero).

Uncertainty in the emission rate will be quantified using the “Evaluation of measurement data — Guide to the expression of uncertainty in measurement” (JCGM 2008). This approach assumes that measurement uncertainty “reflects the lack of exact knowledge of the value” of the emission rate. Uncertainty is “best described by means of a probability distribution over the set of possible values” for the emission rate. To determine the probability distribution for the value of the emission rate, a range of factors that could influence the measured value must be considered. The emission rate is expected to depend on a range of factors including temperature, relative humidity, pressure, flow, exposed membrane area, membrane thickness, and formalin concentration. The first four factors are set points for the experimental system and may have a systematic impact on the emission rate. The last three factors will impact the emission rate in a random manner. Random variation in exposed membrane area, membrane thickness, and formalin concentration will be captured in the standard uncertainty of the emission rate. (Any instability in the values of the set point factors that lead to variations in the data will be included in these standard uncertainties as well.) Systematic errors will not be captured in the standard uncertainty values for flow and concentration. Hence, systematic errors need to be included in the uncertainty in another manner. The measurement equation used to determine the expanded uncertainty is:

$$E = Q(C - C_{in}) * f_{temperature} * f_{relative\ humidity} * f_{pressure} * f_{HCHO\ monitor} * f_{flow\ rate\ dry} * f_{flow\ rate\ wet} \quad (2)$$

Where f values are the influence quantities, which have a value of 1 for computation of the emission rate and a standard uncertainty determined via calibration of the measurement instruments to NIST primary standard reference values. Influence quantities are not required in the definition of the measurand (E in this case) but do have an effect on the measurement result through their contributions to the uncertainty.

The standard uncertainty in flow (Q) and concentration ($C-C_{in}$) will be quantified using standard deviations of the flow and concentration data, respectively. The relative contributions to the total variation seen between bottles, between membranes and ampules, and within each bottle, membrane, and ampule will all be considered as part of the assessment of the standard uncertainty of the emission rate. The standard uncertainties of the values of the influence factors will be calculated from the uncertainty comparison between the measured parameter and the relevant NIST primary standard. For example the uncertainty for the influence factor for the formaldehyde monitor will be determined from the variation seen in comparisons between the concentration values from the formaldehyde monitor and the NIST primary gravimetric standard formaldehyde reference source.

The uncertainty in the emission rate will be quantified using the measurement equation (2). A first-order Taylor series expansion with $n=1$ can be used to determine a linear approximation for the measurement equation near the value of the measurand. The Taylor series then can be used to determine the propagation of uncertainties to determine the combined standard uncertainty. The expanded uncertainty will be calculated from the combined standard uncertainty using a coverage factor of two.

RESULTS AND DISCUSSION

Experiments will commence in February 2015 and complete by June 2015. A summary of the data will be presented at the conference.

In order to develop an acceptable NIST standard reference material based on the FRS approach, additional tests will need to be conducted if the uncertainty from these preliminary experiments is deemed acceptable. Further testing will include testing of a subset of production bottles, membranes and formalin. In addition, a subset will be tested to determine stability of the system after 6 and 12 months. After stability has been confirmed and the final uncertainty deemed acceptable, untested production bottles may be certified and sold.

CONCLUSIONS

Confidence in testing results is needed if emission data are to be submitted to regulatory agencies or is used to meet voluntary product labelling standards. Verification of formaldehyde emission testing data are of particular interest, and therefore merit a reference standard with small, stable level uncertainty. This research will determine if the proposed NIST FRS will have acceptable uncertainty to serve as a verification tool.

ACKNOWLEDGEMENT

Funded in part by EPA Interagency Agreement Number DW-13-92388501-1.

REFERENCES

- Evaluation of measurement data — Guide to the expression of uncertainty in measurement. JCGM 100:2008 GUM 1995 with minor corrections: Joint Committee for Guides in Metrology; 2008.
- Yrieix, C.; A. Dulaurent; C. Laffargue; F.; Maupetit; T. Pacary, and E. Uhde. (2010). Characterization of VOC and formaldehyde emissions from a wood based panel: Results from an inter-laboratory comparison. *Chemosphere* 79: 414–419. doi:10.1016/j.chemosphere.2010.01.062
- Wei, W.; C. Howard-Reed; A. Persily; Y. Zhang. (2013). "Standard formaldehyde source for chamber testing of material emissions: model development, experimental evaluation, and impacts of environmental factors." *Environ Sci Technol* 47(14): 7848-7854.