Evaluation of a Formaldehyde Emissions Reference Material

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Formaldehyde, Emission Testing

1 INTRODUCTION

The development and use of low-volatile organic compounds (VOCs) building materials and products is a key strategy to reduce ventilation and energy use in buildings while preserving the health and sustainability of the indoor environment. Labelling and certification of low emitting products requires accurate and repeatable measurement of VOC emission rates that are comparable between laboratories. Several recent inter-laboratory studies of material emissions resulted laboratory emission rates with relative standard deviations (RSD) on the order of 15 % to 20 % (Yrieix et al., 2010, Risholm-Sundman et. al 2012). The goal of this effort is to produce a prototype formaldehyde reference material with small levels of uncertainty (< 10 % RSD) that can be used in emission chamber system evaluation and assist in identifying sources of measurement error.

The current prototype reference material consists of a NIST-constructed bottle made of polytetrafluoroethylene and stainless steel components, which is loaded with formalin solution (formaldehyde in water). Diffusion of formaldehyde from the bottle is limited by a replaceable polymer film in the cap. The key component of the formaldehyde reference standard is the replaceable polydimethylsiloxane membrane. Each time the reference material is used, a new membrane and new formalin solution are placed in the bottle.

2 MATERIALS/METHODS

Experiments to test the performance of the formaldehyde reference standard are being conducted in the NIST small (50 L) chamber system. A zero air generator supplies formaldehyde free air to the chamber. To achieve the desired relative humidity (50 %), humidified and dry air streams are mixed in a controlled fashion using two mass flow controllers (MFC). Formaldehyde concentrations are measured using a real-time quantum cascade laser trace gas monitor, with an estimated uncertainty of 0.1 $\mu g\ m^{-3}$. Experiments are conducted for at least 18 hours to ensure steady state concentrations have been reached. The steady state formaldehyde concentration was used to determine the emission rate (1) of the six reference systems:

$$E = \left(Q_{wet} + Q_{dry}\right)(C - C_{in})\frac{P}{TR} + \sum_{i=1}^{5} e_i$$

(1)

where E is the emission rate ($\mu g\ h^{-1}$), Q_{wet} is the wet flow rate ($m^3\ h^{-1}$), Q_{dry} is the dry flow rate ($m^3\ h^{-1}$), C is the formaldehyde concentration in the chamber ($\mu g/m^3$), C_{in} is the formaldehyde concentration entering the chamber from sources other than the formaldehyde diffusing out of the bottle ($\mu g/m^3$), (which should be near zero), P is the pressure in the chamber (Pa), T is the temperature in the chamber (K), and R is the universal gas constant. The e_i terms represent the systematic instrument errors (Type B uncertainty) as follows: e_1 temperature measurement, e_2 relative humidity, e_3 total air flow rate, e_4 pressure, and e_5 formaldehyde measurement.

Estimates of systematic error were determined by combining the standard uncertainties of the instrument calibration measurements with single parameter variation experiments to determine the relative impact of any calibration error. The error due to the instrument error of the formaldehyde measurement was not determined at publication time and is not included in the following results. A total of 26 experiments were run to determine Type B uncertainty using a single bottle.

For the assessment of the Type A uncertainty of the emission rate (E), each of the input variables, Q_{wet}, Q_{dry}, C, C_{in}, P, and T were treated as random with a Gaussian probability distribution with measured mean and variance. Using methods of propagation of uncertainties, the Type A (random) uncertainty of the emission rate can be evaluated based on the measurements of the variables in Equation 1. A total of fifteen experiments were run to determine Type A uncertainty using six different bottles.

3 RESULTS AND DISCUSSION

The average emission rate of the preliminary experiments was 1.76 µg h^{-1} (Figure 1). The total average Type A uncertainty was ±0.009 µg h^{-1} (± 0.5 % of the average emission rate). The total average Type B uncertainty was ±0.059 µg h^{-1} (±3.4 %).

Data in Figure 1 were measured within 18 hours of each bottle being prepared. The bottle that was used to quantify the Type B uncertainty was prepared once and re-used. After four months, the same bottle (the formalin and membrane remaining in place) was used to retest six Type B experimental conditions. The emission rates for those six repeated conditions were on average within 2.4 % of the initial values after four months of storage.
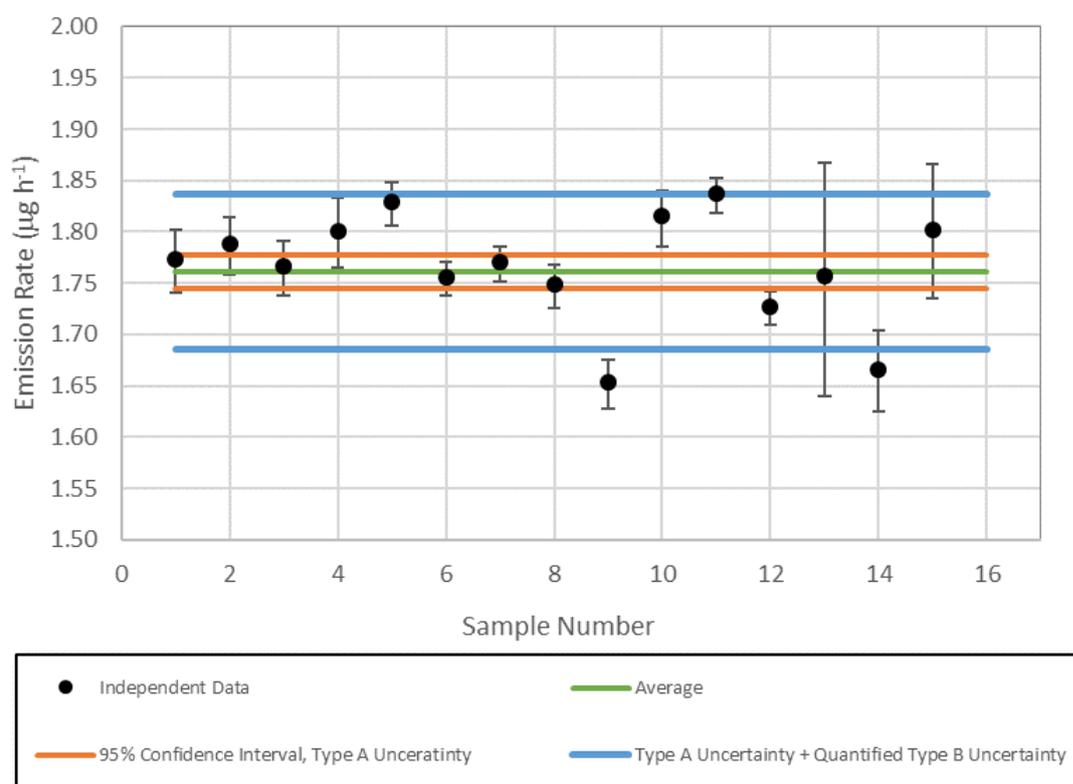

Figure 1: Error bars show 95 % confidence intervals for each experiment (k= 2). Orange lines show the minimum and maximum of the 95 % confidence interval on the Type A error (k=2). Blue lines show the minimum and maximum of the 95 % confidence interval on the Type A error plus the quantified Type B error.

4 CONCLUSION

The results show this prototype formaldehyde reference standard has a quantified emission uncertainty of less than 10 %. This prototype can be used in emission chamber system evaluation and

troubleshooting. The error due to the instrument measurement of formaldehyde measurement will be included in future efforts. An inter-laboratory study of the prototype formaldehyde reference standard will commence in summer 2017. Results of this study will determine the utility of the prototype reference material and/or assist in identifying sources of measurement error.

4 ACKNOWLEDGEMENT

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