

Assessing the uncertainty associated with product emission measurements

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SUMMARY

Volatile organic compounds (VOCs) emitted by building materials and products have been shown to significantly impact human health and comfort. As a result, the market for low emitting building materials and products is growing rapidly. However, existing product labeling programs for ranking and certifying low emitting building products and materials are not yet supported by reliable VOC emission rate measurements. Measuring VOC emissions from building materials and products is a complex multi-step process with numerous sources for measurement uncertainty. These sources include 1) selection, packaging, transport and storage of material/product samples; 2) preparation and conditioning of sample specimens; 3) operation of emission test chambers; 4) gas-phase sampling and storage; and 5) gas sample transfer and analysis. This paper describes methods to evaluate the performance of the emissions testing process and to quantify the associated measurement uncertainty. Improved understanding of emission measurement uncertainty through method validation and performance checks has the potential to increase consensus and confidence in emissions testing as well as to “level the playing field” for product testing laboratories and manufacturers.

KEYWORDS

Material emissions, Volatile organic compounds, Chamber tests, Quality control, Uncertainty

INTRODUCTION

The volatile organic compound (VOC) emissions from building materials and products have been shown to negatively impact human health (Molhave, 1991) and worker productivity (Bako-Biro et al., 2004). As a result, low-emissions or “green” product labeling programs are proliferating and the market for low emitting building materials and products is growing at a rapid rate (Malin, 2006). To demonstrate that products have low VOC emission rates, manufacturers rely on several different emissions assessment programs. Typically, these programs require laboratory measurement of a material’s VOC emission rate in a test chamber. Test chamber emission rates are then compared to specific pass/fail criteria to determine a product’s eligibility for a program’s label. However, existing green product labeling programs are not yet supported by consistent estimates of VOC emission rates. For example, it is common to see large coefficients of variation (> 40 %) in material emission rates measured between different laboratories for the same test material (Howard-Reed et al. 2006). At a recent ASTM workshop on product emissions testing, the general consensus of manufacturers, commercial test laboratories, and product purchasers is that this variability is too high (ASTM, 2006a). However, an “acceptable” or achievable level of variability has not been defined.

To improve measurement reliability and reduce interlaboratory variation, several needs are outlined in a recent paper by Howard-Reed et al. (2007) including standard emissions test methods, performance checks for emissions test laboratories, and a laboratory accreditation program. The current paper focuses on approaches to assess an individual laboratory's measurement performance. Measurement validation is a key part of product emissions testing because reliable data can only be produced when the test procedures are well understood. In this paper, several existing quality control checks and uncertainty techniques for small chamber emissions testing are presented using the steps of the International Organization for Standardization's (ISO) Guide to the Expression of Uncertainty in Measurement (GUM) (ISO 1995). Applying the ISO GUM methods to product emission measurements will undoubtedly strengthen the usefulness of test results by allowing the comparison of measurement results, establishing traceability, improving decision-making regarding product labeling, and obtaining information to improve test methods.

METHODS

The emission rates of organic compounds from building materials and products are typically measured in an environmental test chamber (ranging in size from a few liters to a few cubic meters). Several test methods exist that describe these procedures in detail (e.g., ASTM, 2006b; ASTM, 2002; ECA, 1991; CA DHS, 2004). A small chamber emission test includes the following steps: 1) selection, packaging, transport and storage of material/product samples; 2) preparation and conditioning of sample specimens; 3) operation of emission test chambers at specific environmental conditions; 4) gas-phase sampling and storage; and 5) gas sample transfer and analysis. There is uncertainty associated with each step that either directly or indirectly affects the determination of the emission rate. However, there is limited guidance in existing emissions test methods for determining the uncertainty associated with an emission rate measurement. Measurement results should always be reported with an uncertainty value to aid in interpreting and applying the value.

In 1993, ISO published the GUM to provide guidance for evaluating and expressing uncertainty for a broad spectrum of measurements. Since its publication, most national metrology institutes (NMIs) have incorporated the GUM as part of their policy for reporting uncertainty in measurement results. Several publications summarize the methods described in the GUM and related statistical information (Eurachem/CITAC, 2000; Kirkup and Frenkel, 2006; Taylor and Kuyatt, 1994). Therefore, this paper does not explain the GUM methods, but, rather, associates existing quality control and measurement validation techniques with the process of assessing the performance and uncertainty of key aspects of the product emissions test method.

ISO GUM STEPS FOR SMALL CHAMBER PRODUCT EMISSIONS TESTS

The ISO GUM methods include the following six steps for assessing a measurement result's uncertainty, which are presented below for an emission rate measured in a small test chamber.

Step 1: Define the measurand

The measurand is the unknown quantity that is determined through measurements. For small chamber emissions testing of a material, the measurand is the emission factor (*EF*) of the material being tested with typical units of (mass/area)/time (e.g., mg/(m²h)). The emission

factor is dependent on several mass transfer processes including diffusion within the material, desorption, and evaporative mass transfer, with the dominant process depending on the age and type of material. Based on the many factors that impact EF, the result is generally reported along with the test method employed, the chamber operating conditions and other key parameters.

Step 2: Build the measurement equation

The measurand is then expressed as a mathematical function with the input parameters used in its determination. There are several different mass balance models used to determine the emission factor of a given building product or material (ASTM, 2006b). As discussed above, these models depend on the type of material (e.g., wet vs. dry) and associated mass transfer processes. For example, the model equation for a simple dry material is presented below:

$$V \frac{dC}{dt} = QC_{in} - QC + EF(A) \quad (1)$$

where V is the chamber volume, C is the chamber contaminant concentration, t is the time, Q is the chamber airflow rate, C_{in} is the contaminant concentration in the inlet air, EF is the emission factor, and A is the surface area of specimen. Assuming the inlet air is relatively clean ($C_{in} = 0$), Q is constant, and the change in concentration over time is relatively small, the emission factor for a single compound at a specific time can be directly calculated from the concentration data at that time, using the following equation:

$$EF(t) = \frac{NC(t)}{L} \quad (2)$$

where N is the chamber air change rate (Q/V) and L is the specimen loading ratio (A/V). To avoid potential hidden correlations between inputs, the measurement equation is written in terms of the most fundamental measured input quantities used in its determination. Eqn. 2 then becomes:

$$EF = \frac{QM}{AV_s} = \frac{Q}{AQ_s t_s} \left(\frac{RF_t - b_0}{b_1} \right) \quad (3)$$

where M is the mass of compound in the chamber air collected on a sorbent tube, V_s is the volume of air sampled, Q_s is the sample pump flow rate, t_s is the duration of sample collection, RF_t is the response of the gas chromatograph/mass spectrometer (GC/MS) for the specific compound ion measured, b_0 and b_1 are the y-intercept and slope, respectively of the GC/MS calibration line.

Step 3: Identify the sources of uncertainty

As discussed earlier, there are several components of the emissions test process that have an associated uncertainty contributing to the overall uncertainty of the emission factor measurement. The most obvious sources of uncertainty are those associated with the basic parameters used in Equation 3: Q , RF_t , b_0 , b_1 , A , Q_s , and t_s . In addition, there may be other

parameters that do not appear explicitly in Equation 3 that may affect the measurement results and should also be considered potential sources of uncertainty. Identifying all of the important parameters that affect a measurement is often the most difficult step in assessing uncertainty (Miller and Ohno, 2005).

At a recent ASTM workshop on emissions testing, a comprehensive list of uncertainty sources for each component of the emissions test process was generated (ASTM, 2006a). Results from this exercise are presented in Figure 1. Factors in bold indicate sources of uncertainty the workshop participants listed as significant based on previous experience. Italics indicate parameters from Equation 3.

Step 4: Quantify uncertainty components

Not all of the sources of uncertainty shown in Figure 1 will make a significant contribution to the combined uncertainty of a measured emission factor. In general, it is best to focus on uncertainty sources that “have a magnitude of one-third or more of the largest source.” (Eurachem/CITAC, 2004). The significant uncertainty sources will depend on material type and test method. For the purposes of discussion, this paper considers a simple dry material emitting a VOC that can be collected and analyzed using a sorbent tube and GC/MS.

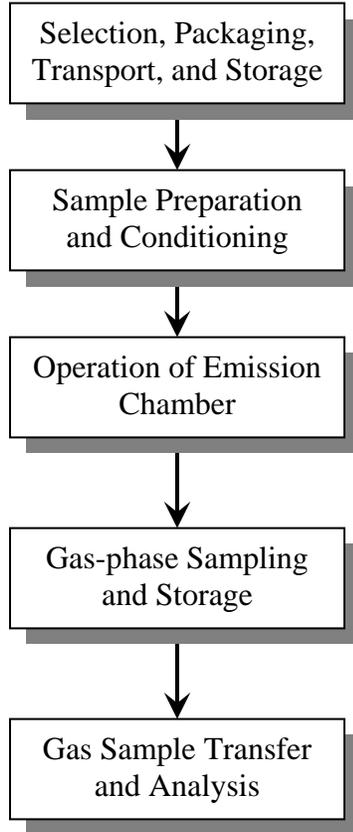
For a dry material, factors such as chamber air velocity and turbulence, material application, substrate effects and material assembly have little impact on the emission result. It is possible to minimize the importance of some factors that are specified in the test method by limitations on accuracy and precision. For example, the chamber temperature can be specified as $23^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ as measured by a traceable thermocouple or thermistor and automatically controlled. Other parameters that are typically specified in the method to minimize impact on the test result include: chamber relative humidity, chamber airflow rate, specimen size, specimen preparation (e.g., minimizing edge effects), conditioning environment parameters and sample times (ASTM, 2006b).

Some potential sources of uncertainty related to the operation of the test chamber can be reduced through performance checks outlined in ASTM D5116. For example, the background concentration of VOCs in the test chamber can be measured to ensure all individual compounds are less than $2 \mu\text{g}/\text{m}^3$ and total concentration is less than $10 \mu\text{g}/\text{m}^3$. If these criteria are not met, the chamber and/or the inlet air may be cleaned to reduce any background interference with the result. An assessment of air mixing can be conducted prior to emissions testing to ensure measured concentrations are representative of the entire chamber volume. If the mixing level as determined by the process described in ASTM D5116 is less than 80 %, a mixing fan or airflow supply can be added. Similarly a compound of interest may be injected in the chamber to assess the potential of the chamber walls to act as chemical sinks.

Information regarding the ability of the sample media to collect and store the compound of interest is often available from the manufacturer or other sources, or can be independently determined through breakthrough tests and sample recovery tests (ASTM, 2003). Use of sample blanks, internal standards and distributed volume pairs can also identify potential sampling issues that should be corrected (ASTM, 2006b; ASTM, 2003). Finally, it is possible

to check the performance of the analytical system through replicate pre-loaded standards of known mass (ASTM 2007).

Product Emission Factor Analysis Steps



Potential Sources of Uncertainty for Each Step:

Test material heterogeneity, packaging materials, packaging configuration, transport conditions, storage duration, storage conditions, product age, product history

Substrate effect, material assembly, conditioning parameters, **edge effects**, **material application**, *sample surface area* (A), sample contamination

Specimen location, chamber size, wall material/sealants, tightness, air mixing, supply air/background concentration, **chamber sinks**, material sinks, **temperature**, relative humidity, *airflow rate* (Q), product loading, specific ventilation rate, turbulence, **surface air velocity**

Sample location, sample lines, **sorbent media**, **sample recovery**, media breakthrough, sample times, *sample duration* (t_s), *sample pump airflow rate* (Q_s), emission test duration, blanks, operator

Analytical equipment, **analytical method**, integration parameters, **calibration** (b_0 , b_1), **chemical type**

Figure 1. Product emissions test steps and associated potential sources of uncertainty.

Of the remaining sources of uncertainty not accounted for in Equation 3 and not discussed above, the sample's homogeneity and product history prior to testing are the most significant. A good measurement equation shall reflect all sources of uncertainty even if they are not part of the analytical solution, thus requiring Equation 3 to be modified to include terms that reflect the uncertainty associated with sample homogeneity (F_{hom}) and product history (F_{ph}).

$$EF = \frac{QM}{AV_s} = \frac{Q}{AQ_s t_s} \left(\frac{RF_t - b_0}{b_1} \right) F_{hom} F_{ph} \quad (4)$$

It should be noted the values of F_{hom} and F_{ph} in Equation 4 are equal to unity, but they have an associated uncertainty.

There are two different ways to assign uncertainty to each source in Equation 4. Type A assignments are empirically determined evaluations of uncertainty based on statistical data obtained by taking a random sample of measurements under identical conditions and are typically reported as a standard deviation or standard error. For example, the chamber airflow rate (Q) can be measured multiple times for a given air change rate using a flow meter calibrated to a traceable standard. If necessary, the mean and standard error from the repeated flow measurements are corrected with information from the flow meter's calibration and uncertainty. The uncertainty associated with the specimen surface area (A), sample pump airflow rate (Q_s), and sample duration (t_s) can be determined similarly.

The quantity $\left(\frac{RF_t - b_0}{b_1}\right)$ is used to determine the mass of contaminant in a sample (M). The standard error associated with the GC response (RF_t) can be determined using the analytical performance checks discussed above. The standard error associated with the y-intercept (b_0) and slope (b_1) of the calibration line can be obtained from the software used to perform a regression on the calibration data. Since the calibration slope and y-intercept are correlated, the following equation is needed to estimate the uncertainty associated with M (Taylor and Kuyatt, 1994):

$$u(M) = \sqrt{c_{RF_t}^2 u_{RF_t}^2 + c_{b_0}^2 u_{b_0}^2 + c_{b_1}^2 u_{b_1}^2 + 2c_{b_0} c_{b_1} u_{b_0, b_1}} \quad (5)$$

where $u(M)$ is the combined uncertainty for M ; $c_{RF_t} = (1/b_1)$; $c_{b_0} = (-1/b_1)$; $c_{b_1} = -(RF_t - b_0)/(b_1)^2$ and u is the uncertainty associated with the GC response and calibration parameters.

The uncertainty associated with the sample homogeneity and product history may also be determined through repetitive measurements, and extensive interlaboratory study and/or reference materials are required for the most rigorous determinations. In lieu of this information, ISO GUM allows the use of non-statistical information such as scientific judgment to estimate uncertainty, which is referred to as the Type B method of uncertainty evaluation.

Step 5: Calculate relative combined standard uncertainty

Each contribution to the overall uncertainty obtained in Step 4 is combined based on the law of propagation of uncertainty (Kirkup and Frenkel, 2006). For Equation 4, the combined standard uncertainty for the emission factor may be written as:

$$u_c(EF) = EF \sqrt{\left(\frac{u_Q}{Q}\right)^2 + \left(\frac{u_A}{A}\right)^2 + \left(\frac{u_{Q_s}}{Q_s}\right)^2 + \left(\frac{u_{t_s}}{t_s}\right)^2 + \left(\frac{u_M}{M}\right)^2 + \left(\frac{u_{F_{\text{hom}}}}{F_{\text{hom}}}\right)^2 + \left(\frac{u_{F_{\text{ph}}}}{F_{\text{ph}}}\right)^2} \quad (6)$$

where $u_c(EF)$ is the combined standard uncertainty for EF and $\left(\frac{u_Q}{Q}\right)$ etc. are the uncertainties in the Equation 4 parameters, expressed as relative standard uncertainties.

Step 6: Calculate the expanded uncertainty

After estimating the combined standard uncertainty of the measurement result, the final task is to compute the expanded uncertainty to show how much the measurement result may deviate from the measurand with a high level of confidence, usually 95 % or 99 %. In many areas, the most common way to compute the expanded uncertainty is by multiplying the combined standard uncertainty by a coverage factor of $k = 2$, which corresponds to an approximate confidence level of 95 % when the effective sample sizes associated with each measurement equation input are large. More information about this process is provided elsewhere (Eurachem/CITAC, 2004; Kirkup and Frenkel, 2006).

DISCUSSION

In general, emission rate uncertainties reported in the literature are standard deviations of emission rates measured for multiple tests at identical conditions. While this approach is statistically simpler than the propagation of error method described in the ISO GUM, it does not provide information about the sources of uncertainty, which could be used to improve the measurement method. However, both approaches to estimating uncertainty can be used to provide more information about the uncertainty associated with the steps of the emissions testing process not included in Equation 3. For example, Magee et al. (2003) estimated the variability in a test specimen by comparing the analytical equation uncertainty (similar to Eqn. 3) determined through the GUM propagation of error approach and the emission factor standard deviation from multiple emissions tests. Results showed the average uncertainty associated with the analytical solution to be 19%, whereas the emission factor standard deviations ranged from 4% to 136%, indicating significant specimen variability. Similar studies are needed to better understand the uncertainty associated with indirect factors that may affect the emission result. Reference materials with known emission rates are also needed to completely assess test chamber performance for improved interlaboratory comparison.

CONCLUSION

Many decisions are being made today regarding low-emitting building materials and products without complete understanding of the measurement results and the associated range of values those results represent. There are many sources of uncertainty that can affect a product's emission factor that should either be considered a significant part of the measurement result, or minimized through existing quality assurance measures and performance testing. As outlined in this paper, a good estimate of uncertainty can be achieved by concentrating efforts on the largest sources of uncertainty. Furthermore, estimation of measurement uncertainty typically does not need to be repeated frequently, since the uncertainty estimate may be reliably applied to subsequent results obtained with the same method and equipment under the same conditions. Thus, the benefits of a well-validated emissions test result are well worth the effort required to achieve them.

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