Short communication

An improved extraction method to determine the initial emittable concentration and the partition coefficient of VOCs in dry building materials☆

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ABSTRACT

Based on the extraction method presented by Smith et al. (2008), this paper proposes an improved method, the multi-emission/flush regression method, to simultaneously determine the initial emittable concentration and the partition coefficient. Compared to the extraction method, the proposed method has the following advantages: (1) it is unnecessary for the target volatile organic compounds (VOCs) to emit completely from the material, thus greatly reducing experimental time; (2) it provides a simpler way to obtain the partition coefficients of VOCs for tested materials and can avoid the measurement uncertainties at low VOC concentrations which often occur during the last few cycles of the extraction method; (3) it does not require grinding the building material into powders thus making this method more convenient to use. Comparisons were made between the initial emittable VOC concentrations determined by the original extraction method and the proposed method. Results show good agreements between these two methods. To further validate the proposed method, the type of static chamber developed by Wang et al. (2006) was used to conduct the experiment for a type of medium density board, and formaldehyde was selected as the target compound. Based on the initial emittable concentration and partition coefficient obtained using the proposed method, and the diffusion coefficient obtained by the mercury intruding porosimetry, the chamber formaldehyde concentration was predicted and compared with the experimental measurements. Results show that the predicted chamber VOC concentration using the measured parameters agree well with the experimental data.

1. Introduction

The initial emittable concentration is one of the key parameters (diffusion coefficient, partition coefficient and initial emittable concentration) that influence VOC emissions from building materials. Over the past two decades, a large number of analytical or numerical models dealing with the emission of VOCs from building materials have been proposed (Little et al., 1994; Haghighat and Zhang, 1999; Guo, 2002; Xu and Zhang, 2003; Lee et al., 2005). To simulate the emissions correctly, it is necessary to determine the aforementioned parameters. However, it is difficult to accurately and easily measure these parameters, particularly the initial emittable concentration. The lack of adequate parameter data makes it difficult to predict or evaluate the emission characteristics.

Several methods capable of determining the initial emittable VOC concentration have been recently presented in the literature. Cox and Little (2001) developed a fluidized-bed desorption (FBD) method to measure the initial emittable VOC concentration in vinyl flooring. Its main merit is that the application of cryogenic milling (CM) together with the FBD technique can accelerate the VOC emission greatly. However, the experimental system is very complicated, and the selection of sampling frequency affects the accumulative results because the concentration changes during the emission process. Yang et al. (2001) applied a numerical method to estimate the initial emittable concentration by using emission chamber data together with emission modeling through curve fitting. In this method, the material/air partition coefficient is pre-determined by empirical correlations (Bodalal et al., 2000), which may cause deviations due to differences of building materials. In addition, the maximum concentration in the chamber is difficult to detect. Wang et al. (2006) proposed a multi-sorption equilibrium regression (MSER) method to obtain the initial

emittable concentration. The building material was placed in a static chamber and emitted VOC until equilibrium. A certain amount of the target VOC was then injected into the chamber several times to produce several equilibriums. According to the peak VOC concentration after injection and the equilibrium VOC concentration, the initial concentration and partition coefficient can be obtained through linear curve regression. However, because the author used an Innova 1312 gas monitor to sample the concentration in the static chamber only every 2 min, it was possible that the peak VOC concentration was missed. Smith et al. (2008) presented an extraction method (see Section 2.1 for details) to determine the initial emittable concentration. This method often takes a long time (4 weeks) and in the last few cycles of the experiment the uncertainty of measurement increases due to the very low VOC concentrations in the chamber.

Based upon the extraction method, this paper proposes an improved method, the multi-emission/flush regression method, to simultaneously determine the initial concentration and the partition coefficient. Its salient features are: (1) it can reduce experimental time significantly (3 weeks) since it is not necessary to let the target VOCs completely emit from the material; (2) it provides a simpler way to obtain the partition coefficients of VOCs of tested materials, the determination of which is based purely on the emission (desorption) process, thus avoiding the inconsistency of the partition coefficient between adsorption and desorption processes; and (3) it does not require grinding the building material into powders, making it convenient to use and ensuring that the emission condition is similar to that in real indoor applications.

2. Principle of the improved method

2.1. Introduction to the extraction method (Smith et al., 2008)

The extraction method involves multiple equilibrium cycles and entails flushing the chamber VOCs multiple times once each VOC emission process has reached equilibrium in the static chamber. The test continues until the equilibrium concentration of the last cycle is less than $x/100$ of the first cycle so that most of the VOCs are extracted from the building materials. The choice of x depends on the experimental conditions. 1–10 are generally recommended. In the extraction method, the test materials are ground (sizes range from 0.038 mm to 4 mm for particle board for example) to minimize the effect of in-material diffusion during the test.

A series of chamber VOC equilibrium concentrations can be obtained using the extraction method. The initial emittable mass in the building material, Mt, is then obtained by using equations (1) and (2):

$$Mt = \sum_{i=1}^{n} VC_i + Ms_n \tag{1}$$

$$Ms_n = \frac{VC_n}{C_{n-1}/C_n - 1} \tag{2}$$

where, V is the volume of the chamber, m^3; C_i is the equilibrium VOC concentration in air for cycle i, µg m^{-3}; n is the last cycle of the experiment; Ms_n is the mass remaining in the building material after cycle n, µg.

The extraction method is effective for obtaining the initial emittable mass or concentration. However, it requires many cycles to reach the aforementioned condition for the equilibrium concentration of the last cycle, and is therefore very time-consuming. Typically, 4 weeks are needed to carry out one experiment. Furthermore, during the last few cycles of the extraction

method, the uncertainty of measurement may increase due to the very low VOC concentration in the chamber.

Considering these problems, this paper proposes an improved method, multi-emission/flush regression method, to determine the initial emittable concentration together with the partition coefficient.

2.2. Principle of the improved method

The improved method is based on mass conservation and Henry's linear sorption law (the specific case of Langmuir isotherm with the condition that KC_i is much less than 1). When the equilibrium state is reached, the relationship between the chamber VOC concentration, C_i, and the VOC concentration in the building material, $C_{m,i}$, can be written as follows:

$$C_{m,i} = KC_i \tag{3}$$

Mass conservation applies for every cycle. Thus, for the 1st equilibrium state, we get:

$$C_{m,0}V_m = KC_1V_m + C_1V \tag{4}$$

where, $C_{m,0}$ is the initial emittable VOC concentration in the building material, µg m^{-3}; V_m is the volume of the building material, m^3.

This can be transformed into:

$$C_1 = \frac{C_{m,0}}{K + R} \tag{5}$$

where, $R = V/V_m$.

For the 2nd equilibrium state, the following mass balance applies:

$$KC_1V_m = KC_2V_m + C_2V \tag{6}$$

And can be written as:

$$C_2 = \frac{KC_1}{K + R} = \frac{KC_{m,0}}{(K + R)^2} \tag{7}$$

Similarly, for the ith equilibrium state, we get:

$$C_i = \frac{KC_{i-1}}{K + R} = \frac{K^2 C_{i-2}}{(K + R)^2} = \cdots = \frac{K^{i-1}C_1}{(K + R)^{i-1}} = \frac{K^{i-1}C_{m,0}}{(K + R)^i} \tag{8}$$

Equation (8) can be represented as:

$$\ln C_i = \ln \frac{K}{R + K} \cdot i + \ln \frac{C_{m,0}}{K} \tag{9}$$

This is the principle mechanism of the multi-emission/flush regression method for handling the experimental data.

There are three primary advantages to the improved method: (1) it can simultaneously determine the initial emittable VOC concentration and the partition coefficient; (2) it only requires a few cycles to obtain the relation between $\ln C_i$ and i and therefore is not necessary for the target VOCs to emit completely; and (3) the determination of the partition coefficient is based purely on the emission (desorption) process, thus avoiding the inconsistency of the partition coefficient between adsorption and desorption processes as described by Jørgensen et al. (1999). These authors showed that it is not justified to apply the partition coefficients obtained from adsorption process to predict the emission characteristics of the building material.

In general, the type of sorption isotherm depends on the VOC-material pair. Tiffonnet et al. (2002) observed a linear isotherm for polar acetone sorption on acrylic paint, but a non-linear isotherm