Factor controlling the formaldehyde emission rate from building materials in small, airtight, glass desiccators

Y Kang\(^1\)*, S-J Yoo\(^2\) and K Ito\(^2\)

\(^1\) Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka, Japan
\(^2\) Faculty of Engineering Sciences, Kyushu University, Fukuoka, Japan
\(^*\) 3ES17306T@s.kyushu-u.ac.jp

Abstract. To clarify the effect of their geometries on the formaldehyde emission rate from building materials, we established a numerical model and analysis method for quantitatively investigating the formation of transient formaldehyde concentration distribution in small, airtight, glass desiccators. The detailed geometries of the desiccators, formaldehyde emission materials and the adsorbent were reproduced as 3D digital models. Numerical analyses were carried out to investigate transient formaldehyde emissions, molecular diffusion, and sorption. We considered the effect of adsorbent evaporation based on a three-component gas mixture theory. The results of the numerical analyses confirmed the impact of the adsorption and diffusion resistance of the water surface on the measured formaldehyde emission rates.

1. Introduction
The method usually adopted to measure the formaldehyde emission rate from building materials in Japan is the desiccator method, which uses a small, airtight, glass desiccator. The desiccator method is a method of measuring the emission rate for the confined space that does not assume the supply of air from the outside and is the mensuration having characteristics corresponding to the headspace method in principle. It is categorized as a passive procedure in which formaldehyde, diffused in a confined desiccator, is adsorbed (here water). This static method has been widely used as an alternative to dynamic methods (e.g., the chamber method specified in ISO 16000-9) because it is relatively inexpensive and straightforward [1]. In this method, the configuration/geometry, and the relative positions of the emission source and adsorbent may have a dominant impact on the formaldehyde emission test results. Therefore, details of the desiccator’s geometry are specified by either the international stand or a domestic standard. In Japan, the geometries of small glass desiccators are specified by the Industrial Standard, JIS R 3503, in accordance with the desiccator method prescribed as JIS A 1460 [1, 2]. However, because the market supply of this desiccator was recently suspended, it is necessary to confirm the emission and sorption characteristics of formaldehyde and to clarify the potential mechanism of emission rate measurement in the desiccator, in order to specify the alternatives. In other words, the impact of differences in desiccator geometries on formaldehyde emission test results must be revealed in order to determine the substitutability of alternative products (i.e., other marketed desiccators with different geometries).

Given this background, we focus on establishing a numerical model and analysis method for investigating formaldehyde emission and sorption characteristics in confined desiccators and discuss the impact of the desiccators’ configurations/geometries on formaldehyde emission test results. In this study, we conduct numerical analyses to examine the emission mechanism in a specific glass desiccator and then report on the factors controlling the characteristics of formaldehyde emissions from building materials.
materials in a small, airtight, glass desiccator. It is considered that these results could be of use to stipulate the formaldehyde emission rates from the international or national standard.

2. Materials and method
We created a three-dimensional (3D) digital model, which reproduces the specific desiccator geometry, formaldehyde emitting materials, and adsorbent (in this case, water). We used the model to conduct numerical analyses for investigating formaldehyde emissions and diffusion in the air, and sorption and diffusion in water. These analyses also considered the change of formaldehyde molecular diffusivity as a function of air humidity by using three-component gas mixture theory.

2.1. Glass desiccator and 3D digital model
Figure 1 shows the glass desiccators studied. This desiccator (Type R) is currently available on the market for use in the formaldehyde emission test and is specified in JIS A 1460. We prepared two versions of the Type R desiccator to explore the effects of geometrical differences and measurement uncertainty.

A 3D digital model of the internal geometry of the desiccators was generated using a laser 3D scanner (EXAscan from CREAFORM). The data error rate of this scanner, after calibration, is approximately ± 5%. In the model, the emission source consisted of ten pieces of the test specimen with a total surface area of 180 cm², and for the adsorbent, a glass crystal dish, which held 300 ml of water, was installed in the desiccator, as specified in JIS A 1460. In order to analyze diffusion and sorption characteristics in the desiccator, the inner geometries of the desiccators were discretized as an unstructured hexahedral mesh.

The two desiccators, Type R-1 and Type R-2, were the same product type and differed only in the vertical distances from the adsorbent surfaces to the bottoms of the test specimens, which were 50 mm and 45 mm.

2.2. Outline of numerical analyses
For numerical analyses, we conducted a transient analysis to investigate the formaldehyde concentration distribution and sorption rate on the water surface, using a 3D digital model. Equation (1) is the governing equation for formaldehyde diffusion in the air within a desiccator.

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_j} \left( D \frac{\partial C}{\partial x_j} \right)
\]

In the transient analysis, it was assumed that formaldehyde adsorption occurred on the water surface, and then the adsorbed formaldehyde diffused into the water. On the adsorption surface, we assumed flux conservation as a boundary condition, and the concept of a partition coefficient was also applied. The
air-water partition coefficient of formaldehyde was estimated by the Van 't Hoff equation, for considering the temperature-dependence of the test [3, 4]. Since the formaldehyde emission test is intended for building materials, the formaldehyde emission properties can be assumed to be of the diffusion-controlled emission type. Therefore, a constant flux boundary condition was assumed for the emission surface, and it was estimated through the experimental formaldehyde emission test. The transient analysis was calculated for 24 h, according to the test duration specified in JIS A 1460.

The molecular diffusivity of formaldehyde in the gas phase is the dominant factor characterizing its emission and adsorption in a confined desiccator. In the confined desiccator environment, the water vapor concentration may affect the formaldehyde diffusion coefficient, because the water (as an adsorbent) evaporates and gradually distributes itself inside the desiccator. To estimate the effect of the change in the formaldehyde diffusion coefficient as a function of water vapor, we performed a transient analysis considering a three-component gas mixture (i.e., air, formaldehyde, and water vapor). In the gas phase, the initial diffusion coefficients of formaldehyde and water vapor were set at the values calculated using the Chapman-Enskog equation; the diffusion coefficient was then estimated over time, using the Wilke equation derived from the theories of Maxwell and Stefan [5, 6]. The formaldehyde diffusion coefficient in water was set at $0.18 \times 10^{-6} \text{ cm}^2/\text{s}$, calculated using the Stokes-Einstein equation.

To discuss quantitatively the diffusion characteristics of formaldehyde in a desiccator, we introduce the concept of equivalent diffusion length of the target desiccator, $L_d$, which is defined by assuming a simplistic hypothetical condition in which the normalized surface concentration $s$ of both the building material and the adsorbent (here assumed to be a perfect sink) are constant, as shown in (3). Equivalent diffusion length of the target desiccator, $L_d$, theoretically represents the concept of one-dimensional diffusion length that is converted from three-dimensional diffusion in a desiccator of complex geometry.

\[
D_d = \frac{1 - Y_d}{Y_B / D_{ab} + Y_C / D_{ac} + \cdots}
\]  

\[
\text{flux}_m = D \frac{0 - C_s}{L_d} = D \frac{C_s}{L_d}
\]

3. Results and discussion

We carried out both experiments and numerical analyses. Firstly, formaldehyde emission tests on the building material, MDF (Medium Density Fibreboard), were conducted in a desiccator (Type R). Test specimens were pre-conditioned under constant environmental conditions of $20 \pm 2 ^\circ\text{C}$ temperature and $65 \pm 5\%$ relative humidity, following the test method specified in JIS A 1460. The total amount of adsorbed formaldehyde in the water after a 24 h test was 0.9566 mg/L (average of five trials).

To assess the prediction accuracy of the numerical analyses, coupled numerical analyses of formaldehyde emission and diffusion in the air, and sorption and diffusion in water were carried out in accordance with the experimental boundary conditions. The formaldehyde concentration in water after 24 h was 0.9103 mg/L (average for two desiccator models). While there was a difference of 5% between the experimental results and those of the numerical analyses, we concluded that this difference was not significant, considering that the standard deviation was 9%.

Figure 2 shows the time-series of the volume-averaged formaldehyde concentrations in the air and the water, from the numerical analyses of the two desiccators. The formaldehyde in the air diffused to the adsorption surface and reached a state of approximate equilibrium within the test period, as shown in Figure 2(a). On the other hand, the formaldehyde concentration in the water did not reach the equilibrium state. The volume-averaged formaldehyde concentrations in water, after 24 h, were 0.9107 and 0.9099 mg/L, respectively, in the numerical analyses for Type R-1 and Type R-2. Figures 3 and 4 show the formaldehyde concentration distribution in a confined desiccator, after 24 h. As formaldehyde was emitted at a constant flux from the emission surfaces, the formaldehyde concentration distribution in the air is gradually stratified, with the upper portion of the desiccator having a relatively high
concentration, which then decreases down to the water surface. The formaldehyde concentration distributions in water were confirmed to be linearly stratified.

We also investigated the influence of humidity on the diffusion characteristics of formaldehyde in a desiccator. Figure 5 shows the time-series of water vapor flux on the water surface and absolute humidity, in the Type R-1 desiccator, for the 24 h test period. The absolute humidity in the confined desiccator reached saturated vapor pressure within 5 hours of the test start, despite setting perfectly dry conditions in the desiccator. The water vapor flux on the water surface also reached equilibrium. Moreover, the diffusion coefficient of formaldehyde in the gas phase changed by about 1%, from 0.136 to 0.137 cm²/s; i.e., it was determined that the water vapor in the desiccator had an almost negligible effect on the diffusion characteristics of formaldehyde for the 24 h experimental period.

Figure 2. Time-series of the volume-averaged formaldehyde concentrations in confined desiccators.

Furthermore, the equivalent diffusion length, \( L_d \), was analyzed to quantify any differences in the substantive diffusion length associated with the different geometries of the desiccators. To calculate the equivalent diffusion length, we assumed a constant concentration at the surface of the building materials.
(emission sources), where the emission flux is highly dependent on the concentration distribution inside the desiccator. Steady-state analyses were then conducted, assuming that the surface concentration was zero \((Cs = 0)\) at the adsorbent surface; i.e., supposing a perfect sink condition. Table 1 shows the equivalent diffusion length, \(L_d\), by steady-state analysis for the two types of the desiccator. The \(L_d\) was evidently affected by the volume of each desiccator, and significantly by the vertical distance from the adsorbent surface to the bottom of the test specimen.

**Figure 3.** Formaldehyde concentration distribution in the air.

**Figure 4.** Formaldehyde concentration distribution in the water.

**Figure 5.** Time-series of water vapor flux on the water surface and absolute humidity.

**Table 1.** Geometric differences and steady-state analysis results for desiccator Type R-1 and Type R-2.

| Desiccator                        | Type R-1 | Type R-2 |
|-----------------------------------|----------|----------|
| Volume [L]                        | 11.45    | 11.74    |
| The vertical distance from the adsorbent surface to the bottom of the test specimen [mm] | 50       | 45       |
| Equivalent diffusion length, \(L_d\) [mm] | 851      | 794      |

4. Discussions and Conclusion
In this study, formaldehyde emission, diffusion, and sorption characteristics in a confined small glass desiccator were investigated by numerical methods. For numerical analyses, 3D digital models with emissive materials and adsorbents were reproduced in accordance with the experimental setup, and
transient analyses were carried out for 24 h. The numerical analysis results were consistent with the experimental results. The results of the transient analyses confirmed that the formaldehyde concentration distributions in the air reached an approximately equilibrium state within 5 hours of the test start, and the constant adsorption flux continued for the duration of the test, due to the high absorption capacity of water. It was also determined that the humidity change in the confined desiccator due to the water vapor generated on the water surface had an almost negligible effect on the formaldehyde diffusion characteristics. The difference in the formaldehyde concentration in water after a 24 h test for two desiccators with different geometries depends on the difference in the transient formation of formaldehyde concentration in the desiccators (in the air and water) within a few hours from the test start. For the two desiccators (Types R-1 and R-2) used in this study, it was confirmed that the impact of the transient formation of the formaldehyde concentration distributions on the measured emissions (i.e., their concentration in the water) was small, and can be considered negligible in terms of experimental uncertainty.

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