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# Standard Formaldehyde Source for Chamber Testing of Material Emissions: Modeling and Preliminary Tests

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Formaldehyde is recognized as a harmful indoor air pollutant for human health (IARC, 2004) and is emitted from building materials, including urea-formaldehyde resin in pressed wood products. Environmental chambers are typically used to measure formaldehyde emission rates from these products. However, there is no formaldehyde standard reference emissions source available to assess the overall performance of these chambers. In this paper, the development of a LIFE (liquid-inner tube diffusion-film-emission) formaldehyde reference is described. A similar LIFE reference was previously developed for toluene (Wei et al. 2012). The formaldehyde source consists of a PTFE container that holds a 16 % formaldehyde-water solution. There is a small hole in the container lid that is covered with a thin polydimethylsiloxane (PDMS) film.

To independently predict the LIFE formaldehyde emission rate, a two-component diffusion model (Figure 1) was developed.

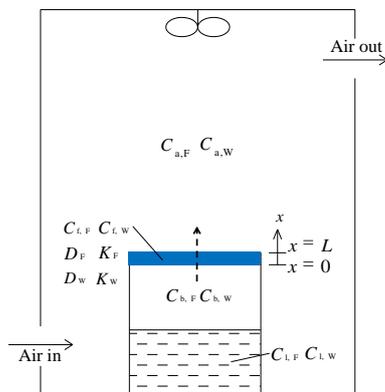


Figure 1: Schematic of emission model

$C_{i,j}$  is chemical concentration ( $\mu\text{g}/\text{m}^3$ ) at location  $i$ , which has the following values: 1 (formaldehyde-water solution), b (tube headspace air), f (film) and a (chamber air). The

subscript  $j$  is the target chemical, either W (water vapor) or F (formaldehyde).  $D_j$  is the diffusion coefficient of each component in the film ( $\text{m}^2/\text{s}$ ); and  $K_j$  is the partition coefficient of each component in the film. Henry's law is used to describe the partition of formaldehyde from the formalin solution to the tube headspace:

$$H = \exp(6548.6/T - 13.816) \quad (1)$$

where,  $H$  is the Henry's law constant ( $\text{mol}/(\text{l}\cdot\text{atm})$ ), and  $T$  is the temperature in the chamber (K) (Roumlck et al. 2010). Formaldehyde concentration in the tube headspace can be calculated as:

$$C_{b,F} = \frac{m_{l,F}}{V_w H} \times 1.013 \times 10^5 / (8.314 \times T) \quad (2)$$

where,  $V_w$  is the volume of the solution ( $\text{m}^3$ ), and  $m_{l,F}$  is the formaldehyde mass in the solution ( $\mu\text{g}$ ). Partition of formaldehyde for the film-headspace is:

$$C_{f,F}|_{x=0} = K_F \cdot C_{b,F} \quad (3)$$

For each component, the diffusion of mass in the PDMS film can be written as:

$$\frac{\partial C_{f,j}}{\partial t} = \frac{\partial^2 C_{f,j}}{\partial x^2} \quad (4)$$

where,  $x$  is the emission dimension of the film (m) and  $t$  is the time (s). Finally, the mass conservation equation for the chamber air is written as:

$$V \frac{dC_{a,j}}{dt} = -AD_j \frac{\partial^2 C_{f,j}}{\partial x^2} \Big|_{x=L} - QC_{a,j} \quad (5)$$

where,  $V$  is the volume of the chamber ( $m^3$ );  $A$  is the emission area of the film ( $m^2$ );  $L$  is the thickness of the film ( $m$ ); and  $Q$  is the airflow rate in the chamber ( $m^3/s$ ).

Equation 5 is solved numerically with the input of the diffusion coefficient ( $D_j$ ) and partition coefficient ( $K_j$ ). To measure the diffusion coefficient ( $D_w$ ) and partition coefficient ( $K_w$ ) for water, a LIFE reference with PDMS film on top and pure liquid water in the tube was put into a ventilated chamber with the temperature of 23 °C and relative humidity of 50 %. An analytical balance was used to test the mass of the tube once a day. The effective mass transfer coefficient ( $DK_w$ ) of water vapor in the film can be calculated by the rate of mass decrease in the LIFE as:

$$DK_w = \frac{dm}{dt} \cdot \frac{L}{A(C_{sat,W} - C_{50\%RH,W})} \quad (6)$$

where,  $m$  is the mass of LIFE ( $\mu g$ );  $C_{sat,W}$  is the saturation gas phase concentration of water in the tube headspace ( $\mu g/m^3$ ).

Next, two pieces of dry PDMS film (approximately 6.35 cm × 6.35 cm × 0.13 mm) were loaded with water vapor in a chamber under 23 °C and 65 % relative humidity. Initial and steady state masses of the films were measured with an analytical balance to calculate  $K_w$ .

$$K_w = \frac{m_{f,w,ini} - m_{f,w,ss}}{V_f C_{65\%RH,W}} \quad (7)$$

Table 1. Emission parameters of water in the PDMS film based on three measurements

	Mean	Standard deviation	Relative standard deviation
$DK_w$ ( $m^2/s$ )	$2.28 \times 10^{-8}$	$\pm 1.51 \times 10^{-9}$	6.61 %
$D_w$ ( $m^2/s$ )	$4.24 \times 10^{-10}$	$\pm 3.90 \times 10^{-11}$	9.18 %
$K_w$	54.13	$\pm 5.25$	9.70 %

To measure the diffusion coefficient ( $D_F$ ) and partition coefficient ( $K_F$ ) for formaldehyde, a para-formaldehyde permeation tube will be used to generate formaldehyde gas that will be

injected into a 100 ml PTFE chamber at 50 % RH. Two pieces of PDMS films will be put in the PTFE chamber. An analytical balance will be used to monitor the chamber's mass increase to steady state.  $K_F$  can be calculated by the total mass increasing while  $D_F$  can be calculated by model regression (Little et al. 1994).

The next step is to evaluate the model's ability to predict the formaldehyde LIFE reference emission rate in a chamber test at 23 °C and 50 % relative humidity (see Figure 2). An analytical balance will be used to monitor the mass change of the reference while duplicate chamber air concentration samples will be analyzed by a Fourier transform infrared spectroscopy (FTIR) and a high-performance liquid chromatography (HPLC) respectively.

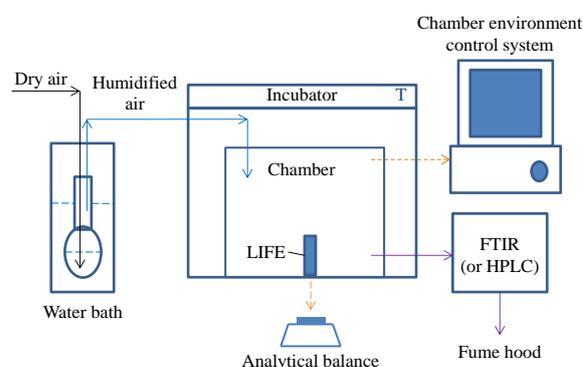


Figure 2: System for chamber test

If successful, the formaldehyde LIFE reference may be used to generate an independently known formaldehyde concentration, thereby providing a tool to evaluate chamber testing performance.

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