

# Development of passive flux sampler (PFS) for measurement of formaldehyde emission rates

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## ABSTRACT

A new type of passive flux sampler (PFS) was developed to find out the formaldehyde emission source in the indoor environment. The controlling step, e.g. the internal diffusion, external diffusion or the combination of these two diffusions, could be determined by carrying out the two or three different diffusion boundary experiments. The processes which decide the surface concentration of emission source could be estimated from the temperature dependence of the flux. As pilot study, the formaldehyde flux was measured in a model house. The flux of the floor, wall and ceiling of a bedroom was measured and those amounts were 1.20–2.56  $\mu\text{g}/\text{m}^2 \text{ h}$  at 10.5°C and 7.77–11.3  $\mu\text{g}/\text{m}^2 \text{ h}$  at 23°C. The variance of flux of the same materials fixed in the same building was sufficiently smaller than that of different materials. The source, which affects the indoor formaldehyde concentration, can be determined from this method from field measurement.

## INDEX TERMS

Flux; Emission source; Passive sampler; Indoor air; Formaldehyde

## INTRODUCTION

Recently, airtight buildings and new building materials have induced indoor air pollution in many houses in Japan. Many people are suffering from sick building syndrome (SBS). The exposure to formaldehyde, emitted from adhesive, bleach fungicide, etc., used indoors has a possibility of causing SBS symptoms, e.g. eye irritation, respiratory tract and neurotoxicity (Kim *et al.*, 2002; Paustenbach, 1997).

It is necessary to remove the source of formaldehyde; however, it is difficult to determine which source affects most, because there are several sources such as flooring, door, closet, desk and bed. An emission chamber (Myers, 1983; Tichenor, 1989; Institute for Health and Consumer Protection, 1999; ASTM, 1996, 1997), a desiccator method (Japanese Industrial Standards Committee, 1999), or Field and Laboratory Emission Cell (FLEC) (Wolkoff, 1991; Uhde, 1998; Risholm-Sundman, 1999) have been used to measure the chemical emission rate from building materials. The flux from the sample materials which are used in real buildings, however, can only be measured in a laboratory by using the chamber or desiccator method. The FLEC can be used in both field and laboratory; however, this system is not adequate to multipoint field sampling because of the size, weight and cost.

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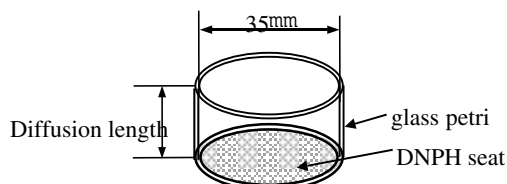
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In this study, a new type of passive flux sampler (PFS), which is a simple method to find out the emission source of formaldehyde was proposed. The target compound in this study was formaldehyde, but VOCs or Phthalate Esters emitted from building materials can also be measured by changing the media.

## METHODS

### Sampler Design

A schematic representation of the PFS is given in Figure 1. The body consists of a glass Petri dish (i.d.: 36 mm, depth: 10 or 20 mm). A 2,4-dinitrophenylhydrazine (DNPH) coated glass filter (OLBO 827, Supelco Co., USA) was used as adsorbent and set on the bottom of the Petri dish. Formaldehyde was captured as DNPH derivatives (formaldehyde–DNPH) in the adsorption filter.



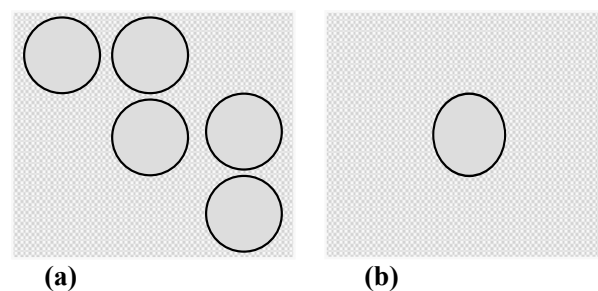
**Fig1** A schematic representation of PFS

### Quality Assurance and Quality Control (QA/QC)

The standard deviations of concentrations of five blank filters were examined to investigate the lower determination limit. The lower determination limit was defined as ten times the standard deviation (10 SD) of the mean amount the blank filters and the minimum absolute amount of the analyte at which point the calibration curve lost linearity. To determine the recovery efficiency, 100  $\mu$ l (7.40  $\mu$ g) of methanol solute formaldehyde was spiked on five filters with a micro syringe. Then the Petri dishes were covered with a tight-fitting glass plate for 60 min to remove the solvent. To evaluate the precision of this method, the flux of formaldehyde from commercially distributed plywood which is classed F<sub>C0</sub> by in the Japanese Agricultural Standard (JAS), were sampled five times on the same point for 2 h (Figure 2a). Side-by-side samplings were also carried out at five points of the same plywood for 2 h (changing samplers every 2 h) (Figure 2b).

### Diffusion Length Dependency and Temperature Dependency

The flux of a plywood board was measured to figure the controlling step of formaldehyde emission by changing the thickness of the diffusion layer. The thickness of the diffusion layer was set at 1, 3, 5, 8, 10, 13, 15, 20, 25 and 28 mm, and the sampling period was set to 2 h. Before sampling the plywood was placed in the controlled clean chamber for 24 h. Moreover, to evaluate the temperature dependence to flux, formaldehyde emission of the plywood was measured at 20, 50, and 80°C for 2 h. The diffusion length was set at 10 and 28 mm during this test.



**Figure 2** Sampler setting points for the precision tests.

### Pilot Study

Flux and indoor concentrations of formaldehyde were measured at some points in a model house. All the windows and doors were opened for air-exchange for 30 min before the sampling was done. In addition, the heating system was turned on 255 min after the sampling had started

to see the effect of heat on Formaldehyde emission in the bedroom. The sampling schedule is shown in Table 1.

**Table 1** Sampling schedule

Time		11:15	12:15	13:15	14:15	15:15	16:15	17:15	18:15
Flux sampling	Bedroom	←		←	←	←	←	←	←
	Japanese room	→		→	→	→	→	→	→
Indoor sampling	Bedroom	←	←	←	←	←	←	←	←
	Japanese room	→	→	→	→	→	→	→	→
Outdoor sampling		←	←	←	←	←	←	←	←

## Analysis

Formaldehyde was captured as DNPH derivative (DNPH-formaldehyde) on the adsorbent. The captured DNPH-formaldehyde was extracted with 5 ml of acetonitrile (HPLC grade, Wako Pure Chemicals Co. Ltd., Japan) by ultrasonication from the adsorption filter. The ultrasonic bath used was W-113 MK-2 (Honda Electronics Co., Japan) and sonication was continued for 30 min at 24 kHz. The extracted DNPH-formaldehyde was analyzed by high performance liquid chromatography (HPLC) (HP1100, Hewlett Packard, USA) with a photodiode array detector at the wavelength of 365 nm. The mobile phase was a mixture of 65% acetonitrile and 35% water with a flow rate of 1 ml/min. Twenty microlitres of the analyte was injected to a XDB-C18 packed column (ZORBAX Eclipse; 250 mm length × 4.6 mm of inner diameter; particle size 5 μm), which was set to 35°C.

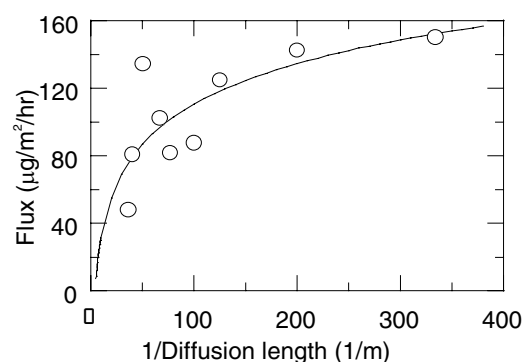
## RESULTS

### Quality Assurance and Quality Control (QA/AC)

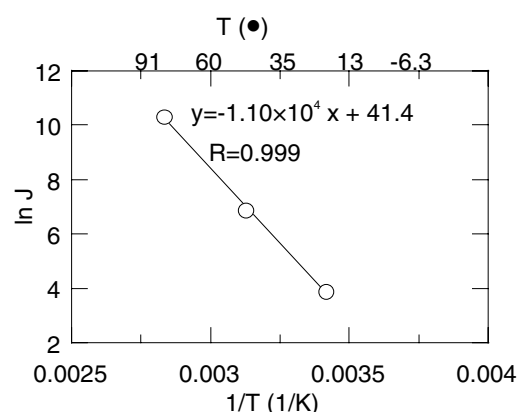
The amounts of formaldehyde in the blank filters were under detection limit (signal/noise=3). The lower determination limit was 0.0375 μg/filter, which is the concentration when the calibration curve lost its linearity. The result of recovery test was 83%. The relative standard deviation (RSD) of five filters sampled at the same point was 8.26% while that sampled at five points was 26.3%.

### Diffusion Length Dependency and Temperature Dependency

The diffusion length dependency of flux is shown in Figure 3. The formaldehyde flux was proportional to the reciprocal of the length of diffusion layer at the range over 10 mm while it was constant regardless of the length of diffusion layer at the range of below 10 mm.



**Fig. 3** Flux and Diffusion Length Reciprocal



**Fig. 4** Arrhenius plot of formaldehyde from plywood (Diffusion length; 10mm)

To estimate the rate-determining step for the surface formaldehyde concentration of plywood, the activation energy was determined by an Arrhenius plot. The Arrhenius plot had a good linearity in the case of both 10 mm (Figure 4) and 28 mm of diffusion length. No significant differences were observed. This means that the surface formaldehyde concentration of plywood was controlled by the same rate-determining step irrespective of the diffusion length.

### Pilot Study

Indoor and outdoor levels are shown in Table 2. The results of formaldehyde flux are shown in Table 3. The formaldehyde fluxes of the floor, wall and ceiling of the bedroom were 1.20–2.56  $\mu\text{g}/\text{m}^2 \text{ h}$  at 10.5°C and 7.77–11.3  $\mu\text{g}/\text{m}^2 \text{ h}$  at 23°C. The RSD of the triplicates measured on the wall and ceiling were 11.3 and 24.7%, respectively.

### DISCUSSION

Assuming that formaldehyde diffuses by only molecular diffusion and the surface concentration is zero, the formaldehyde flux from emission source follows Ficks' law:

$$J = -D \frac{C_0 - C_\infty}{L}$$

$$\left( \begin{array}{l} J [\mu\text{g}/\text{m}^2\text{s}]: \text{Flux } D [\text{m}^2/\text{s}]: \text{Diffusion coefficient} \\ L [\text{m}]: \text{Thickness of boundary layer} \\ C_0 [\mu\text{g}/\text{m}^3]: \text{Surface concentration of material} \\ C_\infty [\mu\text{g}/\text{m}^3]: \text{Indoor concentration} \end{array} \right)$$

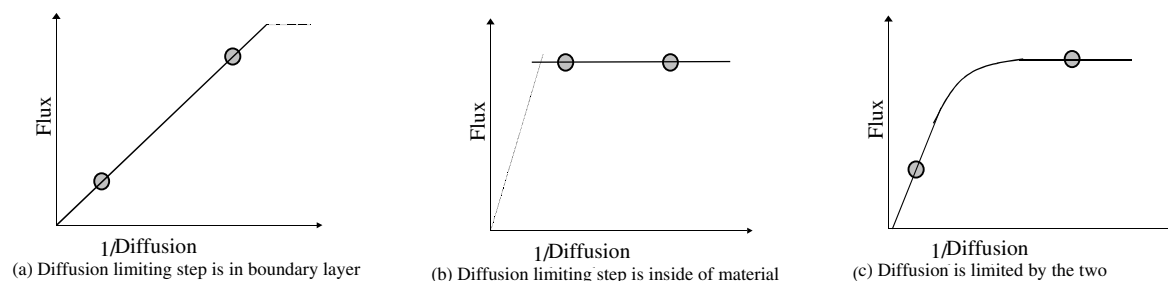
**Table 2** Indoor concentrations of formaldehyde

Location	Sampling	Indoor conc. ( $\mu\text{g}/\text{m}^3$ )
Outdoor	11:16-13:52	1.89
Bedroom	11:15-11:45	4.21
	11:45-12:15	5.15
	12:15-13:14	10.3
	13:15-15:04	14.3
	15:13-17:22	18.2
	17:22-19:28	22.4
Japanese room	11:55-12:26	3.73
	12:30-13:04	4.94
	13:13-15:04	8.94
	15:06-16:40	9.19

**Table 3** Formaldehyde fluxes from each emission source.

Room	Source	Flux ( $\mu\text{g}/\text{m}^2$ )
Bedroom (10.5°C)	Desk	0.675
	Chair	8.27
	Floor	1.20
	Wall	2.52
	Door	1.74
	Closet door	0.906
	Ceiling	2.56
Bedroom (23°C)	Floor	10.8
	Wall 1	12.8
	Wall 2	12.4
	Wall 3	10.3
	Ceiling 1	7.05
	Ceiling 2	6.31
	Ceiling 3	9.94
Japanese room (13.6°C)	Pillar	7.50
	Tatami mat	8.59
	Wood floor	3.93
	Clay wall	8.37
	Ceiling	4.11
	Sliding screen	10.2

In the case when formaldehyde flux depends on external diffusion (diffusion in boundary layer), the surface concentration of the emission source will be maximum in this condition and the flux would be proportional to the reciprocal of the length of diffusion layer (Figure 5a). In the case when formaldehyde flux depends on internal diffusion (diffusion, reaction, absorption or desorption in the materials), flux is maximum and constant (Figure 5b).



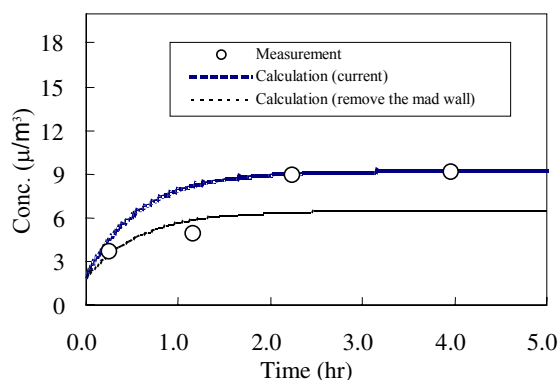
**Fig.5** Example of the Results of Flux Plot

Formaldehyde emission of the plywood, tested in this study, depended on internal diffusion when the diffusion length was over 10 mm. The thickness of the boundary layer depends on the velocity of indoor wind which was reported as 5.3–15 cm/s in previous papers (Hart and Int-Hout, 1980; Schiller and Arens, 1988; Matthews *et al.*, 1989). The thickness of the boundary layer was 14–16 mm when the velocity of indoor wind was 8 cm/s (Bruce, 1993). Thus, we can know whether the formaldehyde emission depends on internal diffusion, external diffusion or mixed diffusion by the flux measurement in two thicknesses (10 and 20 mm) of the diffusion boundary (Figure 5).

The activation energies, calculated by the slope of the Arrhenius plot, were 91.3 (diffusion length: 10 mm) and 87.3 kJ/mol (28 mm). Comparing to the activation energy of molecular diffusion (10–30°C, 3.65 kJ/mol), evaporation of formaldehyde (23.0 kJ/mol) (Kagakukougakukai, 1999) and decomposition of paraformaldehyde (93.5 kJ/mol) (Takaya and Minato, 1997), the surface formaldehyde concentration of this plywood could possibly depend on the decomposition of paraformaldehyde. In the pilot study, temperature dependence of flux from each source was different. Thus, it was suggested that the formaldehyde emission of each material depends on different processes.

The flux variances in the same material were sufficiently smaller than those among the different building materials. Thus, it was confirmed that the largest emission source can be decided among several suspected materials in a room by this method.

The indoor formaldehyde concentration was estimated from the measured flux amounts, indoor volume and fitting parameter (Figure 6). The scale of the room was set at  $3.64 \times 3.64 \times 2.6$  m and perfect mixing was assumed. The fitting parameter was used as air-exchange rate for the calculation. The initial level was set at outdoor level ( $1.92 \mu\text{g}/\text{m}^3$ ). The indoor level after removal of the main emission source was also simulated by this calculation.



**Figure 6** Simulation results of indoor formaldehyde levels after removal the emission source.

## CONCLUSION

A new type passive flux sampler (PFS) was developed and applied to find out the formaldehyde emission source. By the measurement of formaldehyde flux in different diffusion lengths, we can know whether the formaldehyde emission depends on internal diffusion, external diffusion (diffusion in boundary layer) or the combination of internal and external diffusions by carrying out the experiments in two or three thicknesses of the diffusion boundary. From the pilot study, formaldehyde flux was measured in a model house. By using this method, the largest emission source can be found from several suspected materials in a room.

## ACKNOWLEDGEMENT

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## REFERENCES

- American Society for Testing and Materials (ASTM) (1996). E1333-96, Standard Test Method for Determining Formaldehyde Concentrations in Air and Emission Rates from Wood Products Using a Large Chamber.
- American Society for Testing and Materials (ASTM) (1997). D5116-97, Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products.
- Hart, G.H. and Int-Hout, D. (1980). The performance of a continuous linear air diffuser in the perimeter zone of an office environment. *ASHRAE Transactions* **86** (Part 2), 107–124.
- Institute for Health and Consumer Protection (European Commission) (1999). ENV717-1, Wood-based Panels. Determination of Formaldehyde Release, Formaldehyde emission by the chamber method.
- Japanese Industrial Standards Committee (2001). A1460, Building boards; Determination of formaldehyde emission. Desiccator method.
- Kagakukougakukai (1999). *Kagakukougakubinran*, 6th edn. Maruzen, Japan, pp. 17–46.
- Kim, W.J., Terada, N., Cono, A. *et al.* (2002). Effect of formaldehyde on the expression of adhesion molecules in nasal microvascular endothelial cells: the role of formaldehyde in the pathogenesis of sick building syndrome. *Clinical & Experimental Allergy* **32** (2), 287–295.
- Matthews, T.G., Thompson, C.V., Hawthorne, A.R. *et al.* (1989). Air velocities inside domestic environments: an important parameter in the study of indoor air quality and climate. *Environment International* **15**, 545–550.
- Myers, G.E. (1983). Formaldehyde emission of particleboard and plywood paneling: measurement, mechanism; and product standards. *Forest Products Journal* **33** (5), 27–37.
- Risholm-Sundman, M. (1999). Determination of formaldehyde emission with field and laboratory emission cell (FLEC)—recovery and correlation to the chamber method. *Indoor Air* **9**, 268–272.
- Schiller, G.H. and Arens, E.A. (1988). Thermal comfort in office building. *ASHRAE Journal* **39**, 26–32.
- Takaya, Y. and Minato, K. (1997). Mechanism of formaldehyde emission from wood substances and reducing effect by ammonia treatment. *Mokuzai Gakkaishi* **43** (5), 427–433.
- Tichenor, B.A. (1989). Indoor Air Sources; Using Small Environmental Test Chambers to Characterize Organic Emissions from Indoor Materials and Products, EPA-600/8-89-074.

- Uhde, E., Borgschulte, A. and Salthammer, T. (1998). Characterization of the field and laboratory emission cell—FLEC: flow field and air velocities. *Atmospheric Environment* **32** (4), 773–781.
- Wolkoff, P., Clausen, P.A., Nielsen, P.A. *et al.* (1991). Field and laboratory emission cell: FLEC. *Healthy Buildings '91*, ASHRAE, pp. 160–165.
- Yoshida, H. (1998). Zitudai zikkentou wo siyousita formaldehyde kityu noudo no sokutei. *The 19th Mokuzai settyaku kenkyukai*, pp. 1–16.