

# **A new method to measure the emission rate of VOCs with passive flux sampler and evaluation of PFS with reference emission material**

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## **ABSTRACT**

In previous researches, the methods of measurement of VOCs emission rate such as field and laboratory emission cell (FLEC, Wolkoff) or Chamber method have already been established but these methods have a possibility to overestimate the emission in some cases because its airflow near the surface of materials makes the thickness of the boundary layer thin. This research aims to develop a new method to measure VOC emission rates from building materials, using a passive flux sampler (PFS), which is based on the air phase diffusion phenomenon in the sampler. Moreover, a reference emission material (REM), which emits VOCs constantly, was considered. The calculated result implies that REM with liquid toluene as gas dozer can emit about 640  $\mu\text{g}/\text{m}^2/\text{h}$  of toluene converted to the face emission flux of PFS.

## **INDEX TERMS**

Volatile organic compounds; Emission rate; Passive flux sampler; Reference emission materials; Thermal desorption; GC/MSD

## **INTRODUCTION**

Recently, indoor air pollution caused by volatile organic compounds (VOCs) from building materials is known as sick building syndrome or multiple chemicals sensitivity. The ultimate solution to this problem is to use low-VOC-emitting materials. Thus, to evaluate the effects of emission sources on indoor air, we tried to obtain the emission rate of each VOC from building materials. The methods such as field and laboratory emission cell (FLEC) (Wolkoff, 1991) or Chamber method (Afshari *et al.*, 2003), however, may overestimate emission because the clean airflow near the surface of materials makes the thickness of the boundary layer thin and may promote increase of emission. This problem was improved in the passive flux sampler (PFS) method by fixing the diffusion length as 10–20 mm, that is, the length of general boundary layer in the dwelling (Tichenor *et al.*, 1993; Zhang *et al.*, 1995).

The existing methods for emission rate measurement need some large-scale instruments, and so they are suitable for measuring pre-application materials. However, they are not suitable for measuring the building materials in real buildings. PFS is small, light and easy-to-use so that it can be useful to measure emission rate of VOCs from real buildings.

PFS is very inexpensive compared to FLEC or other chambers because of its simple

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structure and principle. PFS contains a Petri dish with carbon adsorbent at its bottom. The adsorbent is fixed to the Petri dish by a steel mesh so that it will not drop off. PFS uses only air phase diffusion. Its concept makes the sampling method very simple. The concentration of adsorbent surface is assumed to be zero during the sampling because it is assumed that the adsorbent trapped VOCs immediately.

In this study, we tried to measure a wood board by the PFS method. The objective of this sampling was to figure out whether the dispersion of the obtained emission rate in the identical material depends on measuring positions or not. In other words, we investigated the representation of emission rate from the material. Moreover, for helping the study of VOC emission rates from building materials, we tried to make a material that is a constant VOC emission source.

The objective of making a reference emission material (REM) is that REM will enable the evaluation of the accuracy of its analysed output data. The reference room where the concentration of VOCs is controlled constantly has already been studied. But the reference emission material that emits constantly and gives emission flux has never been studied. In this paper, we showed the concept of reference emission material and theoretical calculation to imply the realizable possibility.

## PASSIVE FLUX SAMPLER (PFS)

### Structure

The structure of passive flux sampler is shown in Figure 1. The frame consists of glass Petri dish. The bottom of the dish is paved with adsorbent (Carbotrap 20/40 mesh, Supelco, USA) by 360 mg. In order to trap VOCs as much as possible, the maximum amount limited by the volume of thermal desorption tube (ATD tube) was paved on the bottom of PFS. Thus the diameter of the PFS is determined to be 41 mm. Adsorbent is fixed by stainless mesh and BT tube (PTFE tube). The flux from the building material is only ruled by Fick's First Law (Figure 2):



Figure 1 Diagram of PFS.

$$E = D \frac{\partial C}{\partial L} \quad (1)$$

where  $E$  is the emission rate ( $\mu\text{g}/\text{m}^2/\text{h}$ ),  $D$  the diffusion coefficient ( $\text{m}^2/\text{s}$ ),  $C$  the concentration of VOCs ( $\mu\text{g}/\text{m}^3$ ) and  $L$  the diffusion length (m).

This equation shows the emission flux is expressed only by the gradient of the VOC concentrations between the air phase inside the Petri dish and the surface of the adsorbent.

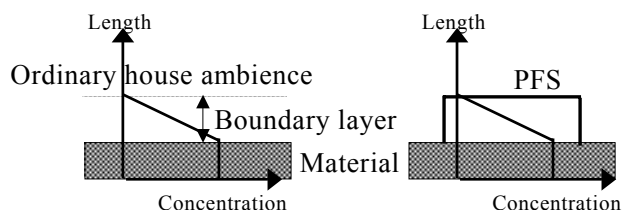


Figure 2 Concept of boundary layer and PFS.

In this study, in order to simplify the model of the diffusion phenomenon, we assumed that the concentration at the adsorbent's surface is hypothesized to zero. The height of the PFS was set to 15 mm

because the thickness of the boundary layer in buildings was estimated to be about 10–20 mm (Tichenor *et al.*, 1993; Zhang *et al.*, 1995).

### Sampling and Analytical Method

The following procedure was used to measure emission from indoor materials such as ceiling, wall, floor and furniture. PFS was placed on various building materials for a specific period. Then the sampler is retrieved and analysed by TDS-GC/MS.

After retrieving the sampler, the adsorbent set on the bottom of the sampler was removed and packed into the thermal desorption tube (Perkin Elmer, USA). The VOCs trapped in the adsorbent were injected into a gas chromatograph (HP6980, Hewlett Packard) introduced by a thermal desorption system (ATD 400, Perkin Elmer Inc., USA). The parameters of the TDS-GC/MSD method are shown in Table.1. From the obtained amount of VOCs by the mass selective detector (MSD), the emission rate was given by

$$E = \frac{n}{ST} \quad (2)$$

where  $E$  is the emission rate ( $\mu\text{g}/\text{m}^2/\text{h}$ ),  $n$  the obtained amount (ng) and  $T$  the sampling time (h).

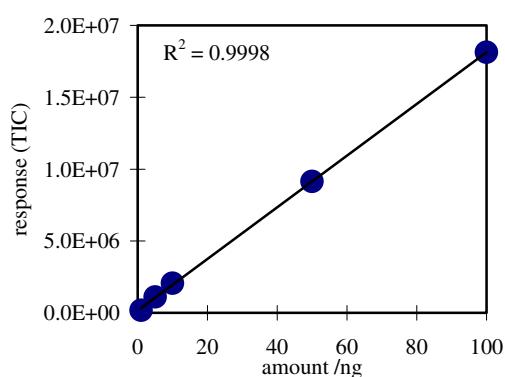
### Experimental Sampling

#### Calibration

The calibration curve of each chemical was drawn by spiking the ATD tube with VOC standards (Japanese Indoor Air Standards Mix, 52 compounds, cat. #47537-U, Supelco, USA) and diluted by methanol. Each standard contains 0, 0.1, 0.5, 1, 5 and 10 ng/ $\mu\text{l}$ . These standards were injected 10  $\mu\text{l}$  into each ATD tube with adsorbent. Thus each standard tube contains 0, 1, 5, 10, 50 and 100 ng of VOCs. The result showed that calibration curve was precisely linear. And the detective and quantitative limit was calculated from the standard deviation (SD) of response of the blanks. The detection limit was defined as three times the SDs, and the quantitative limit was defined as ten times the SDs. The calibration curve and quantitative limits of VOCs are shown in Figure 3 and Table.2.

**Table 1** Analytical conditions

TDS	Prime desorbing time	10 min
	Oven temperature	300°C
	Cold trap temperature	5°C
	Trap hold	10 min
	Out split ratio	1:10•15
	Line temperature	225°C
GC	Prime temperature	40°C
	Prime hold	4 min
	Programming rate	10°/min
	Maximum temperature	280°C
	Carrier gas	He
MSD	Mode	Scan
	Mass range	46–550



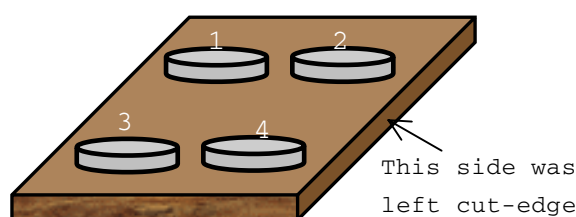
**Figure 3** Calibration curve of benzene.

**Table 2** Quantitative limits of VOCs

VOC	Quantitative limit (ng)
Toluene	5.3
Benzene	0.7
Ethylbenzene	4.2
<i>m,p</i> -Xylene	2.0
Styrene	1.0
1,3,5-Trimethylbenzene	1.1

### Sampling

We tried to measure the emission rate from laminated wood board. In this experiment, four samplers were set on the surface of the board and another four samplers were set on the opposite surface. Sampler-5 was set on the opposite side of sampler-1, sampler-6 was on the opposite side of sampler-2, and so on. In this way, eight samplers were set as shown in Figure 4. The even-numbered samplers were set near the cut-edge of the board, and odd-numbered ones were away from the cut-edge. They had been placed for 24 h under a temperature set to 25°C condition.



**Figure 4** Sampling method: #5 is on the opposite side of #1, #6 is of #2, #7 is of #3, #8 is of #4.

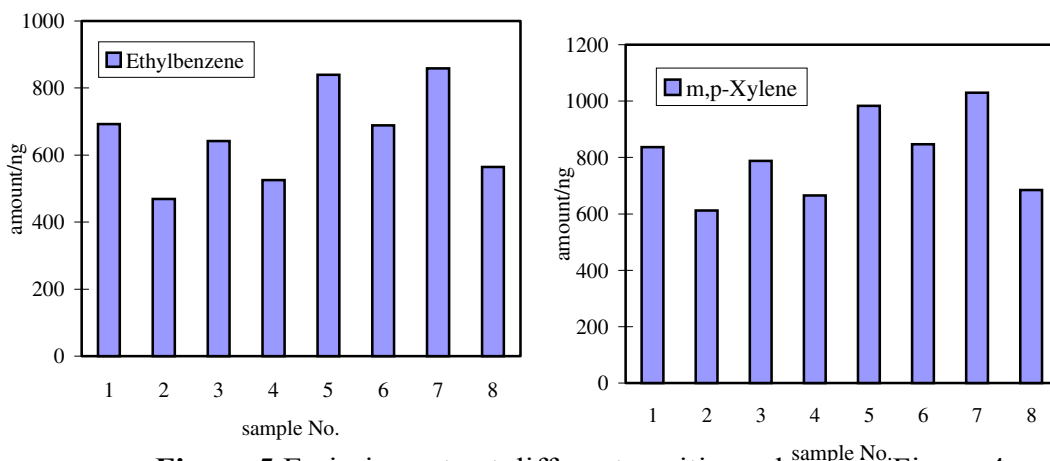
### Results

In this analysis, 30 kinds of VOCs could be determined. The emission rate and relative standard deviation (RSD) at the same material are shown in Table 3. The RSD of the same material is about 19–42%. Hexane, toluene, ethyl benzene, and *m,p*-xylene were emitted relatively more. In addition, analytical errors of VOC amounts are 6% as RSD in average and almost below 10%. Each emission rate was far above the quantitative limit. The results show that the emission from the same material varies widely.

**Table 3** Emission rate and RSD at different positions

VOCs	RSD (%)	Emission rate ( $\mu\text{g}/\text{m}^2/\text{h}$ )	Quantitative limit ( $\mu\text{g}/\text{m}^2/\text{h}$ )*
Hexane	25	17.8	3.6
Benzene	31	1.37	0.24
Trichloroethylene	41	0.651	0.057
Toluene	18	18.7	0.098
Ethylbenzene	21	20.8	0.022
<i>m,p</i> -Xylene	18	25.4	0.10
Nonane	19	1.53	0.055
Alpha-Pinene	20	1.03	0.55
Decane	25	5.89	0.21
<i>p</i> -Dichlorobenzene	40	0.582	0.088

\*Amount of quantitative limit were converted to emission flux.



**Figure 5** Emission rate at different positions shown in Figure 4.

### Discussion

The value of the RSD implied that the emission rate differs among the positions on the board. In this study, however, the variation of emission has recognizable patterns that odd numbers of samplers showed higher levels of emission than even ones. The reason for the difference was that the sites of even numbers are near the cut edge of the board and the edge was exposed by air, while odd number sides was coated with paint.

This study showed that the deviation of emission rate at each position was so large that it must be considered in sampling and analysis and that the effect of cut edges could not be ignored.

### REFERENCE EMISSION MATERIALS

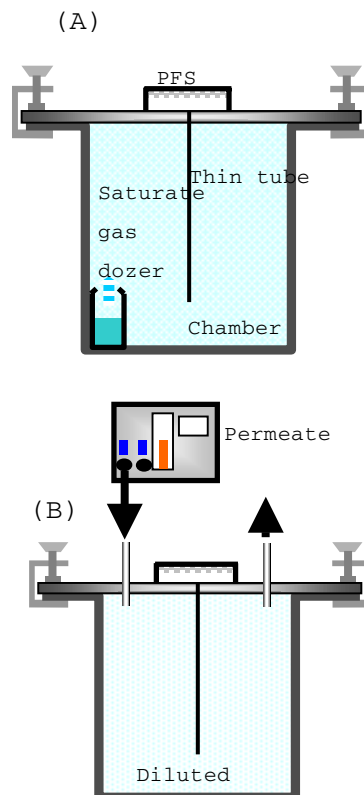
#### Designs and Principles

Two types of REMs are shown in Figure 6. (A)-material consists of a chamber, a saturate gas dozer, and a thin tube. The chamber (SUS304) encloses saturated VOC gas such as toluene. The dozer emits VOC gas by evaporation. The concentration in the chamber is constant because the saturated gas dozer supplies it with gas rapidly. A thin tube (PTFE tube) is set on the chamber. A thin tube works as diffusion resistance and depends on its length and width. The obtained amount of VOCs is measured by weight decrease of liquid sample in the dozer or by using the chamber method.

The structure of (B)-material is also shown. The chamber is filled with diluted VOC gas using a permeater which generates airflow of constant concentration. This compensates for the higher levels of VOC concentrations of (A)-material. In this way, the emission rate can be controlled by changing its parameters.

These methods, using thin and long tubes, have some advantages. The diffusion resistance of the tube is so large that the diffusion resistance of air in PFS can be negligible.

Moreover, the constants related to diffusion are so well known that we may be able to obtain the emission rate that we predicted.



**Figure 6**

### Calculation

Diffusion time in the PFS is far shorter than that in thin tube. Thus the flux was hardly inhibited by the resistance of the boundary layer in PFS. Adsorbent adsorbs more rapidly than the supply rate.

This calculation was performed by

$$Q = S' \frac{D}{L_{\text{tube}}} (C - C^*)T = S \frac{D}{L} (C^* - C_s)T$$

where  $Q$  is the emitted amount (ng),  $C$  the concentration in chamber ( $\mu\text{g}/\text{m}^3$ ),  $D$  the diffusion coefficient of air phase ( $\text{m}^2/\text{s}$ ),  $C^*$  the concentration of the material ( $\mu\text{g}/\text{m}^3$ ),  $S$  the tube cross-sectional area ( $\text{m}^2$ ) and  $T$  the sampling time (h).

The following parameters were assumed. (A)-material was assumed in this calculation. The length of the thin tube was 1000 mm, internal diameter was 0.5 mm, the concentration in the chamber was  $1.4 \times 10^5 \mu\text{g}/\text{l}$ , and the temperature was set to  $25^\circ\text{C}$ .

The results of the calculation implied that the emission rate could be controlled at  $640 \mu\text{g}/\text{m}^2/\text{h}$ . This level was about 10 times that of common building materials such as plywood.

### CONCLUSION

In this paper, we tried to develop a new method for measuring VOC emissions with a passive flux sampler. This method has the advantage to measure VOC emission rates from materials of real houses. This method also involves less troublesome work and is inexpensive compared to previously reported methods. In this study, the emission from different positions of the same material was surveyed. The result showed the obtained emission rate differs among the positions of the board.

In the future, reference emission material is necessary so that we can develop a more foundational investigation into PFS.

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