# THEORETICAL DETERMINATION OF THE SAMPLING RATES OF DIFFUSION SAMPLERS FOR VOCs AND ALDEHYDES

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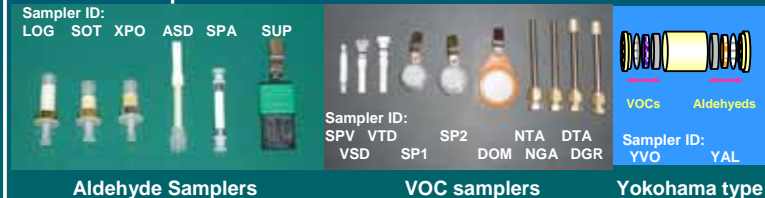
## SUMMARY
This study attempted to derive the sampling rate (SR) for diffusion samplers from the geometry (diffusion area and diffusion length) of the samplers and the physical properties of volatile organic compounds (VOCs) based on Fick's law of diffusion. We tested seven types of diffusion aldehyde samplers and eleven types of diffusion VOC samplers marketed in Japan. SRs were also determined experimentally using simultaneous active (pump) and diffusion sampling. Theoretically determined SRs were nearly the same as the experimentally established SRs. Thus, accurate calculation of SRs for VOCs based on the diffusion theory seems possible without the need to perform experimental measurements.

## INTRODUCTION
Usually, SRs are obtained from literature or a comparative experiment between active and passive sampling. However, the literature does not contain an SR for all compounds, and performing experiments to determine SRs can be burdensome. Therefore, a method is needed to calculate SRs easily and accurately. In this study, we try to establish a method for calculating SRs based on the diffusion theory (Theoretical SRs). In addition, SRs are also determined experimentally (Measured SRs). The theoretical SRs are compared with the measured SRs.

## MATERIALS AND METHODS

### Diffusion samplers

Sampler ID:
LOG SOT XPO ASD SPA SUP

Sampler ID:
SPV VTD SP2 NTA DTA
VSD SP1 DOM NGA DGR

VOCs Aldehyeds

Sampler ID:
YVO YAL

**Aldehyde Samplers          VOC samplers          Yokohama type**

### Theoretical determination of the sampling rate
SRs were derived theoretically based on Fick's law of diffusion:

$$SR = 60 \times A \times D_{12} \times Z^{-1} \qquad (1)$$

where $SR$ $(mL / min)$ is the sampling rate, $D_{12}$ $(cm^2 / sec)$ is the gas diffusion coefficient, $A$ $(cm^2)$ is the diffusion area, and $Z$ $(cm)$ is the diffusion length. The diffusion area and diffusion length of each sampler were accurately measured using an electron microscope.
The diffusion coefficient was calculated using Fujita's Equation, based on the molecular structure of the material:

$$D_{12} = \frac{0.00067 \times T^{1.83}}{\left[\left(Tc_1/Pc_1\right)^{1/3} + \left(Tc_2/Pc_2\right)^{1/3}\right]^3} \times \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \qquad (2)$$

where $Tc_1$ and $Tc_2$ $(K)$ are the critical temperature of the air and the target substance, respectively, $Pc_1$ and $Pc_2$ $(atm)$ are the critical pressure of the air and the target substance, respectively, $M_1$ and $M_2$ $(g/mol)$ are the molecular weight of the air and the target substance, respectively, and $T$ $(K)$ is the ambient temperature. $Tc_1$, $Pc_1$, and $M_1$ were 132.3 $K$, 37.2 $atm$, and 28.97 $g/mol$, respectively. $Tc_2$ and $Pc_2$ were calculated from the critical constant formulas:

$$Tc_2 = \frac{Tb}{0.567 + \sum \Delta T + \left(\sum \Delta T\right)^2} \quad (3) \qquad Pc_2 = \frac{M}{\left(0.34 + \sum \Delta P\right)^2} \quad (4)$$

where $Tb$ $(K)$ is boiling point, and $\Delta T$ and $\Delta P$ are calculated using the addition factor for the critical constant.
When the sampler contained different layers of diffusion resistance, the SR for each layer was calculated and the calculated SRs combined in following equation:
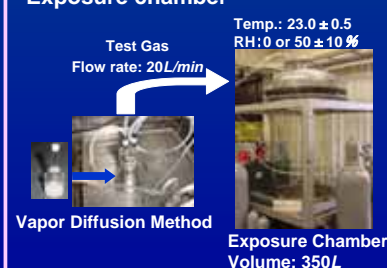
$$SR = (SR_1^{-1} + SR_2^{-1} + \bullet\bullet\bullet + SR_n^{-1})^{-1} \qquad (5)$$

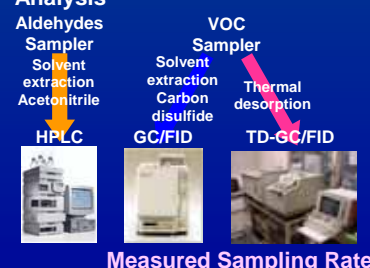where $SRk$ ($k$ = 1 to n) is the sampling rate for each layer of diffusion resistance.

**Theoretical Sampling Rate**

### Experimental determination of the sampling rate
**Exposure chamber**                    **Analysis**

Test Gas
Flow rate: 20 L/min

Temp.: 23.0± 0.5
RH  0 or 50± 10

Aldehydes
Sampler

VOC
Sampler

Solvent
extraction
Acetonitrile

Solvent
extraction
Carbon
disulfide

Thermal
desorption

HPLC          GC/FID          TD-GC/FID

Vapor Diffusion Method

Exposure Chamber
Volume: 350 L

**Measured Sampling Rate**

## RESULTS AND DISCUSSION
### Theoretical SRs derived using diffusion area and diffusion length

ASD, VSD and VTD
Diffusion Area: 1.53 cm²
Diffusion Length: 0.157 cm

SPA and SPV
Diffusion Area: 1.41 cm²
Diffusion Length: 0.173 cm

LOG, SOT and XPO
Diffusion Area: 0.833 cm²
Diffusion Length: 0.37 cm

*Fig. Example of diffusion resistance*     Photo by Hitachi S4800 Scanning Electron Microscope

*Table 1. Theoretical sampling rate for each analyze (mL/ min)*

| Aldehydes Sampler | Formaldehyde | Acetaldehyde | Acetone |
|---|---|---|---|
| LOG, SOT, XPO | 1.40 | 1.06 | 0.86 |
| SUP | 26.7 | 20.7 | 16.9 |
| SPA | 86.0 | 66.7 | 54.4 |
| ASD | 88.7 | 68.8 | 56.0 |
| YAL | 9.76 | 7.58 | 6.13 |
| VOCs Sampler | Benzene | Toluene | Xylene |
| SPV | 43.8 | 37.5 | 32.8 |
| VSD, VTD | 52.3 | 44.8 | 39.2 |
| DOM | 30.3 | 26.0 | 22.7 |
| SP1, SP2 | 18.3 | 15.7 | 13.7 |
| NTA, NGR | 0.75 | 0.65 | 0.57 |
| DTA, DGR | 0.49 | 0.42 | 0.37 |
| YVO | 5.77 | 4.94 | 4.32 |

### Measured SRs by exposure experiment

*Table 2. Measured sampling rate (mL/ min)*

| Aldehydes Sampler | Formaldehyde Measured SR | Measured SR / Theoretical SR | Acetaldehyde Measured SR | Measured SR / Theoretical SR | Acetone Measured SR | Measured SR / Theoretical SR |
|---|---|---|---|---|---|---|
| LOG | 1.11 | 0.80 | 2.50 | 2.36 | 1.54 | 1.79 |
| SOT | 0.96 | 0.69 | 2.00 | 1.89 | 1.26 | 1.46 |
| XPO | 0.69 | 0.49 | 1.73 | 1.63 | 1.14 | 1.33 |
| SUP | 13.4 | 0.50 | 31.7 | 1.53 | 22.8 | 1.35 |
| SPA | 40.7 | 0.47 | 114 | 1.70 | 59.8 | 1.10 |
| ASD | 42.5 | 0.48 | 123 | 1.79 | 67.1 | 1.20 |
| YAL | 9.56 | 0.98 | - | - | - | - |

| VOCs Sampler | Benzene Measured SR | Measured SR / Theoretical SR | Toluene Measured SR | Measured SR / Theoretical SR | Xylene Measured SR | Measured SR / Theoretical SR |
|---|---|---|---|---|---|---|
| SPV | 45.4 | 1.04 | 43.6 | 1.16 | 37.9 | 1.15 |
| VSD | 48.6 | 0.93 | 47.7 | 1.07 | 39.5 | 1.01 |
| VTD | 27.8 | 0.53 | 30.7 | 0.69 | 27.1 | 0.69 |
| DOM | 28.7 | 0.95 | 26.1 | 1.01 | 24.6 | 1.08 |
| SP1 | 13.3 | 0.73 | 11.2 | 0.71 | 6.20 | 0.45 |
| SP2 | 13.7 | 0.75 | 10.3 | 0.66 | 7.30 | 0.53 |
| NTA | 0.423 | 0.56 | 0.449 | 0.70 | 0.490 | 0.87 |
| NGR | 0.412 | 0.55 | 0.485 | 0.75 | 0.507 | 0.90 |
| DTA | 0.364 | 0.74 | 0.442 | 1.05 | 0.426 | 1.15 |
| DGR | 0.378 | 0.77 | 0.418 | 0.99 | 0.460 | 1.24 |
| YVO | 6.05 | 1.05 | 4.64 | 0.94 | 5.17 | 1.20 |

1.00± 0.20

The measured SRs for many samplers except YAL were not equal to the theoretical SRs for aldehydes.
For VOC samplers, the measured SR for each VOC for every sampler except VTD, SP1, SP2, NTA NGR and DGR was nearly identical to the corresponding theoretical SRs.

## CONCLUSIONS
Most SRs for VOCs except VTD, NTA, NGR, SP1 and SP2 could be theoretically calculated accurately, relative to experimental measurements. Thus, our method may be sufficient to calculate many SRs under most conditions. The SRs of various materials can be derived based on their physical properties, but it is important to accurately examine the geometry of the sampler. Also, for this method to be valid, it is important that samplers be uniformly manufactured.

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