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THEORETICAL DETERMINATION OF THE SAMPLING RATES OF DIFFUSION SAMPLERS FOR VOCS AND ALDEHYDES

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ABSTRACT

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. Vapor diffusion was used to generate a stable concentration of sample VOC and aldehyde gases of known concentrations, which were introduced into a 350 L chamber. Each sampler was exposed in the chamber for a specified period. For most samplers and most VOCs, the 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.

INDEX TERMS

Diffusion sampler, VOCs, Aldehydes, Sampling rate, Diffusion theory

INTRODUCTION

Simple and cheap to operate, diffusion samplers are gaining popularity for monitoring indoor air and personal exposure. Diffusion samplers are developed based on the diffusion theory. The sampling rate (SR), corresponding to the absorption rate of active sampling, for each diffusion sampler and each analyte must be known in order to calculate the concentration. 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 from the geometry (diffusion area and diffusion length) of samplers and the physical properties of VOCs based on the diffusion theory.

MATERIALS AND METHODS

Diffusion samplers

Performance tests were carried out on seven types of diffusion aldehyde samplers and eleven types of diffusion VOC samplers marketed in Japan.

- **Aldehyde samplers**

Syringe type (3 types): These samplers use a 2,4-dinitrophenylhydrazine (DNPH) silica syringe type cartridge (one in a long body and one in a short body) for active sampling (sampler IDs: LOG and SOT) and one DNPH silica syringe type cartridge for passive sampling (sampler ID: XPO).

Disk type (1 type): This sampler, containing different layers of diffusion resistance, uses a DNPH filter as the adsorbent (sampler ID: SUP).

Cylinder type (2 types): These samplers use an adsorbent wrapped in a film that serves as diffusion resistance. DNPH silica is used as the adsorbent (sampler IDs: SPA and ASD). The structure of the film in the SPA sampler is different from that in the ASD sampler.

Yokohama type (1 type): This sampler, used for nitrogen oxides and ozone measurements (OSHA 1995, Koutrakis et al. 1993), was remodeled. This sampler uses DNPH silica as the adsorbent (sampler ID: YAL).

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l VOC samplers

Cylinder type for solvent extraction (2 types): These samplers are similar to the cylinder type samplers for aldehydes. They use coconut husk activated carbon or a carbon molecular sieve as the adsorbent (sampler IDs: SPV and VSD).

Cylinder type for thermal desorption (1 type): This sampler is similar to the other cylinder type samplers. Graphite carbon is used as the adsorbent (sampler ID: VTD).

Disk type for solvent extraction (3 types): These samplers are similar to the disk type sampler for aldehydes. An activated carbon disk, charcoal, or Anasorb 747 is used as the adsorbent (sampler IDs: DOM, SP1, and SP2).

Perkin-Elmer type (4 types): These samplers used Perkin-Elmer tubes packed with Tenax TA or GR absorbent (sampler IDs: NTA and NGR). Tubes with a diffusion barrier were also examined (sampler IDs: DTA and DGR).

Yokohama type (1 type): This sampler is a remodeled Yokohama type sampler similar to the one for aldehydes. It uses coconut husk activated carbon as the adsorbent (sampler ID: YVO).

Exposure chamber

The measured SRs for formaldehyde, acetaldehyde, and acetone among aldehydes, and for benzene, toluene, and xylene among VOCs were determined by exposing each diffusion sampler to known concentrations of test gases. Test aldehyde and VOC gases were generated with vapor diffusion and introduced into a 350 L chamber at a rate of 20 L/min. The concentration of each reference gas was monitored continuously with a non-methane hydrocarbon analyzer and a photo-ionization detector (PID)/VOC monitor, and intermittently with gas chromatography/mass spectrometry (GC/MS) and pump sampling. The ambient temperature was held constant at 296.15 K. The diffusion samplers were exposed inside the chamber once the concentration of aldehyde or VOC gas had stabilized in the chamber. The diffusion samplers were exposed for specified times for each sampler.

Analysis

Table 1. *Analysis conditions*

HPLC	
Sample injection volume	5 μL
Eluent	Acetonitrile : Water 55:45
Column	DEVELOSIL ODS-5 250 mm x 4.6 mm
Column temp.	313.15 K
UV detection wavelength	365 nm

Table 1 *(continued)*

Solvent extraction and GC	
Sample injection volume	4 μL
Sample injection temp.	533.15 K
Carrier gas	Helium
Column	HP-5 60 m x 0.32 mm ID Film thickness: 0.25 μm
Column temp.	5 min at 318.15 K; 5 K/min to 373.15 K
FID detection temp.	533.15 K
Thermal desorption and GC	
Sample desorption temp.	573.15 K
Sample desorption time	5 min
ATD 400 secondary trap	Packing: Carbopack B and Carbotrap C Adsorption temp.: 243.15 K; Desorption temp.: 593.15 K
GC carrier gas	Helium
Column	BP-1 50m x 0.22 mm ID Film thickness: 1.00 μm
Coulmn Temp.	15 min at 319.15 K; 5 K/min to 443.15 K; 15 K/min to 473.15 K; 6 min at 473.15 K
FID detection Temp.	533.15 K

Aldehydes in collected samples were eluted with acetonitrile then analyzed by high performance liquid chromatography (HPLC). VOCs in collected samples were extracted with carbon disulfide or thermally desorbed in an ATD 400 (Perkin-Elmer). All VOC samples were analyzed with GC. Table 1 gives further details on the analysis conditions.

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 (HITACHI S-4800 Scanning Electron Microscope).

The diffusion coefficient was calculated using Fujita's Equation, based on the molecular structure of the material:

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

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:

$$Tc_2 = \frac{Tb}{0.567 + \sum \Delta T + \left(\sum \Delta T\right)^2} \qquad (3)$$

$$Pc_2 = \frac{M}{\left(0.34 + \sum \Delta P\right)^2} \qquad (4)$$

where Tb (K) is boiling point, and DT and DP 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:

$$SR = (SR_1^{-1} + SR_2^{-1} + \cdots + SR_n^{-1})^{-1} \qquad (5)$$

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

RESULTS AND DISCUSSION

Theoretical SRs derived using diffusion area and diffusion length

Syringe type: This sampler uses a sep-pak cartridge packed with an adsorbent held in a polyethylene filter. The diffusion area and diffusion length of the polyethylene filter were 0.833 cm^2 and 0.37 cm, respectively. The diffusion area and the diffusion length of the sep-pak cartridge were 0.035 cm^2 and 2.22 cm (thin path), and 0.154 cm^2 and 0.96 cm (thick path), respectively. The theoretical SR was calculated by combining SR_1 for the polyethylene filter and SR_2 for the sep-pak cartridge.

Cylinder type: The diffusion area was calculated as the total area of the pores in the cylinder surface. The diffusion path in the cylinder type sampler is not a straight line to the adsorbent from the cylinder surface. Therefore, the diffusion length is not equal to the film thickness. The diffusion length was estimated as the length of an arc with a diameter equal to the thickness of the film material. SPV and SPA have similar geometries, with 30

% of their total areas being pore space, and a diffusion area and diffusion length of 1.41 cm^2 and 0.173 cm, respectively. ASD, VSD, and VTD have similar geometries. Their diffusion barrier consists of particulate polytetrafluoroethylene. Assuming the tightest possible packing structure, the void ratio was estimated to be 36.8%. Therefore, the diffusion area and the diffusion length were 1.53 cm^2 and 0.157 cm, respectively.

Disk type: This type of sampler contains different layers of diffusion resistance. SUP has a single layer diffusion barrier with 112 holes and a diffusion area and diffusion length of 0.88 cm^2 and 0.30 cm, respectively. DOM has a double-layered diffusion barrier. The first layer (surface layer) is a membrane filter with 20% of the total area being pore space and a diffusion area and the diffusion length of 1.47 cm^2 and 2.54 X 10^{-3} cm, respectively. The second layer is a layer of air supported by a frame with 65 % of the total area being space and a diffusion area and the diffusion length of 4.78 cm^2 and 0.97 cm, respectively. The theoretical SR was calculated by combining SR_1 for the membrane filter and SR_2 for the layer of air. SP1 and SP2 have the equal geometries. These samplers contain 3 layers of resistance. The first layer (surface layer) is a diffusion barrier with 317 holes and a diffusion area and diffusion length of 0.62 cm^2 and 0.18 cm, respectively. The second layer is a membrane filter with a diffusion area and diffusion length of 5.54 cm^2 and 0.002 cm, respectively. The third layer is a stainless steel screen with a diffusion area and diffusion length of 6.39 cm^2 and 0.02 cm, respectively. The theoretical SR was calculated by combining SR_1 for the first layer, SR_2 for the membrane filter, and SR_3 for the stainless steel screen.

Perkin-Elmer type: This sampler's geometry is similar to that of the disk type sampler but has a smaller diffusion area and a longer diffusion length. The diffusion area of NTA and NGR were 0.2 cm^2, obtained by calculating the inside diameter of the stainless tube. The diffusion length was 1.42 cm. DTA and DGR are the same as NTA and NGR except they are fitted with a diffusion barrier. The diffusion barrier is made of 2 layers: a stainless steel screen and a membrane filter. The stainless steel screen had a diffusion area and diffusion length of 8.81 X 10^{-2} cm^2 and 0.03 cm, respectively. The membrane filter had a diffusion area and diffusion length of 5.89 X 10^{-5} cm^2 and 2 X 10^{-4} cm, respectively. The theoretical SR was calculated by combining SR_1 for the stainless steel screen, SR_2 for the membrane filter, and SR_3 for the stainless tube.

Yokohama type: This sampler consists of a solid Duracon cylinder with two openings, each with a tray containing activated carbon (for VOCs) or DNPH silica (for aldehydes). The adsorbent is held in a stainless steel screen, situated behind a diffusion barrier and end-cap with 25 holes. The diffusion areas of the stainless steel screen and end-cap were 0.152 cm^2 and 0.785 cm^2, respectively. The diffusion lengths of the stainless steel screen and end-cap were 0.02 cm and 0.6 cm, respectively. The theoretical SR was calculated by combining SR_1 for the stainless steel screen and SR_2 for the end-cap.

Diffusion coefficient

Table 2. *Diffusion coefficient (D_{12}) for aldehydes and VOCs*

Substance	M (g/mol)	Tc (K)	Pc (atm)	T (K)	D_{12}(cm^2/sec)
Formaldehyde	30.00	408.0	65.0	296.15	0.1517
Acetaldehyde	44.05	464.9	54.8	296.15	0.1176
Acetone	58.08	509.0	46.0	296.15	0.0958
Benzene	78.11	561.9	48.9	296.15	0.0897
Toluene	92.13	594.7	41.4	296.15	0.0768
Xylene	106.16	623.3	36.0	296.15	0.0672

Table 3. *Theoretical sampling rate for each analyte (mL/ min)*

Aldehydes Sampler	**Formaldehyde**	**Acetaldehyde**	**Acetone**
LOG, SOT, XPO	1.400	1.060	0.860
SUP	26.70	20.70	16.87
SPA	86.04	66.72	54.35
ASD	88.71	68.79	56.04
YAL	9.764	7.576	6.170
VOCs Sampler	**Benzene**	**Toluene**	**Xylene**
SPV	43.84	37.53	32.81
VSD, VTD	52.30	44.77	39.19
DOM	26.32	22.53	19.72
SP1, SP2	18.30	15.67	13.71
NTA, NGR	0.756	0.646	0.565

DTA, DGR	0.495	0.423	0.371
YVO	5.770	4.936	4.325

The diffusion coefficients, shown in Table 2, were calculated based on the materials’ structure.

The theoretical SR for each substance was calculated using the diffusion area, diffusion length, and diffusion coefficient in Table 2. Table 3 shows the theoretical SRs.

Measured Sampling Rate

When a small exposure chamber is used, the concentration usually fluctuates during the experiment. A large exposure chamber was used to avoid this. We used the vapor diffusion method, which can generate a gas with a constant concentration throughout the experiment. The short-term measured SRs were determined for an 8 hour period for SUP, YAL, DOM, SP1, and SP2, for a 4 hour period for VTD, and for a 24 hour period for the other samplers. Table 4 shows the experimentally determined SRs.

The measured SRs for many samplers were not equal to the theoretical SRs for formaldehyde and acetaldehyde. With formaldehyde, breakthrough seemed to occur in most samplers because the test gas was at a high concentration. In addition, for the measured SR of acetaldehyde, the discrepancy may be due to high contamination values for the blanks.

Table 4. *Measured sampling rate (mL/min)*

Aldehydes Sampler	**Formaldehyde**		**Acetaldehyde**		**Acetone**	
	Measured SR	**Measured SR / Theoretical SR**	**Measured SR**	**Measured SR / Theoretical SR**	**Measured SR**	**Measured SR / Theoretical SR**
LOG	1.11	0.79	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**		**Toluene**		**Xylene**	
	Measured SR	**Measured SR / Theoretical SR**	**Measured SR**	**Measured SR / Theoretical SR**	**Measured SR**	**Measured SR / Theoretical SR**
SPV	38.8	0.89	37.8	1.01	35.0	1.07
VSD	30.9	0.59	43.6	0.97	37.9	0.97
VTD	43.4	0.83	44.9	1.00	14.6	0.37
DOM	30.5	1.16	22.5	1.00	19.5	0.99
SP1	13.1	0.72	10.7	0.68	-	-
SP2	14.6	0.80	10.8	0.69	-	-
NTA	0.43	0.57	0.45	0.70	0.48	0.85
NGR	0.42	0.56	0.64	0.99	0.48	0.85
DTA	0.35	0.71	0.43	1.02	0.45	1.21
DGR	0.41	0.83	0.42	0.99	0.47	1.27
YVO	-	-	4.70	0.95	-	-

For VOC samplers, the measured SRs for each VOC for every sampler except VTD was nearly identical to the corresponding theoretical SRs. VTD was anomalous because thermal desorption could not be performed sufficiently due to the structure of the sampler.

The effect of temperature and wind will be examined. In addition, the reexamination is necessary for the substances which measured SR was incompatible with theoretical SR.

CONCLUSIONS

Most SRs for VOCs 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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