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 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

Aldehyde Samplers

VOC samplers

Yokohama type

Theoretical determination of the sampling rate

SRs were derived theoretically based on Fick’s law of diffusion:

\[ \text{SR} = 60 \times D \times \frac{L}{Z} \]

where \( D \) is the diffusion rate; \( D_{ij} \) (cm²/sec) is the gas diffusion coefficient; \( A \) (cm²) 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.

1. Test Gas Flow rate: 20L/min
2. Temperature: 23.0 ± 0.5°C
3. Exposure Chamber Volume: 350L

Experimental determination of the sampling rate

Analysis

Test Gas

Flow rate: 20L/min

Aldehyde Samplers

VOC Samplers

NDG

GCFID

TD-GC/FID

Measured Sampling Rate

EXPERIMENTAL RESULTS AND DISCUSSION

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

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Measured SR</th>
</tr>
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<tbody>
<tr>
<td>Benzene</td>
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</tr>
<tr>
<td>Toluene</td>
<td>0.46</td>
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<td>Xylene</td>
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Table 2. Measured sampling rate (mL/min)

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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 molecular structures, and the target substance, respectively, and \( Tc2 \) is the critical temperature of the air and the target substance, respectively. The diffusion coefficient was calculated using Fujita’s Equation, based on the molecular structure of the material:

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\[ D_{ij} = \frac{0.00067 	imes 10^{1.31}}{M_i + M_j} \]

where \( Tc1 \) and \( Tc2 \) (K) are the critical temperature of the air and the target substance, respectively, \( P_{c1} \) and \( P_{c2} \) (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. \( Tc1 \), \( P_{c1} \), and \( M_1 \) were 323.3 K, 37.2 atm, and 28.97 g/mol, respectively. \( Tc2 \) and \( P_{c2} \) were calculated from the critical constant formul:

where \( T_B \) is boiling point, and \( \Delta T \) and \( \Delta P \) are calculated using the add-on factor for the critical constant.

When the sample contained different layers of diffusion resistance, the SR for each layer was calculated and the calculated SRs combined in following equation:

\[ SR = (SR_1^{-1} + SR_2^{-1} + \cdots + SR_n^{-1})^{-1} \]

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

Theoretical Sampling Rate

RESULTS AND DISCUSSION

The theoretical SRs derived using diffusion area and diffusion length

Measured SRs by exposure experiment

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