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Validation of diffusive mini-samplers for aldehyde and VOC and its feasibility for measuring the exposure levels of elementary school children

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Abstract

Exposure to various chemicals can cause adverse effects on health, such as asthma and allergies, especially in children. Data on personal exposure levels in children are scarce, thus small lightweight diffusive mini-samplers for aldehydes and volatile organic compounds (VOCs) were designed to measure the exposure level of children to these chemicals. The aim of the study is to validate and examine the applicability of these mini-samplers for measuring daily chemical exposure. The diffusive mini-samplers are 20 mm in length, 11 mm in diameter, and 1.67 g in weight. The devices are cylindrically shaped with polytetrafluoroethylene membrane filters placed at each end. To measure aldehydes and acetone, 20 mg of 2,4-dinitrophenylhydrazine was used as an absorbent. To measure VOCs, a carbon molecular sieve was used. The sampling rate for each chemical was determined by parallel sampling with active samplers in a closed exposure bag. The blank levels of the chemicals and the storage stability of the device were tested. The mini-samplers were compared to commercially available diffusive samplers. To examine the applicability of the samplers, 65 elementary school children carried them for 24 hours. The sampling rates for formaldehyde, acetaldehyde, and acetone were 20.9, 22.9, and 19.7 mL min⁻¹, respectively. The limits of quantification (LOQ) for the 24-hour sampling by high-performance liquid chromatography/ultraviolet (HPLC/UV) analysis were 8.3, 7.6, and 8.8 µg m⁻³ for formaldehyde, acetaldehyde, and acetone, respectively. The sampling rates for the 11 VOCs were determined and

1 ranged from 3.3 mL min⁻¹ for styrene and 2-ethyl-1-hexanol to 11.7 mL min⁻¹ for benzene. The
2 LOQ for the 24-hour sampling by gas chromatography-mass spectrometry (GC/MS) analysis ranged
3 from 5.9-105.2 µg m⁻³, 1.1 - 24.7 parts per billion. The storage stability after 5 days ranged from
4 94.8 to 118.2%. Formaldehyde, acetone, benzene, and toluene were detected above the LOQ in
5 more than 90% of the children, and the median concentrations were 21.7, 20.9, 10.1, and 21.5 µg m⁻³,
6 respectively. This study shows that the diffusive samplers developed were suitable for children to
7 carry and were capable of measuring the children's daily chemical exposure.

8

1 **Introduction**

2 Exposure to aldehyde and volatile organic compounds (VOCs) is known to have adverse effects on
3 health, such as asthma and allergies, especially in children. According to the latest review, an Odds
4 Ratio (OR) of 1.03-1.17 for an increase of 10 $\mu\text{g m}^{-3}$ of formaldehyde was calculated by
5 meta-analysis ¹. Increased levels of toluene, benzene, and xylene are also reported to increase the
6 risk of asthma or respiratory symptoms ^{2,3}. To assess the health risk of indoor chemicals, their
7 levels in schools and dwellings have been reported ⁴⁻⁷. School children spend time in settings other
8 than their school and home. To assess children's health risk from daily chemical exposures, data on
9 personal exposure levels are needed. However, these data are scarce. Park et al. (2004) measured
10 the personal VOC exposure of four school children using active pump samplers ⁸. However, active
11 pumps are heavy and limit a child's daily activity. In contrast to active sampling with a pump,
12 diffusive samplers are small, lightweight, and easy to handle. Several diffusive sampling devices to
13 measure VOC are commercially available. In the School Health Initiative: Environment, Learning,
14 and Disease (SHIELD) study, outdoor, indoor at school and home, and personal VOC concentrations
15 for inner-city children were measured in Minneapolis, Minnesota, USA ⁹. Adgate et al. (2004)
16 measured the children's personal VOC exposures using diffusive organic-vapour monitors (OVM
17 model 3520; 3M Corporation, St. Paul, MN). OVM 3500 is badge-type diffusive sampler that is
18 approximately 10 x 10 cm in size and 10 g in weight. The alternative diffusive samplers, Supelco

VOC-SD and DND-DNPH (Sigma Aldrich, Co., St. Louis, MO, USA) are tube-type diffusive samplers (approximately 10 cm in length and 3.3 g in weight). However, the commercially available diffusive samplers are cumbersome for small children to carry.

To conduct a personal exposure study for children, a small lightweight sampling device that does not affect the child's daily activity is needed. Therefore, minimised diffusive samplers to measure aldehydes and VOCs were developed for children in this study. The aim of this study is to validate the mini-samplers and use them to measure the personal daily chemical exposure levels for school children.

Material and Methods

Diffusive samplers

Mini-diffusive samplers (20 mm in length, 11 mm in diameter, and 1.67 g in weight) were designed and developed. Figures 1 and 2 shows the outside and expanded views, respectively, with the scale of the mini-sampler. The cylinder tube was made of polyethylene, and both sides were covered by ϕ 10 mm polytetrafluoroethylene (PTFE) membrane filters and metal caps. The face area of each end was 0.55 mm². The interior of the cylinder was separated into two compartments with three ϕ 10 mm, 5-mm-thick urethane sheets. Each cavity was filled with approximately 20 mg of absorbent.

The samplers for the aldehydes and the VOCs were identical except for the absorbent. 2,4-Dinitrophenylhydroazone (DNPH)-coated silica gel (Shibata Scientific Technology Ltd., Saitama, Japan) was used for the aldehydes and acetone. Carbon bead absorbent (Shibata Scientific Technology Ltd., Saitama, Japan) was used for the other VOCs. To distinguish the two samplers, the mini-samplers containing DNPH-silica gel (described as aldehydes mini-sampler hereafter) were marked with red strips, and the mini-samplers containing carbon beads (described as VOC mini-samplers hereafter) were marked with blue strips.

Chemicals for analysis

Fifteen major chemicals commonly detected indoors were selected for analysis in this study. Formaldehyde (density at 20°C, 1.08), acetone (density at 20 °C, 0.791), toluene (density at 20°C, 0.867), m-xylene (density at 20°C, 0.882) and p-xylene (density at 20°C, 0.882) were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Acetaldehyde (density at 20°C, 0.788), 2-butanone (purity, 99; density at 20°C, 0.805), benzene (purity, 99.7%; density at 20°C, 0.878), p-dichlorobenzene (density at 20°C, 1.25), (1S,5S)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (alpha-pinene) (purity, 95%; density at 20°C, 0.86), and (R)-1-methyl-4-(1-methylethenyl)-cyclohexene (limonene) (purity, 97%; density at 20°C, 0.845) were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). 1-Butanol (purity, 99%; density at 20°C, 0.81), ethyl benzene (density at 20°C, 0.866), o-xylene (density at 20°C, 0.882), styrene (density at 20°C, 0.906), and 2-ethyl-1-hexanol (Purity, 99%; density at 20°C, 0.883) were obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). For calibration, SUPELCO T011/IP-6A/ASTM5297 (Sigma

Aldrich Co., Lt. Louise, MO, USA) was used for the formaldehyde, acetaldehyde, and acetone analyses. The VOC standard stock solution mix III (Kanto Chemical Co., Inc., Tokyo, Japan) was used for toluene, ethyl benzene, p-/o-xylene, m-xylene, styrene, and p-dichlorobenzene. For desorption, acetonitrile (high-performance liquid chromatography (HPLC) grade) and carbon disulfide (CS₂) (the reagent grade for working environment determination confirmed, < 0.1 parts per million benzene) were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Analysis

HPLC analysis: HPLC equipped with an ultraviolet detector (HPLC/UV; Hitachi L-7100) (Hitachi, Ltd., Tokyo, Japan) was used for the analysis of formaldehyde, acetaldehyde, and acetone. A one-millilitre sample was injected, and chromatic separation was performed using a solvent gradient elution at a flow rate of 0.3 mL min⁻¹ in an analytical column (SPECLCO Ascentis, semi-micro column, 250 mm x 2.1 mm x 5 µm; Sigma Aldrich Co., St. Louis, MO, USA). The mobile phase was distilled water and tetrahydrofuran (5:1) and acetonitrile (55:45). The temperature of the column was 35 °C. The detection wavelength was 360 nm.

GC/MS analysis: For the VOC analysis, a Hewlett Packard Agilent gas chromatograph with mass spectrometry GC6890/MSD 5983N (GC/MS; Agilent Technologies Inc., Alto, CA, USA) equipped with DB-1 (0.25 mm i.d. x 60 m, 1.5 µm; J & W Scientific, Folsom, CA, USA) was used. The temperature of the injector, the MS ion source, and the interface was set at 250 °C, 230 °C and 220 °C, respectively. The column temperatures were 40 °C (13 min), followed by a temperature

rise of 7 °C min⁻¹ to 280°C (2 min). Helium was used as the carrier gas, with a constant flow rate of 1.0 mL min⁻¹. One-microliter samples were injected in the split mode (5:1). Electron impact ionisation was 70 eV for MS analysis.

Calibration and instrumental quantification limit

Calibration was performed using seven different concentrations. The concentrations of the aldehydes and ketones were 0.015, 0.075, 0.15, 0.75, 1.5, 7.5, and 15 µg mL⁻¹. For the VOC calibration, the following concentrations were used: 0.1, 0.05, 0.1, 0.5, 1.0, 5.0, and 10 µg mL⁻¹. SUPELCO T011/P-6A/ASTM5297 and toluene-d8 were used as the internal standards for HPLC and GC/MS, respectively. The data was acquired by repeating the procedure five times for each concentration. The instrumental quantification limit (IQL) was determined by the method described by the Ministry of Environment of Japan ¹⁰. The IQL was equal to 10 times the standard deviation (SD) of 7-10 repeated measurements of 0.15 µg mL⁻¹ and 0.1 µg mL⁻¹ for HPLC and GC/MS analysis, respectively. The retention times of the target compounds and the corresponding monitor ions for the GC/MS analysis are shown in Table 1.

Determination of the sampling rate with the mini-sampler

To determine the sampling rates for the mini-samplers, parallel measurements with active sampling

1 methods were performed. The generation of the target chemicals vapour was performed using the
2 method described in Araki et al. (2009) ¹¹. To determine the sampling rates of the aldehydes and
3 acetone, a chemical solution containing 10 μL of formaldehyde, 100 μL of acetaldehyde, and 50 μL
4 of acetone was made up to one litre with distilled water. Air was supplied to two 500-mL flasks
5 connected sequentially at a constant rate of 3.5 L min⁻¹ by an air supply pump and was bubbled in
6 200 mL of the aldehydes/acetone solution in the flask located closest to the pump. The vapour
7 generated in the first flask was equilibrated partly in the second flask, which trapped the solubilised
8 gas and stabilised the air flow rate. The vapour was then was collected in a 100-L polyvinyl
9 fluoride exposure bag. An exhaust vent with a control valve was horizontally placed on the
10 opposite side of the air supply to maintain the pressure within the exposure bag at 1 atm. The wind
11 velocity at the air inlet was 0.8-1.1 m sec⁻¹, and it was 0.3 m sec⁻¹ at the exhaust duct. The wind
12 velocity was the same at all ten points for the mini-samplers and active samplers. After 30 min of
13 equilibration, the aldehydes and ketone gas was sampled simultaneously with the aldehyde
14 mini-samplers and the active samplers. For the active sampling, the DNPH active gas tube (Shibata
15 Scientific Technology Ltd.) was used, and the air sampling rate was 1000 mL min⁻¹. The air
16 samplers were calibrated by using soap bubble flow meters. Five pairs of mini-samplers and active
17 samplers were fixed in the exposure bag in parallel at equal heights and exposed to the gas. All of
18 the samplers were replaced with new sets after 1 hour of exposure, and the exposure procedure was

repeated five times. A total of 25 exposed samplers were extracted with 2.5 mL of acetonitrile and used in the HPLC analysis. To determine the VOC sampling rate, the chemical solutions containing 20 μL of each target compound and 15 mg of p-dichlorobenzene were made up to one litre with distilled water. The method of vapour generation and exposure were the as same as for the aldehydes and ketone, except that carbon-bead active samplers (Shibata Scientific Technology Ltd.) were used with an air sampling rate of 100 mL min^{-1} . Twenty-five VOC-exposed samplers were extracted with 1 mL of CS_2 and applied to GC/MS for analysis. During the exposures, the temperature was 25 $^{\circ}\text{C}$, and the relative humidity was 75% inside the exposure bag.

Desorption efficiencies for VOC mini-sampler

The desorption efficiencies of CS_2 from the carbon beads were examined by two different standard solution concentrations. Either 10 μL or 2 μL of the 100- $\mu\text{g mL}^{-1}$ standard solution was added to the carbon beads. After drying with nitrogen gas, the compounds were desorbed by 1 mL of CS_2 and were subjected to GC/MS.

Blank test and storage stability

For the blank test, new mini-samplers that had not exposed to any gases were desorbed by the extract solvent and analysed. Five blank mini-samplers were examined for aldehydes and VOCs. For

storage stability, the mini-samplers were exposed to the chemical vapour for 1 hour in the exposure bag as described above. Five samplers were analysed soon after exposure. Another set of exposed samplers were wrapped in aluminium foil. The aldehyde mini-samplers were stored at -18 °C, and the VOC mini-samplers were stored at 4 °C for 1 day, 3 days, and 5 days after the exposure until analysis. Five samplers were examined at each time point.

Comparison of mini-samplers in the field

The accuracy of the mini-samplers in the field was tested by parallel sampling with the widely used, commercially available diffusive samplers, Supelco DSD-DNPH and Supelco VOC-SD (both from Sigma Aldrich Co., St. Louise, MO). The aldehydes and VOC mini-samplers, the Supelco DSD-DNPH, and the Supelco VOC-SD were placed in parallel and 5 cm apart for 48 hours indoors at 20 dwellings. The formaldehyde concentrations from the aldehyde mini-sampler and the Supelco DSD-DNPH were analysed and compared. The toluene concentrations from the VOC mini-sampler and the Supelco VOC-SD were analysed and compared.

Field study

The mini-samplers were attached to 65 elementary school children in Sapporo City, Japan in September, October and November 2010. The children's personal measurements were conducted

on regular school days. The aldehyde and VOC mini-samplers were attached to the children's school bags or clothes in the morning before leaving for school. The parents were asked to keep both of the samplers as close to the children as possible. The parents were instructed to place the mini-samplers by their children's heads at night. The following morning, after 24 hours of sampling, the samplers were placed in aluminium bags. The aldehydes and VOC mini-samplers were kept at -18 °C and 4 °C, respectively, before and after sampling at home. The investigators collected the samplers, which were sent to the Osaka Occupational Health Service Centre for analysis by HPLC and GC/MS.

This study was conducted with written informed consent from all subjects and was approved by the ethical board for epidemiological studies at Hokkaido University Graduate School of Medicine.

Results and discussion

The newly developed mini-samplers are approximately one-half to one-fifth the size and weight of the commercially available samplers (Figure 1b).

The sampling rates were measured for two aldehydes, acetone, and 11 VOCs. The Japanese Ministry of Health, Labour and Welfare has published an indoor air quality guideline ¹². In addition to the chemicals included in the guideline, alpha-pinene, limonene, and

2-ethyl-1-hexanol were selected as target compounds in this study. Alpha-pinene and limonene are emitted from wooden materials and are commonly detected in Japanese dwellings^{5, 7, 13}. 2-Ethyl-1-hexanol is a possible causative chemical that induces mucous membrane symptoms¹⁴⁻¹⁶. This chemical has been measured in non-domestic buildings¹⁵⁻¹⁷, but no reports have been provided on children's personal exposure levels, to the best of our knowledge.

Calibration of the chemicals and determination of the Instrumental Detection Limits by HPLC and GC/MS analysis

The standard calibration curves were constructed for formaldehyde, acetaldehyde, and ketone by HPLC and for the 11 VOCs by GC/MS. The linear regressions between the internal standards and each compound was highly significant with correlation coefficients of $R=0.997$ for 1-butanol and $R=0.999$ for the other VOCs. The IQLs ranged from 0.033 for ethyl benzene to 0.110 for 1-butanone. The Instrumental Detection Limits (IDLs) were determined to be 0.1-0.5 $\mu\text{g mL}^{-1}$ for the later calculations.

Desorption efficiency

The desorption efficiency of CS_2 from the carbon beads ranged between 91.5-103.4% for 1.0 $\mu\text{g mL}^{-1}$, and 87.3-105.5% for 0.2 $\mu\text{g mL}^{-1}$, except for styrene. The measured desorption efficiencies

were at acceptable levels in the context of the compendium methods of the United States Environmental Protection Agency ¹⁸. The absorbent used in the mini-samplers was the same as those absorbent in the active samplers. Thus, the desorption efficiencies were the same for both the mini-samplers and the active samplers, and this did not affect the results. The desorption efficiency for styrene in this study was 81% and 70.8% for 1.0 and 0.2 µg mL⁻¹, respectively. Styrene's desorption efficiency is known to be varied when the concentration is low ^{19,20}.

Determination of the sampling rate

The sampling rate for the each of the compounds by the mini-samplers was determined experimentally. The correlation between the mini-samplers and active samplers are shown in Figure 3. The correlation coefficients (r) in the linear regressions were greater than 0.98 for all of the compounds. The data from the mini-samplers showed good correlation with the active sampling method, both for the aldehydes and the VOCs. The sampling rates of the target compounds by the mini-samplers were calculated as follows:

$$\text{Mini-sampler sampling rate (}\mu\text{L min}^{-1}\text{)} = \text{slope (m}^3\text{)} \times 10^6 \text{ (mL m}^{-3}\text{)} \div 60 \text{ (min)}$$

The determined sampling rates are shown in Table 2. The sampling rates for formaldehyde, acetaldehyde, and acetone were 20.9 µL min⁻¹, 22.7 µL min⁻¹, and 19.7 µL min⁻¹, respectively. The sampling rates for the VOCs ranged from 3.3 µL min⁻¹ for styrene and 2-ethyl-1-hexanol to 11.7 µL

m⁻² for benzene. The developed mini-sampler has a small cross-sectional area of 1.1 mm³, which results in the low uptake rates ²¹.

By using the IDL and the sampling rate, the limit of quantification (LOQ) values for 24 hours of sampling for the mini-samplers was calculated as follows:

$$\begin{aligned} \text{24-h LOQ } (\mu\text{g}/\text{m}^3) &= \text{IDL } (\mu\text{g mL}^{-1}) \times \text{volume of extraction solvent (mL)} \\ &\div [\text{diffusive sampling rate (mL min}^{-1}) \times 1440 \text{ (min)} \div 10^6 \text{ (mL m}^{-3})] \end{aligned}$$

The 24-h LOQ values for the mini-samplers are also shown in Table 2. The 24-h LOQ ranged from 7 $\mu\text{g m}^{-3}$ for formaldehyde to 105.2 $\mu\text{g m}^{-3}$ for styrene, which were from 1.1 ppb (parts per billion) for limonene to 24.7 ppb for 2-butanone. An indoor VOC-level guideline was enacted by the Japanese Ministry of Health, Labour, and Welfare ¹². The calculated 24-h LOQ were lower than the Japanese guideline. Thus, the mini-samplers were able to measure relatively low environmental exposure levels. Diffusive sampling is based on the free flow of analyte molecules, according to Fick's first law of diffusion ²². Gas standard has been used to determine sampling rate in previous studies^{23, 24}. In this study, the water-bubbling method which forms a gaseous mixture was used ¹¹. This method has been validated in a previous study, and has the following advantages; it is possible to expose samplers to several gaseous compounds at the same time, and furthermore, it is also possible to expose many samplers at the same time. In addition, standard gases for some compounds, such as 2-ethylhexyl-1-ol are not commercially available. The sampling rates of each

compound were determined experimentally by parallel sampling with active sampling in exposure bag. The amounts of target compounds obtained by using the developed mini-sampler and the concentrations measured by the active sampling methods had goodness-of fit linear regression with high correlation coefficients ($r > 0.98$). The amount of gas may vary over time, and the concentrations of the compound within the exposure bag were not stable. The vapours of the target compounds could be absorbed by the polyvinyl fluoride exposure bag. However, the amount of collected compounds for the mini-samplers were compared with the active samplers, so the actual amount of vapour absorbed by the exposure bag did not affect the results. The validation of determined sampling rate by the water-bubbling method was performed in indoor air by parallel sampling of the active and diffusive samplers in a previous study ¹¹. Developed mini-samplers were also diffusive type samplers, and thus, obtained sampling rates which are reliable in the field, despite the fact that sampling rate is affected by temperature, humidity and face velocity.

In this study, however, only the sampling rates of three compounds for aldehyde mini-sampler and 11 compounds for VOS mini-sampler were determined. Sampling rates for additional compounds need to be determined in future field studies that monitor children's exposure to chemicals.

Blank test and storage stability

The average levels of each compound in the blank test were lower than the IQL, except for

2-ethyl-1-hexanol. 2-Ethyl-1-hexanol is the main metabolite of di(2-ethylhexyl)phthalate, which is widely used as a plasticiser for polyvinylchloride (PVC)²⁵. The outer material of the mini-sampler is composed of polyethylene. However, low levels of 2-ethyl-1-hexanol may be emitted from the sampler, and this can be detected by the blank test.

The compounds absorbed onto the mini-samplers were stable upon storage (Figure 4). The differences between the first and fifth days were minor and were comparable within a range of 5%, except for styrene. Thus, the results indicate that most of the target compounds are stable in the mini-samplers. Further examination of 2-ethyl-1-hexanol and styrene should be conducted. The blank tubes show that the mini-samplers do not interfere with their general use.

Comparison of mini-samplers in the field

Parallel sampling of the mini-samplers and the commercially available diffusive samplers²⁶ was conducted as field validation. The relative percentage deviation of the concentration of formaldehyde obtained by the aldehyde mini-samplers and the Supelco DSD-DNPH was 125%. The relative percentage deviation of the concentration of toluene obtained by the VOC mini-samplers and Supelco VOC-SD was 106%. The obtained deviations were within acceptable levels.

Field study

The percentages greater than the 24-h LOQ and the range of concentrations for the 65 children's personal exposure are shown in Table 3. One aldehyde mini-sampler was lost. The most detected compounds were toluene and acetone at 98.5%. Formaldehyde was the third most detected compound at 93.8%. None of the children showed detection levels above the 24-h LOQ levels for styrene and 1-butanol. The results showed that three children were exposed to levels of acetaldehyde, toluene, and p-dichlorobenzene that exceeded the Japanese guideline. In this study, mini-diffusive samplers were developed for children's study. Compared to the commercially available diffusive samplers, the developed mini-samplers are smaller in size and weight, thus easily carried by small children. For further study, the exposure levels will be analysed in terms of the children's health outcomes.

Conclusion

Diffusive mini-samplers for aldehydes and VOC were designed. The sampling rates for the mini-samplers were determined experimentally and examined for their field applicability. The sampling rates for the mini-samplers were 20.9, 22.7, and 19.7 for formaldehyde, acetaldehyde, and acetone, respectively. The sampling rates of the VOC mini-samplers ranged between 3.3-11.7 mL min⁻¹. The sensitivity allows the mini-samplers to be used with a sampling time of 24 hours for

1 concentrations up to 5.9-105.2 $\mu\text{g m}^{-3}$, 1.1-24.7 ppb. Although the tests with styrene and
2 2-ethyl-1-hexanol should be further examined, the developed samplers could be applicable for field
3 measurements. The developed mini-samplers are minimal in terms of size and weight and should
4 be useful for personal measurements, particularly to assess children's daily chemical exposure.

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Table 1. Characteristics of the selected compounds

Compounds	Molecular Weight	Purity (%)	Density (20 °C)	Vapor pressure (kPa)
formaldehyde	30.03	*	1.08	518.6 (25 °C)
acetaldehyde	44.05	*	0.788	101 (20 °C)
acetone	58.08	*	0.791	24.7 (20 °C)
2-butanone	72.11	99	0.805	1.05 (20 °C)
1-butanol	74.12	99	0.81	0.58 (20 °C)
benzene	78.11	99.7	0.878	10 (20 °C)
toluene	92.14	**	0.867	3.8 (25 °C)
ethyl benzene	106.16	**	0.866	0.9 (20 °C)
p/m/o-xylene	106.16	**	0.882	0.7-0.9 (20 °C)
styrene	104.15	**	0.906	0.67 (20 °C)
alpha-pinene	136.26	95	0.86	
p-diclorobenzene	147	**	1.25	0.17 (20 °C)
2-ethyl-1-hexanol	130.23	99	0.883	0.048 (20 °C)
limonene	136.23	97	0.845	0.19 (20 °C)

* SUPELCO T011/IP-6A/ASTM5297 (Sigma Aldrich Co.)

** VOC standard stock solution mix III (Kanto Chemical Co., Inc.)

Table 2 Retention time, and monitor ions for GC/MS

Compounds	Retention time	Monitor ions (m/z)	
		Quantitation	Reference
HPLC			
formaldehyde	5.87	-	-
acetaldehyde	6.96/7.44	-	-
acetone	9.15	-	-
GC/MS			
toluene-d8 ^a	21.1	100	99
2-butanone	9.55	43	72
1-butanol	14.94	56	43
benzene	15.04	78	77
toluene	21.29	91	92
ethyl benzene	25.29	91	106
p/ o-xylene	25.61	91	106
styrene	26.24	104	77
m-xylene	26.43	91	106
alpha-pinene	28.2	93	92
p-diclorobenzene	30.03	146	148
2-ethyl-1-hexanol	30.26	57	83
limonene	30.78	68	67

Table 3 Correlation between mini-samplers and active sampling and determined sampling rate

Compounds	Equation of linear regression	r	Sampling rate (mL/min)
formaldehyde	$Y=0.7972X-0.0069$	0.98	20.9
acetaldehyde	$Y=0.7336X+0.0019$	0.99	22.7
acetone	$Y=0.8532X-0.0267$	0.99	19.7
2-butanone	$Y=0.0006X+0.0115$	0.99	10.0
1-butanol	$Y=0.0004X-0.0352$	0.99	6.7
benzene	$Y=0.0007X+0.1133$	0.99	11.7
toluene	$Y=0.0006X+0.0876$	0.99	10
ethylbenzene	$Y=0.0006X+0.0259$	0.99	10
p/m-xylene	$Y=0.0006X+0.0176$	0.99	10
styrene	$Y=0.0002X-0.0050$	0.99	3.3
o-xylene	$Y=0.0006X+0.0051$	0.99	10
pinene	$Y=0.0005X+0.0166$	0.99	8.3
p-dichlorobenzene	$Y=0.0006X+0.0006$	0.99	10
2-ethyl-1-hexanol	$Y=0.0002X+0.0936$	0.99	3.3
limonene	$Y=0.0004X+0.030256$	0.99	6.7

Y, amount of target compound resulting from mini-samplers (μg)

X, concentration of target compounds resulting from active sampling ($\mu\text{g}/\text{m}^3$)

Sampling rate = Slope (m^3) $\times 10^6$ (mL/m^3) / 60 (min)

Table 4 Personal chemical exposure levels for children

	n	Guide -line ^a	24h LOQ	>24 h LOQ (%)	25%	50%	75%	max
formaldehyde	64	100	8.3	93.8	14.8	21.7	30.7	73.2
acetaldehyde	64	48	7.6	68.8	<LOQ	10.6	16.2	98.6
acetone	64	-	8.8	98.4	16.5	20.9	31.3	147.3
2-butanone	65	-	51.8	0.0	<LOQ	<LOQ	<LOQ	<LOQ
1-butanol	65	-	5.9	92.3	9.5	10.1	11.0	31.4
benzene	65	260	6.9	98.5	18.0	21.5	34.0	328.0
toluene	65	3800	6.9	30.8	<LOQ	<LOQ	7.7	101.8
ethylbenzene	65	870	6.9	61.5	<LOQ	7.9	10.7	52.9
p/m-xylene	65	220	105.2	0.0	<LOQ	<LOQ	<LOQ	<LOQ
styrene	65		6.9	9.2	<LOQ	<LOQ	<LOQ	14.5
o-xylene	65	-	8.4	36.9	<LOQ	<LOQ	14.2	106.2
pinene	65	240	6.9	16.9	<LOQ	<LOQ	<LOQ	607.4
p-dichlorobenzene	65	-	21.0	58.5	<LOQ	31.1	43.5	63.5
2-ethyl-1-hexanol	65	-	10.4	87.7	13.9	23.0	39.6	136.3

unit: $\mu\text{g}/\text{m}^3$ ^a, Guideline from Japanese Ministry of Health, Labour and Welfare

Figure legend

Fig.1 (left) Outside view of the mini-sampler, (right, from top to bottom) 3M #3500, Supelco VOC-SD, developed mini-sampler, respectively.

Fig. 2 Expanded view showing a frame format of the developed mini-sampler: a, metal cap; b, polytetrafluoroethylene (PTFE) membrane filter; c, polyethylene tube; d, absorbent (DNPH-silica gel / carbon beads); e, urethane (5mm thickness x 2)

Fig. 3 The correlations between the target compound collected by mini-samplers, *Y*-axis, and the concentration measured by active sampling, *X*-axis. Closed circles indicate at each concentration.

Fig. 4 The storage stability of the mini-samplers after 1, 3, and 5 days. Bars represent the proportion of each compound as the mean and standard deviation of five determinations. 0 day as a reference (100%).

Fig. 1



Fig. 2

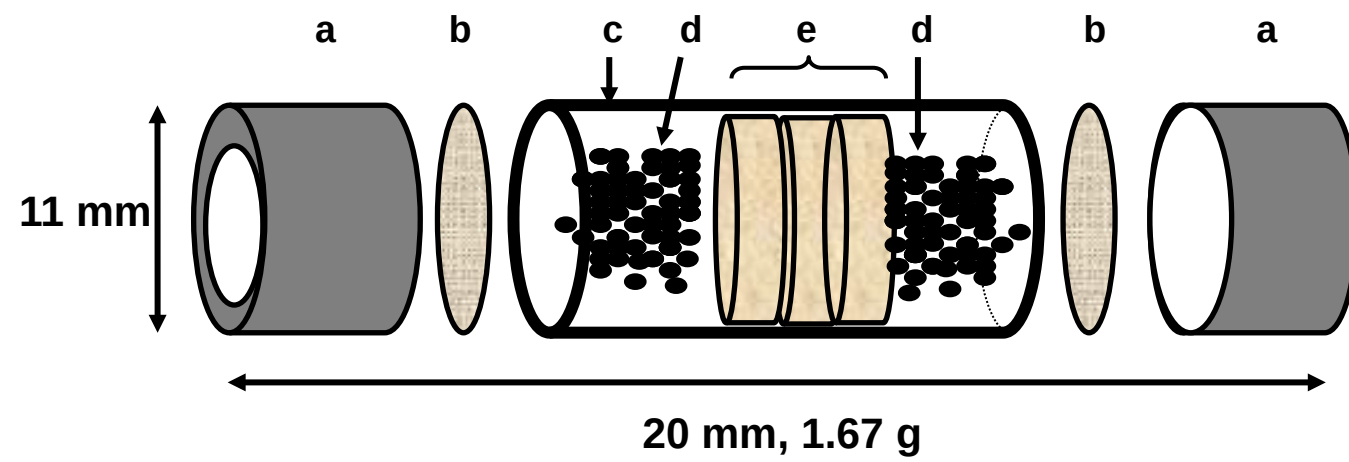


Fig. 3

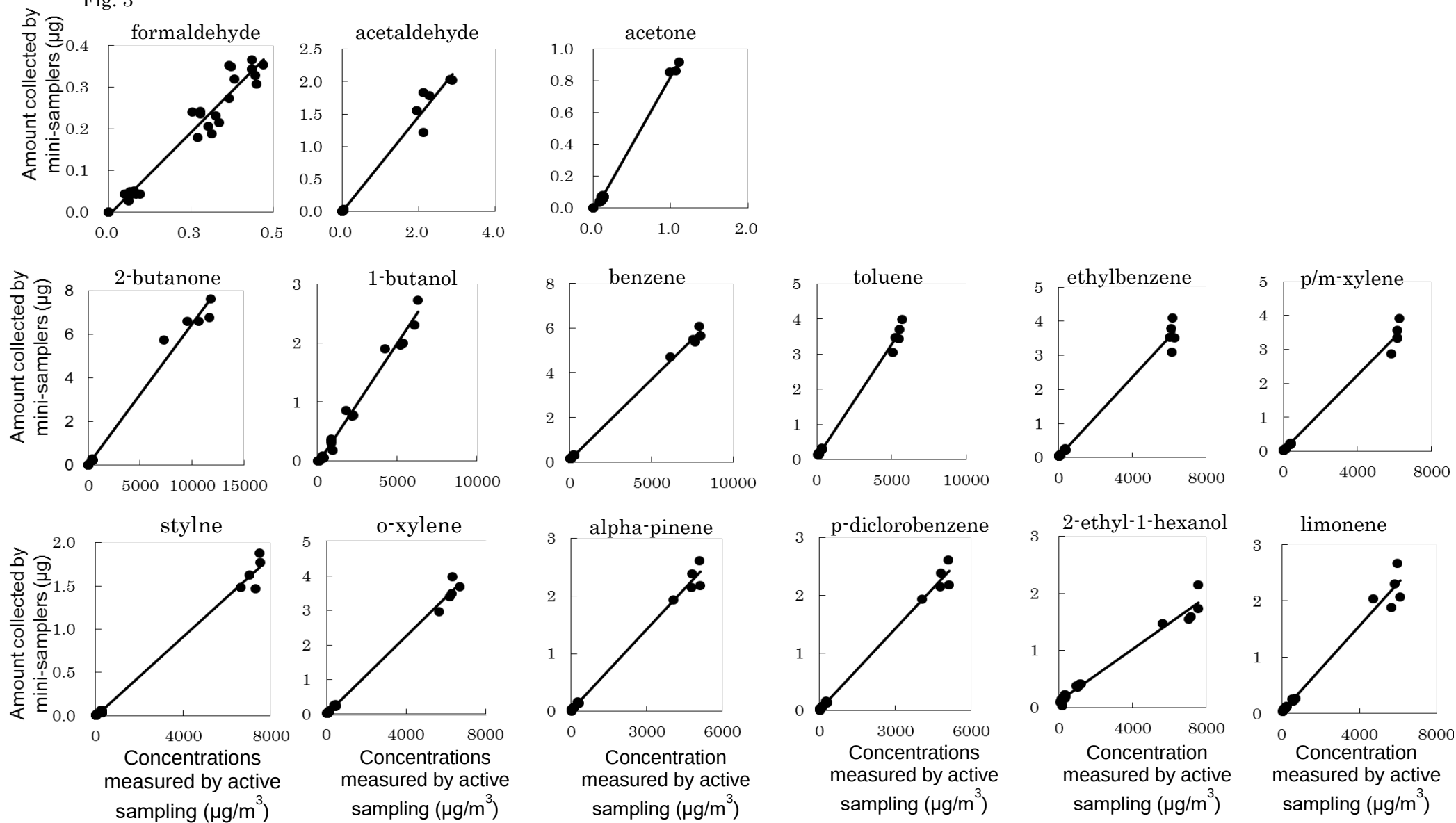


Fig.4

