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Author(s)	Araki, Atsuko; Tsuboi, Tazuru; Kawai, Toshio; Ait Bamai, Yu; Takeda, Tomoya; Yoshioka, Eiji; Kishi, Reiko
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1 **Validation of diffusive mini-samplers for aldehyde and VOC and its feasibility for measuring**
2 **the exposure levels of elementary school children**

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4 Atsuko Araki,^{a,b} Tazuru Tsuboi,^{c,d} Toshio Kawai,^c Yu Ait Bamai,^b Tomoya Takeda,^b Eiji Yoshioka,^b

5 Reiko Kishi*^a

6

7 ^a Hokkaido University Centre for Environmental and Health Sciences

8 ^b Hokkaido University Graduate School of Medicine, Department of Public Health Sciences

9 ^c Osaka Occupational Health Service Centre, Japan Industrial Safety and Health Association

10 ^d Keio University School of Medicine, Department of Preventive Medicine and Public Health

11

12 *Corresponding author

13 Reiko Kishi, MD, PhD, MPH

14 Hokkaido University Centre for Environmental and Health Sciences, Kita 12, Nishi 7, Kita-ku,

15 Sapporo 060-0812, Japan.

16 E-mail: rkishi@med.hokudai.ac.jp;

17 Tel: +81-11-706-4747

18 Fax: +81-11-706-4725

19

1 **Abstract**

2 Exposure to various chemicals can cause adverse effects on health, such as asthma and allergies,
3 especially in children. Data on personal exposure levels in children are scarce, thus small
4 lightweight diffusive mini-samplers for aldehydes and volatile organic compounds (VOCs) were
5 designed to measure the exposure level of children to these chemicals. The aim of the study is to
6 validate and examine the applicability of these mini-samplers for measuring daily chemical exposure.
7 The diffusive mini-samplers are 20 mm in length, 11 mm in diameter, and 1.67 g in weight. The
8 devices are cylindrically shaped with polytetrafluoroethylene membrane filters placed at each end.
9 To measure aldehydes and acetone, 20 mg of 2,4-dinitrophenylhydrazine was used as an absorbent.
10 To measure VOCs, a carbon molecular sieve was used. The sampling rate for each chemical was
11 determined by parallel sampling with active samplers in a closed exposure bag. The blank levels of
12 the chemicals and the storage stability of the device were tested. The mini-samplers were
13 compared to commercially available diffusive samplers. To examine the applicability of the
14 samplers, 65 elementary school children carried them for 24 hours. The sampling rates for
15 formaldehyde, acetaldehyde, and acetone were 20.9, 22.9, and 19.7 mL min⁻¹, respectively. The
16 limits of quantification (LOQ) for the 24-hour sampling by high-performance liquid
17 chromatography/ultraviolet (HPLC/UV) analysis were 8.3, 7.6, and 8.8 µg m⁻³ for formaldehyde,
18 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

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

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

9
10

11 **Material and Methods**

12 **Diffusive samplers**

13 Mini-diffusive samplers (20 mm in length, 11 mm in diameter, and 1.67 g in weight) were designed
14 and developed. Figures 1 and 2 shows the outside and expanded views, respectively, with the scale
15 of the mini-sampler. The cylinder tube was made of polyethylene, and both sides were covered by
16 ϕ 10 mm polytetrafluoroethylene (PTFE) membrane filters and metal caps. The face area of each
17 end was 0.55 mm². The interior of the cylinder was separated into two compartments with three ϕ
18 10 mm, 5-mm-thick urethane sheets. Each cavity was filled with approximately 20 mg of absorbent.

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

9 **Chemicals for analysis**

10 Fifteen major chemicals commonly detected indoors were selected for analysis in this study.
11 Formaldehyde (density at 20°C, 1.08), acetone (density at 20 °C, 0.791), toluene (density at 20°C,
12 0.867), m-xylene (density at 20°C, 0.882) and p-xylene (density at 20°C, 0.882) were obtained from
13 Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Acetaldehyde (density at 20°C, 0.788),
14 2-butanone (purity, 99; density at 20°C, 0.805), benzene (purity, 99.7%; density at 20°C, 0.878),
15 p-dichlorobenzene (density at 20°C, 1.25), (1S,5S)-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene
16 (alpha-pinene) (purity, 95%; density at 20°C, 0.86), and (R)-1-methyl-4-(1-methylethenyl)-
17 cyclohexene (limonene) (purity, 97%; density at 20°C, 0.845) were obtained from Kanto Chemical
18 Co., Inc. (Tokyo, Japan). 1-Butanol (purity, 99%; density at 20°C, 0.81), ethyl benzene (density at
19 20°C, 0.866), o-xylene (density at 20°C, 0.882), styrene (density at 20°C, 0.906), and
20 2-ethyl-1-hexanol (Purity, 99%; density at 20°C, 0.883) were obtained from Tokyo Chemical
21 Industry Co., Ltd. (Tokyo, Japan). For calibration, SUPELCO T011/IP-6A/ASTM5297 (Sigma

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

7

8 **Analysis**

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

16 **GC/MS analysis:** For the VOC analysis, a Hewlett Packard Agilent gas chromatograph with mass
17 spectrometry GC6890/MSD 5983N (GC/MS; Agilent Technologies Inc., Alto, CA, USA) equipped
18 with DB-1 (0.25 mm i.d. x 60 m, 1.5 µm; J & W Scientific, Folsom, CA, USA) was used. The
19 temperature of the injector, the MS ion source, and the interface was set at 250 °C, 230 °C and
20 220 °C, respectively. The column temperatures were 40 °C (13 min), followed by a temperature

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

4

5 **Calibration and instrumental quantification limit**

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

16

17 **Determination of the sampling rate with the mini-sampler**

18 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

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

9

10 **Desorption efficiencies for VOC mini-sampler**

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

15

16 **Blank test and storage stability**

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

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

6

7 **Comparison of mini-samplers in the field**

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

15

16 **Field study**

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

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

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

12

13 **Results and discussion**

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

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

1 2-ethyl-1-hexanol were selected as target compounds in this study. Alpha-pinene and limonene are
2 emitted from wooden materials and are commonly detected in Japanese dwellings^{5, 7, 13}.
3 2-Ethyl-1-hexanol is a possible causative chemical that induces mucous membrane symptoms¹⁴⁻¹⁶.
4 This chemical has been measured in non-domestic buildings¹⁵⁻¹⁷, but no reports have been provided
5 on children's personal exposure levels, to the best of our knowledge.

6

7 **Calibration of the chemicals and determination of the Instrumental Detection Limits by HPLC** 8 **and GC/MS analysis**

9 The standard calibration curves were constructed for formaldehyde, acetaldehyde, and ketone by
10 HPLC and for the 11 VOCs by GC/MS. The linear regressions between the internal standards and
11 each compound was highly significant with correlation coefficients of $R=0.997$ for 1-butanol and
12 $R=0.999$ for the other VOCs. The IQLs ranged from 0.033 for ethyl benzene to 0.110 for
13 1-butanone. The Instrumental Detection Limits (IDLs) were determined to be 0.1-0.5 $\mu\text{g mL}^{-1}$ for
14 the later calculations.

15

16 **Desorption efficiency**

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

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

7

8 **Determination of the sampling rate**

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

$$15 \quad \text{Mini-sampler sampling rate } (\mu\text{L min}^{-1}) = \text{slope } (\text{m}^3) \times 10^6 (\text{mL m}^{-3}) \div 60 (\text{min})$$

16 The determined sampling rates are shown in Table 2. The sampling rates for formaldehyde,
17 acetaldehyde, and acetone were 20.9 $\mu\text{L min}^{-1}$, 22.7 $\mu\text{L min}^{-1}$, and 19.7 $\mu\text{L min}^{-1}$, respectively. The
18 sampling rates for the VOCs ranged from 3.3 $\mu\text{L min}^{-1}$ for styrene and 2-ethyl-1-hexanol to 11.7 μL

1 m² for benzene. The developed mini-sampler has a small cross-sectional area of 1.1 mm³, which
2 results in the low uptake rates ²¹.

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

$$5 \quad 24\text{-h LOQ } (\mu\text{g}/\text{m}^3) = \text{IDL } (\mu\text{g mL}^{-1}) \times \text{volume of extraction solvent (mL)} \\ 6 \quad \div [\text{diffusive sampling rate (mL min}^{-1}) \times 1440 \text{ (min)} \div 10^6 \text{ (mL m}^{-3})]$$

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

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

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

17 **Blank test and storage stability**

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

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

5 The compounds absorbed onto the mini-samplers were stable upon storage (Figure 4).
6 The differences between the first and fifth days were minor and were comparable within a range of
7 5%, except for styrene. Thus, the results indicate that most of the target compounds are stable in
8 the mini-samplers. Further examination of 2-ethyl-1-hexanol and styrene should be conducted.
9 The blank tubes show that the mini-samplers do not interfere with their general use.

10

11 **Comparison of mini-samplers in the field**

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

18

1 **Field study**

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

12

13 **Conclusion**

14 Diffusive mini-samplers for aldehydes and VOC were designed. The sampling rates for
15 the mini-samplers were determined experimentally and examined for their field applicability. The
16 sampling rates for the mini-samplers were 20.9, 22.7, and 19.7 for formaldehyde, acetaldehyde, and
17 acetone, respectively. The sampling rates of the VOC mini-samplers ranged between 3.3-11.7 mL
18 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.

5

6

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12

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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-diclorobenzene	$Y=0.0006X+0.0006$	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

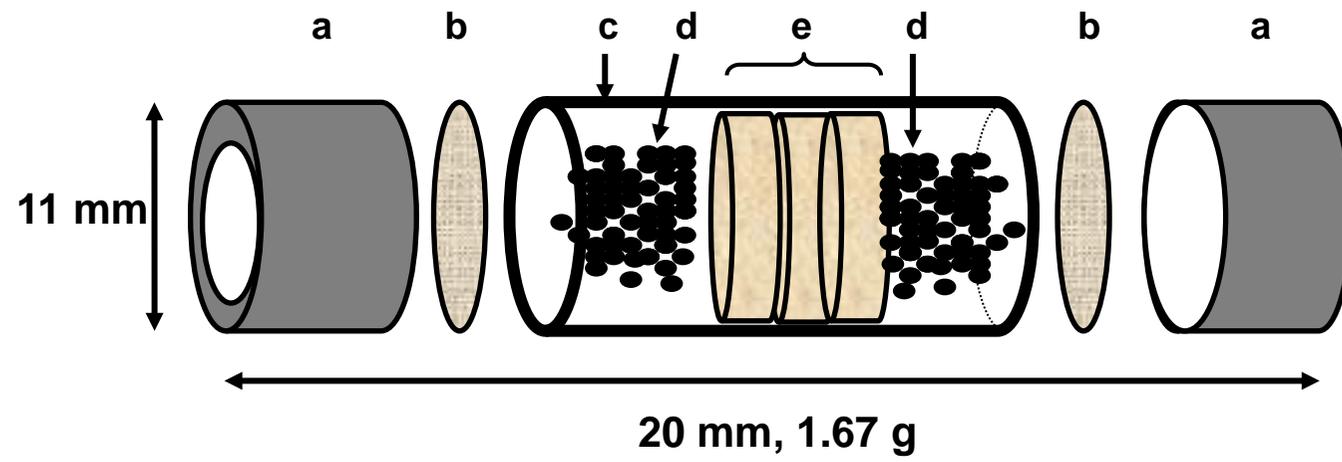


Fig. 3

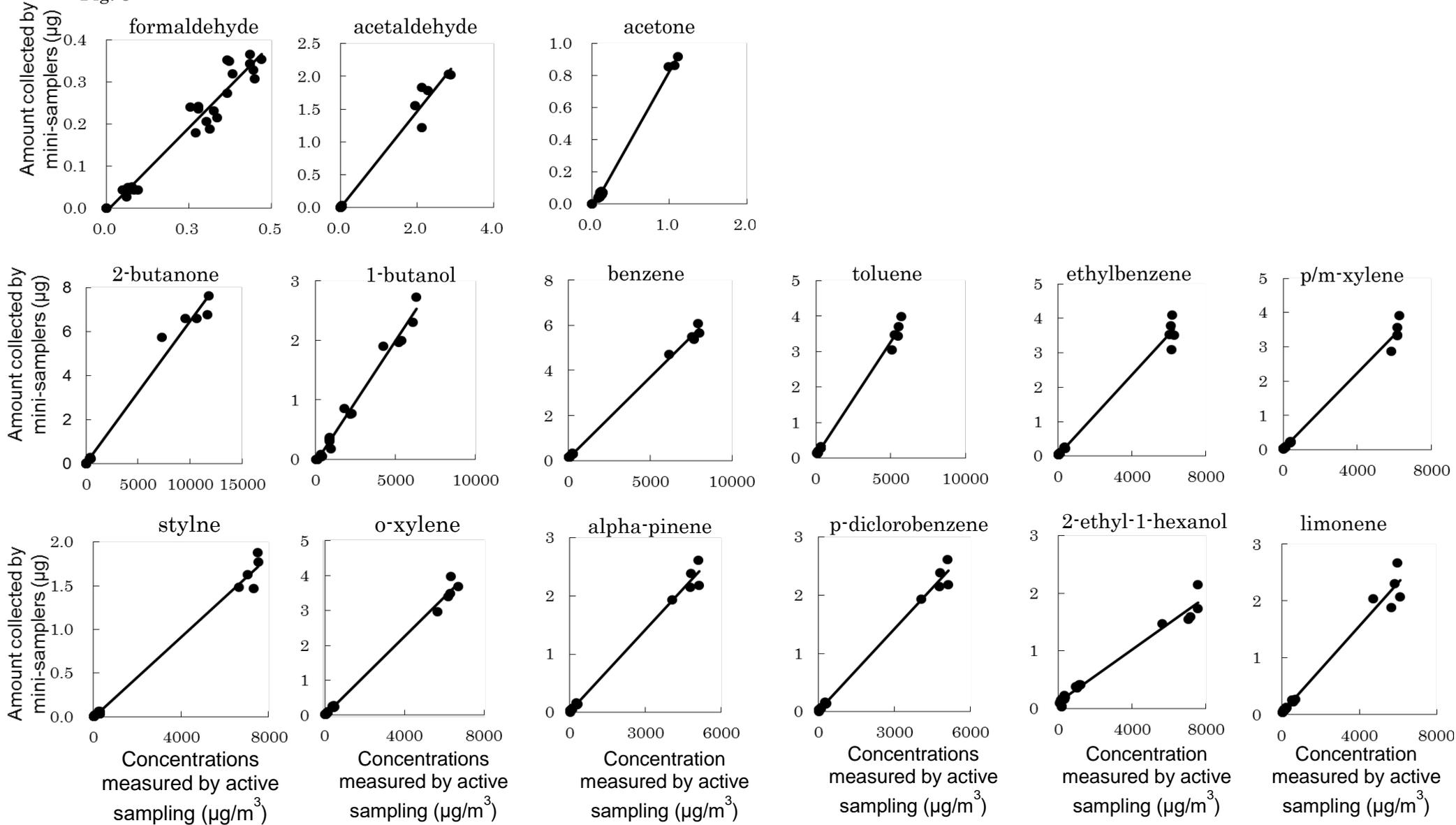


Fig.4

