DEVELOPMENT OF PASSIVE SAMPLER OF VOLATILE ORGANIC COMPOUNDS AND ITS APPLICATION TO PERSONAL EXPOSURE MEASUREMENT OF P-DICHLOROBENZENE

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ABSTRACT

A passive sampler packed with Tenax GC in a porous tube made from polytetrafluoroethylene (PTFE) resin was prepared (30 mm in length, 10 mm in inside diameter, 1 mm in thickness, pore size 2 μm, porosity 50 %). A chamber experiment was performed using the sampler and the proportional constant was found to be 14.14 μg/ppm·hr. Increases in the trapping capacity of about 4 % and 3 % were observed with every increase of 10°C and 1 m/sec of wind velocity, respectively, whereas variations in humidity had no effect on the capacity. Meanwhile, a high correlation (r=0.999) was found between both measured values, in comparison with the active sampler method (Tenax GC tube method). The passive sampler was used to measure the personal exposure levels of various people living in Tokyo (housewives, office workers, students and children). The personal exposure levels were found to range from 7 ppb to 205 ppb.

INTRODUCTION

In fiscal year 1990, 27,000 t of para-dichlorobenzene (p-DCB) was produced in Japan. Most of this output is used to produce deodorant and mothballs. Since p-DCB is irritating to the eye and nose, and has a repressive effect on the central nervous system, the allowable concentration of p-DCB in occupational environments is regulated. TLV of ACGIH (American Conference of Governmental Industrial Hygienists) has decided that the allowable concentration is to be 75 ppm.

Recently, p-DCB has been shown to be a carcinogen in animal experiments (1). In view of the above, the present study was undertaken to develop a passive sampler in order to determine exposure levels of common people in their daily life, and also the effect of this exposure on human health.

Previously, the following two methods have been employed for passive samplers for volatile organic compounds. The first method (2,3) uses active carbon or active carbon felt as the scavenger and the second method (4) employs thermal desorption by Tenax GC. Since the method using active carbon felt was developed for occupational environments, there remain some problems concerning the assay sensitivity in the case of application to general environments. Preparation of the sampler by the thermal desorption method using Tenax GC, is not simple, and this method is expensive. Thus, there are some economic problems with this method.

Accordingly, we examined several methods in order to develop a simple and inexpensive sampler. A sampler packed with Tenax GC was produced by using a PTFE resin tube as a vessel for diffuser and scavengers. The sampler was evaluated with regard to its fundamental properties, such as its proportional constant, the effect of environmental factors, comparative performance vis-a-vis the active sampler method, and other theoretical considerations. Therefore, performance of the passive sampler was evaluated.

In addition, the personal exposure level of various categories of people (housewives, office workers, children and students) was determined by using the sampler developed in this study. The personal exposure levels were found to range from 7 ppb to 205 ppb.

MATERIALS AND METHODS

Scavenger: Tenax GC (60-80 mesh), produced by Enka nv Arnhen, was used. The Tenax GC was used after fully aging at 250°C by admitting N_2 gas.

Generation of p-DCB gas: p-DCB was placed in a glass diffusion tube, and the tube was placed in a standard gas generator. By dilution with purified air, p-DCB was generated at a constant concentration.

Passive sampler: This sampler is composed of a tube made from PTFE resin (2 μm pore size, 50 % porosity), 30 mm length and 1 mm thickness, which was packed with 0.2 g of the scavenger (Tenax GC). At each end of the tube, 5 mm of a teflon stopper 10 mm length was inserted, and the stoppers were fixed with aluminum bands. The sampler was kept in an aluminum preserving bag.

Analytical procedures: The scavenger was taken out of the sampler and placed in a 10 ml stoppered test tube. After addition with 5 ml of n-hexane, the tube was allowed to stand for 15 min at room temperature. After shaking, the supernatant was filtered through a syringe with a filter(0.45 μm). The filtrate was used as a sample for analysis. The sample was applied to capillary gas chromatography.

Experimental determination of the proportional constant: p-DCB gas was generated successively 5 times, and each portion was held in a chamber with 4 passive samplers attached at each concentration. The exposure time was 24 hours. The relationship between the product(CT) of the p-DCB concentration (C) by the exposure time(T), and the amount of p-DCB trapped in the sampler was examined by regression analysis, and the proportional constant(μg/ppm·hr) was estimated. The p-DCB concentration in the chamber was determined by the Tenax GC tube method.

Effects of temperature, humidity and wind velocity on the trapping capacity: The effects of temperature, humidity and wind velocity on the trapping capacity of the sampler were investigated. The test ranges for temperature, humidity and wind velocity were 5-30°C, 30-80 % and 0.2-3 m/sec, respectively.

Comparative measurement: Using the passive sampler method and the active sampler method previously reported by the authors, measurements in typical houses were performed at the same time, and the performance of the passive sampler was evaluated.

RESULTS AND DISCUSSIONS

Preservation of the passive sampler: The naive sampler was stored in an aluminum preservation bag in a desiccator, and an analysis was performed one month later, but no p-DCB contamination was detected. When the post-trapping sampler was stored in the preservation bag in a cool, dark place, the resulting values were not affected by storage for even 2 weeks.

Estimation of the proportional constant: The proportional constant was estimated by the method described in materials and methods. In Table 1, the concentration of p-DCB in the chamber, the amounts of p-DCB trapped in the sampler and the product (CT) of the concentration (C) and the time (T) of the exposure are presented. The relationship of the trapped amount of p-DCB and CT is shown Fig.1. A linear relation between both was found, as seen Fig.1. The first-order regression curve is given by the following equation:

$$y = 14.14\ x + 0.71 \qquad (1)$$

The slope of this straight line is the proportional constant. The variation in the amounts trapped by each of 8 samplers at 194 ppb of p-DCB concentration (Table 1) was 7.5 % of the variation coefficient.

Effects of environmental conditions on the trapping capacity

Temperature: Difference of 10 % was found between the trapped amounts at 5°C and 30°C. Converting it to a value per 10°C, it corresponds to about 4 % increase. This value is approximately the same as the theoretically calculated increase in the molecular diffusion coefficient due to temperature change.

Humidity: For variation in humidity from 30-80 % at a constant concentration of p-DCB in the chamber, no effect or p-DCB amounts trapped in the samplers was observed (exposure time, 24 hrs). This result is reasonable, since a water-repellent tube made from polytetrafluoroethylene resin was used for the sampler.

Wind velocity: When the wind velocity changed from 0.2 to 3m/sec, nearly a 9 % increase in the trapped amount was observed. In other words, the increase was about 3 % per every 1 m/sec increase of wind velocity.

Calculation of the exposure amount

The personal exposure level to p-DCB was calculated from the following equation:

$$ppm = \frac{W}{14.14 \times 24} \qquad (2)$$

Where, W = Weight of p-DCB estimated from the calibration curve (μg), 14.14 = the proportional constant, 24 = hours in a day.

Comparative measurement: The passive sampler method has been shown to be useful in a laboratory setting. It was necessary to ascertain its utility under actual field conditions. Performance of the passive sampler method was evaluated by comparing the values obtained with those obtained by using the active sampler method at the same time. The results shown in Table 2 show that there is a high correlation (r=O.999) between the data obtained by the two methods.

Field study: Using the passive sampler method, the personal exposure levels were determined for various categories of people. The results were 30-205 ppb for housewives, 8-20 ppb for office workers and 7-73 ppb for primary, middle and school students in Tokyo.

CONCLUSION

A passive sampler packed with Tenax GC as the scavenger in a PTFE tube was developed for volatile organic compounds. As the test object, p-DCB, widely used in deodorants and mothballs, was chosen for the present study. Some fundamental investigations, such as estimation of the proportional constant, effects of environmental factors (temperature, humidity and wind velocity), comparative measurements with the active sampler method and theoretical considerations, were made by using the new sampler, and the following results were obtained:

1) Since the sampler is small and lightweight (ca.5 g), it can be used for simultaneous measurement of the concentration of p-DCB at multiple points to determine personal exposure levels to p-DCB.

2) It is found that Fick s first diffusion law is also applicable to a column-type sampler,such as the passive sampler.

3) Concerning the effects of environmental factors on the sampler, it was observed that the trapped amounts at 30°C were larger than those at 5°C by about 11 % (4 % per every 10°C), whereas variations in humidity within the range of 30-80 % had no effect. When the wind velocity was increased from 0.2 to 3 m/sec, about 9 % increase was found in the trapped p-DCB. In other words, a wind velocity increase of 1 m/sec produced about 3 % increase in the trapped amounts.

4) The measurable range of the sampler is 3-500 ppb in the case of a 24 hr exposure.

5) In this study, a fact-finding survey of personal exposure levels under various residential circumstances was carried out using the newly developed passive sampler method. The results showed the personal exposure levels of p-DCB in residences in general to be 7-205 ppb.

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Table 1. Results of calibration experiments for the p-dichlorobenzene diffusion sampler.

p-Dichlorobenzene air concentration ppm, (C)	Duration of sampling time hr, (T)	CT	p-Dichlorobenzene collected μg, *
0.194	24	4.66	67.0
0.302	24	7.25	100.3
0.405	24	9.72	145.1
0.530	24	12.72	171.2
0.596	24	14.30	208.0

Sample gases:Relative humidity 40-60%, Temp. 18-22℃
*:Average of 4 determinations

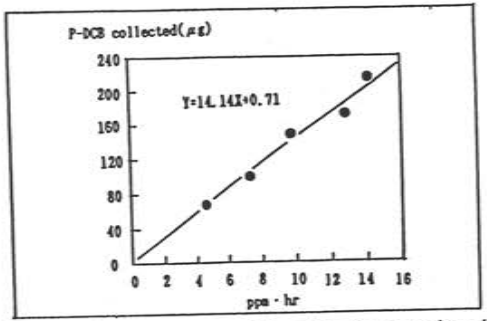

Fig. 1. Amount of p-dichlorobenzene captured by diffusion sampler plotted as a function of p-dichlorobenzene exposure level.

Table 2. Comparison of analytical data obtained by proposed method and active sampler method.

Active sampler method (ppm)* (A)	Passive sampler method (ppm) (B)	(B)/(A)
0.027	0.022	0.81
0.055	0.054	0.98
0.098	0.083	0.85
0.114	0.094	0.83
0.148	0.128	0.87
0.218	0.211	0.97
0.491	0.460	0.94

* :Tenax GC sampling tube method, 100 ml/min x 24hr