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Studies of a Sampling Method Partitioningthe Gaseous and Particulate Phases of Phthalic Acid Esterin Indoor Air

Melikizat Ablat[1+], Shuji Fujii [1]and Naoki Kagi [1]

[1]Graduate School of Information Science and Engineering, Tokyo Institute of Technology
2-12-1, Ookayama, Meguro-ku, Tokyo, 152-8552, Japan

Abstract. Since Phthalic Acid Esters (PAE), which are representative substances of semi volatile organic compounds (SVOCs), have low vapour pressures, the possibility of being present in both the gaseous and particulate phases has been identified. In order to partition and measure the gaseous and particulate phases in an indoor environment, the present study examined the applicability of a VOC denuder as a gaseous and particulate phase partition method. First, the theoretical values were determined for the penetration of the gaseous and particulate phases to a VOC denuder based on the Gormley-Kennedy Equation. Next, experimental values were determined for the Penetration of the gaseous and particulate phases to the denuder using the exposure gas and indoor suspended dust. With a supply flow to the denuder of 5 L/min, almost gaseous wasadsorbed by the denuder, while particulate penetrationratio was 88% or more. Since the results show that the gaseous and particulate phases could be partitioned. In the future, applicability must be studied further through measurements in actual environments.

Keywords: Gaseous phase, Particulate phase, VOC denuder, Penetration

1. Introduction

Phthalic Acid Esters(PAE), known as representative semi volatile organic compounds (SVOCs), are substances added to plastics to provide flexibility and ease of processing [1] and are ubiquitous in our lives. PAE are refractory, but since they are not covalently bonded with polymer materials as addition matrices, it is generated from a variety of products [2]. Since PAE have low vapour pressures, they are hard to volatilize, and since they exist for a long time in indoor air, even though in low concentrations, humans spend 80 percent or more of their time indoors [3] and are thuspotentially exposed. Wensing et al. [1] reported that the PAE concentration in indoor environments was higher than outdoor environments by a few orders of magnitude. While PAE are considered pollutants from the viewpoint of hormone-disrupting substances that cause reproductive impairment, Bornhag et al. [4] reported a correlation between allergic symptoms and SVOC concentration in house dust. As such, there are some doubts that SVOCs may affect human health.

SVOCs in an indoor environment demonstrate low vapour pressures and exist in both the gaseous and particulate phases [5]. N. Kagiet al. [5] showed through chamber experiments that gaseousdi-2-ethylhexyl phthalate(DEHP), which is a representative PAE substance, adsorbs test particles. Although the Filter Empore Disk sampling method is currently used to evaluate the presence and concentration of SVOCs [6], in view of its generally simple operability, there is a problem that gaseous SVOC adsorbs onto a filter at a certain rate, making it impossible to partition gas and particles accurately. Furthermore, denuders have been established for gaseous substances with relatively high reactivity, such as ammonium and NOx, but there have been few measurement examples for PAE. Consequently, it is important to improve sampling methods for PAE in indoor environments in measures of indoor air and studies of the presence of PAE.

[+]Corresponding author. Tel.: +81-3-5734-3153; fax: +81-3-5734-3153
E-mail address: melikizat.a.aa@m.titech.ac.jp

In order to establish a sampling method partitioning the PAE gaseous and particulate phases, the present report evaluated the partitioning of the gaseous and particulate phases using an activated carbon honeycomb denuder. Dibutyl phthalate (DBP), which has been widely used as one of the PAE, was investigated in this study.

2. Experimental Method

2.1. Theoretical Estimation of Penetration of Gaseous and Particulate Phases to Denuder

In order to evaluate the partition of the gaseous and particulate phases of SVOCs by a denuder, first, theoretical values of the Penetration of gaseous and particulate phases to the denuder are determined.

Generally, a theoretical Penetration is determined by the following Gormley-Kennedy equation [7] when an air current flows through a cylindrical denuder in a laminar flow.

$$C/C_0=0.8191\exp(-3.657\mu)+0.0975\exp(-22.3\mu)+0.0325\exp(-57\mu) \quad (1)$$

$$\mu=DL/\bar{U}R^2 \quad (2)$$

Where, μ:deposition parameter, D: diffusion coefficient(cm^2/s), L=length of the denuder, R: radius (cm), $\bar{U}$:mean flow velocity(cm/s), C:outlet concentration of the denuder ($\mu g/m^3$),C_0:inlet concentration of the denuder ($\mu g/m^3$)

For a pipe where the cross section is other than a circular shape, an equivalent diameter δ (=4 x cross-sectional area/wetted perimeter) is used in lieu of the diameter. The Gormley-Kennedy equation was applied to the denuder to determine the relationship between penetration P and the flow rate of particulates (in particle diameters of 10 nm and 100 nm) and gaseous DBP. The theoretical values of penetration were then estimated.

2.2. Studies on Experimental Values of Penetration of Gaseous and Particulate Phases to Denuder

In order to study the transmission characteristics of gaseous PAE to the denuder, studies were performed with the experimental apparatus shown in Fig.1 using the exposure gas DBP. The supply flow rate to the denuder were changed to 2, 5, and 10 L/min. Air at the inlet and outlet of the denuder was sampled by Tenax at 0.2 L/min for 120 minutes and then measured to penetration P of the gaseous DBP to the denuder.

In order to understand the transmission characteristics of the particulate phase to the denuder, the particle diameter distribution of indoor suspended dust at the inlet and outlet of the denuder was determined with a supply flow rate to the denuder of 5 L/min using SMPS with indoor air as the sample air.

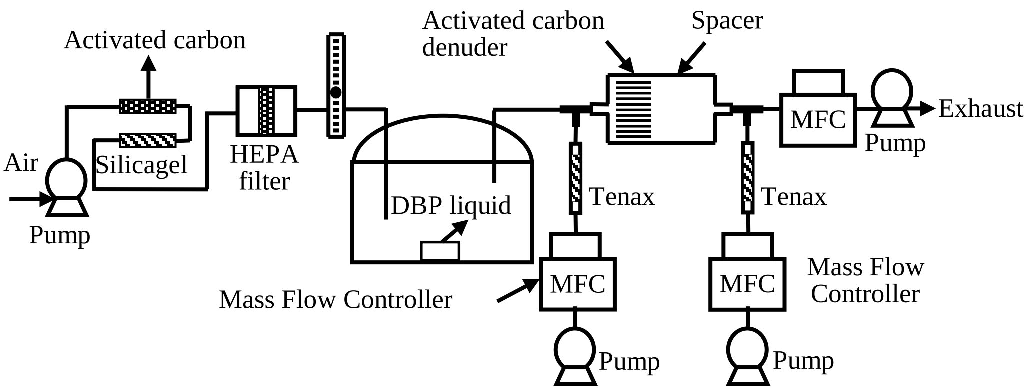

Fig. 1: Experiment for gaseous DBP penetration to the Denuder

2.3. Extraction and Cleaning Operations

Tenax was analyzed by the Thermal desorption method, while the denuder was analyzed by the solvent extraction method.

The cleaning of the denuder was performed two times according to the above-described extraction operation each time after the sampling was completed. 10 ml of the second cleaning liquid was obtained, analyzed as a blank sample, and then subtracted from the quantitative value of the sample. According to this method, the activated carbon denuder was cleaned and used repeatedly.

2.4. Apparatuses Used

Gas chromatogram–mass spectrometry: Analysis was carried out on GC-MS-ATD (QP5050A, GL Science),analysis conditions were summarized Table1.

For measurements of the particle diameter distribution and number concentration of indoor suspended dust during sampling, a scanning mobility particle sizer (SMPS) was used. Since the particle diameter distribution of indoor air fluctuates over time, three sets of data were averaged every 10 minutes.

Table1: Condition of ATD-GC-MS

Instrument	GC—MSQP5050A
Column	30m×0.25μm×0.25μm
Carrier gas	He (99.9999%)
Interface temperature	250 ℃
MS mode	SIM, DEP (149,177), DBP (149,223), DEHP (149,167,279)
Desorption system	Turbo Matrix ATD (Perkin Elmer)
Adsorbent	Tenax-TA
Desorption temperature	300 ℃
Desorption flow	30ml/min
Desorption time	15min
Entrance split	OFF
Trap desorption temperature	300 ℃
Trap desorption time	10min
Exit split	15ml/min

3. Results and Discussion

3.1. Theoretical Values of Penetration of Gaseous and Particulate Phases to Denuder

The length L of the activated carbon honeycomb denuder used in this experiment was 35 mm, and the number of honeycombs was 452, each of which was a square pore with an inner diameter of about 1.5 mm. By using the concept of the equivalent diameter δ for the Gormley-Kennedy equations (1) and (2), a correction equation (3) for a square cross section was determined, Where, Q=flow rate(cm^3/s).

$$\mu = \mathrm{DL}/\bar{\mathrm{U}}R^2 = 4\mathrm{DL}/\mathrm{Q} \quad (3)$$

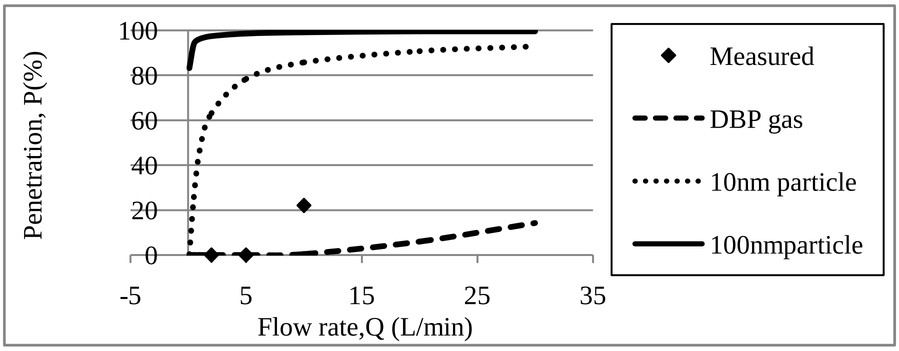

Fig. 2: Relationship between flow rate and theoretical penetration of particulates and measured gas DBP penetration to the denuder

As shown in Fig.2, the penetration increased along with an increase in flow rate, and as the particle diameter increased, the penetration increased within the range of the lower flow rates. In view of the theoretical values, the gas almost adsorbed by the denuder and the penetration was about 89% for particles with less than flow rate of 10 L/min.

3.2. Experimental Values of Penetration of Gaseous and Particulate Phases to Denuder

The results of the penetration of the gaseous DBP to the denuder are shown in Fig.2. As revealed by the results of 2 and 5 L/min, the collection efficiency to the denuder were so high that almost all the DBP gas was adsorbed by the denuder, and no DBP gas was detected at the outlet of the denuder, the theoretical value and the experimental value were in agreement with a flow rate of 2 and 5 L/min. On the other hand, as the supply flow rate increased, the penetration tended to increase: the penetration was 20% or more with 10 L/min. The result was higher than the theoretical value.

The penetration of indoor suspended particles to the denuder was about 88% as a whole, as shown in Fig.3, although there was a loss of about 10%. From this result, it was shown that most particles passed through. Furthermore, the theoretical value and the experimental value were in agreement. From the results show that the present experiments of setting the supply flow rate to the denuder at 5 L/min allowed the partition of the gaseous and particulate phases.

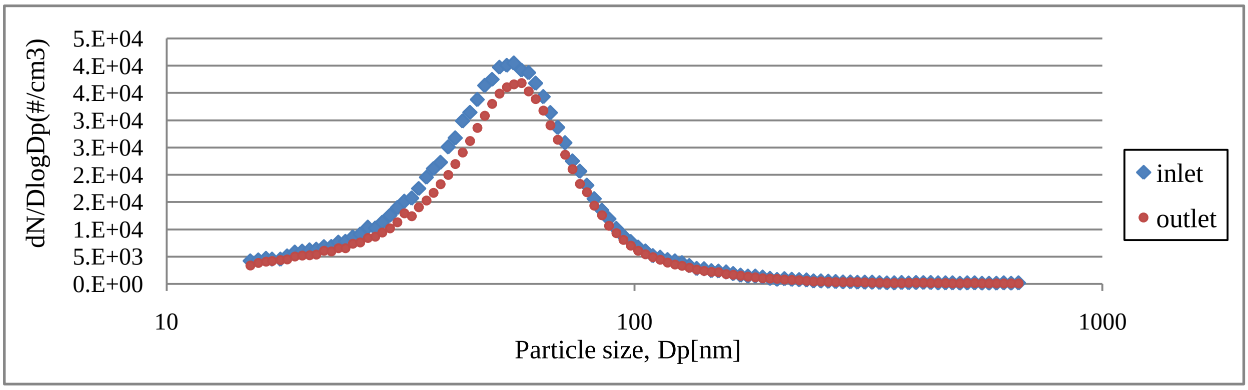

Fig. 3: Penetration of indoor suspended particles to the denuder

4. Conclusion

The present report on the fundamental studies of a partition method for the PAE gaseous and particulate phases by an activated carbon honeycomb denuder came to the following conclusion. The Gormley-Kennedy equation was applied to the denuder to determine the theoretical values of the Penetration of the gaseous and particulate phases to the denuder. Using exposure gas and indoor air, experimental values for Penetration were determined. With 5 L/min, almost all gas was adsorbed by the denuder, and particles with a particle diameter of 10 nm or more produced a Penetration of about 88% or more; consequently, the above condition allowed partition of the gaseous and particulate phases. With 5 L/min, the values of the penetration of the gaseous and particulate phases were in agreement with the theoretical values. In the future, further studies are anticipated through field tests in actual environments.

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