Short Communication

Quantitative Determination of Gaseous Alkanes Adsorbed on Filter Paper During PM_{2.5} Sampling

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Abstract

Atmospheric gaseous alkanes adsorbed onto filter paper during sampling of particulate matter with a diameter less than 2.5 µm (PM_{2.5}) were quantitatively evaluated. Air samples were collected using a high-volume air sampler equipped with a PM_{2.5} impactor. For the determination of gaseous alkanes adsorbed onto the filter paper, two filter papers were introduced into a air sampler. The PM and gaseous compounds were collected on the upstream filter. Part of the gaseous compounds passed through the upstream filter and were also adsorbed onto the downstream filter. The adsorbed alkanes were eluted using ultrasonication with dichloromethane, and subsequently determined using gas chromatography-mass spectrometry. In this study, the gaseous *n*-alkanes C₁₃–C₃₀ were determined from the downstream filter, and the adsorption profiles of these gaseous alkanes varied with air sampling volumes. The adsorption and evaporation profiles of the alkanes were also investigated using deuterium alkanes.

Keywords: PM_{2.5}; Gas adsorption; Alkane; Organic carbon

1. Introduction

The effects of atmospheric particulate matter (PM) on human health have become a critical issue. Specifically, PM with a diameter less than 2.5 µm (PM_{2.5}) can reach deep into human lungs; therefore, monitoring atmospheric air and measures to reduce the occurrence of PM_{2.5} are important [1]. The component analysis of PM_{2.5} is important for source identification and evaluation of its effect on human health. PM_{2.5} is composed of ionic compounds, inorganic compounds, elemental carbons, and organic compounds (organic carbons (OCs)). Research to determine the organic compounds in PM_{2.5} has been performed, and approximately 20–30% of the organic compounds in PM_{2.5} have been reported by mass [2–4].

Gas chromatography (GC) is most widely used method for analyzing volatile organic compounds (VOCs) [5,6] and semi-volatile organic compounds (SVOCs) [7–9] due to its high sensitivity and selectivity. To determine organic compounds in PM_{2.5}, PM_{2.5} is collected on a quartz fiber

filter or a Teflon (PTFE) filter by sampling atmospheric air using an air sampler. The collected PM_{2.5} can be determined using a thermal desorption carbon analyzer, thermal desorption followed by gas chromatography-mass spectrometry (GC-MS), or solvent desorption followed by GC-MS [10,11]. However, during air sampling, part of the gaseous organic compounds are adsorbed onto the filter, and the gaseous compounds are determined together with the organic compounds (positive artifact) [12]. Therefore, the method using filter paper and an air sampler does not accurately measure the organic compounds in PM.

There are many studies determining the amount of alkanes in PM [13,14]; however, investigation on the adsorption of gaseous alkanes onto filter paper during PM sampling is limited. In this study, the adsorption behavior of atmospheric gaseous alkanes onto filter paper during PM_{2.5} sampling with a high-volume air sampler was quantitatively evaluated for each alkane. The amount of adsorbed gaseous alkanes on filter paper was measured by introducing a

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downstream filter paper (backup filter) to the latter side of the upstream filter paper. The adsorption and evaporation behaviors of gaseous alkanes were also investigated using deuterium alkanes.

2. Experimental

2.1. Chemicals

Dichloromethane was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Alkanes (C_{13} – C_{31}) were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). *n*-Nonadecane- d_{40} ($C_{19}D_{40}$) and *n*-hexacosane- d_{54} ($C_{26}D_{54}$) were purchased from CDN Isotopes (Quebec, QC, Canada).

2.2. PM_{2.5} collection and desorption

A high-volume air sampler (HV-500R, Shibata Scientific Technology Ltd., Soka, Japan) equipped with a PM_{2.5} impactor was used for PM sampling. For PM_{2.5} collection, a quartz fiber filter (QR-100) or a PTFE filter (TF98) (both with a 110 mm diameter) were used. Before air sampling, the filters were preheated at 200°C for 1 h. Air samples were collected at 500 L/min. The downstream filter was introduced to adsorb any atmospheric gaseous organic compounds from the latter side of the upstream filter. All air samples were collected at Kofu, Japan. After air sampling, the filters were placed in a glass vial (30 mL volume) and ultrasonicated with dichloromethane (20 mL) for 20 min. This step was performed twice and the combined extract (40 mL of dichloromethane) was filtered using a preheated quartz fiber filter. The obtained solution was concentrated to 1.0 mL under a nitrogen stream. The amount of the analytes detected from the solution obtained by third ultrasonicated elution was less than 1% of the total analytes. The adsorbed amount of the analytes were calculated from calibration curve of each analytes. The calibration curves were prepared by measuring standard solution of the analytes dissolved in dichloromethane.

2.3. GC-MS measurement

A JEOL JMS-Q1000GC Mk-II (JEOL, Tokyo, Japan) was used for all GC measurements. Helium (>99.999%) was used as the carrier gas with a head pressure of 100 kPa. A fused silica HP-5 capillary column (30 m × 0.25 mm, 0.25 µm film thickness, Agilent Technologies) was used for separation of the analytes. The injector and interface temperatures were set at 350°C. Injections were made using the split mode at a ratio of 10:1, and 2 µL of the sample solution was injected. The column temperature was initially maintained at 100°C for 2 min, and then heated to 320°C (maintained for 5 min) at a rate of 20 °C/min. The mass spectrometer was operated in the total ion monitoring (TIM) mode (m/z 46–300) or selected-ion-monitoring (SIM) mode (m/z 56, 71, and 85 for alkanes, and m/z 66, 82, and 98 for deuterium alkanes).

3. Results and discussion

First, the organic compounds found in atmospheric air were confirmed. Atmospheric air (30 m³) was collected onto two PTFE filter papers using the high-volume air sampler equipped with PM 2.5 cut filter (Fig. 1). The collected organic compounds on the two filters were analyzed using GC-MS in TIM mode. From the upstream PTFE filter paper, alkanes C_{13} – C_{30} (branched and *n*-alkanes) were clearly detected, whereas PAHs were not detected (Fig. 2). These alkanes were also detected on the downstream PTFE filter, which were adsorbed as gaseous compounds. To determine straight-chain alkanes, SIM mode was used in the following experiments.

Fig. 1. Illustration of the collection method of air samples using two filter papers and a high-volume air sampler.

To investigate the adsorption of gaseous alkanes onto the quartz fiber and PTFE filter papers, two filter papers were fixed on the air sampler. A PTFE filter was used as the upstream filter, and a quartz fiber or a PTFE filter were investigated as the downstream filter. Figure 3 shows the adsorption amount of the gaseous alkanes on the

Fig. 2. Chromatogram for the determination of organic compounds trapped on the upstream PTFE filter.

downstream filters with an air sampling volume of 90 m³ (0.95 m³/cm²). The results clearly indicate that a significantly larger amount of gaseous alkanes was adsorbed onto the quartz fiber filter, and gaseous alkanes C₂₁–C₂₅ were relatively much adsorbed on both filters in comparison to the other alkanes. The amount of OC in PM has typically determined by thermal optical analysis, where the OC content in PM was determined by heating PM collected on a quartz fiber filter. Therefore possibility of positive artifact for OC by adsorption of gaseous compounds onto the quartz fiber filters has been indicated. The obtained result clearly indicating adsorption of respective gaseous alkanes onto the quartz fiber filter. This result could be useful for investigating positive artifact of OC by thermal optical analysis.

Fig. 3. Gaseous alkanes adsorbed on quartz fiber and PTFE filters used as the downstream filter ($n = 3$).

Two PTFE filters were placed on the high-volume air sampler and different volumes of air samples were collected. Figure 4 shows the amount of adsorbed alkanes on the upstream and downstream filters at air sampling volume of 30, 90, and 150 m³ (0.32, 0.95, and 1.58 m³/cm²). As shown in Fig. 4, the adsorption amount of low-molecular-weight alkanes (C₁₅–C₂₀) reached a plateau at an air sampling volume of 30–150 m³. By contrast, the adsorption amount of the high-molecular-weight alkanes increased with increasing air sampling volume, particularly for the upstream filter. Figure 4 also indicates that high-molecular-weight alkanes were mainly trapped on the upstream filter as PM, although low-molecular-weight alkanes were also found on the downstream filter in equal or greater amounts than the upstream filter. These results are in agreement with a previous study [15]. Higher adsorption of gaseous low-molecular-weight alkanes on the downstream filter paper may be caused by the adsorption of elemental carbon or soot onto the upstream filter paper [16].

To confirm adsorption of gaseous alkanes onto the elemental carbon, further investigation was conducted.

Fig. 4. Adsorption amounts for alkanes adsorbed on the upstream and downstream PTFE filters at different air sampling volumes ($n = 3$). Sampling temperature: 15–27°C.

First, PM_{2.5} was collected on the PTFE filter (air sampling volume of 90 m³). Then, deuterium alkanes, C₁₉D₄₀ and C₂₆D₅₄ dissolved in dichloromethane (100 mg/L, 100 µL), was spiked on a PTFE filter and PM_{2.5} adsorbed filter. Spiked deuterium alkanes were then eluted and measured, and quantitative results obtained by both filter papers were compared ($n = 3$). The result showed that there was no difference between these filters. In the solvent extraction step, the filter paper was ultrasonicated with dichloromethane twice, and detection of the analytes from third extraction for both filters were less than 1% to the sum of the first and second elutions. These results suggest that adsorption of gaseous alkanes onto elemental carbon was not effected to the quantitative determination of alkanes adsorbed on the PTFE filter during PM_{2.5} sampling in this study. Further investigation is required for the evaluation of these variations in adsorption profiles. The adsorption and evaporation of *n*-alkanes were also confirmed using deuterium alkanes. C₁₉D₄₀ and C₂₆D₅₄ were dissolved in dichloromethane (100 mg/L), and a solution (100 µL) was

Table 1. Remaining rate of spiked deuterium alkanes ($n = 3$).

Air sampling volume (m ³)	Upstream filter paper (%)		Downstream filter paper (%)		Evaporation (%)	
	C ₁₉ D ₄₀	C ₂₆ D ₅₄	C ₁₉ D ₄₀	C ₂₆ D ₅₄	C ₁₉ D ₄₀	C ₂₆ D ₅₄
30	2.7 ± 5.0	64.7 ± 7.4	1.3 ± 0.2	0.48 ± 0.04	96	35
90	1.9 ± 1.0	59.8 ± 12	0.88 ± 0.08	0.48 ± 0.02	97	43

spiked onto the upstream PTFE filter. A non-spiked PTFE filter (downstream filter) was placed on the latter side of the spiked filter. Then, atmospheric air (30 m³ and 90 m³) was collected. Table 1 shows the deuterium analytes detected from the upstream and downstream filters at different air sampling volumes. For C₁₉, only 2-3% remained on the upstream filter paper (the spiked filter), indicating that most C₁₉ evaporated. These results also indicate the possibility for evaporation loss of C₁₉ in PM_{2.5} during air sampling. By contrast, 40-60% of C₂₆ remained on the upstream filter paper. In addition, the adsorption of gaseous alkanes onto the downstream filter paper was confirmed, and the ratio of adsorbed gaseous alkanes on the downstream filter was approximately 0.5-1%.

4. Conclusions

Adsorption of gaseous alkanes onto filter paper during PM_{2.5} sampling with a high-volume air sampler was quantitatively evaluated. The results clearly indicated that larger amount of gaseous low-molecular-weight alkanes were adsorbed onto quartz fiber filter than PTFE filter. The results also suggested that most alkanes detected as PM using PTFE filter were gaseous alkanes, especially for C₁₅-C₂₃. Further investigation is required to obtain knowledge about gas adsorption onto filter during PM sampling, although the obtained results could be useful for the evaluation of adsorption profile of other gaseous chemical compounds during PM_{2.5} sampling.

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