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Thermal Extraction of Polycyclic Aromatic Hydrocarbons from Atmospheric 2.5 μm Particulate Matter Collected on a Filter Paper Using a High-Temperature Headspace Method

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Recently, owing to the performance improvement of the headspace (HS)-sampling devices and its consumables, HS vial samples can be analyzed at temperatures up to 300°C. Some studies have attempted to analyze polycyclic aromatic hydrocarbons (PAHs) in atmospheric 2.5 μm particulate matter (PM 2.5) collected on a filter paper by gas chromatography/mass spectrometry (GC/MS) coupled with thermal desorption device. However, no studies have reported the use of an HS-sampling device to quantify PAHs in PM 2.5 filter paper. In this study, we found that the quantification of PAH analysis using HS-GC/MS can be improved by the following steps, so that the accuracy becomes almost the same as that of a solvent-extraction method: 1) replacement of the air in the HS vial with nitrogen, 2) limiting the solvent to toluene, 3) using the hydrolyzed polyimide-covered septum, and 4) optimization of the heating temperature and heating time of the HS vial. As a result, we succeeded in protecting PAHs in an HS vial at a high temperature and in creating an analysis method with a high recovery rate and high repeatability; the limit of quantitation of each PAH in this method was 5.4 pg m^{-3} in the case of a volume of 10080 m^3 of air being collected on the filter paper.

Keywords HS-GC/MS, PM 2.5, PAHs, thermal extraction, hydrolyzed polyimide septum

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Introduction

With the development and improvement of the gas chromatography/mass spectrometry (GC/MS) sample introduction device, corresponding analysis methods have been proportionately developed and the analysis field has been broadened.[1] Recently, owing to the performance improvement of the headspace (HS)-sampling device and its consumables, HS vial samples can be analyzed at temperatures up to 300°C. This greatly expands the application scope of HS-GC/MS. Previously, HS-sampling devices were mainly used to analyze volatile organic substances (VOCs) in water samples. An HS-sampling device that can utilize temperatures up to 300°C is expected to enable the expansion of analysis targets to semi-VOCs (SVOCs). Polycyclic aromatic hydrocarbons (PAHs) are widely recognized as SVOCs in the environment. PAHs originate from fossil fuels and exist in combustion gases and soot. They have been detected in samples of 2.5 μm particulate matter (PM 2.5) in the atmosphere all over the world. Atmospheric PM 2.5 is generally collected on filter paper using a high-volume air sampler. The PAH concentrations extracted *via* filter-paper collection are generally measured using the solvent-extraction (SE) method.[2-6]

An online analysis method that uses an automatic sampling device based on the thermal extraction method for PAH analysis can significantly simplify the analysis procedure. There have been many reports of analysis involving a thermal-desorption sampling device.[7-13] However, there have been no reports on the analysis of PAHs using HS-sampling devices. This may be because PAHs are strongly affected by decomposition, adsorption, and permeation during thermal extraction at high temperatures. Many laboratories possess the latest HS-sampling devices capable of heating samples to high temperatures; despite this, the devices are only used in low temperature fields suitable for, *e.g.*, VOCs analysis in wastewater. In order to expand the application of automatic HS-sampling devices in high-temperature fields, we developed a method for the rapid and accurate quantitative analysis of PAHs in PM 2.5 samples using HS-GC/MS under high-temperature heating conditions.

In the general analysis of HS, the sample to be analyzed usually contacts the air in a sealed HS vial at a high temperature, and then, the oxidation of the component to be analyzed occurs. In addition, the septum used in HS vials is made of silicon and either polytetrafluoroethylene (PTFE) or polyimide (PI), and there have been concerns about the heat resistance and reactivity of the samples on these surfaces. The task of minimizing these effects was also considered in this study.

Material and Methods

Reagents and materials

Two commercially available standard solutions containing PAHs (EPA 525 PAH Mix B in acetone and DIN38407-18 PAH

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solution in acetonitrile) were used as standard samples. The PAH standard n-hexane solution (2.5 μg mL^{-1}) was prepared by diluting a solution of EPA 525 PAH Mix B in acetone (500 μg mL^{-1}) with n-hexane. The PAH standard toluene solution and deuterated PAH (PAHs-d) standard toluene solutions were prepared by dissolving the powdered PAHs and PAHs-d reagents. Stock composite PAH standard solutions of 10 μg mL^{-1} for 16 different PAHs were prepared in toluene. PAHs-d standard solutions were prepared by dilution with toluene to 4 μg mL^{-1}. The compound name, manufacturer, and abbreviations of each PAH used are as follows: Naphthalene (Nap), acenaphthene (Ace), fluorene (Fle), anthracene (Ant), indeno[1,2,3-*cd*]pyrene (IP), fluorene-d10 (Fle-d10) and pyrene-d10 (Pyr-d10), benzo[*a*]pyrene-d12 (BaP-d12), and indeno[1,2,3-*cd*]pyrene-d12 (IP-d12) were obtained from FUJIFILM Wako Pure Chemical Corp., Tokyo, Japan. Acenaphthylene (Acy), phenanthrene (Phe), fluoranthene (Fla), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a*,*h*]anthracene (DaA), and benzo[*ghi*]perylene (BgP) were obtained from AccuStandard, Inc., CT, USA. Fluoranthene-d10 (Fla-d10) and chrysene-d12 (Chr-d12) were obtained from Kanto Chemical Co. Inc., Tokyo, Japan. Toluene, *n*-hexane, acetonitrile, and acetone, which were selected as high-purity-grade solvents, were used for the experiments.

The septa of the HS vials used were made of commercially available silicon covered with a PTFE sheet or a PI sheet. The PTFE septa used were purchased from GL Science, Inc. Tokyo, Japan, and the PI septa were HS septa for ultra-heat resistance purchased from Shimadzu Corp., Kyoto, Japan.

Sampling

Atmospheric PM 2.5 samples were collected using a high-volume air sampler (Sibata Scientific Technology, Tokyo, Japan, HV-RW-1000R) equipped with a Sibata PM 2.5 impactor installed approximately 20 m above the ground in Sakyo-ku, Kyoto, Japan (35°02′54.9″N, 135°46′49.9″E). The samples were collected on quartz filter papers (quartz fiber filter without a blinder, QR-100, 203 × 254 mm, Toyo Roshi, Tokyo, Japan). The sample-collection area of the filter paper was 180 × 140 mm. The collection efficiency (0.3 μm DOP) was 99.99%, and the maximum operating temperature was 1000°C. In order to eliminate the influence of organic matter in the filter paper, it was wrapped with a thin aluminum foil, heated at 300°C for 3 h in an electric furnace, and then naturally cooled to room temperature. The sampling was performed at a flow velocity of 1000 L min^{-1} for one week, and a volume of 10080 m^3 was collected. The collected samples were dried in a desiccator for 24 h and stored in a cryogenic freezer at –80°C.

Equipment and analysis conditions

In the HS method, the desorption of samples was conducted with the HS-20 HS-sampling device (Shimadzu Corp.). The HS vials were heated at 255 – 300°C for 0.5 – 5.0 min with a vial pressure of 150 kPa. The sample line and transfer line temperature were set to 300°C to avoid the absorption of high-boiling-point compounds. GCMS QP-2010 Ultra (Shimadzu Corp.) was used with the HS-20 for GC/MS with automatic HS sampling. The chromatographic column was SH-Rxi-5Sil MS model (30 m length, 0.25 mm inner diameter, and 0.25 μm film thickness: Shimadzu Corp.), and the carrier gas used was helium. In the SE method, the GCMS QP-2010 Ultra with the AOC-20i auto injection device (Shimadzu Corp.) was used. The column used for SE-GC/MS was the same as that used for HS-GC/MS. The analysis conditions of GC/MS for the HS and SE methods were the same as well. The GC oven program was set at 90°C, and after holding for 1 min, the temperature was then increased to 320°C at 15°C min^{-1} and held for 8 min with a carrier gas flow line velocity of 35 cm s^{-1}. The mass spectrometer was operated *via* an electron ionization method using a full scan that selected an ion-monitoring mode (SIM/SCAN mode), and a 70 eV electron was used for ionization. The mass-to-charge ratio (*m*/*z*) of the quantitative ions of each PAH were as follows: Nap (*m*/*z* 128), Acy (*m*/*z* 152), Ace (*m*/*z* 153), Fle (*m*/*z* 166), Fle-d10 (*m*/*z* 174), Phe (*m*/*z* 178), Ant (*m*/*z* 178), Fla (*m*/*z* 202), Fla-d10 (*m*/*z* 212), Pyr (*m*/*z* 202), BaA (*m*/*z* 228), Chr (*m*/*z* 228), Chr-d12 (*m*/*z* 240), BbF (*m*/*z* 252), BkF (*m*/*z* 252), BaP (*m*/*z* 252), BaP-d12 (*m*/*z* 264), IP (*m*/*z* 276), IP-d12 (*m*/*z* 288), DaA (*m*/*z* 278), and BgP (*m*/*z* 276).

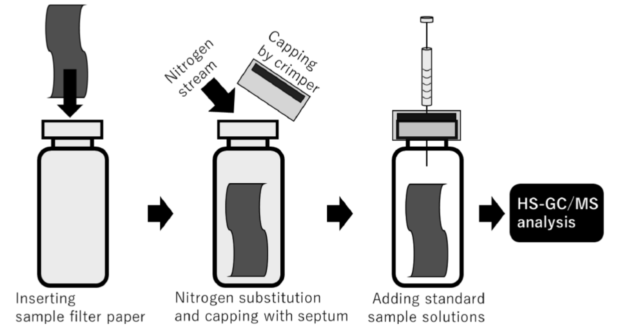

Fig. 1 Schematic of the HS analytical sample preparation procedure.

Sample preparation

The filter paper samples used for analysis were cut from a PM 2.5 sample-collection filter paper or blank filter paper using a self-made 25.5 × 15.5 mm square drilling punch and then placed in an HS vial (10 mL size). The nitrogen substitution inside the HS vial was realized by capping the vial with a septum while expelling the air inside using a stream of nitrogen gas. Then, the standard solution and internal standard solution required for each of the following experiments were added to the prepared HS vial using a syringe pump (Fig. 1).

When optimizing the gas atmosphere in HS vials, air atmosphere and nitrogen atmosphere were compared. The air atmosphere vial preparation was capped with a septum with hydrolyzed PI film (hydrolyzed PI septum) without the nitrogen-substitution procedure. In this experiment, a blank filter was placed in the vial. Then, 2.0 μL of 2.50 μg mL^{-1} PAH standard toluene solution and 3.0 μL of 10.0 μg mL^{-1} *n*-hexadecane toluene solution as the internal standard solution were added, respectively. In order to investigate the effect of different solvents on the detection intensities of PAHs, four PAH standard samples were prepared using four different solvents: acetone, acetonitrile, n-hexane, and toluene. This evaluation was performed using a blank filter. The PAH solutions of the four different solvents were added to each HS vial in a nitrogen atmosphere and were capped with hydrolyzed PI septa. In this investigation, 2.0 μL of 2.50 μg mL^{-1} PAH standard solution and 3.0 μL of 10.0 μg mL^{-1} n-hexadecane solution as the internal standard solution were diluted with an appropriate solvent, and added into HS vials. In order to evaluate the influence of different types of septa on PAH analysis, three types of septa—a septum with PTFE film (PTFE septum), a septum with PI film (PI septum), and a hydrolyzed PI septum—were used. In this experiment, a blank filter was placed in the

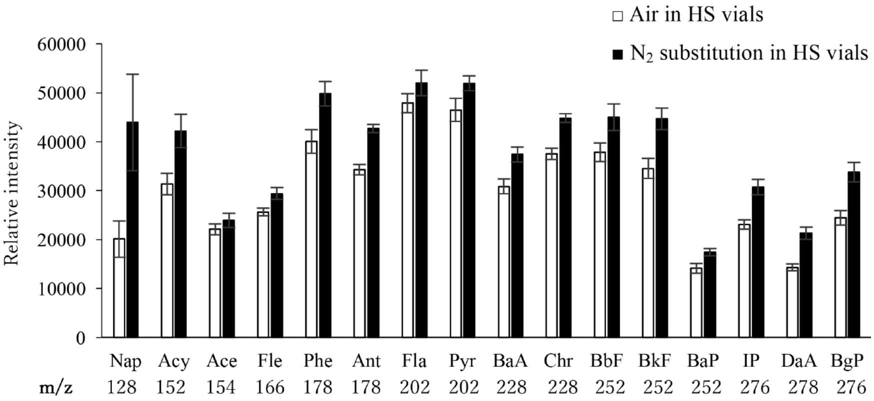

Fig. 2 Effect of nitrogen substitution on the PAH detection intensity (n = 3).

HS vial. The HS vials contained nitrogen atmosphere inside, to which 2.0 μL of 2.50 μg mL^{-1} PAH standard toluene solution and 3.0 μL of 10.0 μg mL^{-1} n-hexadecane toluene solution were added. The sample used in the experiment for investigating the heating temperature and heating time was prepared by placing a blank filter paper in an HS vial, substituting with nitrogen, and capping with a hydrolyzed PI septum. Then, 2.0 μL of 2.50 μg mL^{-1} PAH standard toluene solution and 3.0 μL of 10.0 μg mL^{-1} n-hexadecane toluene solution were added.

As a standard sample used for a calibration-curve method, a blank filter paper was used, and an HS vial was prepared by substituting with nitrogen and capped with a hydrolyzed PI septum. Then, 2.0 μL of PAH standard solution (0, 0.10, 0.25, 0.50, 1.00, 2.50, and 5.00 μg mL^{-1} toluene solution) and 3.0 μL of 10.0 μg mL^{-1} *n*-hexadecane toluene solution were added to the vial. A PAH concentration analysis sample was prepared by placing PM 2.5-collecting filter paper in a vial instead of blank filter paper and adding 2.0 μL of toluene instead of a PAH standard solution. A sample, to which PAHs-d was added as a surrogate substance, was prepared by placing a blank filter paper in an HS vial, substituting with nitrogen, and capping with a hydrolyzed PI septum. Then, 2.0 μL of PAHs standard toluene solution and 3.0 μL of 2.50 μg mL^{-1} PAHs-d toluene solution were added. For the standard sample used in the standard addition method, a vial was prepared by inserting PM 2.5-collecting filter paper, substituting with nitrogen, and capping with a hydrolyzed PI septum. Then, 2.0 μL of PAH standard solution (0, 0.10, 0.25, 0.50, and 1.00 μg mL^{-1} toluene solution) and 3.0 μL of 10.0 μg mL^{-1} n-hexadecane toluene solution were added to the vial.

Except for experiments that examined the heating temperature and heating time, the heating temperature and heating time of the HS vials of the HS sampler were all set to 300°C and 2.5 min, respectively.

Hydrolysis of the PI septum

The PI surface was converted into a polyamic acid surface by immersing the PI septum in a 1.5-M Na_2CO_3 solution for 1 – 5 h to render it hydrophilic. To confirm the degree of hydrophilicity, the contact angle was visually evaluated when water droplets were dropped on the sheet surface.

Method of SE

The PAHs from the PM 2.5 samples were solvent-extracted using ultrasonic extraction with dichloromethane as the solvent. PM 2.5 filter paper (36 × 70 mm: three pieces) was cut with ceramic scissors into fine pieces, placed in a cylindrical filter paper (Toyo Roshi, silica fiber), and set in a glass centrifuge tube. Further, 100.0 μL of 1.0 μg mL^{-1} PAHs-d standard toluene solution was added to the PM 2.5-collecting filter paper, and then, 50.0 mL of dichloromethane was added so that the PM 2.5-collecting filter paper was immersed in the solvent, and the lid for the centrifuge tube was closed. After irradiation with ultrasonic waves for 30.0 min, the cylindrical filter paper was removed and its inside was washed with dichloromethane. The sample solutions were concentrated by nitrogen purging until they were almost dry, and then, up to 1.0 mL of toluene was added to prepare an analytical sample. The concentrations of PAHs in the PM 2.5 samples were determined using the calibration-curve method after correcting the recovery rate with an internal standard (the PAHs-d standard solution).

Results and Discussion

Effect of nitrogen substitution

The detection intensities of PAHs were compared between the case where the atmosphere in the HS vial was substituted with nitrogen and the case where the atmosphere in the indoor air was not substituted with nitrogen. The result was compared with the case of indoor air in the HS vial (Fig. 2). The PAH recovery rate was found to improve for all PAH components. The recovery rate was greatly reduced in the presence of oxygen and moisture, which caused oxidative decomposition in the thermal extraction process, but it was improved by the nitrogen substitution.

Selection of solvent

The effects of different solvents on the detection intensities for the PAH standard solutions were investigated. The PAH standard solutions in four different solvents were compared. Figure 3 shows the detection intensity at the value of m/z corresponding to the molecular weight of each PAH. The results showed that Nap exhibited a high coefficient of variation (CV: 11.2 – 22.5%) and low quantitativeness in all solvents. However, the cause for this observation was not identified. Therefore, it was judged that the quantitative analysis of Nap using the HS sampler in this method was not suitable. Except for Acy, Ant, and BaA, the detection intensities of 3 – 4-ring PAHs tended to be higher when using hexane solutions. In the case of hexane as the solvent, a peak due to the component derived from septum was observed at the same time as the retention time of 3 – 4-ring PAHs, and the matrix was believed to have affected the detection intensity. Acetone and acetonitrile, which are polar solvents,

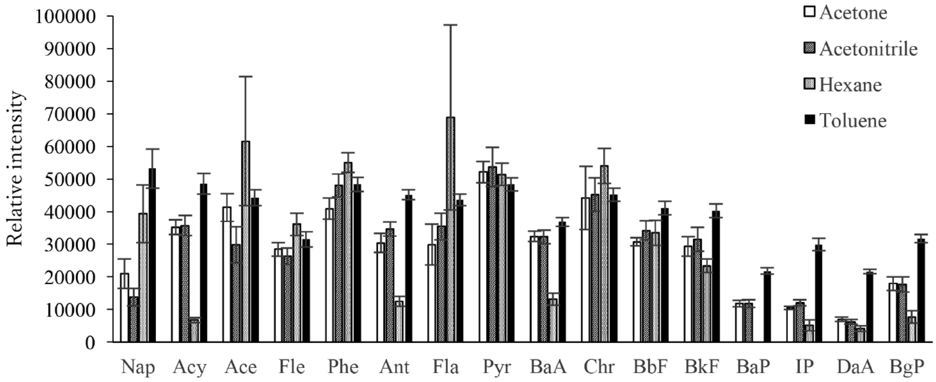

Fig. 3 Effect of the solvent on the PAH detection intensity (*n* = 3). Acetone, acetonitrile, *n*-hexane, and toluene were used as the solvents of the PAH standard solutions.

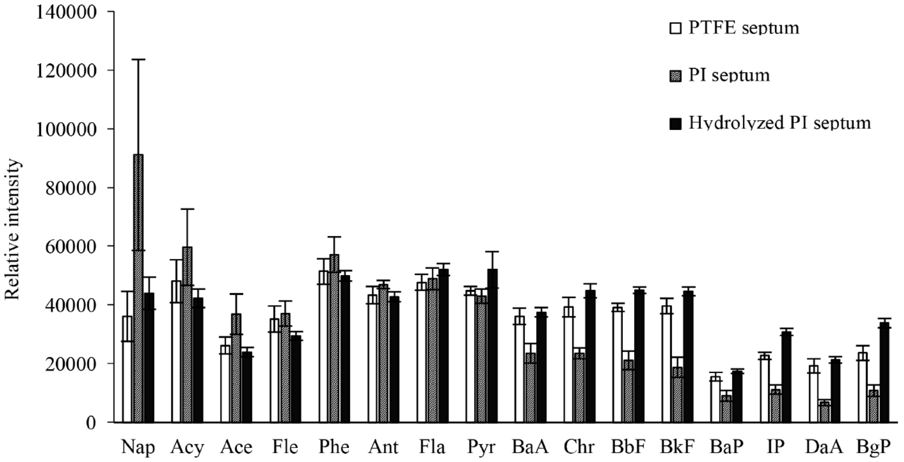

Fig. 4 Effect of the septum (PTFE septum, PI septum, and hydrolyzed PI septum) on the PAH detection intensity (*n* = 3).

exhibited the same detection intensities as other solvents for 4-ring PAHs; however, the detection intensities of other PAHs were low (31 – 82%). The detection intensity of PAHs was particularly outstanding when the toluene solvent was used, especially for 5 – 6-ring PAHs, which are particularly difficult to extract by heating. It was speculated that toluene exhibited some interaction with the septum and glass surface of the HS vials. π-π interactions have also been reported to exist in the gas phase,[14–16] and toluene may have pi-stacked with PAHs and stabilized in the gas phase. However, the strength of the interaction was not confirmed. It may also be due to a combination of this effect with other effects.

Selection of septum

Figure 4 shows the results of evaluating the effect of the septum on the detection intensity of each PAH when 2.0 μL of 1.0 μg mL^{-1} PAH standard toluene solution and 3.0 μL of 10.0 μg mL^{-1} *n*-hexadecane toluene solution as an internal standard were added to a blank filter. The PTFE septum demonstrated good detection intensity for 3 – 4-ring PAHs. The PI septum exhibited the highest detection intensity for 3-ring PAHs, but for 4 – 6-ring PAHs, it exhibited 65% lower intensity than the PTFE septum. The cause of this decrease was considered to be the effect of adsorption and decomposition on the surface of the PI sheet. Therefore, for a surface treatment of the PI sheet, the surface was converted into polyamic acid using alkaline hydrolysis to make it hydrophilic (Fig. 5).[17–19] As a result, the detection intensity was significantly improved for most of the 4 – 6-ring PAHs; the detection intensity of the hydrolyzed PI septum was 107 – 124% higher than that of the PTFE septum. It was speculated that the reason for this phenomenon was that PAHs might have been stabilized in the hot gas phase by being repelled by the hydrophilic surface and protected by toluene vapor. In addition, because the slight gas permeability of the PTFE sheet is stronger than that of the PI sheet,[20] PAHs may have partially adsorbed on the rubber of the septum through the PTFE sheet.

Furthermore, the treatment time for the hydrolyzed PI septum was optimized. The detection intensities obtained for BgP were compared using PI septa immersed in a 1.5-M Na_2CO_3 aqueous solution for 0, 1, 3, and 5 h. The detection intensities improved by factors of 1.32, 1.44, and 1.40, for treatment times of 1, 3, and 5 h, respectively. This confirmed that a sufficient effect could be obtained in the 3 – 5-h range. It was confirmed that the contact angle of the water droplets on the surface of the PI sheet became almost 0° after the alkali treatment for 3 h or more.

Investigations of the heating temperature and heating time of HS vials

The heating temperature and heating time of each HS vial

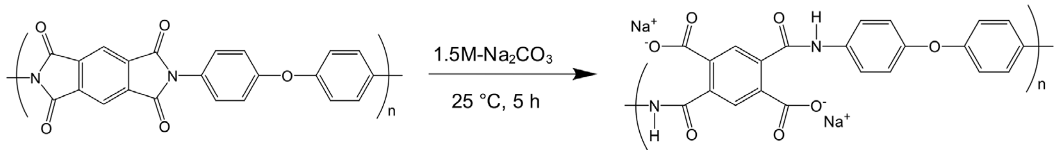

Fig. 5 Reaction scheme of the alkaline hydrolysis treatment of the PI sheet surface.

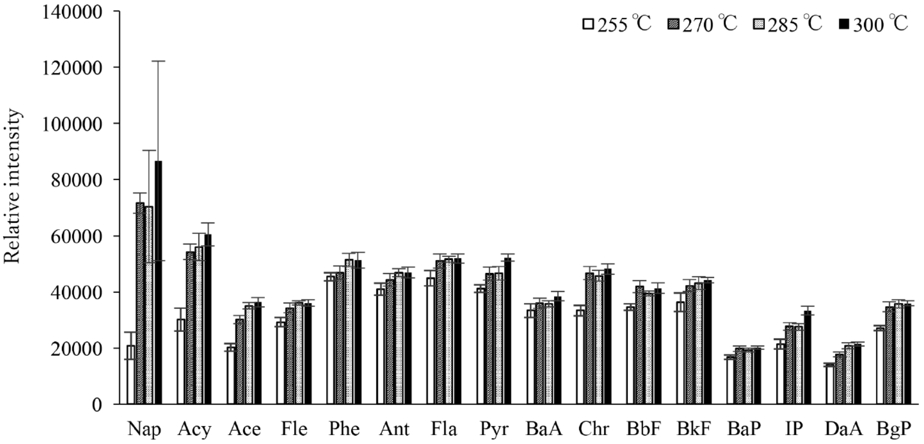

Fig. 6 Effect of a heat-retention temperature (at 2.5 min) on the PAH detection intensity (n = 3) set at 225, 255, 285, and 300°C.

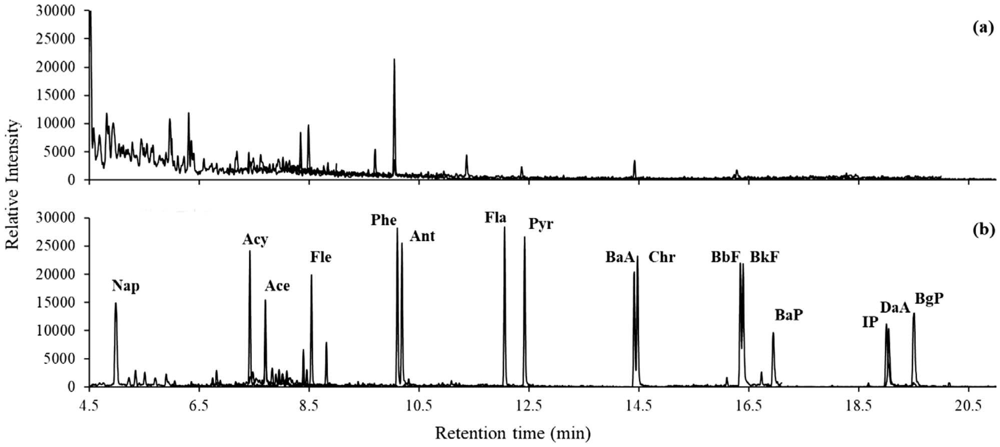

Fig. 7 Absolute strength of PAHs-d chromatograms of PAH standard samples obtained using HS-GC/MS (a) before and (b) after investigating the conditions.

were investigated. When the heating time of an HS vial was 2.5 min, for most PAHs, the highest detection intensity was obtained at 300°C, which is the maximum temperature available with the HS-sampling device (Fig. 6). Even the detection intensities of the 2 – 3-ring PAHs with low boiling points were the maximum at 300°C. In addition, when the heating time was varied over the range of 0.5 – 4.0 min, a duration of 2.5 min was found to provide the maximum detection intensity for all PAHs. It was speculated that the optimal heating time for PAH analysis is much shorter than that for VOC analysis owing to the rapid attainment of dynamic equilibrium at a high temperature. The optimum heating temperature and time found in this study were 300°C and 2.5 min. Figure 7(a) shows the results from analyzing a PAH standard acetone solution using an untreated PI septum without replacing the air inside the HS vial with nitrogen. Figure 7(b) shows the results of the PAH analysis obtained with the HS method used in this study under optimum conditions. Analyzing the PAHs with the HS method was not possible without optimizing the analysis conditions in the HS vial. After the analysis of the PAH samples under the optimum analysis conditions, we succeeded in significantly improving the analytical sensitivity of 5 – 6-ring PAHs, which had been considered difficult to achieve because of the thermal desorption. In addition, the 5 – 6-ring PAHs were 65 – 93% of the intensity of the molecular weight ion fragment of chrysene, which was a high detection sensitivity.

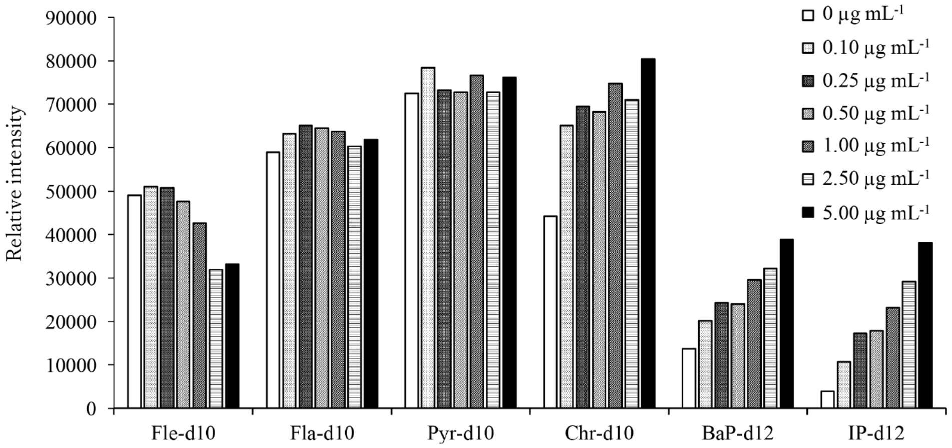

Fig. 8 Influence of the PAH concentrations (0, 0.10, 0.25, 0.50, 1.00, 2.50, and 5.00 µg mL^{-1}) on the relative intensity of PAHs-d as the internal standard substance.

Table 1 PAH concentrations in PM 2.5 samples obtained using the HS and SE methods

PAHs	April 4 - 12, 2019			May 18 - 24, 2019			July 12 - 18, 2019		
	HS/ng m^{-3}	SE^{a,b}/ng m^{-3}	Ratio of HS/SE	HS/ng m^{-3}	SE^{a,b}/ng m^{-3}	Ratio of HS/SE	HS/ng m^{-3}	SE^{a,b}/ng m^{-3}	Ratio of HS/SE
Acy	0.010	0.0094	1.07	0.0045	0.0041	1.10	0.0045	0.0042	1.07
Ace	0.0043	0.0037	1.16	0.011	0.011	1.05	0.0095	0.010	0.92
Fle	0.0024	0.0019	1.26	0.0055	0.0053	1.04	0.0051	0.0055	0.93
Phe	0.0067	0.0061	1.10	0.022	0.021	1.06	0.016	0.014	1.09
Ant	0.0024	0.0025	0.96	0.018	0.019	0.99	0.012	0.013	0.99
Fla	0.032	0.032	1.02	0.041	0.038	1.08	0.0081	0.0090	0.90
Pyr	0.016	0.017	0.96	0.034	0.035	0.98	0.013	0.013	1.05
BaA	0.0037	0.0033	1.12	0.011	0.011	1.05	0.012	0.011	1.13
Chr	0.028	0.027	1.03	0.040	0.039	1.03	0.030	0.028	1.06
BbF	0.056	0.055	1.02	0.066	0.063	1.05	0.060	0.056	1.07
BkF	0.0039	0.0034	1.15	0.016	0.019	0.81	0.016	0.018	0.88
BaP	0.0064	0.0060	1.07	0.018	0.019	0.96	0.018	0.016	1.14
IP	0.016	0.016	1.03	0.045	0.043	1.05	0.030	0.031	0.98
DaA	0.0084	0.0081	1.04	0.018	0.015	1.16	0.016	0.015	1.05
BgP	0.037	0.038	0.96	0.051	0.050	1.02	0.031	0.030	1.04

a. The limit of quantitation of the SE method was 8.2 pg m^{-3} in the case of a volume of 10080 m^3 of air collected on the filter paper.
b. The CV value of the SE method was 8.7% or less for all PAHs.

Examination of the quantitative method

When the internal standard n-hexadecane toluene solution (3.0 µL of 10.0 µg mL^{-1}) and PAH standard toluene solution (2 µL of 0.1, 0.25, 0.5, 1.0, 2.50 and 5.00 µg mL^{-1}) were added to the blank filter paper and measured under the optimum conditions, good linearity was obtained (coefficient of determination $R^2 = 0.987 - 0.999$). The relative slope values (relative detection intensities/concentrations) of the calibration curves for the PAHs Acy, Ace, Fle, Phe, Ant, Fla, Pyr, BaA, Chr, BbF, BkF, BaP, IP, DaA, and BgP were 0.42, 0.47, 0.82, 0.74, 0.95, 0.93, 0.81, 0.81, 1.0, 0.93, 1.04, 0.64, 0.74, 0.61, and 0.69, respectively. Furthermore, the absolute intensities of PAHs-d detected upon adding five types of PAHs-d standard solutions as internal standards varied greatly depending on the concentration of the PAH standard solution (Fig. 8). These results showed that the reference PAHs-d did not function as an internal standard owing to the self-matrix effect of PAHs in the standard solution. Therefore, the calibration-curve method using an internal standard (PAHs-d) was considered to be unsuitable for analyzing the quantification of the PAHs obtained by thermal extraction. Accordingly, the standard addition method, which was capable of suppressing the matrix effect, was considered suitable for quantifying the PAHs collected on PM 2.5 filter paper. Moreover, the repeatability (CV, $n = 3$) in the minimum concentration standard solution (0.1 µg mL^{-1}) was 4.8% or less. Therefore, the limit of quantitation of each PAH in this method was 5.4 pg m^{-3} in the case of a volume of 10080 m^3 of air being collected on the filter paper. This limit of quantitation was sufficiently sensitive compared with the SE method.

Comparison between HS and SE

Table 1 presents the results of measuring the PAH concentrations in the collected atmospheric PM 2.5 samples using the HS (standard addition method) and SE methods. The results of the analysis obtained using the HS method tended to be slightly higher, although they showed agreement with the results obtained using the SE method. However, the BkF concentrations in the May 18, 2019 and July 12, 2019 samples obtained with the HS method were 81 and 88% lower when using the HS method, respectively. It was speculated that this affected the evaluation of the peak separation because the retention time was close to that used for BbF. In addition, the relatively higher HS results (compared with the SE results) were attributed to the pretreatment steps in the SE method, and losses due to sublimation and adsorption might be reduced using the HS method.

Conclusions

To analyze PAHs using the high-temperature HS method, establishing an appropriate analysis condition in the HS vial is important. By investigating the conditions for analyzing the PAHs in PM 2.5 samples collected on a filter paper, replacing air with nitrogen in the HS vial, using hydrolyzed PI septum, limiting the solvent to toluene, and setting the heating temperature to 300°C and the heating time to 2.5 min was most effective. It was conjectured that toluene vapor stabilized the PAHs by pi stacking in the gas phase and a hydrophobic-hydrophilic repulsion occurred between the hydrolyzed PI septum surface and the toluene vapor containing PAHs; as a result, the detection intensity of the PAHs was improved. In other words, an untreated PI septum caused degradation and adsorption in the high-temperature HS method, which could result in a significant adverse effect on analytical accuracy.

This study was the first investigation demonstrate that PAHs (a type of SVOC) can be analyzed at 300°C using the HS method. In addition, this study specifically proposes a method for maximizing the utility of the most convenient and most popular GC sampling device.

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