

## RESEARCH ARTICLE

# Analysis of Parent/Nitrated Polycyclic Aromatic Hydrocarbons in Particulate Matter 2.5 Based on Femtosecond Ionization Mass Spectrometry

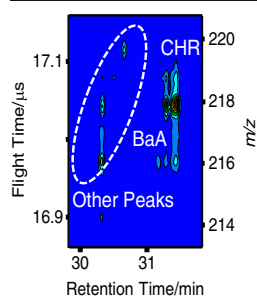
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**Abstract.** Particulate matter 2.5 (PM<sub>2.5</sub>), collected from ambient air in Fukuoka City, was analyzed by gas chromatography combined with multiphoton ionization mass spectrometry using an ultraviolet femtosecond laser (267 nm) as the ionization source. Numerous parent polycyclic aromatic hydrocarbons (PPAHs) were observed in a sample extracted from PM<sub>2.5</sub>, and their concentrations were determined to be in the range from 30 to 190 pg/m<sup>3</sup> for heavy PPAHs. Standard samples of nitrated polycyclic aromatic hydrocarbons (NPAHs) were examined, and the limits of detection were determined to be in the picogram range. The concentration of NPAH adsorbed on PM<sub>2.5</sub> in the air was less than 900–1300 pg/m<sup>3</sup>.

**Keywords:** Gas chromatography, Multiphoton ionization, Time-of-flight mass spectrometry, Particulate matter 2.5, Polycyclic aromatic hydrocarbons, Nitrated polycyclic aromatic hydrocarbons

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## Introduction

Carcinogenic compounds adsorbed on particulate matter (PM) are becoming more important in the field of environmental science. The concentration of PM<sub>2.5</sub>, particulate matter with a diameter less than or equal to 2.5 μm, has attracted considerable attention in Asian countries. It should be noted that this type of particulate matter, because of its small size, can penetrate deeply into human lungs [1]. Polycyclic aromatic hydrocarbons (PAHs), some of which are known to be carcinogenic, are frequently adsorbed on PM<sub>2.5</sub>. Therefore, high concentrations of such PAHs pose a carcinogenic risk to the general population [2]. The organic compounds associated with PAHs can be classified mainly to parent (PPAH), nitro (NPAH), hydroxyl (OHPAH), and methyl (MPAH) PAH types [3]. Among them, PPAH are present in the highest concentration, but NPAH pose the highest carcinogenic risk. The concentration of NPAH in ambient air, however, is much lower than that of PPAH, since NPAH is produced by a radical

reaction of PPAH with a nitro compound such as NO or NO<sub>2</sub> that are formed in the exhaust gas of automobiles [4]. For this reason, it would be desirable to develop a sensitive analytical method not only for PPAHs but also for other PAHs such as NPAHs, especially when the origin emitting PM<sub>2.5</sub> is being investigated (e.g., NPAHs are more abundant in the environmental aerosols from the traffics).

Gas chromatography combined with mass spectrometry (GC/MS) has been successfully utilized for the analysis of PAHs. GC coupled with high-resolution MS (GC/HRMS) is one of the known methods with excellent sensitivity [5, 6]. On the other hand, GC combined with time-of-flight mass spectrometry (GC/TOF-MS) is useful for comprehensive analysis of PAHs, which provides a useful means to determine the composition of PAHs and then to identify the origin of the environmental pollution. Multidimensional gas chromatography (e.g., GC×GC/TOF-MS) is more useful because of its better separation resolution and has been applied for the measurement of an aerosol extract [7]. A technique involving electron ionization (EI) is most frequently used as an ionization source in MS [8]. In this case, many fragment ions appear, especially for NPAHs, which makes measuring the target

molecule a difficult task. In MS, multiphoton ionization (MPI) has been successfully employed for soft ionization of PAHs (i.e., for suppressing fragment ions and for enhancing the molecular ion peak). This technique is especially useful for analyzing a sample containing numerous chemical species, and even unknown compounds can be simultaneously recorded on the two-dimensional display of GC/MS. In fact, PPAHs specified by the Environmental Protection Agency of the United States (US-EPA), dioxins/dibenzofurans/biphenyls, explosives, pesticides, and polybrominated diphenyl ether, have been measured to date [9]. It should be noted that PPAHs in a surface water sample in China was measured using GC/MPI/TOF-MS [10]. Three different laser-based techniques for on-line analysis of particles (i.e., one-step laser desorption/ionization, two-step laser desorption/photoionization, and thermal desorption/photoionization) were used for the measurement of aerosol samples such as a wood ash and exhaust fumes of a gasoline-driven car [11]. More recently, this laser ionization technique has been combined with Curie-point pyrolysis for measuring PPAHs present in a certified reference material (CRM) of PM10 supplied by the National Institute for Environmental Studies, Japan [12].

There are several studies reporting the measurement of NPAHs. In MS, EI or negative chemical ionization (NCI) has been employed for this purpose [13, 14]. However, fragmentation is more serious for NPAHs than PPAHs, which deteriorates reliability in the determination of NPAHs. It is interesting that 1-nitronaphthalene has been measured using a single photon ionization (SPI) technique and that only a molecular ion was observed in the mass spectrum [15]. A technique of two-photon ionization is more sensitive, and trinitrotoluene (TNT) has been measured using a femtosecond laser as the ionization source [16]. The signal intensity of the molecular ion is enhanced by the resonance effect at the specified wavelength.

In this study, we first report on the comprehensive analysis of PAHs in a real sample of PM2.5, which was collected in Fukuoka City, based on GC/MPI/TOF-MS using a femtosecond laser as the exciting source. Using this technique, it was possible to detect numerous chemical species for a pattern recognition of the constituents in the sample extracted from PM2.5, some of which were assigned as PPAHs. Moreover, when standard samples of NPAHs were examined using this technique, a molecular ion was observed as well as several fragment ions. The present GC/MPI/TOF-MS technique was applied to the trace analysis of NPAHs in PM2.5.

## Experimental

### Apparatus

Details of the analytical TOF-MS instrumentation are reported elsewhere [17–19]. One micro liter of a sample solution was injected into a GC (6890GC; Agilent Technologies, Santa Clara, CA, USA) with an autosampler (7683B Series; Agilent Technologies). The analytes were separated using a DB-5 ms GC column (length, 30 m; inner diameter, 0.25 mm; film

thickness, 0.25  $\mu\text{m}$ ). The flow rate of helium used as a carrier gas was adjusted to 1 mL/min. The eluted analytes were introduced into a linear-type TOF-MS (HGK-1; Hikari-GK, Fukuoka, Japan) through a transfer line made of an inactive silica capillary (length, 1 m; inner diameter, 0.25 mm; Agilent Technologies). For the measurement of the PPAHs, the temperature of the inlet port and the transfer line were set at 310°C. The temperature of the GC oven was programmed to increase at a rate of 20°C/min from 40°C to 120°C with a 1 min hold, followed by an increase at a rate of 5°C/min to 250°C and then a 3 min hold. Finally, the temperature was increased at a rate of 5°C/min to 310°C and was then maintained for 5 min [9]. For the measurement of NPAHs, the temperature of the GC oven was programmed to increase at a rate of 10°C/min from 50°C to 220°C followed by a 1 min hold. The temperature was further increased to 310°C at a rate of 5°C/min and was then maintained at 310°C for 2 min [20]. When measuring a real sample, the separation conditions were the same as those used for the PPAHs. The third-harmonic emission (267 nm, 90 mW) of a femtosecond Ti:sapphire laser (800 nm, 85 fs, 1 W, 1 kHz; Libra, Coherent, Santa Clara, CA, USA) was used as the ionization source. The laser beam was focused onto a molecular beam introduced from the transfer line, the focal point of which was optimized by translating the position of a focusing lens to maximize the ratio of the signals for molecular and fragment ions. The induced ions were detected by micro channel plates (MCP; F4655-11; Hamamatsu Photonics, Shizuoka, Japan). After passing through an amplifier (Timing Amplifier 574, ORTEC, Atlanta, GA, USA), the signal was recorded with a computer-interfaced digitizer (Acquisiris AP240; Agilent Technologies). The data were analyzed using a program made with LabVIEW 8.6 (National Instruments, Austin, TX, USA). The signal-to-noise ratio was calculated from the baseline drift of the chromatogram according to the manual reported by Ministry of the Environment, Japan [21] and a limit of detection (LOD) was calculated as a concentration providing a signal-to-noise ratio of three. The maximum concentration range was 4.5  $\text{pg}/\mu\text{L}$  for PPAHs and 100  $\text{pg}/\mu\text{L}$  for NPAHs.

### Reagents

A sample solution containing 16 PPAHs specified by the US-EPA [22] [i.e., naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IND), dibenzo(a,h)anthracene (DBA), and benzo(ghi)perylene (BPY)] was supplied by Kanto Chemical Co., Inc., Tokyo, Japan. The sample solution was diluted to 4.5  $\text{pg}/\mu\text{L}$  with acetonitrile (Wako Pure Chemical Industries, Ltd., Osaka, manufactured for application to chromatography) and was used in the experiments.

**Table 1.** Concentration of PPAHs in PM2.5

PPAH	LOD [pg/ $\mu$ L]	Concentration [pg/ $\mu$ L]				Concentration in PM2.5 [ $\mu$ g/g]	Concentration in Air [pg/m <sup>3</sup> ]
		DCM	Hexane	Toluene	Acetonitrile		
NAP	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ACY	0.099	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ACE	0.084	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FLU	0.068	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PHE	0.033	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ANT	0.156	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FLT	0.095	0.60	0.18	0.34	0.49	2.5	190
PYR	0.080	0.44	0.18	0.26	0.35	1.8	140
BaA	0.055	0.12	0.040	0.088	0.12	0.49	38
CHR	0.032	0.53	0.17	0.32	0.50	2.2	170
BbF	0.044	0.51	0.14	0.26	0.44	2.1	160
BkF	0.044	0.22	0.054	0.094	0.16	0.93	72
BaP	0.034	0.22	0.098	0.10	0.21	0.92	71
IND	0.038	0.17	n.d.	n.d.	0.19	0.72	56
DBA	0.024	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BPY	0.034	0.42	n.d.	n.d.	0.21	1.8	140

n.d. = not detected

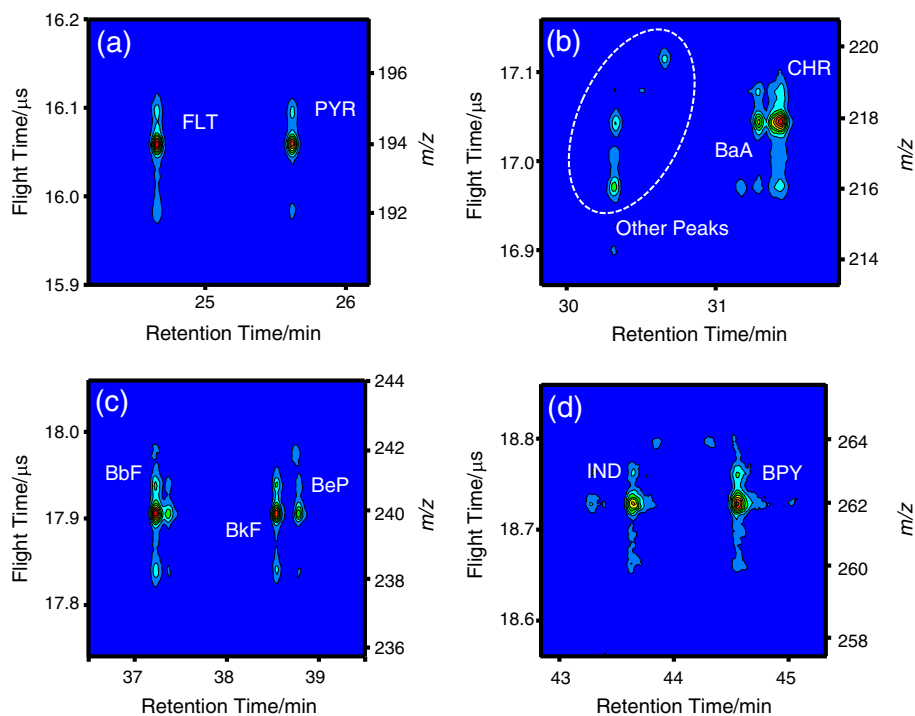
DCM = dichloromethane

Three sample solutions of NPAHs (i.e., 9-nitroanthracene (9-nitroANT), 3-nitrofluoranthene (3-nitroFLT), and 1-nitropyrene (1-nitropyrene)) were purchased from AccuStandard Co., Inc, New Haven, CT, USA. These three NPAHs were selected because of their relatively large abundance in diesel exhaust gas, and 1-nitropyrene has the highest toxicity among the NPAHs [23]. The solutions were diluted to 100 pg/ $\mu$ L with

acetonitrile (Wako Pure Chemical Industries, Ltd., manufactured for chromatographic applications).

### Sample Pretreatment

In order to collect the PM2.5, a sampling device (HVI-2.5, Tokyo Dylec Co., Inc., Tokyo, Japan) was operated for 24 h. A filter made of quartz fiber (401 cm<sup>2</sup>) was attached to the device



**Figure 1.** Expanded views of the two-dimensional display obtained for a real sample extracted from PM2.5 with dichloromethane. Location, (a) FLT, PYR, (b) BaA, CHR, (c) BbF, BkF, BeP, (d) IND, BPY. Several unassigned peaks in the figure are attributed to compounds different from the 16 PPAHs specified by US-EPA. No signal was observed for DBA, and the data is not shown here

and the PM<sub>2.5</sub> was trapped by passing ambient air at a sampling point (Dazaifu City, Fukuoka Prefecture, Japan). The total volume of the air that passed through the filter was 829 m<sup>3</sup>. The concentration of the PM<sub>2.5</sub> was 77.3 μg/m<sup>3</sup>, as determined from the difference in the filter weights measured before and after sample collection. This value was larger than the daily standard of 35 μg/m<sup>3</sup> in Japan, and was smaller than the reported values (68–345 μg/m<sup>3</sup>) for different cities in the Asian countries [24]. The resulting filter was cut into small pieces with a dimension of 1.0 × 1.5 cm. The surrogates (0.44 pg for each PAH) were added, and the analytes were extracted from the filter with 1 mL of dichloromethane (Wako Pure Chemical Industries, Ltd., manufactured for dioxin analysis) under ultrasonic agitation for 45 min. After evaporating the dichloromethane under a stream of nitrogen gas, 1 mL of acetonitrile was added. The sample solution was passed through a syringe filter (GL Chromato Disk; diameter, 13 mm; pore size, 0.2 μm; GL Science,

Tokyo, Japan) to remove small particles from the solution. Finally, 0.44 pg of naphthalene-d<sub>8</sub> (Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA), chrysene-d<sub>12</sub> (Wako Pure Chemical Industries, Ltd.), and pyrene-d<sub>10</sub> (AccuStandard Co., Inc.) were added as surrogates. Fluoranthene-d<sub>10</sub> (Wako Pure Chemical Industries, Ltd.) and benzo(a)pyrene-d<sub>12</sub> (Cambridge Isotope Laboratories, Inc.) were used as syringe spikes.

### Quantum Chemical Calculation

Spectral parameters were evaluated based on quantum chemical calculations. The procedure has been reported elsewhere and is briefly described here [25]. In the previous study, the optimized geometry of the ground state and the energies of the ground and ion states were evaluated using B3LYP at the level of cc-pVTZ basis sets [26]. In this study, the data were calculated at a level of cc-pVDZ basis set for comparison. The

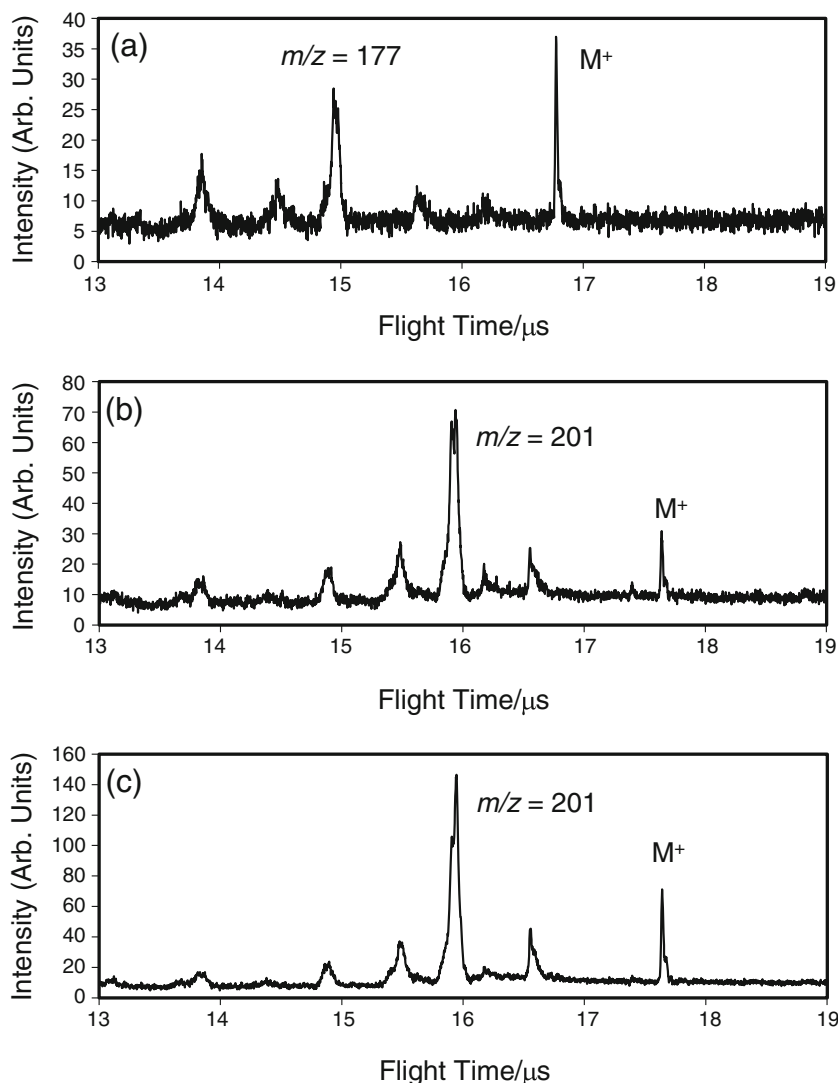


Figure 2. Mass spectra of NPAHs. (a) 9-nitroANT, (b) 3-nitroFLT, (c) 1-nitroPYR. The  $m/z$  value of the base peak is shown in the figure

lowest 40 singlet excitation energies were obtained by using time-dependent density functional theory. All computations were performed with the Gaussian 09 program series package [27].

## Results and Discussion

### Parent Polycyclic Aromatic Hydrocarbons

A standard sample mixture containing 16 PPAHs specified by US-EPA was measured, and the LODs were determined to be in the range from 0.024 to 0.16 pg/ $\mu$ L (see the second column in Table 1). These values are lower than the LODs obtained by quadrupole mass spectrometer (picogram levels) but are higher than those (subfemtogram levels) reported in the previous study [28]: The higher LODs in this study would be attributed to a lower average power of the laser and deterioration of the ion detector used in this study. Figure 1 shows expanded views of the two-dimension display obtained for a real sample extracted from the PM2.5 sample. All of the heavy PPAHs were observed in the display except for DBA. Lack of the signal for DBA would be due to a low concentration of this compound in the PM2.5 sample, since the LOD is relatively lower than those of the other compounds (see Table 1) and the concentration of DBA in the standard reference material (SRM1650b) is reported to be more than an order of magnitude lower than that of BPY [29]. The concentrations of the PPAHs in PM2.5 were measured after extraction with different solvents to find the optimum condition for pretreatment using a real sample. The results are summarized in Table 1. No light PPAHs ranging from NAP to ANT were observed, suggesting that these compounds contain smaller numbers of aromatic rings (<3 rings) and are not adsorbed on PM2.5 but are present in gaseous form in the atmosphere [30–33]. The extraction efficiency was the highest when dichloromethane and acetonitrile were used as solvents. However, many signal peaks arising from impurities were observed when acetonitrile was used as an extraction solvent. As a result, dichloromethane was used as the extraction solvent in this study. Since dichloromethane has a low boiling point (40°C at 313 K) and high volatility, it is difficult to use this solvent in the pretreatment process. In addition, it is somewhat toxic. For this reason, the solvent was changed from dichloromethane to acetonitrile after extraction. Validity of this sample preparation process was checked by measuring the recovery of PPAHs to be in the range of 50%–150%, in which deuterated PPAHs were used for this purpose; they were also added to the sample for calibration of the analyte signals to cancel the drift of the laser output power. The values of the recoveries were found to be in the range from 78% to 90%. This result suggests that the extraction and pretreatment procedures are suitable for the analysis of PPAHs in PM2.5. A signal peak with an  $m/z$  value of 252 ( $C_{20}H_{12}$ ), which is identical to that of BaP ( $C_{20}H_{12}$ ), was observed at a retention time slightly earlier than that of BaP. This signal could be assigned to

benzo(e)pyrene (BeP,  $C_{20}H_{12}$ ,  $m/z = 252$ ), an isomer of this compound. Thus, the present approach using GC/MPI/TOF-MS allows a comprehensive analysis to be done, and it is possible to observe all of the chemical species, even for unassigned compounds that can be determined using a standard chemical to be synthesized in the future.

The concentrations of the PPAHs adsorbed on the PM2.5 were calculated, and the results are summarized in the last two columns of Table 1. The concentrations were in the order of 1  $\mu$ g/g or 100 pg/m<sup>3</sup>. The abundance ratios calculated for IND/(IND + BPY), BaP/(BaP + CHR), BbF/BkF, BaP/BPY, and IND/BPY were 0.29, 0.29, 2.28, 0.52, and 0.41, respectively, suggesting that these PPAHs are produced by local traffic in the area [14]. As suggested, such information would be useful for

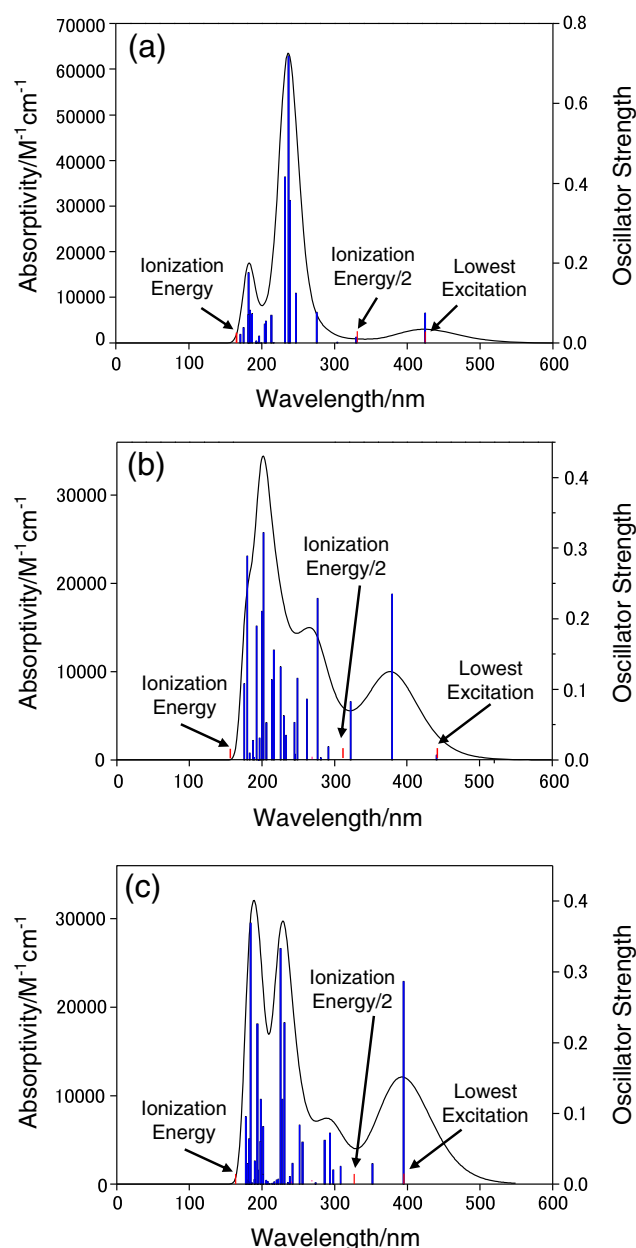


Figure 3. Ionization energies and absorption spectra calculated for (a) 9-nitroANT, (b) 3-nitroFLT, (c) 1-nitroPYR

identification of the origin emitting the PPAHs and then for protection of the environment.

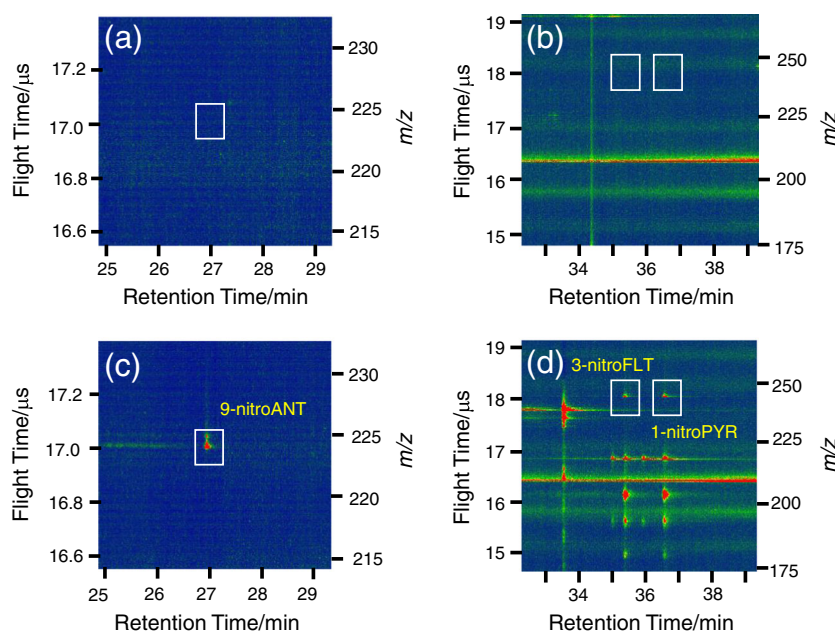
### Nitrated Polycyclic Aromatic Hydrocarbons

A sample containing a mixture of NPAHs was measured using GC/MPI/TOF-MS. The data for retention times corresponding to 9-nitroANT, 3-nitroFLT, and 1-nitroPYR were extracted for construction of their mass spectra. As shown in Figure 2, several fragment ions were observed, in addition to the molecular ion. In the present study, a UV femtosecond laser emitting at 267 nm was utilized as the ionization laser, which corresponds to 4.64 eV as a photon energy. On the other hand, the ionization energy was estimated to be 7.5–8.0 eV for NPAHs based on quantum chemical calculations as shown in Figure 3, which was not significantly changed from the data calculated using a different basis set [26]. Assuming that the NPAHs are ionized through a two-photon process, the excess energy is calculated to be 1.2–1.7 eV. A nitro group substituted on a benzene ring can easily be dissociated after a rearrangement because of the excess energy in the ion state [34]. The dissociation of a nitro group, which corresponds to  $[M - \text{NO}_2]^+$ , is observed as a base peak for all the mass spectra, e.g.,  $m/z = 223 - 46 = 177$  for 9-nitroANT and  $m/z = 247 - 46 = 201$  for 3-nitroFLT and 1-nitroPYR. It should be noted that broad peaks observed for the fragment ions would arise from the excess energy occurred in the process of fragmentations.

There are two approaches for reducing the excess energy by changing the laser wavelength. One approach is the use of a laser emitting at shorter wavelengths for SPI. As shown in Figure 3, the ionization energy corresponds to the wavelength of 150–160 nm, suggesting that a vacuum-ultraviolet light source such as the third harmonic emission (118 nm) of the

third harmonic emission (355 nm) of a Nd:YAG laser is needed. It is, however, rather difficult to decrease the excess energy by changing the laser wavelength. The other approach is the use of a laser emitting at longer wavelengths for resonance-enhanced two-photon ionization, which is achievable at a wavelength of 300–400 nm [26].

Figure 4 shows expanded views of a two-dimensional display measured for a sample extracted from PM2.5. As shown in Figure 4a and b, NPAH ion signal was not observed from the extracted sample. However, signals arising from NPAHs were clearly observed when standard chemicals were added to the sample as shown in Figure 4c and d, suggesting that the concentrations of NPAHs are lower than the LODs of these compounds. The LODs were determined from the data of Figure 4c and 4d to be 4.0, 4.1, and 2.8 pg/ $\mu\text{L}$  for 9-nitroANT, 3-nitroFLT, and 1-nitroPYR, respectively. Therefore, the concentration of NPAHs in this real sample would be lower than these values, suggesting that the concentrations of these NPAHs in the atmosphere are less than 12–17  $\mu\text{g/g}$  in the PM2.5 or 900–1300  $\text{pg/m}^3$  in the atmosphere. Since NPAHs are produced by a radical reaction between PPAHs and a nitro compound, the concentrations are, in principle, much lower than the concentrations of the corresponding PPAHs. As reported in Table 1, the concentrations of the PPAHs in the sample extract are in the range from 0.12 to 0.60  $\text{pg}/\mu\text{L}$ . Poorer LODs for NPAHs could arise from efficient fragmentation and from a very short lifetime because of rapid energy relaxation from the electronic excited state. It is known that the abundance ratio of NPAHs and PPAHs is ca. 0.1 or less [35]. Accordingly, improving the sensitivity of the analytical instrument by two orders of magnitude would be highly desirable. Such an improvement could be achieved by increasing the size of the filter used for extraction (e.g., 1.5  $\text{cm}^2 \rightarrow 401 \text{ cm}^2$ )



**Figure 4.** Expanded views of the two-dimensional display. (a) (b) Real samples extracted from PM2.5. (c) (d) Standard samples of 9-nitroANT, 3-nitroFLT, and 1-nitroPYR were added to the extract before the measurement

and by concentrating the sample solution (e.g., 1 mL → 20 µL) before it is injected into the GC: it was difficult to demonstrate this in the present study because of a limited amount of the PM<sub>2.5</sub> sample, since the major part of the sample was used in the study of PAHs and additional sampling of PM<sub>2.5</sub> for the study of NPAHs can only be performed on the day providing a high level of PM<sub>2.5</sub> that is exceptional in Japan. It should be noted that a high-power laser with a higher repetition rate (e.g., 20 kHz) would be a distinct advantage in terms of improving the sensitivity of the analysis. In fact, the LODs of PPAHs were improved to subfemtogram levels by using a high-power picosecond laser and an ion counting technique requiring a high-repetition-rate ionization source [28]. Thus, the concentration of the NPAHs in the PM<sub>2.5</sub> could be determined by concentrating the sample solution and by using a laser with a superior performance than the one used here.

## Conclusions

In this study, we report on the analysis of PPAHs/NPAHs in PM<sub>2.5</sub> based on GC/MPI/TOF-MS using a femtosecond laser as the ionization source. The present technique was found to be applicable for the analysis of PPAHs in PM<sub>2.5</sub>. For NPAHs, several fragment ions were observed at 267 nm probably because of large excess energy. Although no signals were assigned to NPAHs, their concentrations could be determined by concentrating the sample solution from a larger amount of PM<sub>2.5</sub>, judging from the sensitivity of the instrument for the PPAHs and the relative concentration ratio of NPAHs/PPAHs. The present GC/MPI/TOF-MS technique described herein, combined with a UV femtosecond ionization source has the potential for use in the comprehensive analysis of PAHs contained in PM<sub>2.5</sub> samples.

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