



# Multiphoton ionization mass spectrometry of nitrated polycyclic aromatic hydrocarbons



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## ABSTRACT

In order to suppress the fragmentation and improve the sensitivity for determination of nitrated polycyclic aromatic hydrocarbons (NPAHs), the mechanism of multiphoton ionization was studied for the following representative NPAHs, 9-nitroanthracene, 3-nitrofluoranthene, and 1-nitropyrene. The analytes were extracted from the PM<sub>2.5</sub> on the sampling filter ultrasonically, and were measured using gas chromatography/multiphoton ionization/time-of-flight mass spectrometry with a femtosecond tunable laser in the range from 267 to 405 nm. As a result, a molecular ion was observed as the major ion and fragmentation was suppressed at wavelengths longer than 345 nm. Furthermore, the detection limit measured at 345 nm was measured to be the subpicogram level. The organic compounds were extracted from a 2.19 mg sample of particulate matter 2.5 (PM<sub>2.5</sub>), and the extract was subjected to multiphoton ionization mass spectrometry after gas chromatograph separation. The background signals were drastically suppressed at 345 nm, and the target NPAHs, including 9-nitroanthracene and 1-nitropyrene, were detected, and their concentrations were determined to be 5 and 3 pg/m<sup>3</sup>, respectively.

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## 1. Introduction

Particulate matter 2.5 (PM<sub>2.5</sub>) has increasingly attracted the attention of the public in recent years, since it contains polycyclic aromatic hydrocarbons (PAHs) and nitrated polycyclic aromatic hydrocarbons (NPAHs), which are highly mutagenic and carcinogenic. A few papers have reported that the content of NPAHs in PM<sub>2.5</sub> is 2 or 3 orders of magnitude lower than those of non-nitrated PAHs but their mutagenicity and carcinogenicity can reach 100,000 times and 10 times higher than the corresponding values for non-nitrated PAHs [1,2]. While the total amount of NPAHs and oxidized PAHs (OPAHs) is reported to exist only in 8% of the total PAHs, the mutagenicity arising from these compounds can be 200% higher than the mutagenicity caused by PAHs [3]. In general, there are two main sources of NPAHs: (1) the incomplete combustion of organic matter such as fossil fuels by motor vehicles [4,5] (2) reactions of corresponding PAHs with NO<sub>x</sub> or OH radicals in the atmosphere or heterogeneous reactions of PAHs adsorbed on ambient particles with N<sub>2</sub>O<sub>5</sub>/NO<sub>3</sub>/NO<sub>2</sub> [6–9]. Due to the low concentrations of NPAHs in the environment and their high

mutagenicity and carcinogenicity for human beings, it is important to develop a sensitive analytical instrument with a high selectivity for NPAHs, in conjunction with a simple pretreatment procedure before the measurement of NPAHs extracted from PM<sub>2.5</sub> [10,11]. It should be noted that a large amount of interfering species arising from non-nitrated PAHs is unavoidable in practical trace analysis.

Some analytical methods have been developed to date for the measurement of NPAHs. High-performance liquid chromatography (HPLC) combined with mass spectrometry (MS) and gas chromatography (GC) combined with MS are the most common techniques used for this purpose [12,13]. However, these methods suffer from limitations in sensitivity or selectivity, and the sample pretreatment process can be time consuming. Gas chromatography combined with multiphoton ionization time-of-flight mass spectrometry (GC/MPI/TOF-MS) has recently been developed and subfemtogram detection limits have been reported for PAHs by using an ultraviolet femtosecond laser as the ionization source [14]. This technique has been applied to trace analyses of dioxins [15,16], PAHs [14,17], pesticides [18,19] present in real samples. Thus, GC/MPI/TOF-MS represents a potential method for use in the trace analysis of NPAHs. Compared with other ionization techniques such as electron ionization (EI), this approach provides soft ionization and is useful for enhancing the intensity of the molecular ion and for suppressing background arising from interfering

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species such as PAHs [14,20]. Mass spectrometric techniques based on negative-ion laser desorption ionization and nanosecond desorption followed by femtosecond ionization have been used for the measurement of NPAHs, although numerous fragments are observed in the mass spectrum [21–23].

In this study, we used an ultraviolet femtosecond laser for the efficient ionization of NPAHs. A tunable output of an optical parametric amplifier was employed to determine the optimal conditions for the sensitive as well as selective ionization and for the observation of a molecular ion to improve the reliability of the analysis. The effect of excess energy in mass spectrometry was investigated by changing the wavelength of the laser. Moreover, the background signals arising from interfering substances such as PAHs were examined using a real sample containing standard chemicals. To our knowledge, this is the first study reporting the ionization mechanism involved when a tunable ultraviolet femtosecond laser is used for trace analysis of NPAHs extracted from a PM<sub>2.5</sub>.

## 2. Experimental

### 2.1. Apparatus

The analytical instrument used in this study has been described in detail elsewhere [24,25]. Briefly, a GC (6890N, Agilent technologies) equipped with an auto sampler 7683B, Agilent technologies) was combined with a TOF-MS developed in our laboratory and now commercially available (HGK-1, Hikari-GK, Fukuoka, Japan). The fundamental beam of a Ti:sapphire laser (800 nm, 35 fs, 1 kHz, 4 mJ, Elite, Coherent Co.) was used as the pump source for an optical parametric amplifier (OPerA-Solo, signal beam, 650 μJ at 1200 nm, idler beam, 260 μJ at 2400 nm, Coherent Co.), the frequency of which was further converted into the ultraviolet (UV) region. The laser beam was introduced into the TOF-MS, the pulse energy of which was adjusted to 15 μJ using a neutral density filter at different wavelengths except 390 and 395 nm (8 μJ). A sample mixture containing NPAHs was separated using a DB-5MS column (30 m long, 0.25 mm inner diameter, 0.25 μm film thickness). The temperature program of a GC oven for separation of NPAHs was as follows: initial temperature 50 °C held for 1 min, a rate of 10 °C/min to 220 °C, then 5 °C/min to 310 °C, held for 2 min [26]. For the measurement of a sample extracted from PM<sub>2.5</sub>, the temperature was programmed to increase from 40 °C to 120 °C at a rate of 20 °C/min, and held for 1 min, and increased to 250 °C at a rate of 5 °C/min, then held for 3 min at 250 °C. Finally, the temperature was increased to 310 °C at a rate of 5 °C/min, and held for 15 min [14,17]. For both the standard sample mixture and the extract from PM<sub>2.5</sub>, the temperature of the inlet port and the transfer line to the MS were set at 300 °C. The flow rate of helium used as a carrier gas was 1 mL/min. A 1-μL aliquot of sample solution was injected into a GC system using an auto sampler. Then, the analyte molecule in the molecular beam was ionized by a femtosecond laser. The ions induced by multiphoton ionization were accelerated toward a flight tube and were detected by microchannel plates (F4655-11, Hamamatsu Photonics). The signal was recorded using a digitizer (Acqiris AP240, Agilent Technologies), and the data were analyzed using a home-made software programed by LabVIEW. The detection limit was calculated using this software by measuring the peak intensity and the baseline noise in the observed chromatogram.

### 2.2. Reagents and chemicals

Standard samples of 9-nitroanthracene (9-nitroANT), 3-nitrofluoranthene (3-nitroFLT), and 1-nitropyrene (1-nitroPYR), the concentrations of which were adjusted at 100 μg/mL, were purchased

from AccStandard Inc. A standard mixture sample containing the above three NPAHs was prepared at a concentration of 1 ng/μL for each NPAH by dissolving in acetonitrile. Dichloromethane (analytical grade) and acetonitrile (LC/MS grade) used as solvents were supplied by Wako Pure Chemical Industries.

### 2.3. Pretreatment procedure of PM<sub>2.5</sub>

A sample of PM<sub>2.5</sub> was collected on the roof of a building at the Fukuoka Institute of Health and Environmental Sciences using an instrument reported elsewhere [27]. The sampling equipment was placed 16.4 m from the ground level. The PM<sub>2.5</sub> was collected during a period of 1430 min on March 20, 2013 at a flow rate of 580 L/min. A quartz filter (22.8 × 17.6 cm<sup>2</sup>) was placed on the equipment for the collection of PM<sub>2.5</sub> in ambient air. The amount of PM<sub>2.5</sub> trapped on the filter was 37.6 mg, the concentration of PM<sub>2.5</sub> in the ambient air being calculated to be 45.3 μg/m<sup>3</sup>. The amount of PM<sub>2.5</sub> was evaluated from the difference in the weights of the filter measured before and after the sample collection.

Several circular filters (diameter, 4.7 cm) and rectangular filters (1.0 × 1.5 cm<sup>2</sup>) were taken from the above filter. One particle-loaded circular and four rectangular filters with a total area of 23.3 cm<sup>2</sup> (weight of PM<sub>2.5</sub>, 2.19 mg) were cut into small pieces using a clean stainless-steel scissors. The small pieces were then placed into a vial containing 10 mL of dichloromethane. Organic compounds such as PAHs and NPAHs were extracted three times using an ultrasonic extraction method with dichloromethane for 45 min [11]. The extraction solvent was evaporated, and the residue was dissolved by adding 1 mL of acetonitrile. The sample mixture containing PAHs and NPAHs was filtered through a syringe with a membrane filter (GL-13N, pore size 0.2 μm), and was then concentrated to 70 μL using a stream of nitrogen. In order to evaluate the detection limits of the NPAHs present in the extracted sample and the effect of interference arising from other organic substances such as PAHs, the sample was measured with and without adding sufficient amounts of the standard chemicals. The sample, to which 500 pg/μL for each NPAH was added, was stored in the refrigerator in prior to the measurement.

### 2.4. Computational methods

Quantum chemical calculations were performed for studies on the ionization mechanism of NPAHs using a Gaussian09 program series package. Minimum geometries were obtained using the B3LYP method based on the density functional theory (DFT) with a cc-pVDZ basis set [28]. The harmonic frequencies were calculated so as to ensure an optimum geometry providing a global energy minimum. A vertical ionization energy was evaluated from the difference between the energies of the ground and ionic states, which were obtained at the level of B3LYP/cc-pVTZ [29]. The lowest 40 singlet transition energies and the oscillator strengths were calculated using time-dependent DFT (TD-DFT), and the predicted absorption spectra were generated using the Gauss View 5 software program.

## 3. Results and discussion

### 3.1. Ionization mechanism

Resonance-enhanced multiphoton ionization (REMPI) is known to be one of the advanced techniques for the efficient ionization of organic compounds such as aromatic hydrocarbons. This approach has superior selectivity and reduces the background arising from interfering compounds. In addition, it can be utilized as a tool for soft ionization, producing a molecular ion in mass spectrometry.

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