

Analysis of Nitro-polycyclic Aromatic Hydrocarbons in Particulate Matter 2.5 by Gas Chromatography/Multiphoton Ionization/Time-of-flight Mass Spectrometry Using a Femtosecond Laser

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論 文 名 : Analysis of Nitro-polycyclic Aromatic Hydrocarbons in Particulate Matter 2.5 by Gas Chromatography/Multiphoton Ionization/Time-of-flight Mass Spectrometry Using a Femtosecond Laser
(ガスクロマトグラフィー/フェムト秒レーザー多光子イオン化飛行時間型質量分析法のよる超微粒子(PM2.5)の中ニトロ多環芳香族化合物の分析)

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論 文 内 容 の 要 旨

Particulate matter 2.5 (PM2.5) has increasingly become a major concern in recent years since it contains parent polycyclic aromatic hydrocarbons (PPAHs) and nitrated polycyclic aromatic hydrocarbons (NPAHs), which are highly mutagenic and carcinogenic. To date, the health risk posed to PPAHs and their derivatives have been assessed. It should be noted that NPAHs have been shown to have indirect-acting mutagenicity and carcinogenicity for human beings, compared with direct-acting mutagenicity for PPAHs; up to 40% of the mutagen potency can be attributed to NPAHs especially to nitropyrene, dinitropyrene, and nitrohydroxypyrene. Biologically-active APAHs influence human cells through different pathways compared to that of NPAHs. The mutagenicities of aminofluoranthene (AFLU) and aminopyrene (APYR) have been proven to be the strongest among various types of two-, three-, and four-ring APAHs. Therefore, exposure to the air containing PM2.5 has become a major, world-wide concern for human health.

Since numerous interfering organic species are present in PM2.5, a sensitive and selective analytical method is needed for the determination of NPAHs. Several analytical techniques, based on gas chromatography coupled with mass spectroscopy (GC-MS) or electron-capture, nitrogen-selective-thermionic, and flame-ionization detections, have been used for the analysis of PPAHs, NPAHs, and APAHs in complex matrices. In addition, high-performance liquid chromatography (HPLC) has been combined with MS or fluorescence detection; a chemiluminescence detection technique has also been utilized after a chemical reaction using a column for reducing NPAHs. However, there are several limitations to these established methods even for GC-MS, e.g., the dominant fragmentation in electron-ionization MS. In our previous study, a combination of GC and time-of-flight MS (TOFMS) using a femtosecond laser as the ionization source provided femtogram detection limits and was applied for the trace analysis of PPAHs and NPAHs. This technique has several advantages; the two-dimensional display of GC-MS can be used for comprehensive analysis, and the analytes can be more selectively and softly ionized through the multiphoton ionization (MPI) process.

In chapter 1, the research background of this dissertation including PM2.5, the analytical techniques were

introduced to investigate the meaning and the objective of this research. The principle of MPI and the effect factors of ionization efficiency were also stated for the better understanding of the basic knowledge.

In chapter 2, 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_{2.5} 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_{2.5}), 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/m³, respectively.

In chapter 3, Multiphoton ionization processes of parent-polycyclic aromatic hydrocarbons (PPAHs), nitro-PAHs (NPAHs), and amino-PAHs (APAHs) were examined by gas chromatography combined with time-of-flight mass spectrometry using a femtosecond Ti:sapphire laser as the ionization source. The efficiency of multiphoton ionization was examined using lasers emitting in the far-ultraviolet (200 nm), deep-ultraviolet (267 nm), and near-ultraviolet (345 nm) regions. The largest signal intensities were obtained when the far-ultraviolet laser was employed. This favorable result can be attributed to the fact that these compounds have the largest molar absorptivities in the far-ultraviolet region. On the other hand, APAHs were ionized more efficiently than NPAHs in the near-ultraviolet region because of their low ionization energies. A sample extracted from a real particulate matter 2.5 (PM_{2.5}) sample was measured, and several signal peaks arising from PAH analogs were observed at 345 nm. The identifications of these compounds were, however, difficult when measured at 200 and 267 nm, due to the large number of interfering species present in the real sample.

In last chapter, the application of GC/MPI/TOF-MS for the measurement of the trace NPAHs was summarized for the better understanding the influences of ion source and absorption characteristics on the sensitivity and selectivity of this technique.

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