# Use of chemical conversion for determination of nitrated aromatic hydrocarbons using femtosecond ionization mass spectrometry

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HIGHLIGHTS

- A chemical conversion system was employed to identify nitrated aromatic hydrocarbons.
- A reaction mimicking a chemical conversion in a diesel engine system was used for analysis.
- Femtosecond ionization mass spectrometry was utilized for observing a molecular ion.
- A sample extracted from exhaust gas emitted from a diesel engine was measured.

GRAPHICAL ABSTRACT
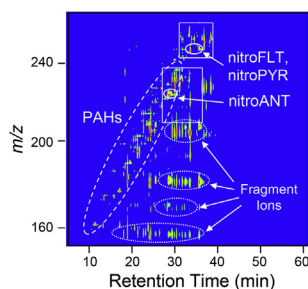
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ABSTRACT

A sample containing nitrated aromatic hydrocarbons (NPAHs) was injected into the sample inlet port of a gas chromatograph (GC), along with hydrazine, a reducing reagent. The analytes that eluted from the GC column were measured by mass spectrometry (MS) using an ultraviolet femtosecond laser as the ionization source. When no reducing reagent was used, large numbers of polycyclic aromatic hydrocarbons (PAHs) including NPAHs were observed in the two-dimensional GC/MS display. In contrast, when hydrazine was present, reduced forms of NPAHs, which included amino PAHs, were detected. When a palladium or platinum catalyst was placed in the GC inlet port, the compounds were further reduced to non-aromatic hydrocarbons. The present approach would be useful for studies to evaluate the chemical reaction that converts the constituents contained in exhaust emitted from a diesel engine.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are produced by the incomplete combustion or pyrolysis of a fossil fuel and are emitted into the atmosphere [1]. In order to make this type of combustion more efficient, it is necessary to increase the temperature of the

chemical reaction. For this reason, an automobile with a diesel engine that operates at high temperature would be preferable for use in traffic. However, undesirable reaction products such as particulate matter (soot particles) are produced by the incomplete combustion of the fuel. To minimize this, the exhaust gas is passed through the first converter containing a diesel oxidation catalyst (DOC) where they are oxidized to species such as nitrogen oxides (NO_x) and hydroxide (OH) [2—4]. These species can be used to advantage for burning the soot. The remaining toxic species, such as

NO_x, are subsequently decomposed by injecting an aqueous solution of urea into the second converter for selective catalytic reduction (SCR), where they are reduced. Finally, remaining particulates are trapped with a diesel particulate filter (DPF). However, nitrated PAHs (NPAHs), which are more toxic and more stable than NO_x, remain in the exhaust gas and would be adsorbed on particulate matter [2,3,5].

Airborne particulates, referred to as particulate matter 2.5 (PM2.5), i.e., particles with diameters equal to or less than 2.5 μm, are reported to contain PAHs and NPAHs, which are suspected to be carcinogenic for humans by the International Agency for Research on Cancer (IARC) [6,7]. Therefore, these compounds are of interest and have been studied in several international assessment programs, in attempts to evaluate the carcinogenic risks posed by them. The concentrations of NPAHs that are adsorbed on PM2.5 in ambient air are 10–100 times lower than those of PAHs [8–10]. However, the mutagenicity and carcinogenicity of NPAHs are reported to be 10–10000 times higher than the corresponding values for PAHs [11]. It is interesting to note that 3-nitrobenzanthrone, a potential mutagen, as evidenced by an Ames bacterial mutagenesis assay, has recently been reported to induce the formation of tumors in rodents [6]. When tested in *Salmonella typhimurium* (strain TA98) in the absence of exogenous metabolizing enzymes, l-nitropyrene, 1,3-dinitropyrene, 1,6-dinitropyrene, and 1,8-dinitropyrene are reported to be 200, 63000, 80000 and 11000 times more mutagenic than benzo[*a*]pyrene [12]. For this reason, it would be highly desirable to convert these highly toxic compounds into non-toxic compounds by means of a chemical reactor. It is known that NPAHs can be converted into amino derivatives as well as nitroso- and hydroxyamino-compounds under anaerobic conditions [13]. Although the allowed concentration of NO_x in air is regulated by law, no attempts have been made to reduce the concentrations of NPAHs in exhaust gas, probably due to their low concentrations. Therefore, developing a research platform for controlling these compounds in exhaust gas would be highly desirable. For this purpose, it would be necessary to develop an analytical technique that can be used for a comprehensive analysis of PAHs/NPAHs and their reaction products in order to evaluate the effectiveness of reducing reagents and catalysts used in the chemical conversion.

A variety of analytical methods have been developed for determining the levels of PAHs and NPAHs [5,6,14–20]. Because of the complexity of an environmental sample, a chromatographic separation needs to be applied prior to detection. Liquid chromatography (LC), combined with electrochemical detection (ECD), fluorescence detection (FLD), or chemiluminescence detection (CLD), can be used for this [17]. However, NPAHs must be converted into APAHs before the measurement [13]. Gas chromatography combined with mass spectrometry (GC/MS) provides a powerful tool because of the excellent performance with respect to separation and for the identification of organic compounds. A variety of techniques, based on electron ionization MS (EI-MS) [21], positive and negative ion chemical ionization MS (PICI-MS and NICI-MS) [22,23] and high-resolution MS (HRMS) have been developed for this purpose [24]. An intense molecular ion is observed in NICI-MS for NPAHs, which is in contrast to extensive fragment ions that are produced in the case of EI-MS [21]. The MS-MS technique, e.g., the formation of a negative ion by NICI followed by EI-MS, has been employed [25]. These traditional techniques of GC/MS have been successfully used for trace analysis of PAHs and NPAHs in the urban particulate matter [18]. More recently, an advanced technique such as two-dimensional GC coupled with MS has been reported, e.g., GC × GC/MS-MS, GC × GC/HRMS or GC × GC/quadrupole MS (QMS) [26]. These methods, however, make a comprehensive analysis of unknown PAHs and their analogs difficult.

Gas chromatography combined with multiphoton-ionization time-of-flight MS (GC/MPI-TOFMS) using an ultraviolet femtosecond laser as the ionization source has been utilized for the trace analysis of organic compounds in actual samples. Dioxins in soils, pesticides in foods, and NPAHs and APAHs in PM2.5 have been measured to date [27–31]. In this approach, specific molecules can be efficiently ionized by adjusting the laser wavelength to the absorption band in the ultraviolet region for two-photon ionization (TPI). It should be noted that, using this technique, fragmentation can be suppressed by reducing the excess energy in TPI, resulting in the selective as well as the sensitive analysis of the constituents in the sample. Indeed, a comprehensive analysis of NPAHs an APAHs was demonstrated in a previous report [28].

In this study, we report on the development of an analytical system to study the sequence of reactions of NPAHs using a standard sample mixture and also a real sample obtained from the exhaust gas of a diesel engine. Hydrazine, a reducing reagent, was mixed with the sample and the mixture was allowed to react in the inlet port of the GC in both the presence and absence of a palladium or platinum catalyst. The original and chemically-reduced compounds such as PAHs, NPAHs, and APAHs were then measured using GC/MPI-TOFMS. This type of approach, which is similar to the redox system currently used after a diesel engine, was employed to identify the redox components such as NPAHs and to measure trace toxic substances in exhaust gas from an automobile.

2. Experimental section

2.1. Analytical instrumentation

A 1-μL sample solution was injected into a GC (6890N, Agilent Technologies, Santa Clara, CA, USA) from an auto sampler (7683B Series, Agilent Technologies). The analytes were separated on a DB5-MS column (30 m long, 0.25 mm inner diameter, 0.25 μm film thickness, Agilent Technologies) and then introduced into a TOFMS that was developed in this laboratory and is now commercially available (HGK-1, Hikari-GK, Fukuoka, Japan) [27]. The third harmonic emission (267 nm) of a Ti:sapphire laser (800 nm, 85 fs, 1 kHz, 1 mJ, Libra, Coherent Inc., Santa Clara, CA, USA) was used as the ionization source. The laser beam was focused with a fused-silica lens with a focal length of 30 cm into the molecular beam to produce ions that were accelerated into a flight tube by potentials applied to the electrodes to reach a microchannel plate detector (F4655-11, Hamamatsu Photonics, Shizuoka, Japan). The signal was recorded by a computer-interfaced digitizer (Acqiris AP240, Agilent Technologies), and the data were processed using a home-made software program that was developed in this laboratory.

2.2. Sample

A standard sample of 9-nitroANT was supplied from Sigma-Aldrich Japan Co. (Tokyo, Japan) and 1-nitroFLT and 3-nitroPYR from AccuStandard Inc. (New Haven, CT, USA). Acetonitrile (LC-MS grade) purchased from Wako Pure Chemical Industries. Ltd (Tokyo, Japan) was used to dissolve the standard samples of NPAHs and APAHs. Hydrazine monohydrate ($H_2NNH_2 \cdot H_2O$) obtained from Sigma Aldrich Japan Co. was used as a reducing reagent in this study, since urea ($CO(NH_2)_2$) was not reactive even at the maximum temperature of the inlet port of the GC; urea is currently reacted at above several hundred °C in a diesel engine system, which is much higher than the highest temperature usable for the GC inlet port. Palladium-activated carbon (Pd/C, 5%) and platinum-activated carbon (Pt/C, 5%) were purchased from Wako Pure Chemical Industries Ltd. and Sigma-Aldrich Japan Co., respectively, and were