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

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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.

Keywords:

Polycyclic aromatic hydrocarbons

Diesel exhaust

Femtosecond ionization mass spectrometry

Reducing reagent

Catalyst

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 to 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 used as typical catalysts, since the catalysts used in a diesel engine system should be used at above several hundred °C and were not commercially available. A diesel particulate extract (SRM1975) was obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). A unit of SRM1975 contains approximately 1.2 mL of a dichloromethane extract of diesel particulate matter collected from an industrial diesel-powered forklift.

2.3 Procedure

Two standard samples were prepared by mixing three NPAHs, i.e., 9-nitroanthracene (9-nitroANT), 3-nitrofluoranthene (3-nitroFLT), and 1-nitropyrene (1-nitroPYR), or three APAHs, i.e., 9-aminoanthracene (9-aminoANT), 3-aminofluoranthene (3-aminoFLT), and 1-aminopyrene (1-aminoPYR). These compounds were selected as representatives of NAPHs and APAHs, since they have different numbers of aromatic rings and have sufficiently different physical and spectroscopic properties. The standard sample mixture containing NPAHs or APAHs was prepared at a concentration of 1 ng μL^{-1} for each compound using acetonitrile as the solvent. A 50-μL portion of hydrazine monohydrate was added to the sample and the volume was made up to 500 μL. This solution was injected into a glass liner (5190-2293 Ultra Inert Liner, Splitless, Single Taper, Wool, Agilent Technologies) installed in the sample inlet port of the GC. The standard sample mixture

containing NPAHs or APAHs was injected into the GC inlet port that was maintained at 300 °C with or without a catalyst. The temperature of the GC oven was programed from 60 °C, a 1-min hold, to 200 °C at a rate of 40 °C min^{-1} and finally increased to 280 °C at a rate of 20 °C min^{-1}, followed by a 5-min hold. The temperature of the sample inlet port was set at 300 °C. For a sample extracted from the diesel engine, the original solution was injected into the GC inlet port maintained at 350 °C. The temperature of the GC oven was programed from 40 °C to 120 °C at a rate of 20 °C min^{-1}, a 1-min hold, and increased to 250 °C at a rate of 5 °C min^{-1}, a 3-min hold, and increased to 320 °C at a rate of 20 °C min^{-1}, a 5-min hold, and finally increased to 310 °C at a rate of 5 °C min^{-1}, then a 15-min hold. The temperature program was modified for the measurement of the real sample, which contained a variety of unknown compounds with different volatilities. In fact, it was necessary to increase the temperature more carefully to higher temperatures to precisely elute all the components. The temperature of the transfer line connecting the GC and the MS was always set at >300 °C. The flow rate of helium used as a carrier gas was 1 mL min^{-1}.

2.4. Quantum chemical calculations

To investigate the ionization mechanism of PAHs, NPAHs, and APAHs, their spectral properties were evaluated by quantum chemical calculations using the Gaussian09 program [32]. Geometries were calculated using the B3LYP method based on density functional theory (DFT) with a cc-pVDZ basis set [33,34]. The harmonic frequencies were calculated to ensure an optimum geometry providing a global energy minimum. A vertical ionization energy was calculated from the difference between the energies of the ground and ionic states. The enthalpy of the reaction was calculated by subtracting the formation enthalpy of the product from that of the reactant.

3. Results and discussion

3.1. Standard sample

Fig. 1A shows the two-dimensional GC/MS display for a sample mixture containing 9-nitroANT, 3-nitroFLT, and 1-nitroPYR without using hydrazine as the reducing agent. Sharp signals corresponding to the molecular ions of NPAHs were clearly observed, in addition to several signals arising from fragment ions. Small signals also appeared at a retention time of approximately 7 min, which are assigned to impurities such as PAHs that were contained in the standard sample. As shown in the mass spectrum for nitroPYR, the peak arising from $[M\text{-}NO]^+$ is sharp, which is in contrast to the broad peak for $[M\text{-}NO_2]^+$. This result has been explained by the difference in the excess energy in TPI [29]. Fig. 1B shows the two-dimensional display obtained for a sample mixed with hydrazine. The enthalpy of the following reaction calculated by DFT was ΔH = -330, -340, and -341 kJ mol^{-1} (or -79, -81 and -82 kcal mol^{-1}) for 1-nitroANT, 3-nitroFLT, and 2-nitroPYR, respectively.

$$\text{hydrazine} + \text{NPAH} + (1/2)\ O_2 \rightarrow \text{APAH} + NO_2 + (1/2)\ N_2 + H_2O \quad (1)$$

Accordingly, the NPAHs were easily decomposed, and the signals in the two-dimensional display then disappeared. Three components assignable to the corresponding APAHs were then observed in the data: this assignment was confirmed by measuring standard samples of APAHs. These results suggest that NPAHs are completely reduced to APAHs by the hydrazine. It is interesting to note that a few components are observed in the two-dimensional display, which is probably due to the formation of thermal decomposition products such as FLT (*m/z* = 202 at 7.1 min) and PYR (*m/z* = 202 at 8.2 min) that were produced in the sample inlet port. The signal intensity increased and the

fragmentation was suppressed for APAHs, as shown in Fig. 1B. The signal intensity of the molecular ion was 450 mV for aminoPYR, which was larger than 67 mV observed for nitroPYR. This signal enhancement can be attributed to the improvement in ionization efficiency and also the suppression of fragmentation by reducing the nitro group. The detection limit obtained using a molecular ion peak was 20 pg μL^{-1} for nitroPYR, which was decreased to 5.9 pg μL^{-1} for aminoPYR that was produced from nitroPYR by reaction with hydrazine.

3.2. Performance evaluation of the catalyst

Fig. 2 shows the two-dimensional display obtained for the standard sample mixture of NPAHs for evaluating the performance of the Pd/C catalyst. The signals corresponding to NPAHs and APAHs disappeared, and numerous additional signals appeared as the result of the catalytic reaction with hydrazine. As demonstrated, NPAHs are more efficiently decomposed when hydrazine is present along with the catalyst. Many signals were observed in the ranges of m/z = 200-206 and 228-234, and some could be assigned to PAHs with no substituent groups, e.g., FLT and PYR (m/z =202) and benzo[a]anthracene and chrysene (m/z = 228). This result remained essentially unchanged, even when the catalyst was replaced with Pt/C. It has been reported that PAHs can be reduced by hydrogenation in the presence of catalysts containing palladium and platinum: such the transition metals are known to be effective for breaking the double bonds in the aromatic rings of PAHs [35-37]. Indeed, a series of signals spaced by $\Delta m/z$ = 2 was observed in the data, suggesting that two hydrogen atoms are incorporated into the sample, thus breaking the aromatic ring. To avoid the serious chemical reduction of NPAHs, the following studies were performed without the use of a catalyst.

3.3. Sample extract from diesel exhaust gas

Fig. 3A shows the two-dimensional displays obtained for a sample extracted from diesel exhaust gas. Many components were observed, most of which were assigned to PAHs with no substituent group and alkylated PAHs. It should be noted that several NPAHs, such as nitroANT, nitroFLT, and nitroPYR, were observed, which is in good agreement with the data reported by NIST [38]. Fig. 3B shows the two-dimensional display obtained when hydrazine is added as the reducing reagent. Many signals arising from PAHs and their alkylated compounds were observed, suggesting that such these PAHs are stable against hydrazine. However, several peaks that can be assigned to APAHs are clearly observed. These results suggest that the reaction process can be studied by a comprehensive analysis of NPAHs and APAHs using the constituents in the real sample. Fig. 4 shows the expanded views of the area indicated by solid square lines in Fig. 3. The signal peaks arising from nitroANT, nitroFLT, and nitroPYR disappeared, as the result of reduction by hydrazine. Therefore, the present technique appears to be useful for monitoring the chemical reaction of NPAHs. It is interesting to note that, similar to the findings for these NPAHs, some of the unassigned signals disappeared as shown in Fig. 4B-D. These molecules have odd numbers of molecular weights, suggesting that an odd number of nitrogen atoms is contained in a molecule, as is referred to as the nitrogen rule in mass spectrometry. Then, unknown NPAHs would be also reduced to corresponding APAHs. Thus, the decomposition of these highly-toxic NPAHs can be realized by carefully checking the data measured before and after the chemical reaction, even when standard chemicals are not available.

3.4. Advantage in the studies of chemical reaction and environmental protection

Studying a chemical reaction can be time consuming and can also result in measurements at

different conditions using different chemical reagents, catalysts, temperatures very costly. This is particularly true for many types of organic compounds that are suspected to be present in exhaust gas. However, it would be possible to examine the performance of a reactor that is intended to reduce the concentration of undesirable compounds such as NPAHs. Needless to say, this technique can be applied, not only to reducing but also oxidizing systems. Then, the present technique would be useful as a tool for developing a diesel engine with lower emissions of highly toxic species. In this case, the GC inlet port should be replaced with a high-temperature gas-processing unit of the diesel engine, in which a solution of urine would be injected and reacted with redox organic compounds in exhaust gas on the surface of a catalyst embedded on the supporting material. The converted species would be subsequently measured using GC/MPI-TOFMS. It is interesting to note that some of the NPAHs, e.g., nitroFLT and nitroPYR, have large *m/z* values (see Fig. 3) and the molecular ions can be clearly observed in MPI-TOFMS. Because of this, they could be measured with minimal interference without the need for a chromatographic separation, possibly allowing the on-line measurement of these toxic compounds, in addition to highly concentrated NO_x compounds such as NO_2, NO, N_2O and other radical species such as OH and O_3 that are present in exhaust gas. Due to its superior sensitivity and selectivity, the present instrument can be used to assure the limits of hazardous PAHs and their analogs such as NPAHs, APAHs, nitrosoPAHs, and hydroxyPAHs, to be regulated by law in the future, although their concentration levels are considerably low in exhaust gas. Thus, this analytical system has significant potential for use in solving environmental issues.

4. Conclusions

A sample containing NPAHs was analyzed by GC/MPI-TOFMS using an ultraviolet

femtosecond laser as the ionization source in the absence/presence of hydrazine as a reducing reagent with/without palladium/platinum catalysts being placed in the inlet port of the GC. The use of a two-dimensional display permitted a comprehensive analysis of a sample comprised of numerous constituents and was useful for monitoring changes in their composition caused by a chemical reaction. For this reason, this technique can be advantageously used to evaluate the performance of a chemical reaction system using the compounds present in an actual exhaust gas sample, reducing the time and the cost of research directed at controlling the level of constituents in exhaust gas from a diesel engine with the view of protecting the global environment.

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Figure Captions

Fig. 1. Two-dimensional displays measured for a standard sample mixture containing NPAHs. Reducing reagent: (A) none (B) hydrazine. The mass chromatogram (*m/z* = 247) of the region where nitroFLT and nitroPYR appear is shown as an insert in (A). Mass spectrum measured at a retention time of 12.0 min, where the nitroPYR appears, is shown in the right-hand side of (A). The mass spectrum measured at a retention time of 10.7 min, where aminoPYR appears, is shown in the right-hand side of (B). The locations of the molecular ions are indicated by solid circle lines and those of the fragment ions by dotted circle lines.

Fig. 2. Two-dimensional displays measured for a standard sample mixture containing NPAHs. Reducing reagent, hydrazine; catalyst, Pd/C.

Fig. 3. Two-dimensional displays measured for a sample extracted from diesel exhaust gas. Reducing reagent: (A) none (B) hydrazine. The locations of nitroANT, nitroFLT, nitroPYR, and their reduced products of aminoANT, aminoFLT, and aminoPYR, are indicated by solid circle lines. The fragment ions from PAHs and NPAHs are indicated by dotted circle lines. The expanded views of the areas indicated by solid square lines are shown in Fig. 4.

Fig. 4. Expanded views of the two-dimensional displays shown in Fig. 3. Reducing reagent: (A) (C) none (B) (D) hydrazine. Locations: (A) (B) nitroFLT and nitroPYR (C) (D) nitroANT (see the square parts shown in Fig. 3). The signals disappeared by reduction are indicated by dotted circle lines.