

Simultaneous Measurements of Aromatic Hydrocarbons in Exhaust using a Laser Ionization Method

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ABSTRACT

A simultaneous multi-composition analyzing (SMCA) resonance enhanced multi-photon ionization (REMPI) system was used to investigate gasoline engine exhaust. Observed peaks for exhaust were smaller mass numbers than those from diesel exhaust. However, large species up to three ring aromatics were observed suggesting that soot precursor forms even in the gasoline engine. At low catalyst temperature condition, the reduction efficiencies of a three-way catalyst were higher for higher mass numbers. This result indicates that the larger species accumulate in the catalyst or elsewhere due to their lower vapor pressures. To evaluate the emission of low volatility species, the accumulation should be taken into account. In the hot mode, reduction efficiencies for aromatic species of three-way catalyst were almost 99.5 % however, they fall to 70% in the cold start condition.

INTRODUCTION

The exhaust gas from automobiles has been improving gradually over the last 20 years. However, some places, especially metropolitan areas, still have air pollution problems [1]. Exhaust gas contains various hydrocarbon species, such as aromatics and paraffin. Although their toxicity with respect to humans varies [2] from species to species, total hydrocarbons have been used to regulate exhaust gas emissions [3]. In order to determine the effects of exhaust gas from automobiles on the human body and to reduce air pollution, the chemical composition of automotive exhaust must be determined. In addition, more information about the processes by which toxic species form in an engine is needed [4]. Chemical analysis should help to clarify the formation process. Although GC-MS and HPLC techniques have often been used [5-7], real time measurements cannot be performed. Since automotive exhaust constantly changes synchronized with engine operation, a sampling frequency of more than 1 Hz is required to analyze the species in exhaust gas.

One of the latest techniques to achieve real-time molecule-specific observation is a supersonic jet/resonance enhanced multi-photon ionization (Jet-REMPI) method. This method has been used in molecular spectroscopy [8–11], and some groups have used it to measure the VOCs in automobile exhaust gas [12–17]. The sensitivity has been reported to be approximately on the parts per million volume level. However, since emission levels have recently decreased due to progress in engine and catalytic system technology, we have improved the sensitivity to the parts per billion volume level [18,19]. Although Jet-REMPI has been shown to be effective for detecting VOCs and PAHs, since only one species at a time can be measured in a specific driving mode, it is difficult to detect all of the components of the exhaust gas.

In our previous study, we used a simultaneous multi-composition analyzing (SMCA)-REMPI system for analyzing diesel engine exhaust [20]. This system consists of a time of flight (TOF) mass spectrometer (MS) with untuned laser light for ionization. This technique detects fewer species than normal jet-REMPI does and cannot be used to determine which isomers are present. However, since SMCA-REMPI does not require a tunable light source, the system is simpler than a normal Jet-REMPI system. By using the fourth harmonic of a YAG laser for ionization, various aromatic species can be detected simultaneously because the resonance wavelengths of these species are located close to the wavelength of the laser. In this study, the SMCA-REMPI system was used to study the exhaust gas from a gasoline vehicle. In addition, by comparing the results using the SMCA-REMPI system with those using GC-MS, the accuracy of this method was verified.

EXPERIMENTAL

A schematic diagram of the experimental apparatus is shown in Fig. 1. The sample gas was introduced directly into the ionization chamber from a pipe located upstream or downstream of the catalyst of the test vehicles. The length and diameter of the sample line were approximately 5 m and 3 mm, respectively, and it had an inline filter. The sample line was heated to about 80 °C to prevent the exhaust gas from depositing. Sample gas was introduced into the chamber through a pinhole with a diameter of 150 μm to afford a supersonic jet. The fourth harmonic of a YAG laser with a frequency of 100 Hz was used as the ionization source. The YAG laser head had dimensions of 5 mm $\times$ 5 mm $\times$ 20 mm. Since the wavelength of the YAG laser was near the resonance wavelength of many of the aromatic species, other species, such as CO_2 , H_2O and NO_x , in the exhaust gas did not affect the measurements. The ions produced by the laser light were introduced into a TOF-MS. The maximum mass detected in this chamber was approximately 300 amu because the drift length of the TOF chamber was set to 800 mm. The above-mentioned chambers and the small YAG laser were set up in one

rack. Therefore, the system could be moved easily, and system handling was easier than that for the normal Jet-REMPI system [18,19].

The results obtained using the SMCA-REMPI system were only calibrated in the case of naphthalene using a GASTEC permeator. The results, excluding those for naphthalene, are not absolute values. Thus it is not possible to compare those species by the heights of peaks because the ionization efficiencies vary each other. However, relative comparisons of the same species in the different experiments are possible, because the intensities of those peaks in the results were expressed as the normalized results to those for naphthalene, which were obtained simultaneously. This procedure avoids the constant change in sensitivity mainly due to a fluctuation in laser power.

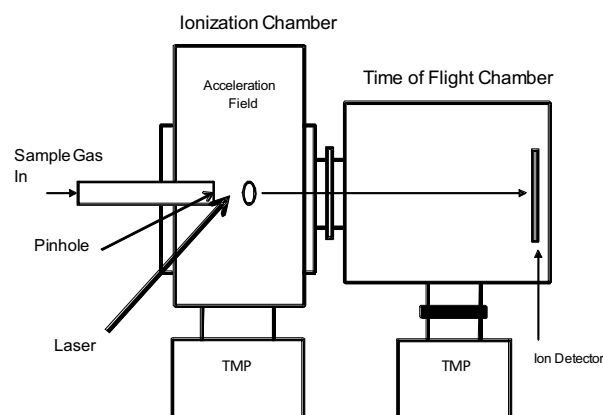


Fig. 1 Schematic diagram of the SMCA-REMPI

Table 1 Specifications of the test vehicle.

Engine Type	L4, MPI Gasoline
Intake air management	NA, EGR
Displacement (L)	1.495
MAX. Power (KW/rpm)	80/6000
Transmission	4AT
After treatment device	3-way catalyst
Weight of Vehicle(kg)	1050
Emission Regulation	'05 JAPAN

Table 2 Specifications of tested diesel vehicle

Engine Type	L4, DI
Intake air management	NA, EGR
Displacement (L)	4.8
MAX. Power (KW/rpm)	96/3000
Injection System	Common rail
Aftertreatment device	DOC
GVW (kg)	4485
Emission Regulation	'03 JAPAN

Simultaneous measurement using GC-MS (Shimadzu QP2010) was performed under steady state operation conditions. The GC-MS was equipped with a DB-1 column (length: 60 m; inner diameter: 0.32 μ m). The test vehicle specifications are listed in Table 1. The vehicle had an MPI gasoline engine system, which is the most common among Japanese passenger vehicles. A three-way catalyst was located in the exhaust manifold. The exhaust gas was sampled in the exhaust manifold and the exhaust pipe downstream of the catalyst for engine-out and catalyst-out exhaust gases, respectively. Adding to the exhaust gas observation for gasoline vehicle, the diesel exhaust gas was measured at a constant speed of 60 km/h for a comparison. The tested diesel vehicle was a light duty truck and equips a DOC for the after treatment system. And it has a common rail injection system. The specifications of the vehicle were listed in Table 2.

RESULTS AND DISCUSSION

STEADY STATE OPERATION – Figure 2 shows a TOF mass spectrum of the engine exhaust of the gasoline vehicle upstream of the catalyst obtained by using our SMCA-REMPI system. Several mass peaks were detected. Ionization potentials of alkane and alkene species are quite higher than those of aromatics. Thus with the wavelength of laser light adopted to this study, three photons are required to ionize these species. On the other hand, the most of aromatic species are ionized with two photons by this wavelength. Ionization efficiencies of two photons process are quite higher than three photons process. Thus the observed mass peaks in this study can be assumed for aromatic species only. The aromatic which has the simplest structure is benzene. SMCA-REMPI system can not detect benzene, because the resonance wavelength of benzene does not located close to the laser wavelength. However benzene concentration in the resent gasoline is quite little, thus exhaust amount of benzene is considered also little.

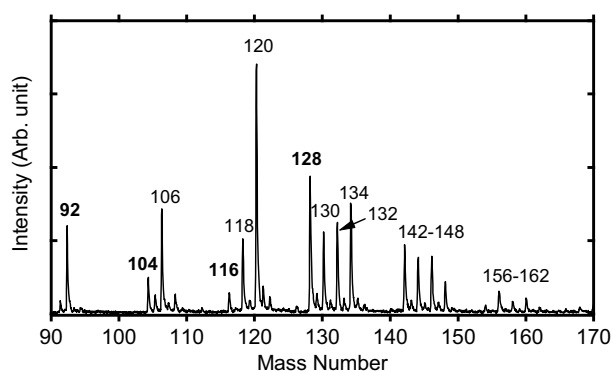


Fig. 2 TOF mass spectrum obtained upstream of the catalyst at 60 km/h by using SMCA-REMPI system.

As discussed in our previous study [20], the observed peaks can be classified into four groups: toluene [92

(toluene's mass number) + 14 $\times$ n (n = the number of CH₂ groups)], styrene, indene, and naphthalene groups. In the case of n = 1 for the toluene group, the mass number is 106, which corresponds to a structure from which one H atom of toluene is replaced by a CH₃ group, such as ethyl-benzene and xylene. N = 2 for toluene group as trimethylbenzene, ethylmethylbenzene. The classification of the mass peaks in Fig. 2 is summarized in Table 3. The parent mass peaks of the groups were expressed with bold text.

Table 3 List of detected species at a constant speed of 60 km/h by using the SMCA-REMPI system.

Mass number	Species
92	toluene
106	toluene+CH ₂
120	toluene+2(CH ₂)
134	toluene+3(CH ₂)
148	toluene+4(CH ₂)
162	toluene+5(CH ₂)
104	styrene
118	styrene+CH ₂
132	styrene+2(CH ₂)
146	styrene+3(CH ₂)
160	styrene+4(CH ₂)
116	indene
130	indene+CH ₂
144	indene+2(CH ₂)
158	indene+3(CH ₂)
128	naphthalene
142	naphthalene+CH ₂
156	naphthalene+2(CH ₂)

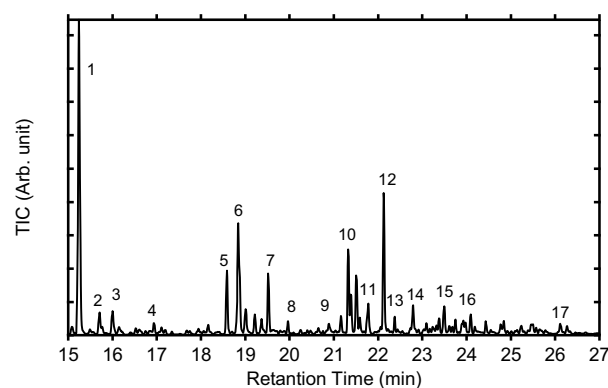


Fig. 3 TIC obtained upstream of the catalyst at a constant speed of 60 km/h by using GC-MS.

GC-MS was performed simultaneously with the experiment depicted in Fig. 2. A total ion chromatogram (TIC) and identification of each peak are shown Fig. 3