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Aerosol Spectrometer for On-Line Measuring Diameters and Chemical Compositions of Volatile Organic Nanoparticles

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Abstract – We describe the design and performance of an aerosol spectrometer that simultaneously measures size-dependent concentration and chemical composition of volatile organic nanoparticles ranging from 10 to 470 nm. The spectrometer consists of a differential mobility analyzer (DMA) for size classification and a gas chromatography mass spectrometer (GC-MS) for composition analysis. The size-classified particles of two kinds of hydrocarbons, an aliphatic hydrocarbon and aromatic hydrocarbon, were directly introduced into the GC-MS after vaporization of the particles. The relationships between the concentrations of classified particles measured with an aerosol electrometer and the peak area of major fragment ions measured with the GC-MS were given to show the detection limit of our spectrometer. For a particle size of 330 nm, the lower detection limit of the spectrometer for particle concentration was approximately 7.5×10^4 particles cm^{-3}.

Key Words : Volatile Organic Nanoparticles, Differential Mobility Analyzer, Gas Chromatography Mass Spectrometer, Composition Analysis.

1. Introduction

There has recently been much concern regarding the unfavorable influence of nanoparticles emitted by diesel engines（Kittelson, 1998）on human health（Sagai and Ichinose, 2001）. The diesel nanoparticles usually consist of volatile organic and sulfur compounds（Kittelson, 1998; Sagai and Ichinose, 2001; Sakurai *et al.*, 2003）. Unfortunately, off-line analysis of these diesel nanoparticles changes the composition of the volatile components. On-line measurements are therefore essential for precise analysis of the chemical composition and particle size of the diesel exhaust particles. Precise analysis should provide a wealth of useful information in developing new diesel engines for reduction of emissions of harmful diesel nanoparticles.

Several studies described below have reported that analytical equipment composed of a sequential combination of a DMA and a mass spectrometer provides a powerful tool for measuring the size-dependent chemical composition of aerosol nanoparticles. DMAs are suitable for particle classification based on particle size, since DMAs have higher resolutions for size classification than other equipments such as impactors and aerodynamic lenses.

Okada *et al.*（2002）have developed for metal nanoparticles a system that measures the size-dependent chemical composition of gas-borne metal nanoparticles by using an inductively coupled plasma mass spectrometer combined with a DMA. For organic nanoparticles emitted from diesel engine exhaust, the chemical compositions can be measured by a time-of-flight mass spectrometer（Deguchi and Tanaka, 2004; Deguchi *et al.*, 2008）or a thermal desorption particle beam mass spectrometer（Sakurai and Takami, 2004; Tobias

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et al., 2001） after size classification with a DMA. But these measurements of the chemical compositions for organic diesel nanoparticles cannot identify the chemical species of the organic compounds. The fragmentation that occurs in the ionization process of these mass spectrometers usually causes a complicated overlapping of fragmented ions generated from all compounds in the mass spectra. No possibility of distinction of the parent ions from the fragmented ions in the mass spectra makes the identification of chemical species impossible. In the case of the thermal desorption particle beam mass spectrometer, it is equipped with a system for separation of organic species based on differences in the desorption temperatures. The system can distinguish sulfur compounds from hydrocarbon compounds （Sakurai and Takami, 2004; Tobias *et al.*, 2001）. It, however, does not have adequate resolution to identify the chemical species of these compounds. We therefore believe that a gas chromatography mass spectrometer is most suitable for identifying the chemical species.

Myojo *et al.* （2002） have reported analysis of the chemical species using a GC-MS for diesel exhaust particles after size-classification by a DMA, which involves an off-line step for introduction of particles collected on the filters into the GC-MS. In the present study, however, we developed a system for on-line measurement by directly introducing the vapor of particles size-classified by a DMA into a GC-MS. This system enables one to simultaneously measure the size distribution and the size-dependent chemical composition of volatile organic nanoparticles.

2. Description of the spectrometer

A schematic of our spectrometer equipped with a nebulizer is shown in **Fig. 1**. Particles of hexadecane （$C_{16}H_{34}$, molecular weight=226.44） or nonylbenzene （$C_{15}H_{24}$, molecular weight=204.35） are generated by atomizing of the liquids from a nebulizer with N_2 carrier gas at 0.26 MPa. Hexadecane and nonylbenzene are major components of aliphatic hydrocarbons and aromatic hydrocarbons contained in the diesel fuels, respectively.

The particles are first charged in a charger containing ^{241}Am with 0.5 standard L/min of N_2 carrier gas and then classified in a DMA （WYCKOFF Co., Ltd., D1） with 3.0 standard L/min of N_2 sheath gas. The ^{241}Am is used as an α-ray source of 22.4 MBq to generate bipolar ions of particles. The charged particles have size-dependent electrical-mobility and therefore are classified in the electrical field inside the DMA at 0.10 MPa. The inner radius of the DMA's outer electrode is 33 mm, and the outer radius of the inner electrode is 25 mm, and the classification length is 300 mm. The concentrations of the classified monodispersed particle emitted by the DMA are measured using a Faraday cup electrometer.

A volume corresponding to 0.5 cm^3 at standard temperature and pressure of classified monodispersed aerosol is introduced into a pre-evacuated stainless steel pipe heated to 150°C, of which the inner volume is 6 cm^3, through a needle valve, of which the flow rate is set at 0.5 standard cm^3/min. After this introduction of aerosol into the heated pipe during 1 min for vaporization of particles, a part of the gas is fed from the pipe into the GC-MS （Shimazu Ltd., GCMS-QP5050A） during 1 sec through a three way valve. After a turn of the three way valve, the gas pressure in the pre-evacuated space upstream from the chromatography column instantaneously increases, because the inner diameter of the column is too small and the column is too long to make the gas pass through quickly. The difference in pressures between this space and the heated 6 cm^3 pipe disappears within 1 sec. Therefore the

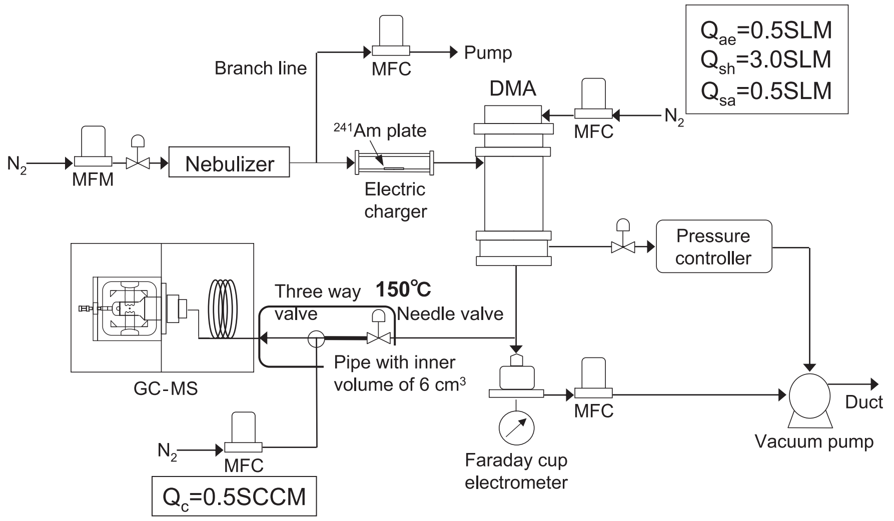

Fig. 1 Schematic of the spectrometer for size and composition analysis of organic particles. MFC: mass flow controller, MFM : mass flow meter.

time period for feeding longer than 1 sec does not increase the volume of the gas fed into the GC-MS very much. This time for feeding gives us the start of the retention time for the chromatograms. The analytical conditions of the GC-MS are shown in **Table 1**.

Table 1 Analytical conditions of GC-MS

Model	: GCMS-QP5050A
-GC-	
Column	: Rtx-35MS 15 m × 0.32 I.D. df=0.25 μm
Column Temp.	: 40°C (1 min)-10°C/min-250°C (8 min)
Carrier Gas	: N_2 0.5 standard cm^3/min
Injection Temp.	: 150°C
-MS-	
Injection Temp.	: 230°C
Ion Source Temp	: 180°C
Ionization Method	: EI
Scan Range	: m/z 60–300
Scan Interval	: 0.5 sec

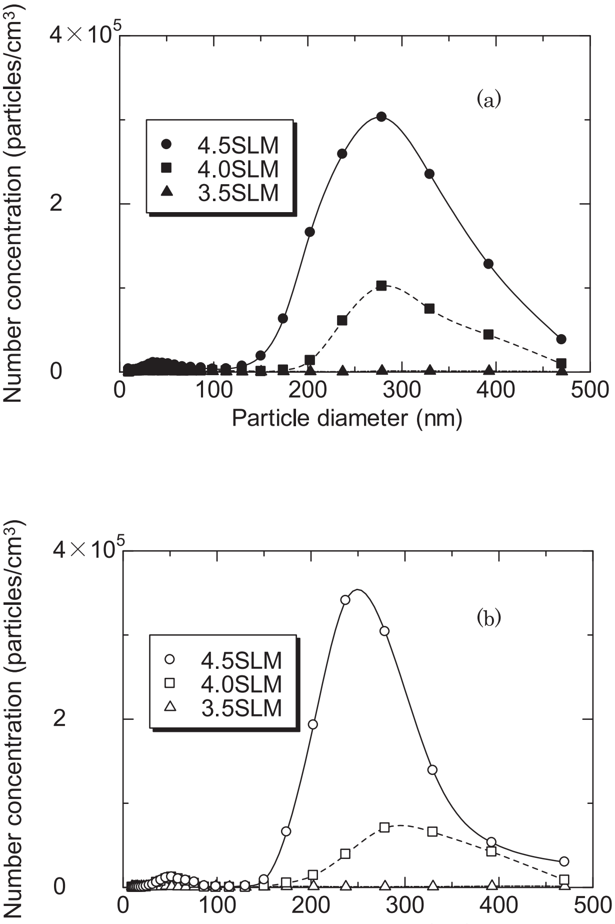

Fig. 2 Size distributions of (a) hexadecane particles and (b) nonylbenzene particles measured by using the DMA.

3. Results and discussion

Fig. 2 (a) and 2 (b) show the size distributions of hexadecane and nonylbenzene particles, respectively, measured with the DMA and Faraday cup electrometer for three flow rates of the carrier gas into the nebulizer. Our results show that the bimodal distributions ranged from approximately 10–470 nm and had higher peaks with increases in the carrier gas flow rate. We performed experiments described below using hexadecane and nonylbenzene particles generated at the nebulizer with 4.5 standard L/min of N_2 carrier gas.

Fig. 3 (a) and 3 (b) show the chromatograms measured when monodispersed hexadecane and nonylbenzene particles classified at a size of 330 nm by the DMA (the voltage of the inner electrode: 1840 V) were introduced into the GC-MS after vaporization at 150°C. The chromatograms show the peaks at 13.31 min and 13.91 min for hexadecane and nonylbenzene particles, respectively. Fig. 3 also shows the chromatograms (Figs. 3 (c) and 3 (d)) measured when hexadecane and nonylbenzene vapors generated from the liquids at 150°C were directly introduced into the GC-MS. The peaks observed with the classified particles and vapors coincided in their retention times for both organic substances.

When the voltage of the inner electrode of the DMA was set at 0 V and the flow exiting the DMA was introduced into the GC-MS, no peaks at these retention times were observed in the chromatograms. From this result, we understood that any hexadecane or nonylbenzene vapor present in the aerosol flow entering the DMA was not detected by the GC-MS after diffusion from the outer to inner DMA cylinder. We confirmed that hexadecane and nonylbenze molecules originated only from the classified particles were observed in the chromatograms (Figs. 3 (a) and 3 (b)) at 1840 V of the classification voltage of the DMA.

Fig. 4 (a) and 4 (b) show the mass spectra measured at the retention times of 13.31 min and 13.91 min for hexadecane and nonylbenzene particles, respectively. For hexadecane, the spectrum shows a series of peaks due to aliphatic hydrocarbons every 14 m/z and a peak of the parent ions at 226 m/z. For nonylbenzene, the spectrum shows a large peak of tropylium ions ($C_7H_7^+$) at 91 m/z and a peak of the parent ion at 204 m/z. The characteristics of these spectra coincide with those of the spectra (Figs. 4 (c) and 4 (d)) reported in NIST libraries. These results show that our spectrometer enables us to simultaneously measure the size distribution and size-dependent chemical composition of volatile organic nanoparticles.

In order to determine the temperature most suitable for vaporization of hexadecane and nonylbenzene particles, we investigated the temperature dependence of the vaporization

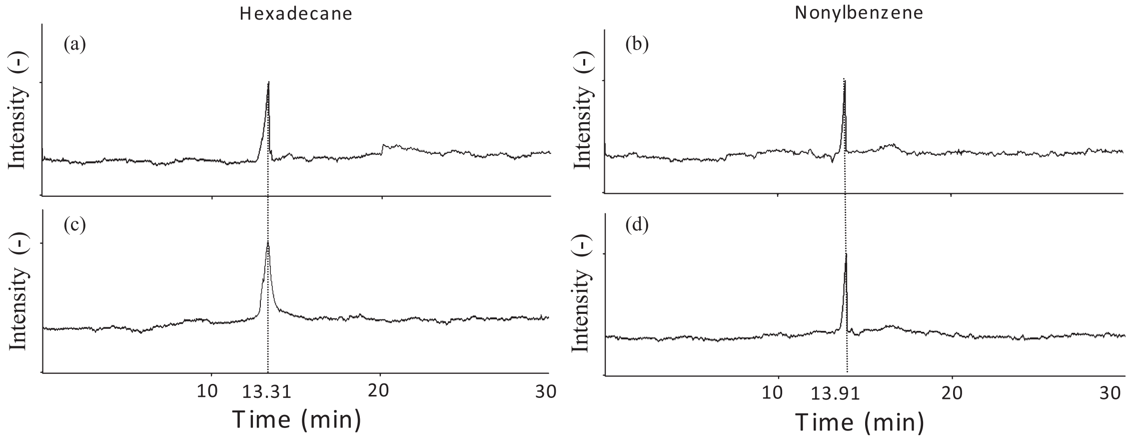

Fig. 3 Chromatograms measured by using the GC-MS when monodispersed (a) hexadecane and (b) nonylbenzene particles classified at a size of 330 nm by the DMA were introduced into the GC-MS after vaporization at 150°C. Chromatograms measured when (c) hexadecane and (d) nonylbenzene vapors were directly introduced into the GC-MS.

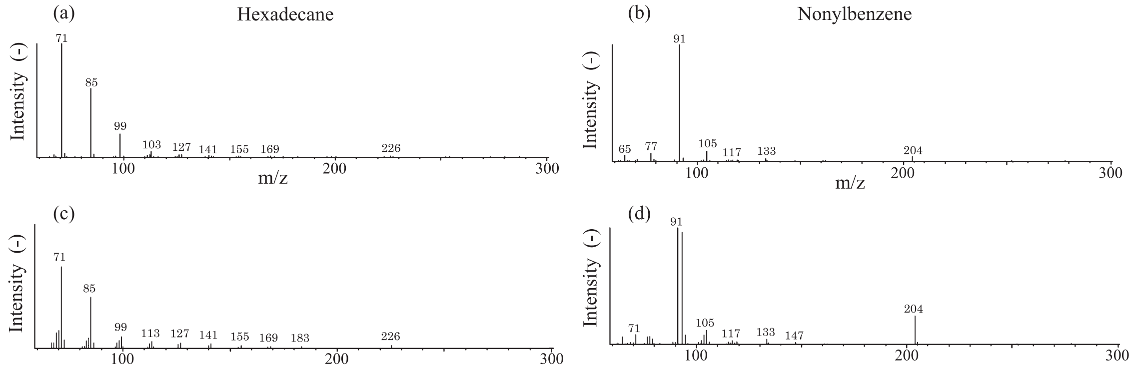

Fig. 4 Mass spectra measured at a retention time of 13.31 min and 13.91 min for (a) hexadecane and (b) nonylbenzene particles. Mass spectra reported in NIST libraries for (c) hexadecane and (d) nonylbenzene.

rate of these organic particles classified at 330 nm. When a droplet, for which the surface temperature is T_0 and the vapor pressure is p_0 (T_0), is present in gaseous media for which the temperature is T_m and the vapor pressure is p_m, the time period t required for the droplet to decrease the diameter, D_p, from D_{p1} to D_{p2} due to the vaporization is given by the following equation (Wagner and Pohl, 1975),

$$\int_{D_{p1}}^{D_{p2}} D_p dD_p = \int_0^t \frac{4\beta_M D_v M}{R\rho_L} \left\{ \frac{P_m}{T_m} - \frac{p_0(T_0)}{T_0} \right\} dt \qquad (1)$$

where β_M is the correction coefficient, D_v is the diffusion coefficient of the vapor in the gaseous media, R is the gas constant, M is the molecular weight of the vapor, and ρ_L is the density of the droplet. When we estimated the vaporization time t for the classified particles to decrease from 330 nm to 0 nm at 150°C, t was 9.0×10^{-6} sec for hexadecane particles and 5.6×10^{-6} sec for nonylbenzene. We understood that these classified particles could evaporate in a moment which is shorter than the vaporization period of 1 min in the heated pipe at 150°C.

We experimentally investigated the relation between the vaporization temperature of the particles classified at 330 nm and the area of the peaks shown in the chromatograms of the GC-MS. Also from the data in **Fig. 5** and the thermal decomposition temperatures of hexadecane and nonylbenzene, we found that a temperature of 150°C was suitable for vaporization of these organic particles.

To examine the sensitivity of our spectrometer, we measured the dependence of the signal intensity of the GC-MS on the particle concentrations. **Fig. 6** shows the relation between the number concentration of 330 nm organic particles classified by the DMA and measured with the Faraday cup electrometer at the outlet of the DMA, and the peak area of the organic compounds in the chromatograms measured with the GC-MS. We found that the peak areas measured with the GC-MS were zero when the particle concentrations of hexadecane and nonylbenzene were less than approximately 5×10^4 particles/cm^3, and monotonically increased with increasing concentrations. The curve gradients were not the same between hexadecane and nonylbenzene, possibly because of

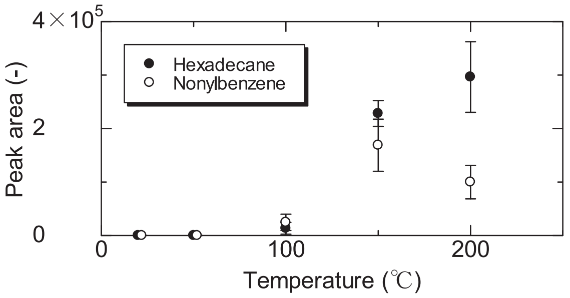

Fig. 5 Relation between the vaporization temperature of classified particles and the peak area of the organic compounds in the chromatograms measured with the GC-MS.

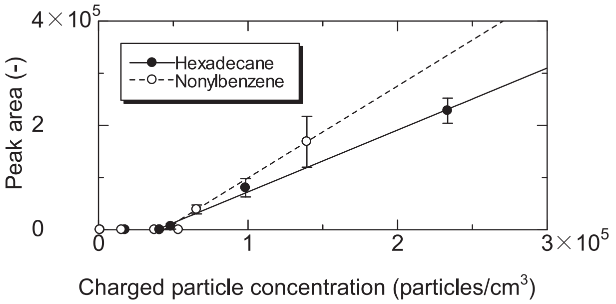

Fig. 6 Relation between the number concentration of classified 330-nm organic particles measured with the Faraday cup electrometer at the outlet of the DMA, and the peak area of the organic compounds in the chromatograms measured with the GC-MS.

the difference in the fragmentation pattern. The results show that for a particle size of 330 nm, the lower limit of the particle concentrations measurable by the GC-MS was approximately 5×10^4 particles/cm^3 for both hexadecane and nonylbenzene particles. The theoretical peak concentration for ideal classification in a DMA is 66.7% of the total concentration of aerosol particles supplied to the DMA (Kousaka, Okuyama, Adachi, and Miura, 1986). Charged 330-nm particles at concentrations higher than 7.5×10^4 particles/cm^3 can therefore be measured with our spectrometer.

In conclusion, our spectrometer, which involves using a DMA coupled with a GC-MS, can simultaneously measure the size distribution and size-dependent chemical composition of volatile organic nanoparticles ranging from 10 to 470 nm. The spectrometer identifies the chemical species of organic compounds from the retention times and mass spectra measured with the GC-MS for organic particles size-classified by the DMA. In addition, it was found that charged 330-nm particles at concentrations higher than 7.5×10^4 particles/cm^3 can be measured with our spectrometer.

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