Development of a new on-line measurement system for organic substances in nano particles from diesel exhaust

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1. Introduction

Nano particles in the atmosphere are mainly emitted by automobiles from the combustion of fossil fuels (e.g., [1]). For instance, nano particles typically contain 1-20% of the particle mass and more than 90% of the particle number in diesel exhaust (e.g., [1]). Nano particles that enter the human body during respiration are often deposited in the lung and deeper areas, and are suspected of causing various diseases such as lung cancer (e.g., [2], [3]). In addition, the toxicity of nano particles is reported to vary depending on the chemical substances on/in the particles, such as heavy metals ([3]-[5]). Hence, it is important to analyze the concentrations and distributions of chemical substances in nano particles from the atmosphere and exhaust gases.

In this study, we examine a new measurement system for organic substances in nano particles, using a differential mobility analyzer (DMA) and laser ionization time-of-flight mass spectrometer (laser ionization TOFMS). In this system, nano particles are classified from other particles using DMA, and then directly transported to the laser ionization TOFMS. Finally, chemical substances in the particles are ionized using a laser in an ionization chamber and measured using the TOFMS. The detection limit of chemical substances using the laser ionization TOFMS is below 10^{-15} g, enabling a high-resonance measurement[6]. Accordingly, this system is suitable for the measurement of trace chemical substances in nano particles in real time.

In this study, we manufactured the new system described above, and evaluated the suitability of the system for the measurement of organic substances in nano particles in diesel exhaust.

2. Experimental

For the classification of nano particles from bulk particles, Model 3071 DMA (TSI) equipped with a condensation particle counter (CPC; Model 3021, TSI) was used. The diameters of the classified particles ranged from 10 to 500 nm. In this study, 10 to 500nm diameter particles were randomly collected.

For the measurement of chemical substances in nano particles, the laser ionization TOFMS manufactured by Mitsubishi Heavy Industry was used. The schematic of the instrument is shown in Fig. 1.

The instrument mainly consists of an ionization part, a flight tube, a control unit and a vacuum system. The mechanism of the measurement using the laser ionization TOFMS is described as follows. Sample gases are transferred to the ionization chamber, whose pressure is maintained at $<10^{-8}$ Torr by a jet valve, as a molecular jet. The repetition of the molecular jet was 10 Hz, i.e., sample gases were transferred to the ionization chamber 10 times per second. The gas samples in the ionization chamber were then ionized by laser irradiation, using a wavelength four 4 times that of a YAG laser (266 nm wavelength), which is approximately the same as the resonance vibrational energy of polycyclic aromatic hydrocarbons (PAHs), and were transferred to the flight tube. The transferred ions were led into an ion detector after rebounding the reflector. The detected signals were amplified and measured using an oscilloscope and a photon counter. Measurement conditions using the laser ionization TOFMS were optimized by a preliminary measurement using a standard reagent of anthracene.

Diesel exhaust samples were collected as shown in Fig. 2. Sample gases were lead to the DMA via the dilution device in which the gases were diluted fifty fold by the volume.

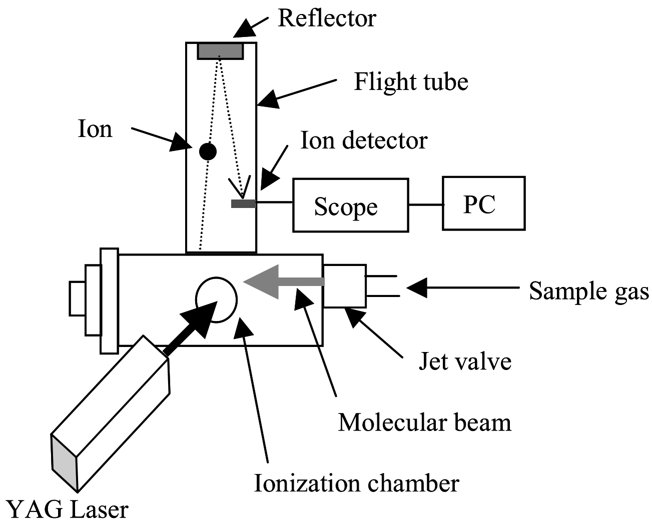

Fig. 1 Schematic of the laser ionization TOFMS.

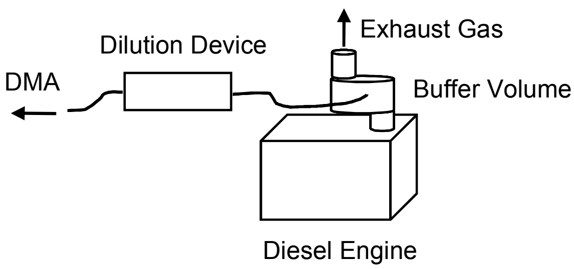

Fig. 2 Schematic of sample gas collection.

3. Results and discussion

The chemical substances in the nano particles from diesel exhaust samples were measured using the system manufactured in this study. The diameter distributions of the diesel exhaust particles are shown in Fig. 3. The diameter distribution of the diesel exhaust particles (0 W load: solid line) had two peaks; one was a sharp peak at 50 nm and the other was a “shoulder” peak at 150 nm. In contrast, a different pattern of particle diameter distribution was observed at the diesel engine load of 500 W (dotted line) and had two peaks; one peak was at 200nm and the other was at 70nm.

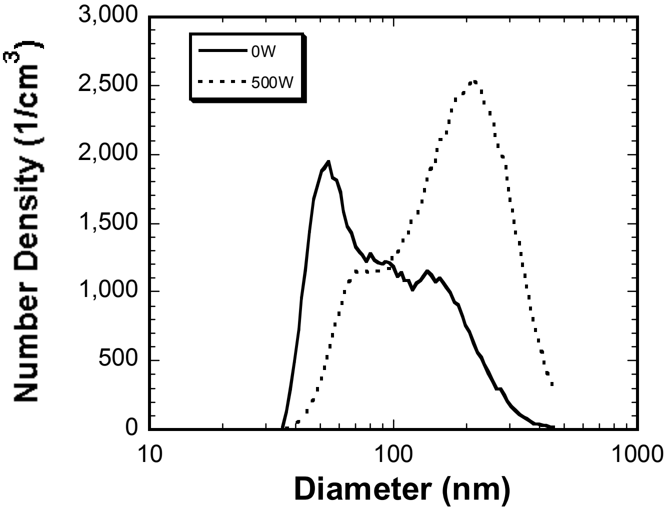

Fig. 3 Diameter distributions of diesel exhaust particles.
Solid line: 0W load. dotted line: 500W load.

Next, on-line and real-time measurement results for the chemical substances in the classified particles (70 nm and 150 nm diameter) of the diesel exhaust samples (500W engine load) using the laser ionization TOFMS are shown in Fig. 4. Figure 4 shows that several clear mass spectra were detected in the wide m/z range of 50 to 300. Several “big” peaks in the case of the 70 nm diameter particles are presumed to be some of polycyclic aromatic hydrocarbons (PAH) because of their correspondence to the mass number of standard PAH: for example, m/z 252 is same as molecular ion of benzo(a)pyrene, benzo(e)pyrene and pelyrene. However, qualification and quantification of each peak has not been performed yet.

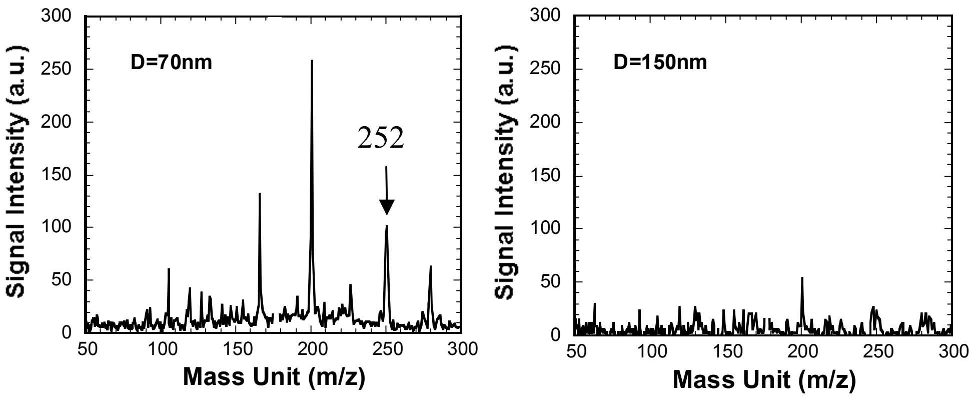

Fig.4 Mass spectra patterns of nano particles in diesel exhaust gases (500 W engine load).

Left: 70nm diameter, right: 150nm diameter.

In addition, the mass spectra of the diesel exhaust particles of 70nm diameter were clearly different from those of the 150 nm diameter particles (Fig.4). Furthermore, the signal intensities of the 150nm diameter particles were smaller than those of the70 nm diameter particles. This result shows the differences in the chemical substances found in the particles. At the first peak (70 nm diameter particles), relatively volatile organic substances were the major components, whereas non/semi-volatile substances (e.g., soot and heavy metals) were the major components at the second peak (150 nm-diameter particles).

4. Conclusion

In this study, the system using a combination of DMA and laser ionization TOFMS was manufactured for on-line and real-time measurements of chemical substances in from nano particles. Next, the measurement of chemicals in nano particles in diesel exhaust samples using the system resulted in the successful classification of nano particles from bulk samples and in obtaining clear mass spectra of the chemicals. Accordingly, it was apparent that the system manufactured in this study is suitable for the measurement of chemical substances in nano particles in fossil fuel exhaust gases.

5. Reference

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