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REAL-TIME, SIZE-RESOLVED, QUANTITATIVE MEASUREMENTS OF DIESEL EXHAUST PARTICLES SEMI-VOLATILE CHEMICAL COMPOSITION BY MEANS OF AEROSOL MASS SPECTROMETER

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ABSTRACT - Atmospheric aerosols and particulate matter from a wide variety of emissions sources measurements are conventionally performed by recording PM mass. The ambient standards are written in terms of mass concentrations, and emission regulations are based on mass rates. However, in order to understand better the nature of the mobile source contribution to ambient PM, many research groups are currently extending their investigations to include measurements of the speciation of particles in automotive exhaust.
Usually, organic fraction of automotive exhaust particles are concentrated to 1 mL by Kuderna-Danish concentrator after extracted into dichloromethane by soxhlet extraction. Then, these extracts are analyzed by GC/MS. In this time, it need long time to get analytical results although we can get precise results.
Progress in understanding and mitigating these problems is limited by the ability of existing instruments to provide real-time, size-resolved, quantitative measurements of aerosol mass and chemical composition. A number of measurement techniques possessing some of the required aerosol analysis capabilities have emerged recently. Real-time aerosol mass spectrometers aim to provide information on chemical composition of particle ensembles. Most of these instruments also provide information on particle size.
An Aerosol Mass Spectrometer (AMS) developed at Aerodyne Research, which has been designed to provide real-time quantitative information on size-resolved mass loadings for semi-volatile chemical components present on ambient aerosol particles.
In this study, semi-volatile chemical composition of automotive exhaust particles are continuously measured by improved aerosol mass spectrometer. In this result, it is found out that diesel exhaust particles semi-volatile size resolved chemical compositions are changed according to driving condition.

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1. INTRODUCTION

Atmospheric aerosols and particulate matter (PM) from a wide variety of emission sources are receiving increasing attention because of their influence on human health(1), visibility, acid deposition, and global climate (2). These measurements are conventionally performed by recording PM mass. The ambient standards are written in terms of mass concentrations, and emission regulations are based on mass. However, in order to understand better the nature of the mobile source contribution to ambient PM, many research groups are currently extending their investigations to include speciation of particles in automotive exhaust.
Progress in understanding and mitigating these problems is limited by the ability of existing instruments to provide real-time, size-resolved, quantitative measurements of aerosol mass and chemical composition (3). A number of measurement techniques possessing some of the

required aerosol analysis capabilities have emerged recently(4). Real-time aerosol mass spectrometers aiming to provide information on chemical composition of particle ensembles or individual particles. Most of these instruments also provide information on particle size. An Aerosol Mass Spectrometer (AMS) developed at Aerodyne Research, which has been designed to provide real-time quantitative information on size-resolved mass loadings for semi-volatile chemical components present on ambient aerosol particles. This conventional AMS equipped with quadrupole mass spectrometer was not enough ability of particle composition analysis for example continuous measurement, particle size depend composition analysis, etc. Thereupon, we combined AMS to time of flight mass spectrometer to get continuous speciation data depend on particle size and to know particle size depend composition information.
Trials result of continuous measurement of diesel exhaust particles size depend on composition are introduced in this paper.

2. METHOS AND APPARATUS

2.1 Aerosol mass spectrometer

An Aerosol Mass Spectrometer (AMS) developed at Aerodyne Research, which has been designed to provide real-time quantitative information on particle size-resolved mass loadings for volatile and semi-volatile chemical components present in/on ambient aerosol particles (5). In its present configuration, the AMS cannot detect refractory aerosol components such as sea salt, soil dust, and elemental carbon. A schematic of the AMS is presented in Figure 1.
The AMS consists of three main parts: an aerosol inlet(6,7), a particle sizing chamber, and a particle composition detection section. The different sections are separated by small apertures and differentially pumped. A computational fluid dynamics simulation of the AMS inlet system shows nearly 100% transmission efficiency to the detector for particles in the aerodynamic diameter range 70–500 nm, and shows substantial transmission for particles in the 20–70 nm and 500 nm to 2.5 mm ranges for spherical particles. Irregularly shaped particles may have lower transmission efficiencies (5). Size-dependent particle velocities created by expansion into vacuum are used to determine particle size through a particle time-of-flight measurement. The focused particle beam is modulated by a rotating wheel chopper operating at about 100 Hz. Time-resolved particle detection after a known flight distance gives the particle velocity from which the particle aerodynamic diameter is obtained. Detection is performed by directing the particle beam onto a resistively heated, roughened surface under high vacuum. On this surface, the volatile and semi-volatile components in/on the particles flash vaporize. The vaporization source is integrally coupled to an electron impact ionizer at the entrance of a quadrupole mass spectrometer. When the quadrupole is tuned to a representative m/z, bursts of ions are produced that are averaged to produce a size-resolved mass distribution.

2.2 Improvement of aerosol mass spectrometer

Conventional AMS is good apparatus for measurement of real-time quantitative information on particle size-resolved mass loadings for volatile and semi-volatile chemical components present in/on ambient aerosol particles. Although, conventional AMS equipped with quadrupole mass spectrometer was not enough ability of organic particle composition analysis, second by second continuous measurement and particle size depend composition analysis, etc. Thereupon, we tried to combine AMS and time of flight (TOF) mass spectrometer (MS). TOF/MS made by TOFWERKS was selected for these purpose because of fast scan speed. Figure 1 shows photo of conventional AMS and improved AMS. This TOF/MS can get over 80 kHz full scan data. The chopper of AMS is rounding about 100Hz, then we get over 800 full scan in one chopper round. When 100 scan data was add up, we can get over 800 full mass spectrum in one chopper rounding every one second. In this result, we get 800 average mass spectrum along particle size axis, and this measurement is perform every second. This improved AMS is named TOFAMS.

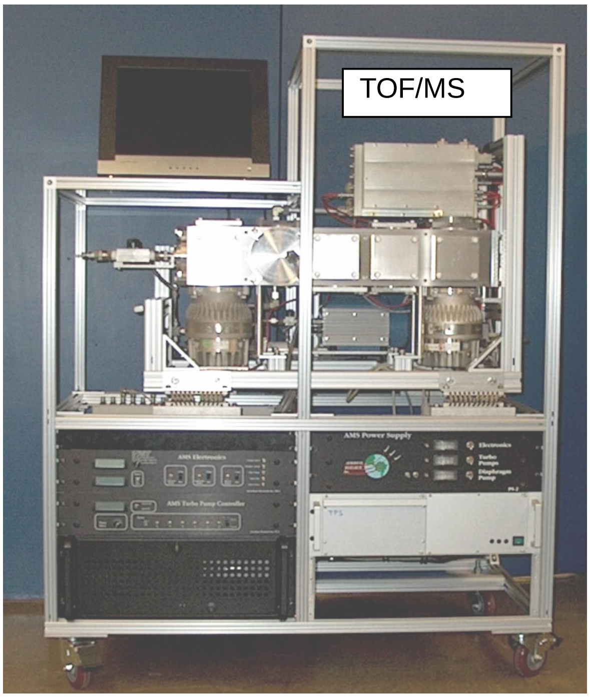

Fig.1 Photo of conventional AMS and improved AMS (TOFAMS)

3. RESULT AND DISCUSSION

Trial particle size depend mass spectrum measurement and every second continuous measurement of automotive exhaust particle was implemented.

<u>3.1 Trial of automotive exhaust particle size depend composition measurement</u>

Automotive exhaust trial measurement is performed with TOFAMS. Figure 2 shows DMS (DMS500, Cambustion LTD.) measurement result of diesel (3000cc, without cat.) exhaust particles number depend size distribution diluted by full tunnel when idling. In this result, mode diameter of particle number distribution is around 40nm and theses particles are almost consist with nano particles (<50nm). Figure 3 shows TOFAMS result of same driving condition. This figure indicate that theses particles are almost consist with organics although there are size distribution of organics, sulfate, nitrate, ammonium and water. This size distribution of organics has two peaks of mode diameter is 50nm and 150nm. These difference is caused by definition of particle size and Y axis. Unit of particle size in figure 2 is mobility diameter and figure 3 is vacuum aerodynamic diameter. Unit of Y axis in figure 2 is particle number and figure 3 is mass of every components. When particle number of figure 2 is changed to particle volume, difference of these distributions is decrease.

Figure 4 shows mass spectrum of every particle size. Figure 4(a) is mass spectrum of add up 20-50nm size range, figure 4(b) and 4(c) are mass spectrum of add up 50-100nm and 100-200nm size range, respectively.

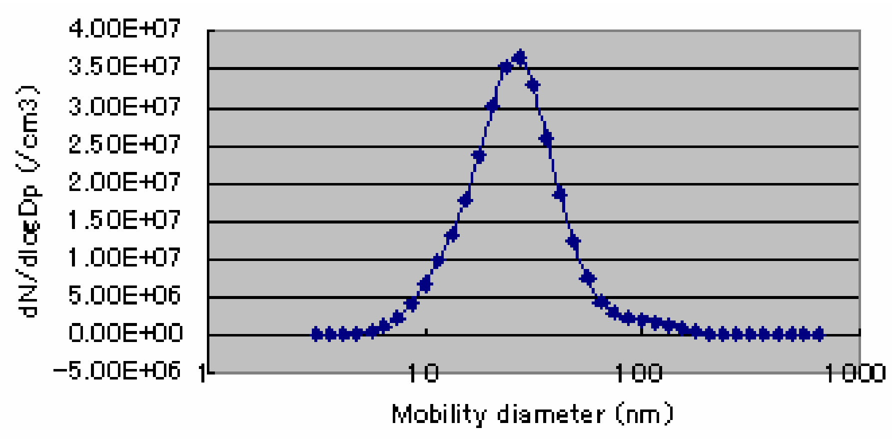

Fig.2 Particle size distribution of diesel exhaust measured by DMS (Idling)

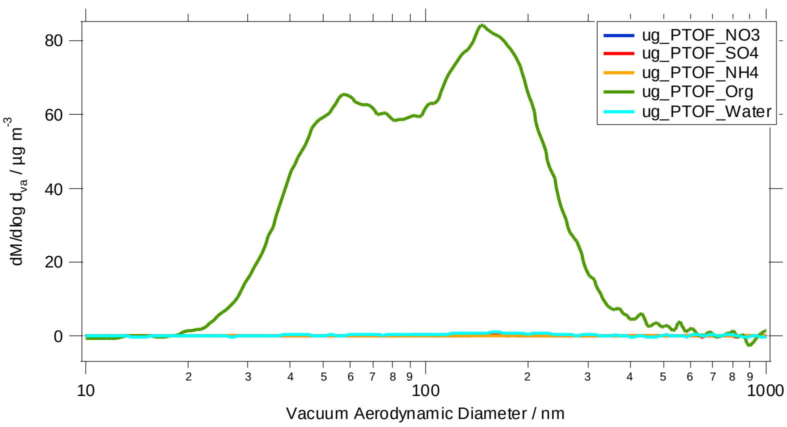

Fig.3 Particle size distribution of diesel exhaust measured by TOFAMS (Idling)

These tree mass spectrums are bear close resemblance. Figure 5 shows relationship of mass fragment signal. X axis is mass fragment signal of 20-50nm and Y axis are mass fragment signal of 50-100nm and 100-200nm. Only signal of m/z 41 and m/z 28 are not on the straight line, although another plots in this figure are on the every straight line. It is thought that m/z 41 indicate fragment ion of $C_3H_5^+$ and C_2HO^+ and m/z 28 indicate fragment ion of $C_2H_4^+$ and CO^+. In this results, composition portion of include oxygen are not constant according to particle size, although composition portion of consist of only carbon and hydrogen are not change according to particle size. This result indicate large size particles include rich oxygen include components. Such analysis is able to make possible by means of development of TOFAMS.

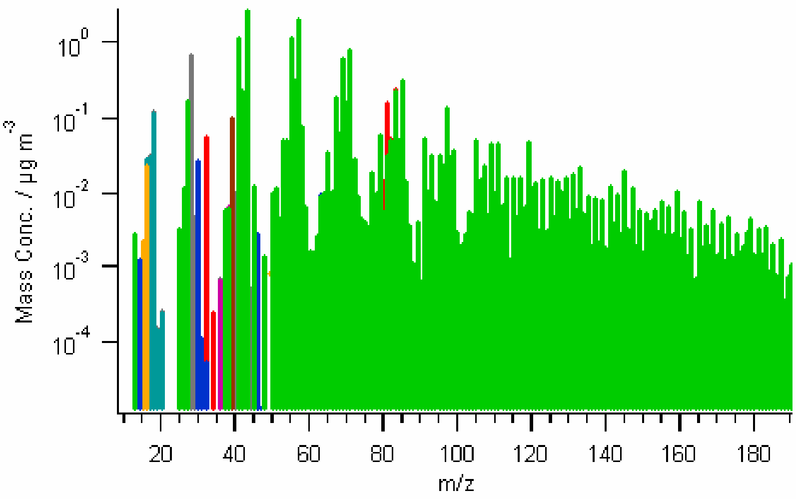

Fig.4(a) Mass spectrum of particle size add up 20-50nm

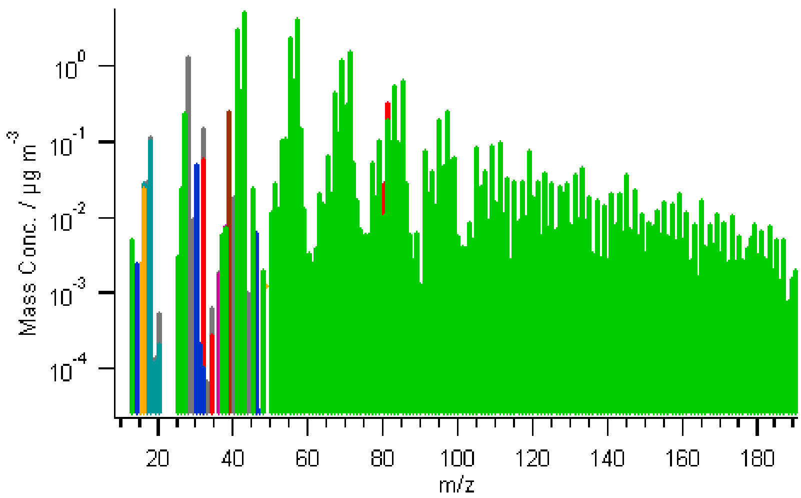

Fig.4(b) Mass spectrum of particle size add up 50-100nm

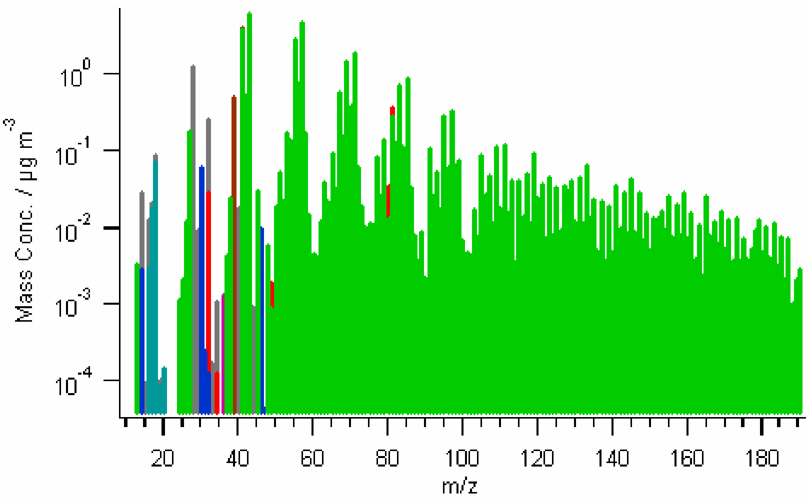

Fig.4(c) Mass spectrum of particle size add up 100-200nm

Fig.4 Particle size depend mass spectrum of diesel exhaust particles. (Idling)

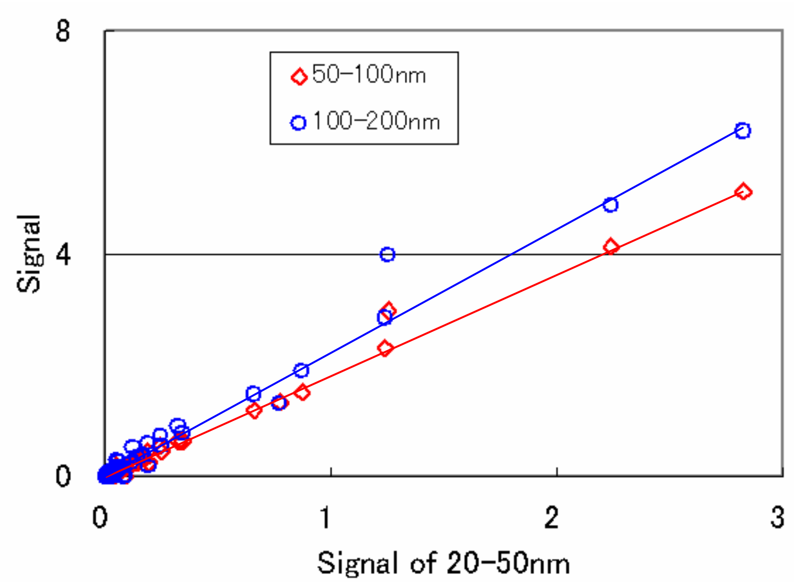

Fig.5 Comparison of signal of every mass fragment.

3.2 Trial of automotive exhaust particles continuous measurement

Automotive exhaust trial measurement is performed with TOFAMS. Figure 6(a) shows continuous measurement result of direct diesel (3000cc, without cat.) exhaust particles organics composition when trapezoid mode running. Figure 6(b) shows enlargement of this data. There are every second size distribution of organics. In this result, it is observed that mode diameter of organic particle decrease when deceleration. When 50km/h running, mode diameter of organic particle is about 100nm, after deceleration, mode diameter of organic particle changed to about 40nm.

Figure 7 shows continuous measurement result of mass fragment signals of m/z69 and m/z71. Ratio of these two fragment ions indicate oil and fuel ratio. When fuel ratio is rich in organic composition, signal of m/z71 is higher than signal of m/z69, when oil ratio is rich, signal of m/z69 is higher than signal of m/z71. In this result, when car speed is stable, oil/fuel ratio in organic composition is not stable, although oil portion increase when deceleration.

4. CONCLUSIONS

Particle size depend mass spectrum measurement and second by second continuous measurement of automotive exhaust particle was established in this study by means of development of TOFAMS.

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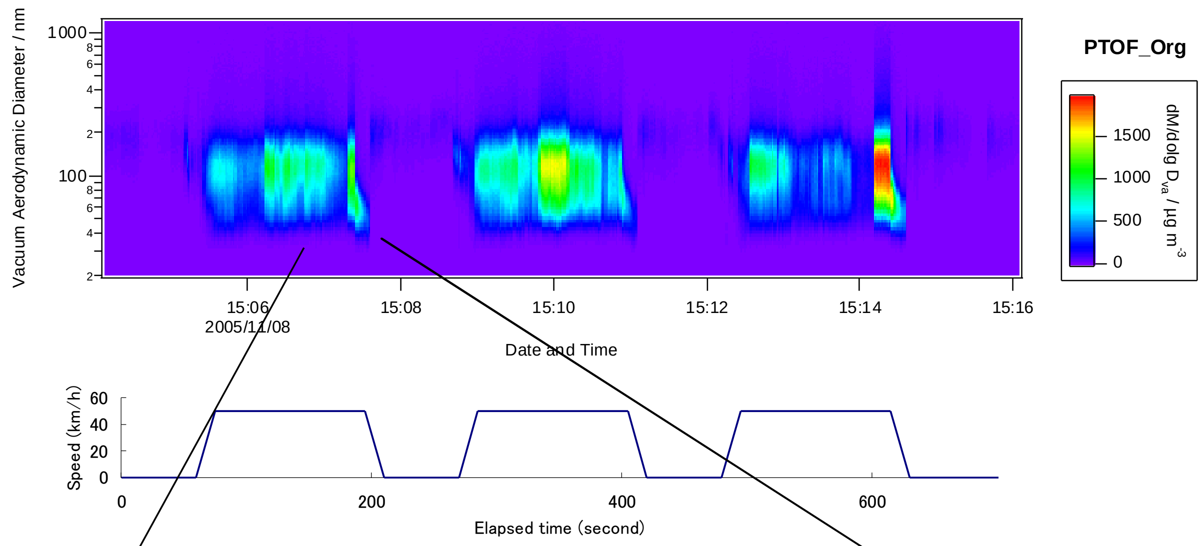

Fig.6(a) Continuous measurement result of organic particle size distribution.

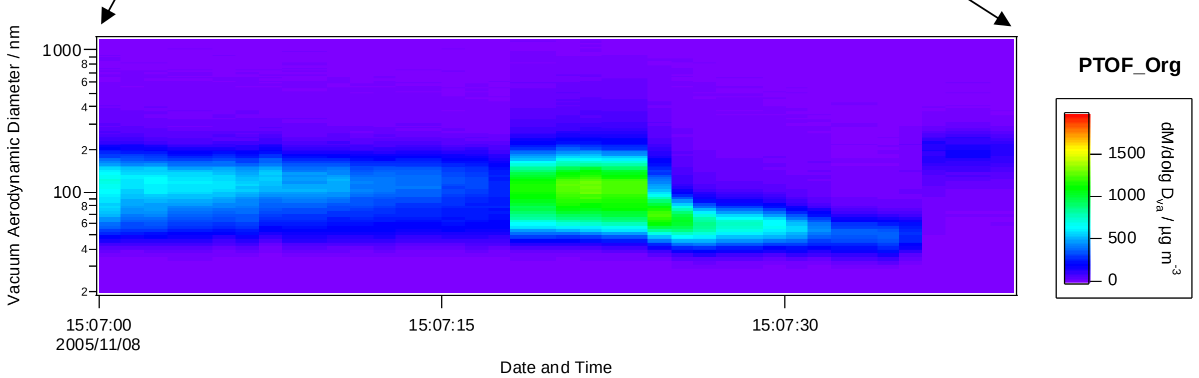

Fig.6(b) Continuous measurement result of organic particle size distribution (enlargement).

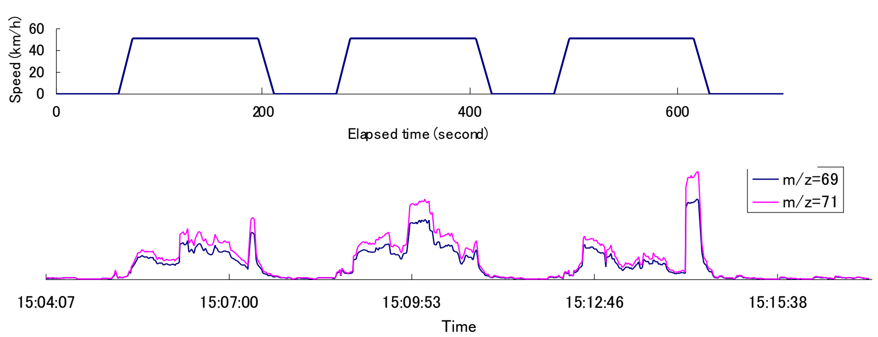

Fig.7 Continuous measurement of m/z 69 and m/z71 (oil fuel ratio)