11 Probe of Different Generation Routes for Organic Carbon and Elemental Carbon Diesel Particles Using Single Particle Mass Spectroscopy

-Statistical data analysis of DPM using SPMS-

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Diesel particulate matters (DPM) often contain small amounts of metal as a minor component but major contributor to adverse health effects. The knowledge of mechanism for formation as well as size preference of the trace metal is highly needed to mention about health concerns. To achieve this, size and composition of each particle should be measured at the same time. A single particle mass spectroscopy (SPMS) would be a best tool for the objectives. Here, we will introduce newly finding with SPMS about the mechanism and distribution of the trace metals.

***Keywords*: Single Particle Mass Spectroscopy, Diesel Particulate Matter, Characterization, Metal Contents**

1. INTRODUCTION

Diesel Engine emits tri-modal particulate matters at the concentration as high as 10^9 particles/cm^3 [(1)]. Nuclei- and accumulation-mode particles among them are known as species of the most harmful aerosols because of their deep penetration and easy deposition into human lung. Also coarse-mode DPM often contain alkali and transition metal species such as Ca, Al, Na, Ba, Zn, Fe, Se, Mg and so on [(2)]. It have been thought that the metals originate from lube oil via reverse blow-by process, mechanical wear of break pad, and combustion of metal-containing fuel additives such as ferrocene or cerium. But, there have been no report to give answers on the following questions: how much metals are in a particle (single particle analysis of metals), whether or not metal contents are the same in particles with different sizes (size preference of metals), and how and where they form (mechanism of metal formation). These fundamental questions motivate this research.

Recent interest in adverse health effects of DPM initiated researches relevant to in-situ measurement of size of DPM at various engine modes. For examples, Kittelson and Zachariah's group have reported that metal contents in DPM played a catalytic role in carbon oxidation inside engine or even flame using tandem differential mobility analyzer (TDMA) [(3-5)]. Hence, the technology for sizing nanoparticles seems to be well established, while in-situ quantitative single *nanoparticle* mass analysis doesn't do that to date. An ideal tool if exists should be capable of measuring size and chemical composition of single nanoparticle at the same time. Aerosol time-of-flight mass spectroscopy (ATOFMS or AMS) might be closest to the tool. Prather group indeed reported the simultaneous measurement of size and compositions of particles [(2,6)].

But, as AMS employs light scattering for sizing particles as well as triggering the ionizing laser, the measurable size of particles are often limited larger than 200nm. This hinders the use of that machine to the nuclei- and accumulation-mode particles that are more important in the health effect. Also the power of conventional laser installed to AMS may appear to be not enough for complete ionization of a particle, because their mass spectra consist of only molecular positive and negative ions. The different polarity of such ions facilitates the rapid recombination and charge transfer from ions with larger ionization potential (IP) from those with less IP [(7)]. This yields some bias in the composition of the particle. From this reason, majority of researches are focused to report qualitative assignment of molecular species composing an environmental particle rather than quantification. Here, we recently showed that a use of much stronger laser pulse seemed very likely to solve these problems [(8)]. Also we demonstrated that the SPMS with the capability of simultaneous measurement of size and composition of particles could be used to elucidate various nanoscale phenomena, for examples, finding solid state reaction kinetics inside a nanoparticle [(7)], and size-resolved surface reaction kinetics [(9)]. In this study, we applied the SPMS to explore the origin of metals and size preferences of metals originating from metallic fuel additives and lube oil. In addition, we extract statistical data from the single particle analyses and eventually, address the mechanism of formation of metals.

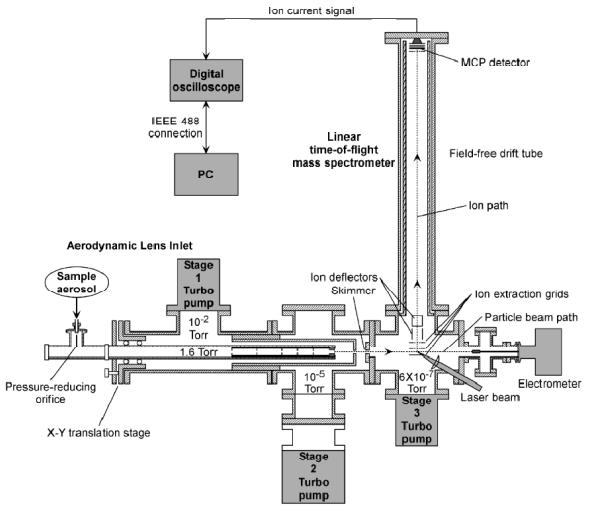

Fig. 1. Schematic of Single Particle Mass Spectrometer.

2. EXPERIMENTAL

Our SPMS consists of an aerodynamic inlet, a source region for particle-to-ions conversion with a free firing high powered Nd:YAG laser, a linear time-of-flight (TOF) tube and a multichannel plate detector (MCP), as shown in Fig. 1. The aerodynamic lens inlet is employed to separate particles from the carrrier gas and collimate them such that they can be injected with traveling losses through differentially pumped chambers to the ionization region. As configured, positive ions formed from a particle by multi-photon laser ionization are accelerated along ~1 m long linear TOF tube and detected with MCP. More details for the instrumentation of SPMS are described elsewhere (7-9).

The source of diesel particulate for this work was an Onan-Cummins "QuietDiesel" genset powered by a three cylinder, 1.5 liter Isuzu engine. This unit is capable of providing 10kW of continuous AC power at a fuel flow rate of about 4 kg/hr. In order to maintain a steady 60Hz of AC current from the generator, the fuel flow to the engine is controlled by an electronic governor actuator that maintains a constant engine speed of 1800 rpm. The load on the engine is provided by loading the generator outlet with a resistive load bank made by the Simplex Company.

For most of our experiments, the engine was run at two conditions i.e. no-load and 6kW load unless otherwise noted. The corresponding fuel flow rates were 1.0kg/hr and 2.25kg/hr. It should be noted that the size distribution of particles generated by this relatively small engine varies somewhat from that of typical heavy duty engines. Under normal operating conditions it produces no discernable nuclei mode and the accumulation mode decreases with engine load rather than increases as it does for most larger engines. The dilutions of exhaust gases and DPM were made using a probe of 3mm ID inserted into 10cm ID tube.

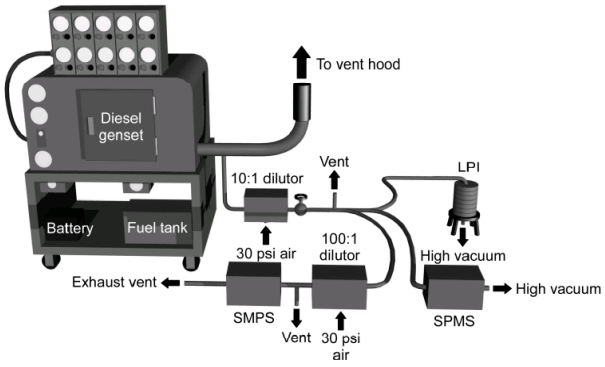

Fig. 2. Sampling and dilution of DPM using exhaust probe. and ejector dilutor.

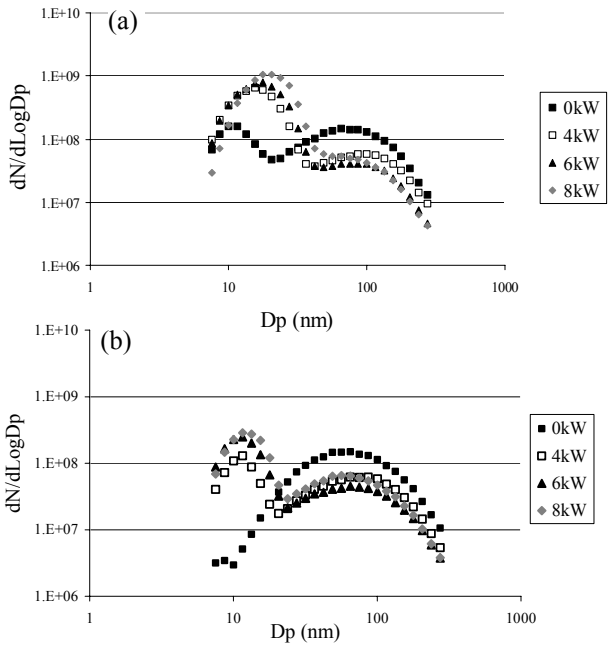

Fig. 3. Size distributions of DPM at various engine loads which is doped with (a) 60 ppm Fe and (b) 20 ppm Fe.

Cold-flow calibration using a bubble flow meter at the dilutor inlet and a rotameter at the outlet, yielded a dilution ratio of approximately 10:1 for this setup. For measurements of particle size distribution with the SMPS, the flow was further diluted as shown in Fig. 2, using a second ejector dilutor. To investigate the effects of metals on DPM formation, we added first a ferrocene as an iron source, the amount of which was varied from 20 ppm to 60 ppm. Secondly 1% lube oil (SAE 15W-40) was directly doped to the fuel tank to see the effect of metal intake through the reverse blow-by. The amount of doped metals is too large to simulate normal lube oil consumption, but is used as a means of adding metals to particles for catalytic effects.

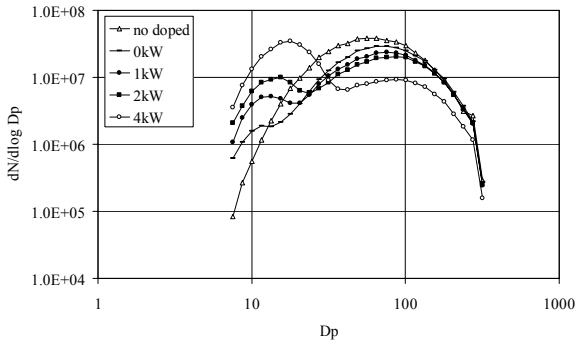

Fig. 4. Size distributions of DPM at various engine loads which is doped with 1% lube oil.

Table 1. Elemental components and their properties of l;ube oil of SAE 15W-40 (John Deere TY6391).

Elements	Weight (%)	IP (kJ/mol)	Psat	
			torr	°C
Ca	0.29	590	$\sim 10^{-8}$	282
Zn	0.14	960	8×10^{-4}	280
P	0.13	419	1	261
Mg	0.04	738	$\sim 10^{-5}$	282
S	0.33	1000	1	189
C		1087	$\sim 10^{-8}$	1657
Fe		762	$\sim 10^{-8}$	892

3. EFFECTS OF METALS ON DPM SIZE

As described in the previous section, we tested two metal sources such as ferrocene and lube oil. First we would like to show the effect of the ferrocene on DPM size. Fig. 3a shows that when the fuel is doped with 60ppm iron, the size distribution of particles contains a distinct nuclei mode that increases with engine load. This increase in self nucleated metal particles reflects higher metal throughput, since the increase in load results in higher fuel flow rates and thus higher metal throughput. As the doping rate is reduced to 20ppm (Fig. 3b), the iron content is lowered and the nuclei mode eventually disappears at 0kW engine load as illustrated in the figure.

For both doping levels (Figures 3a and 3b), the size distribution is strongly bimodal in the range measured by the SMPS and the dilution-corrected total number concentrations vary from about 5×10^7 #/cc to about 5×10^8 #/cc (higher numbers being reflective of the increasing number of nuclei mode particles at high engine load). The accumulation mode particles are shown to decrease as load (and thus both engine temperature and metal content) goes up, especially during the initial increase from 0 kW to 4 kW load.

When 1% lube oil is doped to the fuel, the nuclei mode of DPM begins to appear even at relatively low engine load (1kW). The remarkable difference between the ferrocene and lube oil may be amounts of metals introduced to the engine. Note that 1% doping of lube oil corresponds to more than 1000ppm of total metals in the mixed fuel (see table 1).

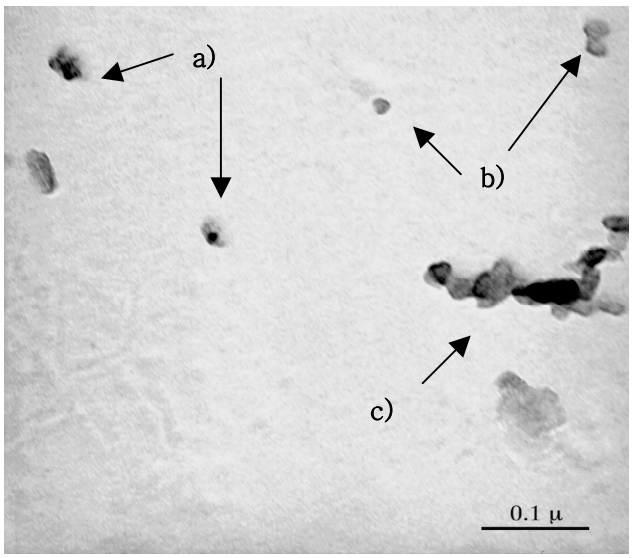

Fig. 5. TEM images representing the three classes of DPM doped with Fe at 6kW load and high Fe doping.

As compared to the doping level of ferrocene, much higher metals may enhance carbon oxidation in engine, leading to reduction in number of preexisting carbon particles [12]. In turn, gaseous metals do not find sufficient sites for condensation. It is probable that the metals instead tend to self-nucleate. The self-nucleation process should be pronounced at higher dose of metal source, i.e. in the lube oil case, which may explain the more pronounced nuclei mode. The same trend was observed by Kyto et al. [13]. Another interesting thing is that the absolute number concentration of DPM is lower than that of Fe-doped DPM by a factor of 3 especially for accumulation mode. This may be also resulted from the enhanced catalytic effects of metals.

4. COMPOSITIONAL ANALYSIS OF DPM

Classes of DPM according to mass spectra

The nuclei mode of DPM is generally considered to consist of two particle types; nonvolatile inorganic ash that nucleates at high temperatures in the engine [10], and condensed volatile materials such as sulfates and unburned fuel or oil which self nucleate later during the dilution/cooling of the exhaust aerosol [11]. The accumulation mode on the other hand, which would be the third type of particle, is said to consist mainly of "spherules" i.e. primary particles of elemental carbon, coagulated into agglomerates, with other materials adsorbed onto the surface. Particle mass spectra are sorted into two classes according to the ratio of hydrogen (H) to carbon (C) as a criterion, i.e. organic carbon (OC when $H/C > 1$) and elemental carbon (EC when $H/C < 1$). The third class is pure metal where metal to carbon ratio is larger than 10. These are metal nanoparticles (presumably self-nucleated in the engine). Fig. 5 shows distinct differences in morphology and size for the three classes of particles at the dose of iron.

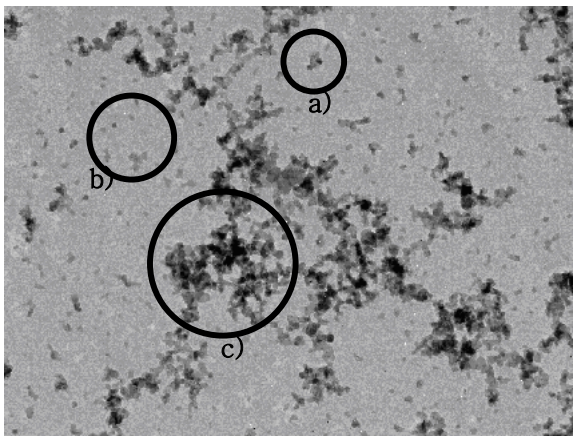

Fig. 6. TEM images representing the three classes of DPM doped with 1% lube oil at 6kW engine load.

The dark spot of the figure, say a), corresponds to Fe rich particles, i.e. the third class, which was confirmed by energy dispersive X-ray spectroscopy (EDS). The non-agglomerate light gray particles of (b) are organic carbon, while large agglomerate of (c) contains elemental carbon and iron as well, which is attributed to coagulation between them. Typical mass spectra also show consistently the changes in composition (not shown here).

The classification process was carried out for the dose of lube oil. According to Table 1, the oil contains various metals, so one may predict that TEM images and EDS of the DPM should show a composite of the four metal elements such as S, Ca, Zn, and P. Also the relative abundance of each element in such composite may have to decrease in that order. But, surprisingly, the particle mass spectra show that the metals as a form of isolated metal-rich spherule primarily consist of Ca rather than other metal elements. Actually, this is not that big surprise because S, the most abundant species, are likely to exist in vapor phase due to their high saturation vapor pressure (refer Table 1). Fig. 6 shows that the morphology of the DPM with dose of lube oil is pretty similar to that of the Fe-doped DPM. EDS measurements for DPM denoted by circle in the figure clearly show that the dark areas in DPM contain a lot of Ca and the nuclei mode particles are self-nucleated hydrocarbon and metal rich particles. The difference of this from Fig. 5 is that the light gray particles, i.e. organic carbon particles are more abundant than metal-rich nuclei.

Species size distribution

More than 500 mass spectra for each condition are collected and analyzed by our own computer program that is able to search, assign elements to, and analyze peaks in a mass spectrum. Such given total area of peaks versus time of flight in a mass spectrum is converted to volume equivalent size of the corresponding particle by an adequate volume-peak area correlation [8]. The whole analyses for 500 mass spectra data is finished within half an hour. We can extract any statistical relations from a collection of the analysis results.

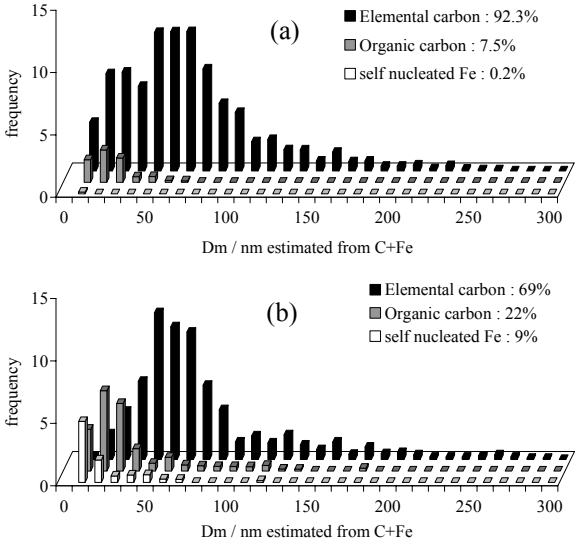

Fig. 7. Size distributions of three species of DPM doped with 60ppm Fe at (a) 0kW (b) 6kW engine load.

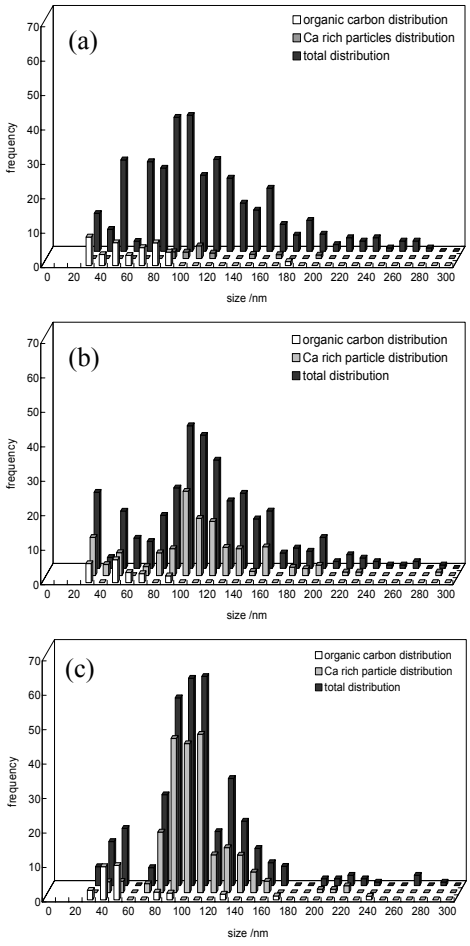

Fig. 8. Size distributions of three species of DPM doped with 1% lube oil at (a) 0kW, (b) 2kW, (c) 6kW engine loads.

This is a unique and striking benefit of single particle analysis and makes SPMS so useful in nanotechnology and any research fields dealing with nanoparticles as well.

A. Fe-doped DPM

Before looking at detailed particle stoichiometry, we present the SPMS results for the three classes of DPM (explained in the previous section), in terms of the frequency distribution of each class as a function of particle size. Fig. 7a shows that at low engine load and high ferrocene doping rate, the "elemental carbon" particles are widely distributed, with a peak at around 70nm, and constitute the bulk of the particulate material, which coincides with the distribution of agglomerate particles i.e. the accumulation mode particles shown in Fig. 3a. Fig. 7a also shows that the "organic carbon" particles are distributed in the lower size range (< 50 nm) i.e. the lower-side tail of the accumulation mode. Under the conditions for Fig. 7a we see virtually no "pure iron" particles. This is probably due to higher carbon generation at low load, preferentially facilitating Fe adsorption onto carbon particles rather than nucleation of Fe. The result is that at the lower load, the nuclei-mode iron particles as measured by mobility diameter (Fig. 3a), are fewer in number and almost all less than 30 nm in diameter, and in that range the mass-spectrometer has poor particle transmission efficiency [7].

At higher engine load, the increase in Fe throughput combined with inherent soot reduction yields a higher Fe/C ratio, so the pure iron particles have increased in number and grown in size to a point where the aerodynamic lens is able to transmit them more efficiently to the ionization laser. Fig. 7b shows that at 6kW engine load, about 9% of the detected particles (by number) are pure iron nanoparticles. Note that in this figure the size distribution of the elemental carbon particles has not changed significantly, which is consistent with the SMPS measurement in Fig. 3a.

B. 1% lube oil-doped DPM

When various metals in the form of lube oil are added to the fuel, the species distribution is somewhat different from the previous. Three interesting things are found in this case as follows: 1) no distinct self-nucleation of metals even at higher total dose of metals, 2) dominance of Ca rich particles even in accumulation mode, i.e. they are already not in nuclei mode, 3) seemingly underestimation of nuclei mode particles as compared to in the iron doping case. All points are essentially inter-related through the thermo-physical properties (vapor pressure) of metal and the mechanism of metal forming. Though more Ca is added than Fe, the higher vapor pressure of Ca enables itself to exist in vapor phase during expansion process. The vapor is in turn condensed into the preexisting DPM. This is a possible route for Ca forming.

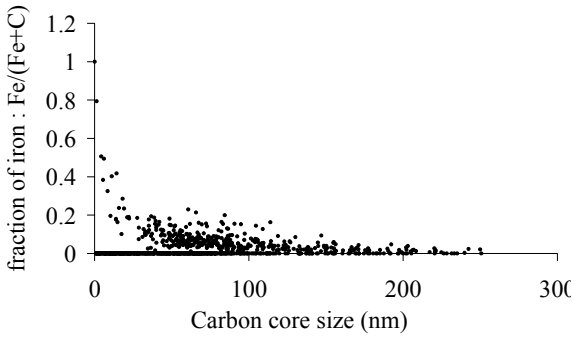

Fig. 9. Metal fraction in 20ppm Fe-doped DPM as a function of carbon core size at no engine load.

But, here one may raise an issue related to the amount of Ca exceeding the other species (contained inthe oil) and even carbon. Elemental carbon seems very likely to be much more reduced due to catalytic effect and high dose of Ca (compare Figures 3 and 4). The function of Ca for enhancing carbon oxidation was demonstrated with thermo-gravimetric analysis by Miyamoto et al (14). Also, since much of the sulfur leaves the tailpipe as vapor-phase SO2 due to its high vapor pressure, only a few percent of sulfur is known to convert to particulate sulfate. Thus, the recondensed Ca may be primary species detected by SPMS.

But, we are not at the position where to give an answer to whether Ca is self-nucleated or not, because it is also possible that the Ca particles in accumulation mode may be resulted from violent coagulation between self-nucleated Ca particles. There remains another question, why big nuclei-mode peak in Fig. 4 are not shown in Fig. 8, which is not consistent with Fe-doped DPM.

We would note that the size measured by SMPS is electrical mobility size (~ aerodynamic size), while the size by SPMS is volume equivalent size. In other words, even if the Fe rich and Ca rich particles have same aerodynamic size and pass though the aerodynamic lens with the similar transmission efficiency, the heavier Fe rich particles can have smaller volume. Therefore, in contrast to Ca, detectable size range of Fe particles with SPMS spans to smaller size. This may be the reason for the question or the third point (apparent underestimation of nuclei mode).

Stoichiometry of species in metal-doped DPM

To confirm the above-mentioned mechanism of metal forming, we draw a plot of metal-to-carbon ratios against carbon core size. Fig. 9 represents the ratio is strongly correlated with preexisting carbon core size and proportional to $D_{m,c}^{-1.3}$ that is mobility size of the carbon core. Again we would note that in the free molecular regime, recondensation rate of volatile species is proportional to the surface area of preexisting particles, while in the continuum regime it is directly to the size. In turn, the ratio should have size dependence of $D_{m,c}^{-2}$ for continuum regime or $D_{m,c}^{-1}$ for free molecular regime. The proximity of the dependence to $D_{m,c}^{-1}$ reflects that the iron

vapors condense onto the carbon cores just after engine and/or through tail pipe, because if the condensation occurs inside engine, high pressure condition(continuum regime) should show the $D_{m,c}^{-2}$ dependence.

On the other hand, as engine load or the amount of dose increases, nucleation and subsequent coagulation between nuclei and carbon agglomerate make the data scattered from the correlation seen in Fig. 9. This becomes more pronounced at all conditions of lube-oil doping case, which is explained mainly by the higher dose of metals.

5. CONCLUSIONS

We demonstrate for the first time that single particle mass spectroscopy can be successfully used to characterize individual diesel exhaust particles in terms of size and composition. From the data sets, we extract several interesting relations which are meaningful in statistical view. When small amount of metal is introduced to the engine as fuel additives, the metal vapor from the disintegration of metals in engine condenses onto the pre-existing carbon spherules somewhere along tailpipes. As more metals are added, the governing mechanism is shifted from condensation to nucleation and subsequent coagulation between nuclei and pre-formed agglomerates. The relative dominance between nucleation and coagulation is determined by not only the dose of metals but thermo-physical properties of metal vapor.

ACKNOWLEDGEMENT

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