Available online at www.sciencedirect.com

ScienceDirect

Journal of Environmental Sciences 21(2009) 452–457

JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Morphological and semi-quantitative characteristics of diesel soot agglomerates emitted from commercial vehicles and a dynamometer

LUO Chin-Hsiang[1,*], LEE Whei-May[2], LIAW Jiun-Jian[3]

1. Department of Safety, Health and Environmental Engineering, Hungkuang University, Taichung 43302, Taiwan, China. E-mail: andyluo@sunrise.hk.edu.tw
2. Graduate Institute of Environmental Engineering, "National" Taiwan University, Taipei 10617, Taiwan, China
3. Graduate Institute of Information and Communication Engineering, Chaoyang University of Technology, Taichung 41349, Taiwan, China

Received 11 April 2008; revised 24 September 2008; accepted 20 October 2008

Abstract

Diesel soot aggregates emitted from a model dynamometer and 11 on-road vehicles were segregated by a micro-orifice uniform deposit impactor (MOUDI). The elemental contents and morphological parameters of the aggregates were then examined by scanning electron microscopy coupled with an energy dispersive spectrometer (SEM-EDS), and combined with a fractional Brownian motion (fBm) processor. Two mode-size distributions of aggregates collected from diesel vehicles were confirmed. Mean mass concentration of 339 mg/m^3 (dC/dlogd_p) existed in the dominant mode (180–320 nm). A relatively high proportion of these aggregates appeared in PM1, accentuating the relevance regarding adverse health effects. Furthermore, the fBm processor directly parameterized the SEM images of fractal like aggregates and successfully quantified surface texture to extract Hurst coefficients (H) of the aggregates. For aggregates from vehicles equipped with a universal cylinder number, the H value was independent of engine operational conditions. A small H value existed in emitted aggregates from vehicles with a large number of cylinders. This study found that aggregate fractal dimension related to H was in the range of 1.641–1.775, which is in agreement with values reported by previous TEM-based experiments. According to EDS analysis, carbon content ranged in a high level of 30%–50% by weight for diesel soot aggregates. The presence of Na and Mg elements in these sampled aggregates indicated the likelihood that some engine enhancers composed of biofuel or surfactants were commonly used in on-road vehicles in Taiwan. In particular, the morphological H combined with carbon content detection can be useful for characterizing chain-like or cluster diesel soot aggregates in the atmosphere.

Key words: diesel soot; fractal morphology; carbon; fractional Brownian motion

DOI: 10.1016/S1001-0742(08)62291-3

Introduction

Exhaust soot from internal combustion engine is a complete mixture consisting of unburned carbon solids and toxic elements that are associated with a number of adverse public health by inducing respiratory diseases. Typically, fractal morphology of diesel soot aerosols is a physical property of interest for agglomerate formation, source identification, and relative oxidation. According to the definition by Mandelbrot (1983), the major fractal parameter, fractal dimension (D_f), can be successfully determined by various techniques, such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM) image analysis, light scattering, and size- and concentration-dependent investigations, which are usually based on the mobility of particles. When calculating D_f of soot agglomerates through numerical calculation or semi-empirical estimation, several pre-factors, such as diameters of spheroids and aggregates, distance and overlap coefficients between two spheroids, number of spheroids in an aggregate and radius of gyration of an aggregate, must be considered (Wentzel *et al*., 2003; Park *et al*., 2004). Furthermore, D_f derived from two-dimensional (2D) image projection of three-dimensional (3D) structures inherent in real particles was 10%–20% lower than the true D_f (Rogak and Flagan, 1992). Considering neither the interaction between these geometric variables nor a projection-induced error, D_f value for fractal-like diesel soot agglomerates was effectively obtained by a fractional Brownian motion (fBm) processor (Luo *et al*., 2005a).

Briefly, fBm analysis can derive the fractal parameter, Hurst coefficient (H), as Eq. (1) (Wen and Acharya, 1998; Luo *et al*., 2004).

$$B_H(t) = \frac{1}{\Gamma(H+\frac{1}{2})}\left(\int_{-\infty}^{0}((|t-s|^{H-\frac{1}{2}} - |s|^{H-\frac{1}{2}}\,\mathrm{d}B(s) + \int_{0}^{t}|t-s|^{H-\frac{1}{2}}\,\mathrm{d}B(s)\right) \quad (1)$$

where, $B_H(t)$ is a non-stationary zero-mean Gaussian

* Corresponding author. E-mail: andyluo@sunrise.hk.edu.tw

random function. The fluctuation of soot aggregate textures can be presented by $B_H(t)$, where two time variables are t and s. The H value ranges from 0 to 1, and is related to the fractal dimension by $D_f = 2 - H$ for 2D images. The surface roughness of selected subject, such as a soot aggregate, is represented by the specific function in Eq. (1). The fractal parameter, H is evaluated by the fBm processor, an image processing program. Luo *et al*. (2005a) directly confirmed that the average H for soot agglomerates from a diesel dynamometer was about 0.284. The multiscale H for gunpowder, industrial particles with Fe, clay particles from soil, carbon-rich particles, and soot aggregate from wood combustion were 0.455, 0.332, 0.439, 0.567, respectively (Luo *et al*., 2004), and 0.170 transformed from the average D_f of 1.830 (Gwaze *et al*., 2006). Additionally, the average H for four kinds of airborne allergenic pollens that are prevalent in Taiwan was about 0.905 determined using fBm analysis (Luo *et al*., 2005b). Consequently, H is a also useful classification index between diesel soot aggregates and particles emitted from other sources.

X-ray energy-dispersive spectrometer (EDS) coupled with SEM or TEM/EDS has been wildly used to detect elemental fractions of single airborne particles (Paoletti *et al*., 1999; Allouis *et al*., 2003; Chen *et al*., 2006). Soot aggregates are the predominant carbonaceous aerosols containing high level of carbon. Carbon fraction and size, microstructure and external shape for diesel soot were determined by the fuel quality and engine operational conditions (Burtscher, 2005).

Previous results discussed above implied that the combustion process and fuel influence the morphology and chemical composition of exhaust particles. Therefore, fBm processor was performed in this study to obtain the fractal parameter (H) of the soot aggregates, which were sampled from a diesel engine dynamometer and 11 on-road diesel vehicles, by calculating the texture fluctuation signal in the SEM image. Moreover, the elemental fractions of single soot aggregates were also investigated by SEM/EDS. The combination of H quantification and chemical element detection is likely an effective approach for identifying and classifying diesel soot emissions in an atmospheric environment.

1 Experiment

1.1 Soot collection

Commercial vehicles in use and a model dynamometer were set for producing diesel soot. Eleven tested vehicles (a–k) were equipped with three types (L4, L6, V8) of diesel engine and mounted on an electric dynamometer and control systems that were varied in engine speed (r/min) and relative loading rate. A larger number of cylinders generates large displacement (c.c.) and a high peak power. All vehicles were used for 9–16 years and had a mileage of 1.5×10^5–2.8×10^5 km. Under peak power/engine speed (kW/(r/min)) for each vehicle (Table 1), tract sampling for combustion particles was programmed run for 5 min. To follow the US Transient Cycle Test for well-characterized fuel load and combustion, the laboratory dynamometer (Model GS 350, Schenk, Germany) was fed with the heavy diesel with a specific density 0.95 and < 50 ppmw of sulfur. Although the exact concentration of sulfur was not detected, the same tank of fuel was used for the whole test. With exhaust temperature/torque of 726/367 (°C/Nm), the operational condition of a high power/engine speed of 112/2900 (kW/(r/min)) was selected to closely simulate the energy output of test vehicles.

Figure 1 presents the overall setup of the soot agglomerate sampling. Exhaust soot samples from the model dynamometer and test vehicles were collected by a stainless probe, and then passed through the dilutor (Model VKL 100S, Palas GmbH, Germany) and a modified chamber to dilute to a ratio of 1:2000 with air pretreated by a high-efficiency particulate air (HEPA) filter and an activated carbon column. Dilution air was at about 25°C and 50% relative humidity. After dilution, final temperature was about 30–50°C. Some heat transfer is obvious when warm dilution is performed, but this effect should be negligible at this low temperature. The systematic loss for small particles of a diameter < 50 nm was about 25%, but it became negligible for larger particles. Under isokinetic sampling at flow rate 30 L/min, 3 cm^2 cleaned mica slice partially coated for the each stage of the 10-stage micro-orifice uniform deposit impactor (MOUDI, Model 110, MSP Co., US) was utilized to segregate individual soot particles separated from the output dilutor

Table 1 Technical information and usage status for 11 diesel vehicles

Vehicle code	Engine type	Displacement (c.c.)	Vehicle weight (kg)	Mileage (km)	Vehicle age (year)	Peak power/engine speed (kW/(r/min))*
a	L4	2545	3500	285655	12	60/2700
b	L4	2659	3490	189075	14.5	60/3500
c	L4	2476	2400	240608	11	60/2400
d	L4	2476	2400	156733	9	60/2400
e	L4	2835	3490	172278	12	65/3400
f	L4	2184	2660	146317	15	46/4250
g	L4	2835	3490	199309	12	65/3400
h	L6	6925	8900	276509	13	119/3000
i	L6	7412	13500	281808	12	145/2900
j	L6	6919	10300	198602	16	130/2900
k	V8	13688	21000	242590	12.5	250/2200

* An electric dynamometer was in control of engine speed value for a peak power output.

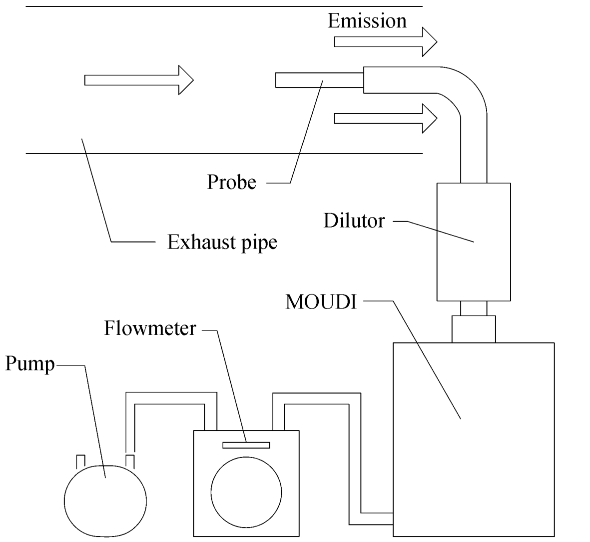

Fig. 1 Sampling setup for exhaust soot aggregates from the vehicles and dynamometer.

flow. This MOUDI collected particulate samples with cut-off diameters of 56 nm to 18 μm. Dilution of exhaust was critical for the following SEM/EDS detection to preserve the integrated structure of single soot aggregates by preventing aggregates overlapping during one sampling. To decrease moisture interference, soot samples on the mica slices were conditioned under relative humidity of 40% and 20–25°C for 24 h before the SEM/EDS investigation.

1.2 SEM and fBm analysis

The abundant individual diesel soot aggregates dramatically on the mica slices of MOUDI stages were examined to obtain 2D digital images using a field emission scanning electron microscope (Model LEO 1530 FEG-SEM, Gemini, Germany) with a narrowed and focused electron beam at 1 nm. Subsequently, gray level (digital brightness) change in SEM images (magnification $\times 10^5$) was automatically parameterized as a mathematical matrix function. A 2D window size and the number of segmentation regions depend on individual soot size. Figure 2 briefly presents the segmentation size of an aggregate image can be increased from 65 × 65 to 80 × 80 pixels with equimultiple under a software adjustment. Furthermore, considering uniform sampling to the exclusion of mica background, 2–4 segmentation regions which were crowed and occupied with partially-overlapping spheroids on each image were selected to calculate the mean H value by the computer-controlled fBm processor. A four-segmented example of an aggregate image is shown in Fig. 3. Operational details of the fBm processor have been found by Luo *et al*. (2005a).

2 SEM/EDS for elemental analysis

The elements with low atomic number (6–92) embedded in the soot aggregates were determined qualitatively and quantitatively by their SEM/EDS spectra. The EDS was equipped with four sets of X-ray wavelength dispersive spectrometers. A small acceleration voltage of 10 kV was

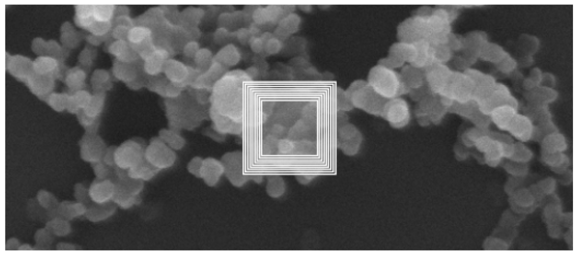

Fig. 2 Mapping H is extracted inside the window which the size is controlled with 65×65–80×80 pixels. Image magnification is $\times 10^5$.

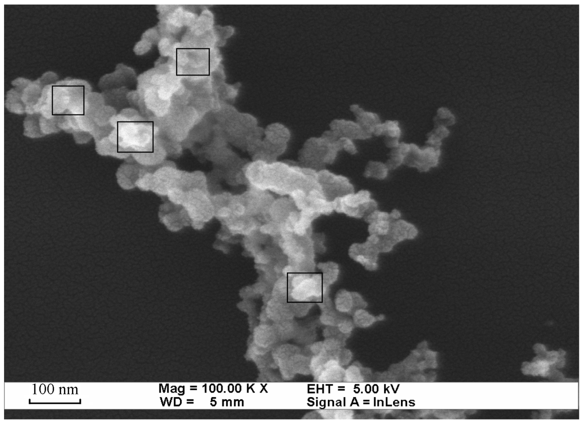

Fig. 3 Four segmentation windows are diagrammed on an aggregate SEM image by the computer-driven fBm processor. Image magnification is $\times 10^5$.

chosen to eliminate the interference caused by background and overheated deformation of aggregate structure, such as collapsed or lumpy states. Collection time of 128 s was utilized to enhance the signal accumulation for each sample. Because the focus diameter and digging depth of the X-ray detection beam in practice was approximately 0.5 μm, the background interference should be eliminated for the EDS detection on aggregates with diameter > 1 μm . Conservatively, aggregates of 2 and 5 μm in diameter were selected for the EDS approach.

3 Results and discussion

3.1 Size distribution for vehicle exhaust

Cluster or chain-like aggregates belonging to the well-defined accumulation mode with diameters of 100 nm–1 μm dominated vehicle exhaust particles which were collected in diesel vehicle exhaust. These aggregates were composed of several primary spheroids whose diameter by SEM was around 20 nm. This experimental result was close to mean spherule diameters reported in the range of 20–35 nm for diesel engine exhaust under different operational conditions (Neer and Koylu, 2006). Figure 4 shows the two-mode mass size distribution of these aggregates for the 10-stage MOUDI measurements of 11 tested vehicles. The principal mode with a mean mass concentration (C) of 339 ± 134 mg/m^3 under its size lognormal distribution (dC/dlogd_p) was located at 180–320 nm. This result was similar to an experimental result for 8-stage MOUDI measurements obtained by Moh'd *et*

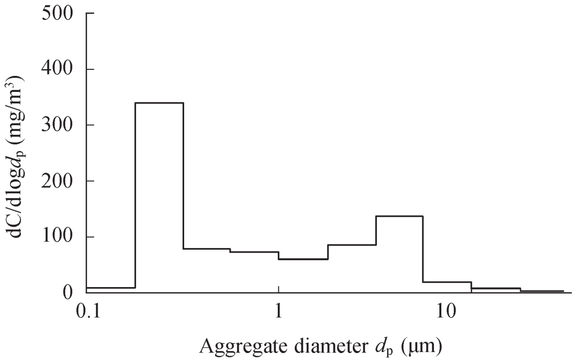

Fig. 4 Two-mode size distribution of soot aggregates emitted from 11 tested vehicles.

al. (2001). The other mode aggregates of 1.8–3.2 μm had mean mass concentration of 140 ± 47 mg/m^3. Furthermore, the total mass concentrations of $PM_{3.2}$ and PM_1 calculated by direct weight measurements were 161.36, and 124.68 mg/m^3, respectively. Consequently, PM_1 was the dominant suspended diesel soot aggregates.

3.2 Morphological Hurst coefficient for soot agglomerates

To process SEM images of soot aggregates exhausted from the dynamometer and 11 vehicles, the fBm analysis was used to estimate the fractal parameter, H. Table 2 displays the H extraction results from the soot aggregate SEM images. The numbers of analyzed aggregates (N_S) for each exhaust sample was in the range of 6–13. The number of total segmentation windows (N_W), for one sample was in the range 19–37, and dependent on aggregate size.

For 7 vehicles (a–g) with 4-cylinder engines, the arithmetic means of H for all selected segmentation regions were in the range 0.271–0.359. Mean H value was 0.245, 0.250, and 0.260 for vehicle h, i, j, respectively, which had a 6-cylinder engine. The only 8-cylinder vehicle (k) produced the fractal aggregates with the smallest H value (0.225). No obvious influence existed for H of emitted aggregates for vehicle status, such as age, weight, and mileage. Moreover, for seven 4-cylinder vehicles, H values were not connected with their displacement and peak power. Indeed, the morphological properties were also independent of engine operational conditions for three 6-cylinder vehicles. The average displacement of each cylinder was 161, 197, 214 c.c. for 4-, 6-, 8-cylinder engines, respectively. Finally, no significant calculation uncertainties appeared for all fBm measurements in Table 2.

Table 2 Fractal parameter (H) of diesel soot aggregates sampled from vehicle and dynamometer exhaust

Emission source	N_S	N_W	H	SD	Variance (%)
Vehicle					
a	13	29	0.359	0.045	12.5
b	12	31	0.359	0.068	18.9
c	6	23	0.308	0.046	14.9
d	7	24	0.271	0.040	14.8
e	6	19	0.321	0.053	16.5
f	9	29	0.321	0.051	15.9
g	7	23	0.290	0.041	14.1
h	7	22	0.245	0.057	23.2
i	7	21	0.250	0.059	23.6
j	8	31	0.260	0.049	18.8
k	8	24	0.225	0.043	19.1
Dynamometer*	9	37	0.287	0.056	20.7

N_S: the number of analyzed aggregates; N_W: the number of total segmentation windows for analyzed aggregate images; H: arithmetic mean value of H computed by fBm processor; SD: standard deviation for H.
* Controlled under a high power/engine speed of 112/2900 (kW/(r/min)).

A large number of cylinders provides a high peak power under the nearly identical engine speed. As the number of cylinders increases, relative displacement increases and provides the fuel-powered cars with efficiency improvement. High power output promotes oxidation and combustion efficiency of diesel fuel. Figure 5 presents the relationship between the number of cylinders in a vehicle and H of soot aggregates. Obviously, H value extracted from an aggregate image decreased when the number of cylinders increased. Furthermore, mean H of aggregates emitted from the dynamometer was 0.287, which was the median H value of aggregates collected from the 4- and 6-cylinder vehicles. The power output of the dynamometer at 112/2900 (kW/(r/min)) is ranged in the peak power/engine speed of the 4- and 6-cylinder vehicles. If condensation and dilution processes from the cylinder to tail pipe were equal, the H characteristics for diesel soot aggregates should be significantly affected by operational conditions supported by a various number of cylinders. Because $D_f = 2 - H$, small H means large D_f. A small H value, near to zero indicates that the segmented texture of the image fluctuates markedly (Fortin *et al*., 1992). Fluctuation implies the appearance of increased roughness in the overlapping region of primary spheroids. Therefore, the texture roughness increases as H decreases. This result can be confirmed by the DLCA calculation by Oh and Sorensen (1997). Because the morphology of aggregates can influence their reactive and toxicological properties, our results implied that the Hurst coefficient should be more concerned in future studies for the diesel exhaust.

3.3 Elemental characteristics

To control background influence, the mica slice for the sample supply was previously analyzed by EDS. Figure 6 presents the spectrum of a pure mica slice. According to

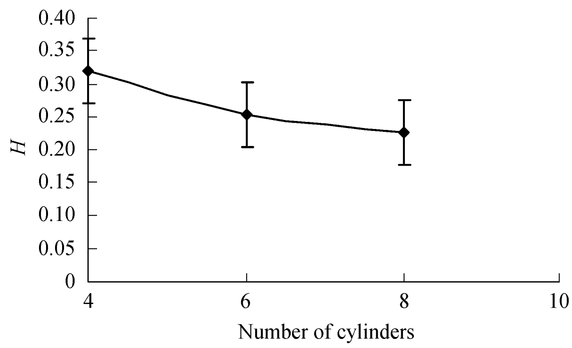

Fig. 5 Relationship between mean H values of soot aggregates and the number of cylinders equipped with three types of vehicles. Error bar means relative standard deviation.

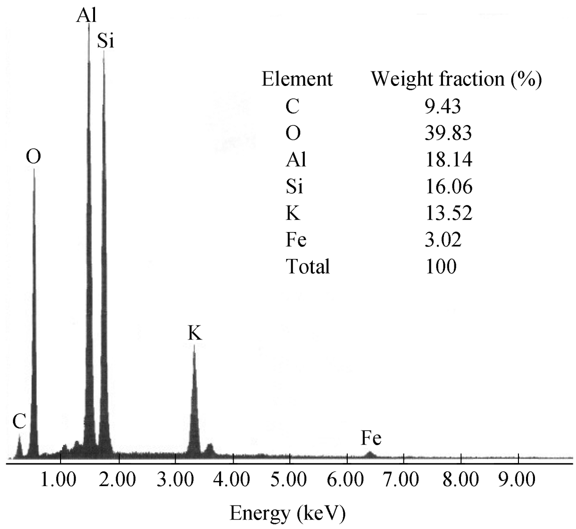

Fig. 6 EDS X-ray counts and relative contents by weight (%) for different elements in background of mica slice.

the relative amount of X-ray counts for chemical elements, the major elements in mica slices were oxygen, silicon, and aluminum; the content of each was > 15%. Element K and Fe were also found in this background measurement and thus, were not related to soot aggregates.

Without considering above five elements, carbon and some elemental traces were detected in diesel soot aggregates which had diameter of 2 or 5 μm (Table 3). Vehicles *c*, *i*, and *k* equipped with 4-, 6-, and 8-cylinders, respectively, had nearly identical mileage, age, and engine power. The observed high carbon contents in 7 soot aggregates from the dynamometer and three selected vehicles were significantly larger than 10%, which was the upper limit for the mica slice investigation. The relative carbon composition reached 63.47% (*W/W*) in the dynamometer aggregate because several trace metals, such as Na, Mg, Ti, Cr, Mn and Zn, were not detected. The heavy diesel for the laboratory dynamometer can be considered as a control fuel. In Taiwan, no regulations currently exist for functional additives or biofuel addition to on-road vehicles. However, several modified surfactants and biodiesel products should have been utilized to enhance the performance of engines, as Na and Mg elements were always detected in the aggregates from those three tested vehicles. Furthermore, Zn content (19.9%) was elevated, and the carbon fraction was then 25.98% for aggregates 5 μm in diameter from vehicle c exhaust. Generally, relative carbon content by weight was about 30%–50% for diesel soot aggregates. The true origins of the metal traces have not been resolved, implying that these traces are from fuel additives, lubricators, catalysts, and erosion loss of internal pipes, rather than the diesel fuel.

4 Conclusions

Combining fBm extraction and SEM/EDS detection was developed to investigate the fractal morphology and elemental contents of diesel soot aggregates generated by a well-controlled dynamometer and 11 commercial vehicles. Several contributions derived from our results can be summarized as follows:

(1) Signature size distribution of exhaust aggregates from commercial diesel vehicles had a high PM_1/PM_{10} ratio, implying a negative impact on human health.

(2) The fractal information for soot aggregates can be presented by a parameter of H which ranged from 0 to 1 and was related to D_f via a simple mathematical equation, $D_f = 2 - H$, for 2D SEM images. The H values of soot aggregates were 0.225–0.359, and the related D_f values were 1.775–1.641. This experimental result agrees with the findings using TEM studies reviewed by Neer and Koylu (2006).

(3) Mean H value derived from 2D SEM images of soot aggregates was markedly affected by the number of cylinders in a vehicle, suggesting that a small H value was a morphological property of exhaust aggregates from vehicles with a large number of cylinders. However, the H value was conservative for vehicles with the same number of cylinders.

(4) Based on the EDS approach, carbon content by weight was 30%–50% for diesel soot aggregates from vehicle exhaust. Different heavy metals were identified occasionally due to the variety of fuel additives and catalytic converters. However, an engine efficiency enhancer, such as modified biodiesel, was likely added into on-road vehicles in Taiwan because of the regular appearance of Na and Mg. For model dynamometer exhaust, soot aggregates produced by burning heavy diesel were composed of high levels of carbon; however, no trace metals were detected.

Considering carbon fraction and morphological H merged in soot aggregates, this study established a fingerprint for identifying particulate pollution from diesel vehicles into the atmosphere.

Table 3 Relative contents by weight (%) for different elements in 2 or 5 μm diameter diesel soot aggregates according to their EDS spectra

Sample	Diameter (μm)	C	Na	Mg	Ti	Cr	Mn	Zn
Dynamometer	2	63.47	–	–	–	–	–	–
Vehicle c	2	49.03	0.82	0.64	–	–	–	1.39
	5	25.98	4.24	0.51	–	0.21	0.90	19.9
Vehicle i	2	32.88	0.39	0.68	–	–	–	–
	5	41.21	0.50	0.64	–	–	–	–
Vehicle k	2	36.55	0.51	0.60	0.28	–	–	–
	5	48.77	0.43	0.53	0.29	–	–	–

–: Non-detectable.

Acknowledgments

This work was financially supported by the "National" Science Council of Taiwan, China (No. NSC 92 -2211-E-241-008, 96-2221-E-241-011-MY3). The authors would like to thank LEE Yuan-Tzu, a researcher at the Instrumentation Center of "National" Taiwan University for her assistance in SEM/EDS detection.

References

Allouis C, Beretta F, Alessio A, 2003. Structure of inorganic and carbonaceous particles emitted from heavy oil combustion. *Chemosphere*, 51: 1091–1096.

Burtscher H, 2005. Physical characterization of particulate emissions from diesel engine: A review. *Journal of Aerosol Science*, 36: 896–932.

Chen Y, Shah N, Huggins F E, Huffman G P, 2006. Microanalysis of ambient particles from Lexington, KY, by electron microscopy. *Atmospheric Environment*, 40: 651–663.

Fortin C, Kumaresan R, Ohley W, Hoefer S, 1992. Fractal dimension in the analysis of medical images. *IEEE Engineering in Medicine and Biology*, June: 65–71.

Gwaze P, Schmid O, Annegarn H J, Andreae M O, Huth J, Helas G, 2006. Comparison of three methods of fractal analysis applied to soot aggregates from wood combustion. *Journal of Aerosol Science*, 37: 820–838.

Luo C H, Wen C Y, Liaw J J, Chiu S H, Lee W M, 2004, Texture characterization of atmospheric fine particles by fractional Brownian motion analysis. *Atmospheric Environment*, 38: 935–940.

Luo C H, Lee W M, Lai Y C, Wen C Y, Liaw J J, 2005a. Measuring the fractal dimension of diesel soot agglomerates by fractional Brownian motion processor. *Atmospheric Environment*, 39: 3565–3572.

Luo C H, Chuang L C, Wen C Y, Liaw J J, 2005b. Projected texture characteristics of allergenic bioaerosols (pollens). *Journal of the Chinese Institute of Environmental Engineering*, 15: 199–204.

Mandelbrot B B, 1983. Fractals: Form, Chance and Dimension. San Francisco, USA: W. H. Freeman and Co.

Moh'd A Q, Matson A, Kittelson D, 2001. Combination of characterization methods for diesel engine exhaust particulate emissions. *JSME International Journal*, 44: 166–170.

Neer A, Koylu U O, 2006. Effect of operating conditions on the size, morphology, and concentration of submicrometer particulates emitted from a diesel engine. *Combustion and Flame*, 146: 142–154.

Oh C, Sorensen C M, 1997. The effect of overlap between monomers on the determination of fractal cluster morphology. *Journal of Colloid and Interface Science*, 193: 17–25.

Paoletti L, Diociaiuti M, Berardis B De, Santucci S, Lozzi L and Picozzi P, 1999. Characterization of aerosol individual particles in a controlled underground area. *Atmospheric Environment*, 33: 3603–3611.

Park K, Kittelson D B, McMurry P H, 2004. Structural properties of diesel exhaust particles measured by transmission electron microscopy (TEM): relationships to particle mass and mobility. *Aerosol Science and Technology*, 38: 881–889.

Rogak S N, Flagan R C, 1992. Characterization of the structure of agglomerate particles. *Particle and Particle System Characterization*, 9: 19–27.

Wen C Y, Acharya R, 1998. Self-similar texture characterization using a Fourier-domain maximum likelihood estimation method. *Pattern Recognition Letters*, 19: 735–739.

Wentzel M, Gorzawski H, Naumann K H, Saathoff H, Weinbruch S, 2003. Transmission electron microscopical and aerosol dynamical characterization of soot particles. *Journal of Aerosol Science*, 34: 1347–1370.