



DIESEL PARTICULATE ANALYSIS USING SEM-EDX AND LASER-INDUCED BREAKDOWN SPECTROSCOPY

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Abstract- In this paper, composition analysis using scanning electron microscopy/energy-dispersive X-ray spectroscopy analysis (SEM-EDX) and laser-induced breakdown spectroscopy (LIBS) for particulate matter in diesel exhaust is presented. Conventionally, scanning mobility particle sizer (SMPS) has been widely used to obtain particle size distribution of the suspended particles. However, real-time analysis of the composition of diesel particulate matter is difficult because of the small sized particles and rapidly exhausted. The particulates are less than a few micrometers in diameter. Real-time chemical analysis of the very small sized particles emitted from diesel fuels is facilitated with LIBS technique.

Index terms: LIBS, particulate matter, aerosol.

I. INTRODUCTION

Renewable energy sources play an important role in environment protection, particularly in preventing global warming. Hence, numerous organizations are actively involved in research programs for the development of processes that utilize biodiesel sources, hydrogen-powered fuel cells, etc. A diesel engine is more fuel efficient than a gasoline engine, and further, gas emission is very less in the case of the former. Diesel engines based on a new multistep fuel injection technique (electronically controlled common-rail injection) have been designed; in these engines, NO_x and diesel soot emission is considerably reduced. However, the exhaust gas from these engines contains fine particulate matter (PM) that cannot be filtered by diesel particulate filters (DPF) and catalytic filters.

It is known that inhalation of PM causes several health problems [1-4]. While larger particulates are filtered out in the nose and throat, smaller particulates can reach the deepest recesses of the lungs. Particulates that are less than 10 μm in size (PM₁₀) tend to settle in the bronchi and lungs. PMs that are smaller than 2.5 μm in size (PM_{2.5}) can penetrate the gas-exchange region of the lung. Therefore, it is important to develop a system for the qualitative and quantitative analysis of airborne PM and for identifying the sources of PM in the atmosphere.

Laser-induced breakdown spectroscopy (LIBS) is a useful tool for the determination of the elemental composition of various materials, and it does not require any pre-processing step. In particular, LIBS is sensitive to particulates having the smallest possible diameter (30 nm). Our research group has been developing LIBS techniques that have potential applications in various fields. A large amount of fundamental reference data on plasma emission intensity, particle size, and ambient gas pressure has been obtained [5, 6]. In addition, a quantitative calibration technique that makes use of a microdrop ejection system has been established. [7]

The LIBS technique has been used for the practical detection of diesel PM, and baseline experiments have been carried out on a sample material.

II. PRELIMINARY MEASUREMENTS

Before the LIBS analysis of PM in diesel, observations were carried out on the PM trapped in an exhaust gas filter made of Teflon-coated glass fiber. Figure 1 shows a photograph of a diesel particulate trap filter. Particulates of various sizes ranging from a few hundred nanometres to 20 μm were deposited on the filter after use. The trap filter (TX40HI-20-WW) was used to test the exhaust emissions from a diesel engine operating in the JE05 mode. Figures 2 and 3 show the enlargement of portions of Figure 1. These images are scanning electron microscopy (SEM) images of the surface of the exhaust filter before and after use, respectively. Particulates of various sizes ranging from a few hundred nanometres to 20 μm were deposited on the filter after use. Figure 3 shows PM_{2.5} adsorbed on the filter. Three sample filters (TX40HI-20-WW) were provided by Tokyo Metropolitan Research Institute for Environmental Protection. According to the information provided, these filters had been used to test the exhaust emission from a diesel engine operating in the JE05 mode; the distance covered by the engine during the test was 14 km.

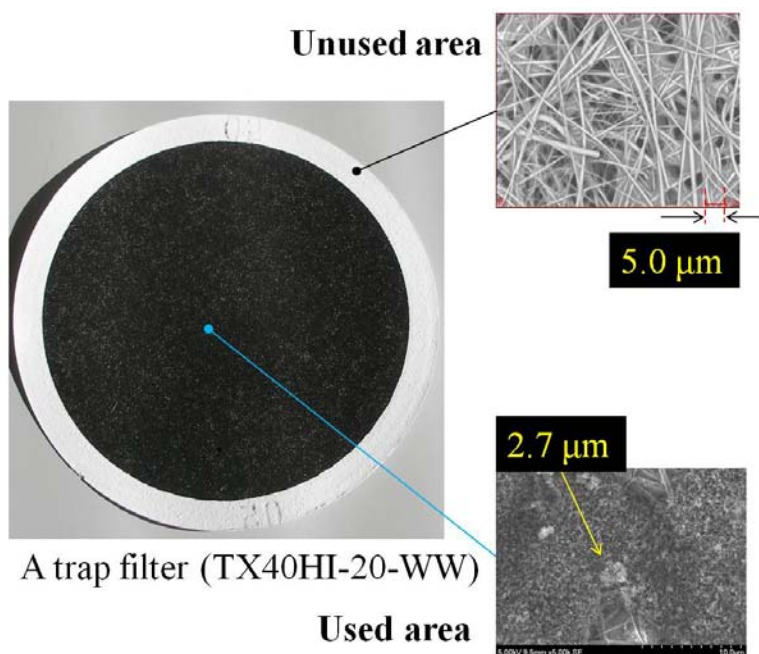


Figure 1. Diesel particulate matter deposited on filter after use: trap filter (left); and SEM images (right)

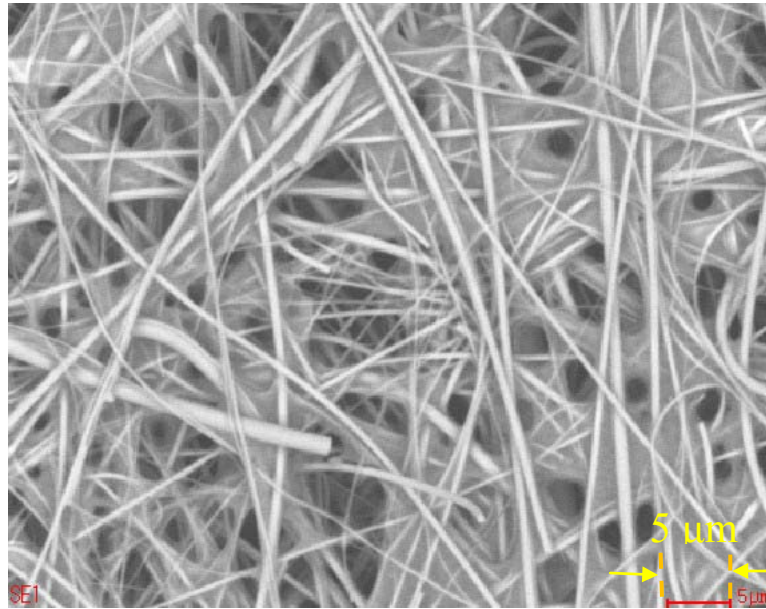


Figure 2. SEM image of unused filter

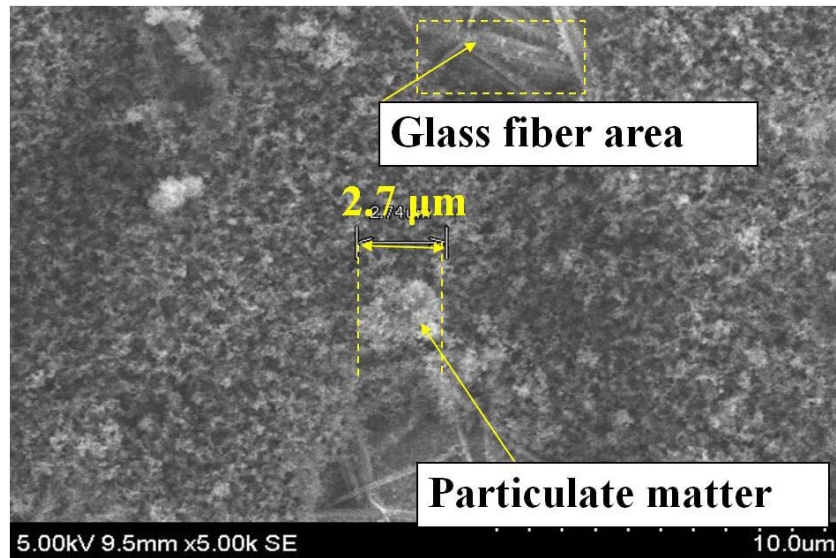


Figure 3. SEM image of particulate matter (PM) deposited on used filter

Figures 4–6 show the results of scanning electron microscopy/energy-dispersive X-ray spectroscopy analysis (SEM-EDX) of an unused filter, used filter, and PM.

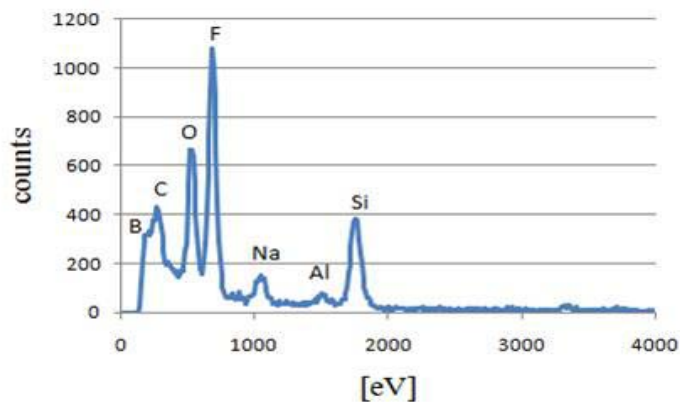


Figure 4. Results of SEM-EDX analysis of unused filter

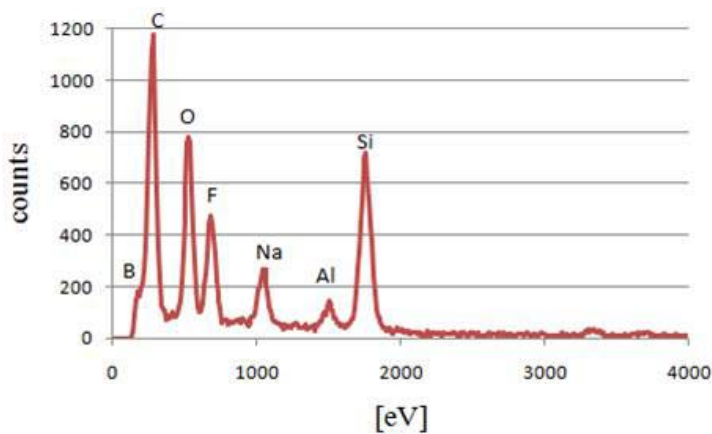


Figure 5. Results of SEM-EDX analysis of the glass fiber matrix of used filter

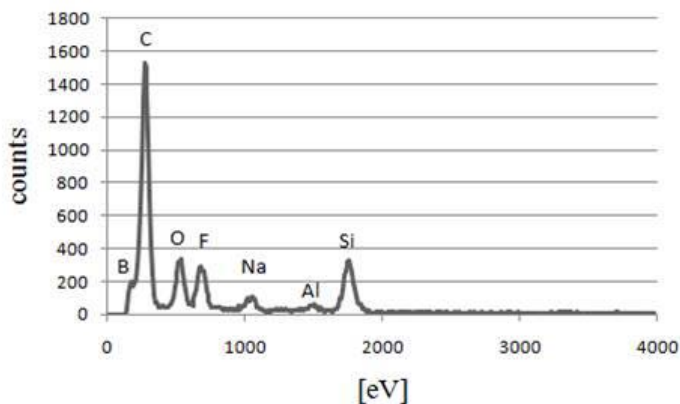


Figure 6. Results of SEM-EDX analysis of particulate matter (PM)

Table 1 shows the results of SEM-EDX quantitative analysis performed with a combination of matrix correction and atomic number, absorption, and fluorescence correction. The results indicate that the main component of diesel PM is carbon. The concentration of sulfur in diesel PM is very low, indicating the efficient desulphurization of the fuel. Boron, oxygen, silicon, and fluorine in the PM are assumed to have been generated from the Teflon-coated borate glass fiber used for constructing the filter. The source of aluminum in the PM is thought to be the experimental stage used for the SEM-EDX analysis.

Table 1: Results of SEM-EDX quantitative analysis using ZAF correction

Element	Unused filter At (Wt) %	Used filter At (Wt) %	Particulate At (Wt)%
C	22.09 (23.60)	52.80 (45.54)	68.74 (62.26)
B	50.23 (42.53)	17.87 (13.88)	11.03 (8.99)
O	6.57 (8.23)	12.31 (14.15)	7.54 (9.10)
F	8.84 (13.15)	5.17 (7.05)	4.33 (6.20)
N	6.99 (7.67)	4.46 (4.49)	3.99 (4.22)
Si	1.57 (3.45)	4.74 (9.55)	2.84 (6.01)
Na	0.52 (0.93)	1.42 (2.34)	0.72 (1.24)
Al	0.20 (0.42)	0.57 (1.10)	0.41 (0.82)
K	---	0.38 (1.07)	0.20 (0.58)
Ca	---	0.26 (0.74)	0.10 (0.31)
S	---	0.00 (0.00)	0.03 (0.07)

III. LIBS MEASUREMENT FOR DETERMINATION OF CARBONE SPECTRUM

A schematic representation of the LIBS system is shown in Figure 7. The Nd:YAG laser was operated at 1064 nm to generate a 50-mJ Q-switched pulse with a width of 8 ns (full width at half maximum, FWHM). The breakdown emissions were dispersed by a grating with a groove density of 1200 lines/mm, and the resulting electrical signal was recorded using a streak camera. The signal was processed, and the data were stored in a PC.

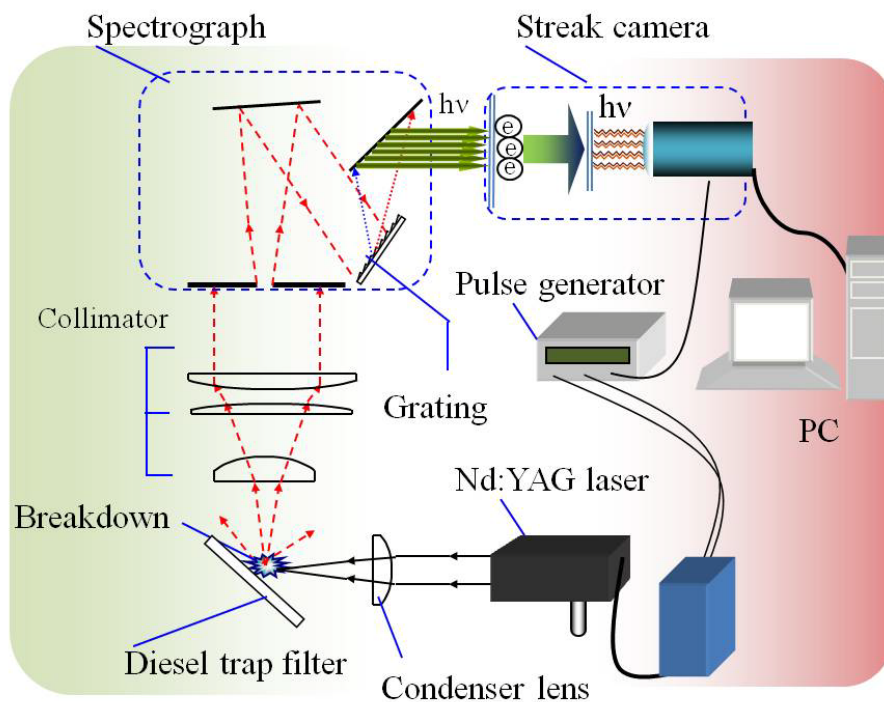


Figure 7. Schematic of the LIBS system

Formation and subsequent dissipation of the laser plasma occurred very rapidly. Within 1 μ s of plasma initiation, intense continuum radiation was observed, along with ionic lines over a broad wavelength range. This emission was caused by bremsstrahlung spectra and recombination radiation from the plasma as free electrons and ions recombine in the cooling plasma. The plasma intensity was optimized with respect to the background. Spectral measurements were carried out after an appropriate delay time to allow for the decay of the continuum radiation. In the exploratory experiment, the bright-line spectra obtained from charcoal were recorded in air ambient. (Figures 8 to 12) In the experiments, 100 laser shots were used.

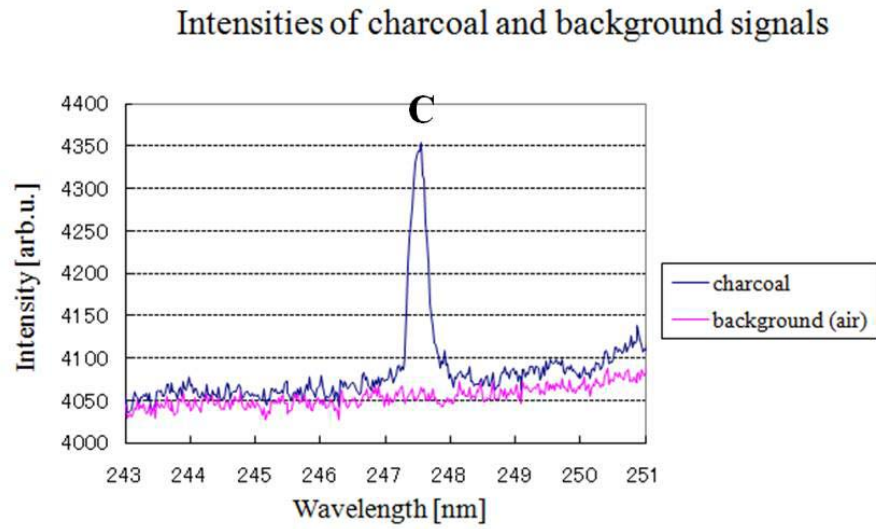


Figure 8. Spectra of charcoal and plasma background in air ambient recorded using LIBS system ($\lambda = 243\text{nm} - 251\text{nm}$)

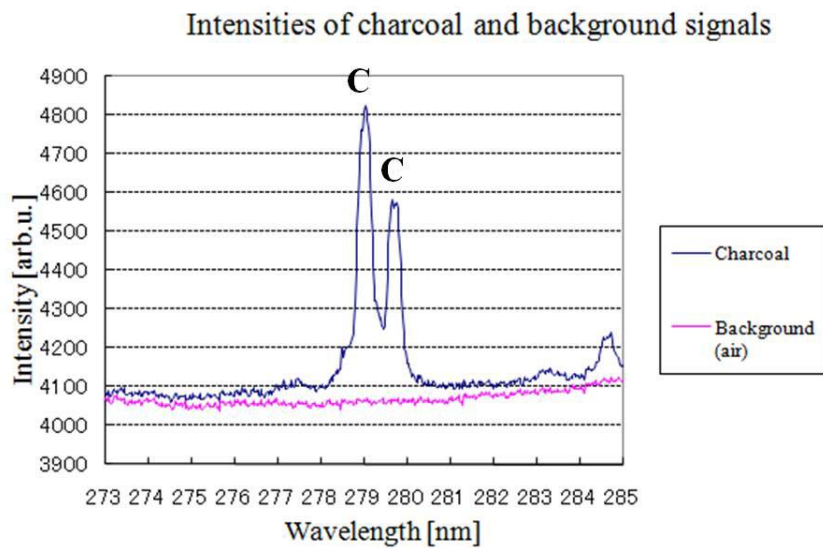


Figure 9. Spectra of charcoal and plasma background in air ambient recorded using LIBS system ($\lambda = 273\text{nm} - 285\text{nm}$)

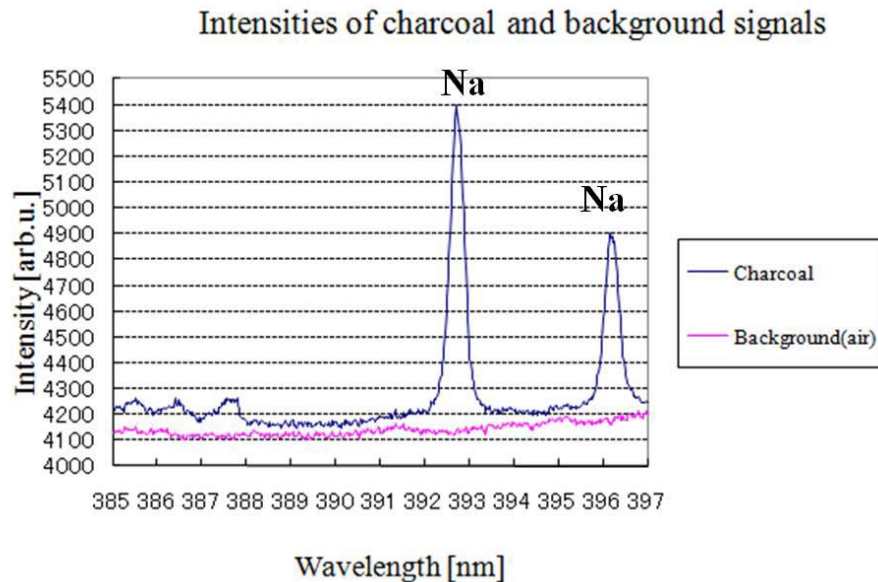


Figure 10. Spectra of charcoal and plasma background in air ambient recorded using LIBS system ($\lambda = 273\text{nm} - 285\text{nm}$)

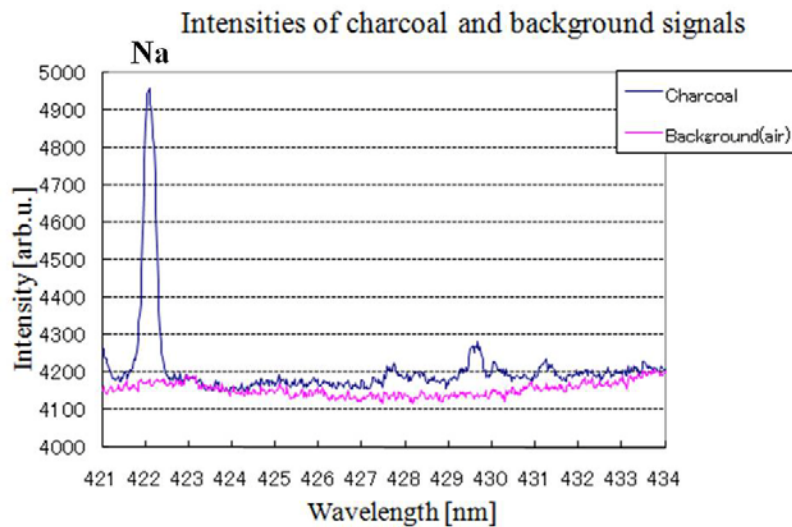


Figure 11. Spectra of charcoal and plasma background in air ambient recorded using LIBS system ($\lambda = 421\text{nm} - 434\text{nm}$)

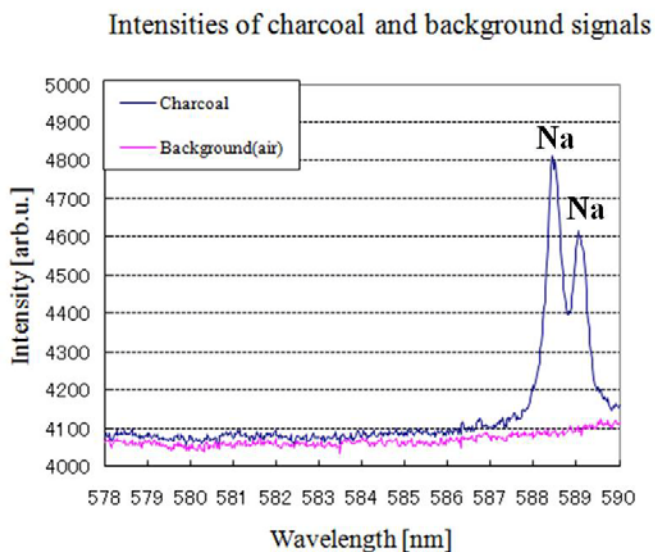


Figure 12. Spectra of charcoal and plasma background in air ambient recorded using LIBS system ($\lambda = 578\text{nm} - 590\text{nm}$)

Figure 8 and figure 9 show the atomic spectra of carbon recorded using our LIBS system. Figure 10 to figure 12 show the atomic spectra of sodium. The atomic spectra of carbon were recorded at 247.856 nm, 279.477 nm and 280.094 nm in this experiment. At the noise level shown in those figures, there were no interferences from the plasma background signals.

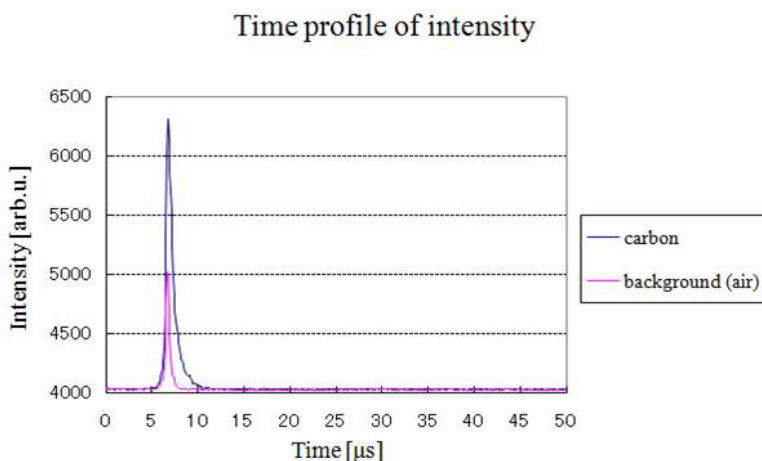


Figure 13. Time profile of intensity of carbon spectrum ($\lambda = 247.856\text{ nm}$) and background plasma signals

Figure 13 indicates that in the experiment performed in air ambient, the effective gate time required for separating the fluorescence signals from the peak intensity of background signals were 6.85–12.72 μ s after laser trigger.

IV. LIBS MEASUREMENT PERFORMED ON DIESEL PM

Figure 14 shows the atomic signals corresponding to the diesel PM, as obtained by LIBS measurements. Peaks due to carbon, boron, and silicon are observed in this wavelength range (245nm - 253nm). Figure 15 shows the spectra of charcoal, diesel PM, silicon and air plasma. Atomic signals due to carbon and silicon were observed in this wavelength range (277nm - 289nm).

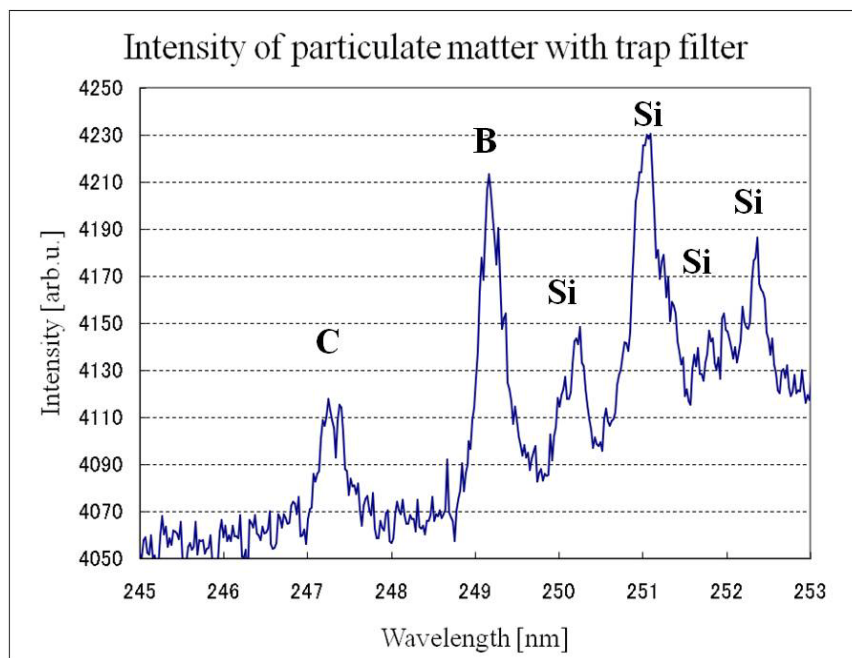


Figure 14. Atomic signals obtained using LIBS measurement using 100 laser pulses for particulate matter deposited on glass fiber filter

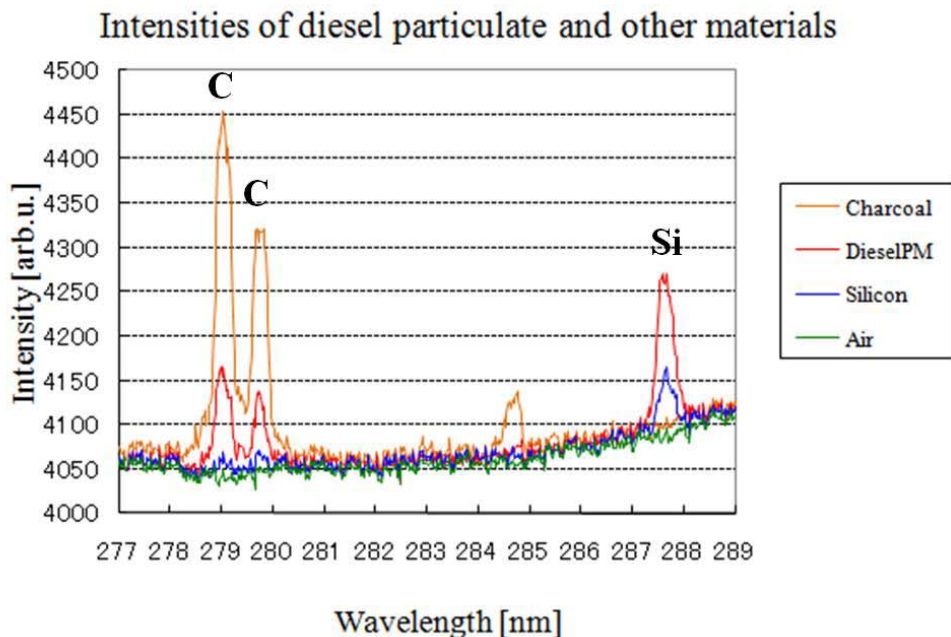


Figure 15. Spectroscopic data of diesel PM, charcoal, silicon, and plasma background in air ambient recorded using LIBS system ($\lambda = 277\text{nm} - 289\text{nm}$)

Figure 16 shows the atomic signals corresponding to the diesel PM and trap filter, as obtained by LIBS measurements. Peaks due to fluorine is observed in this wavelength range (679nm – 691nm).

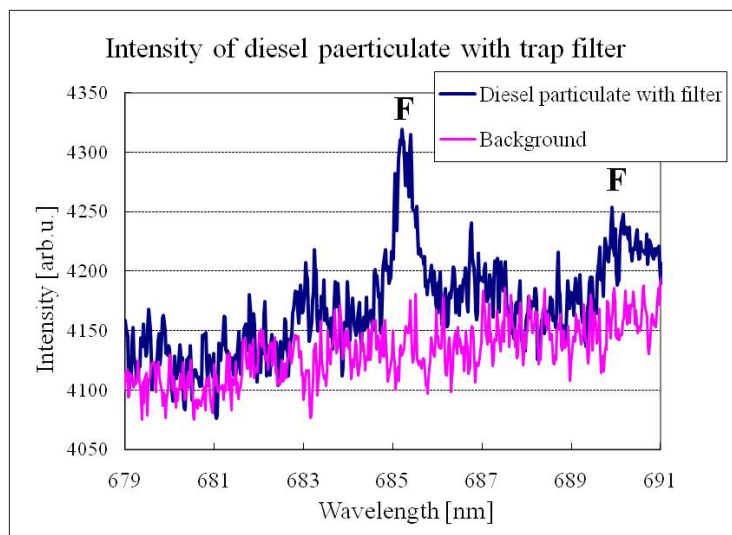


Figure 16. Atomic signals obtained using LIBS measurement using 100 laser pulses for particulate matter deposited on glass fiber filter

Table 2 shows the typical wavelengths obtained from the results of LIBS analysis on major elemental compositions of diesel particulate. Oxygen and nitrogen were difficult to separate from air plasma on the LIBS measurement under the air ambient condition.

Table 2: Typical wavelengths obtained from the results of LIBS analysis on major elemental compositions of diesel particulate

Element	Typical wavelength obtained by LIBS		
C	247.856 nm	279.477 nm	280.094 nm
B	249.676 nm	249.772 nm	
O	---	---	---
F	685.603 nm	687.022 nm	690.248 nm
N	---	---	---
Si	250.690 nm	251.432 nm	252.411 nm
Na	422.381 nm	588.995 nm	589.592 nm

V. CONCLUSIONS

We carried out LIBS analysis of suspended particulates in diesel exhaust. According to our results, the diesel exhaust contains PM as well as elements from the glass fiber filter used. This is possibly because the laser causes vaporization of the diesel particulates as well as the elements present on the filter surface. Elements present on the filter surface may also be included in the exhaust when the filter is used for the removal of diesel soot.

This method of analysis of diesel particulates may be affected by the presence of filter-surface elements in the sample. In order to improve the sensitivity of the method for the analysis of diesel particulates, it is necessary to develop a method for separating the sample material from the undesired elements.

During carbon detection, good peak resolutions were obtained when the spectra were recorded at wavelengths of 247.856 nm, 279.477 nm and 280.094 nm. In this case, carbon was found to be the main component of the diesel particulates, indicating that the obtained spectrum could be used for quantitative calibration.

Biodiesel fuels obtained from used vegetable oils may contain several impurities. The increased use of such biodiesel fuels makes real-time analysis of the exhaust gas important. Monitoring of biodiesel-powered systems by LIBS is expected to help in the establishment of a recycling-oriented society.

VI. ACKNOWLEDGEMENTS

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