Proceedings of the
International Conference on Mechanical Engineering 2011
(ICME2011) 18-20 December 2011, Dhaka, Bangladesh

ICME 11-TH-003

NANO-SIZED CARBON PARTICULATES IN THE GASOLINE ENGINE EXHAUST

B. Paul and A. Datta

Department of Power Engineering, Jadavpur University, INDIA.

ABSTRACT

In this experimental work attention has been focused on the characterization and quantification of nano-sized organic carbon (NOC) particulates from the exhaust of a small non-road SI engine. A hydrosol of the sample has been prepared by collecting the sample from the engine exhaust manifold, operating at no load condition. Existence of NOC particles has been confirmed using absorption and fluorescence spectroscopy. DLS and TEM image of the sample shows that the particles are below the size range of 5 nm. Chemical structure of the sample analyzed by measuring the band gap energy shows that the NOC particles are having three to five aromatic ring in their structure. A quantitive analysis of the sample at this operating condition shows the number and mass concentration of the particles of the order of 3.02×10^{12} cm^{-3} and 2.19×10^{-8} g/cm^3. The corresponding emission index at the same condition has been found out to be 0.27 g/kg of fuel.

Keywords: Nano-Sized Organic Carbon, Gasoline Engine, Engine Emission, Spectroscopy, TEM.

1. INTRODUCTION

Emission of particulate matter from the gasoline engine exhaust is getting attention due to its adverse effects on the environment and human health. Particulate matter generated in hydrocarbon combustion can be classified as organic carbon (OC), having diameter smaller than 10 nm, and elemental carbon (EC) or soot in the size range of 20 -100 nm. The large surface area to mass ratio and typical surface characteristics of these nano-sized organic carbon (NOC) particles make them highly toxic in comparison to the particles in the micrometer size range. Epidemiological studies confirm a direct relationship between the exposure to nano-scaled ultrafine particles and respiratory and cardiovascular syndrome [1, 2]. Toxicological properties of the NOC particles emitted from gasoline vehicles showed an effective interaction with the biological cells in animals and increased mutagenicity depending upon the inflicted dose [3]. The NOC particles are hydrophilic in nature and readily form a colloidal suspension in water. Besides that the NOC particles affect the earth's radiation balance by back scattering or absorbing the incident radiation and also act as a cloud condensation nucli [4].

Recently a lot of study has been performed on the formation of NOC particles in different types of flames. D'Anna et al. [5] found a comparable concentration of NOC particles and soot in a co-flow laminar diffusion flame. The NOC particles (mean size 2 - 3 nm) are found to form on the fuel side of the flame front closer to the flame axis than soot particles. Some of the studies in premixed flames [6-9] show the existence of particles finer than 5 - 6 nm in the early region of the flame before the inception of soot. Experimental studies in partially premixed hydrocarbon jet flame [10] also show the existence of NOC particles in the blue region of the flame, which is devoid of soot, and the particle size was found to increase gradually with the elevation of the flame. NOC particles having size below 5.5 nm has been reported in this study. The band gap energy of NOC particles, in the range of 2 to 4 eV has been reported in most of the studies.

The emissions of carbon nanoparticle from the gasoline engine exhaust have been reported in some literature. Borghese et al. [11] performed the optical analysis on the air-diluted and water trapped samples collected from the exhaust of both diesel and gasoline engines. They reported a number concentration of the order of 10^{14} cm^{-3} in the engine exhaust having particle size in the range of 3 - 4 nm. They also reported the presence of fully grown soot particle having band gap energy less than 0.5 eV in the air diluted diesel engine exhaust, which has not been observed for the other cases. The ex-situ and in-situ absorption and fluorescence investigations on the exhaust from the engines and stationary burners show the presence of one to two ring aromatics in the samples attributed by the fact that there is no absorbance beyond 250 nm [12]. The fluorescence spectra of the water diluted samples from the engine exhaust also shows two broad bands at around 320 and 400 nm with varying intensities. The presence of engines emitted carbonaceous particulate matter in the urban atmosphere has been evidenced in this work by

collecting and testing the rain samples. The particle size measured by using time-resolved fluorescence polarization anisotropy (TRFPA) [13] of the samples collected from the gasoline engine exhaust shows the presence of mainly smaller particle having size of about 1.3 nm. The combustion formed nano-organic particles has been observed to have a coagulation efficiency several orders of magnitude lower than the particles of d_p = 10 nm at flame temperature [14]. The low coagulation efficiency of the ultrafine particles at high temperature may be one of the causes of survival of the NOC particles upto the engine exhaust. A study by Sgro et al. [14] shows a number concentration and mass concentration of the order of 10^{12} cm^{-3} and 1×10^{-7} g/cm^3 for the condensed water samples collected from the SI engine exhaust having the particle size of 2 - 4 nm. However, another experimental work performed by Sgro et al. [15] on laboratory flame and vehicle exhaust shows some contradictory result in comparison to the previous study. UV-extinction has been used to characterize the nano-organic carbons and to find out the size distribution, electrospray-differential mobility analysis (E-DMA) and atomic force microscopy (AFM) has been performed. The results from the E-DMA and AFM shows a uni-modal and bimodal distribution of particles for the gasoline and diesel powered vehicles. The reported size of the particle from the gasoline engine exhaust is in the size range of 1 – 3 nm and for diesel powered engine the size range is from 1 – 150 nm. While a recent study by Grotheer et al. (2009) [16] using photo ionization mass spectrometry (PIMS) and DMA on the exhaust of a Otto engine shows a considerably lower emission of the order of 20 $\mu g/m^3$ corresponding to 6×10^9 particle/cm^3 for particles having size of 1.8 nm. The discrepancy in the results among the studies may be due to the use of different types of engines.

In this experimental work we have used a small non-road gasoline engine. This type of engines are mainly used in household and commercial applications, including lawn and garden equipment, utility vehicles, generators, and a variety of other construction, farm, and industrial equipment. Recently, emission from these small engines is receiving serious attention from environment protection agencies, who are introducing separate norms for them [17]. In view of that we have performed a qualitative and quantitative analysis of the engine emitted ultrafine particles from this small non-road engines.

2. EXPERIMENTAL

In this study a single cylinder, 4-stroke gasoline powered engine with a displacement volume of 256.7 ml has been used for performing the experimental work. The gasoline engine (model – MK 25 HSP) has a rated output of 2.5 kW at 3600 rpm. For our work we have operated the engine at CR = 4.67 and at a speed of 3000 rpm at no load condition. The engine was equipped with a carburetor to deliver a homogeneous gasoline (RON = 91, MON = 81 and density of 720 - 775 kg/m^3) air mixture into the cylinder. Sample has been collected (refer Fig. 1) from the exhaust manifold of the engine, using a quartz

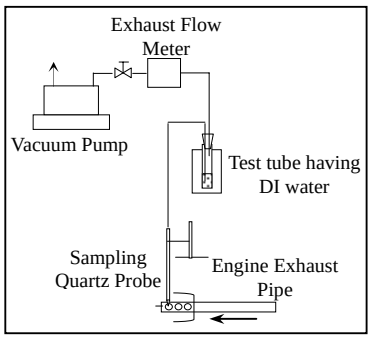

Fig 1. Schematic of the sample collection system

probe connected to a vacuum pump and by sucking the exhaust through 10 ml de-ionized water in a test tube. This type of sampling has been used previously by many researchers [6, 8 & 10] to isolate only the nano-organic carbon particles from the other combustion generated gaseous compounds and hydrophobic soot. This amount of sampling water is used so that the nanoparticles get enough time to diffuse into the whole mass of the sampling water. The sample gas flow rate is measured using a calibrated gas flow meter placed after the test tube. The temperature of the exhaust gas has been measured to be 660 ± 20°C. The sample has been collected for a period of 900 seconds. The sample has been collected after an initial warm-up period of the engine. After collection, the sample has been kept in a desiccator for 24 hrs before sparged by nitrogen gas for 30 mins to remove any dissolved volatile organic compounds in the hydrosol. Finally the sample has been poured in a quartz cell and analyzed by using UV–visible absorption, fluorescence and dynamic light scattering. UV-visible absorption has been carried out by using a UV-visible spectrometer (Shimadzu UV-1601PC). Two types of light sources, namely Deuterium and Halogen lamps, have been used to provide energy in the spectral range of 190 - 1100 nm. The Deuterium light source is used to measure the absorption spectra in the UV range (from 190 to 361nm) and the Halogen lamp is used for the visible absorption measurement extended up to 1100 nm. For measuring the fluorescence spectra of the same sample a steady state fluorescence measurements has been performed using a Perkin Elmer Luminescence Spectrometer (Model No. LS-55). A 20 kW discharge xenon lamp for 8μs duration has been used as the source for excitation of the samples. All measurements were carried out using a quartz cuvette of 1x1 cm^2 dimension supplied by Perkin Elmer. The size distribution of the sampled material has been carried out by using dynamic light scattering technique (Model DLS—Zetasizer Nano ZS, Malvern Instruments). A 4 mW He-Ne gas laser provided the light source to illuminate the sample at 633 nm and an avalanche photodiode was used as detector to measure the intensity of the scattered light. For DLS measurements, the samples have been filtered several times through a 0.22 μm Millipore membrane filter. Samples were prepared for transmission electron microscopy (TEM) by placing a drop of the hydrosol containing the NOC particulates on a 300 mesh copper

grid coated with a thin amorphous carbon film and drying it. The TEM (TECNAI S-TWIN, FEI Company) was operated at 200 kV with a magnification of 71000.

3. RESULTS AND DISCUSSIONS

We are reporting here results on NOC particles emitted from the engine running at no load. When a spark ignition engine operates at NO load a fuel-air mixture richer than stoichiometric is prepared in the carburetor. Fuel and air flow measurements show the air-fuel ratio to be 11.72:1, indicating a rich mixture of gasoline. We prefer the rich air-fuel mixture as the chance of particulate formation is high under this situation.

Figure 2 shows the absorption spectra of the water trapped gasoline engine exhaust at no load condition collected from the tail pipe of the gasoline engine. The absorption spectra of the sample decrease monotonically from its maximum value at 200 nm and become almost negligible beyond 400 nm. Besides this the spectra show a small hump at around 250 nm. The qualitative nature of the spectrum is the typical of a nano-organic carbon particulate generated from the combustion sources [6-7, 10]. The small hump at around 250 nm in the hydrosol samples collected from the non-sooting zone of the flame has also been reported by many researchers [6, 10] and attributed to the absorption due to nano-organic carbon particulates. No absorbance in the visible range of the spectra indicates that there is no elemental carbon present in the samples and the absorption is due to the nano-sized organic particles. The similarities in the spectra from the engine and the flame suggest that the samples collected from the engine exhaust contain similar NOC particles as obtained from the hydrocarbon flame.

The fluorescence spectra of the gasoline engine exhaust at no load condition have been shown in figure 3. An excitation wavelength of 266 nm has been used to excite the sample. The fluorescence spectra show two distinctive peaks at around 310 nm and 380 nm. The fluorescence peak at around 310 nm is a typical of nano-organic carbon particulate having one to two aromatic rings [18]. While the presence of fluorescence emission at higher wavelength range indicating towards

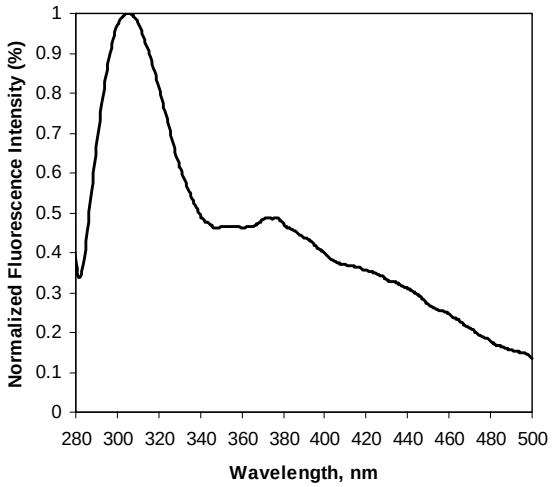

Fig 3. Fluorescence spectra of the NOC particles collected from gasoline engine exhaust

the presence of more aromatized particles having more than two aromatic rings. This is because of the fact that the fluorescence spectra of aromatic compounds shifts to the red with the growth in aromatic ring structure [18].

In order to characterize the size distribution of the NOC particles in the engine exhaust, we have performed dynamic light scattering (DLS) on the sample collected from the engine. Figure 4 shows the particle size distribution in the sample collected from the engine exhausts. The size distribution of the particles in the collected sample analyzed using the DLS (Fig. 4) shows a particle size in the range from 1.5 – 3.6 nm. This has been verified from the TEM images taken from the sample (Fig. 5). The TEM results show some low contrast, faint marks for the particles without having clearly defined boundaries. This indicates towards the semi-transparent nature of the NOC particles under the electron beam. Such nature of the NOC particles was reported earlier by other researchers while studying in laminar premixed and diffusion laboratory flames [19]. Direct measurement from the TEM image shows the diameter of the particulates to be higher. However, liquid

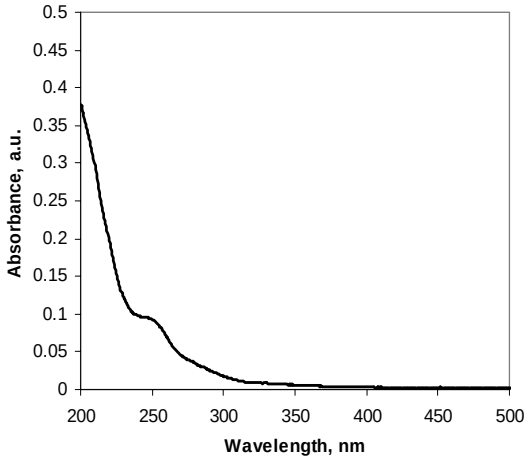

Fig 2. Absorption spectra of the NOC particles collected from gasoline engine exhaust

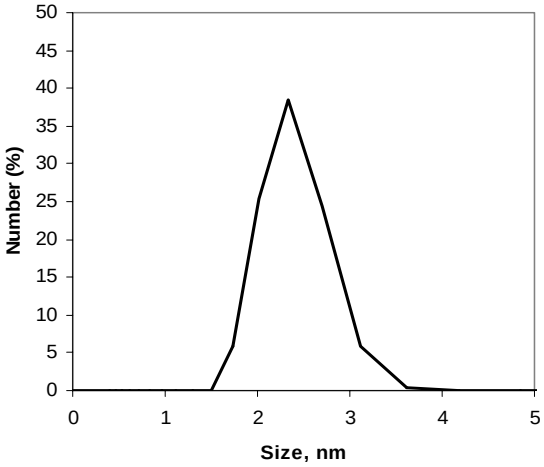

Fig 4. DLS size distribution of the NOC particles collected from gasoline engine exhaust

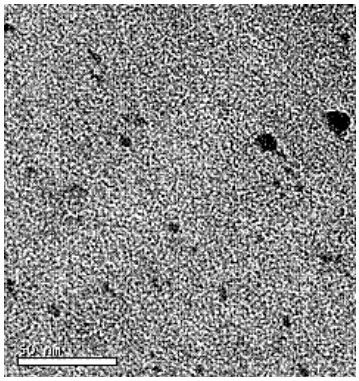

Fig 5. Particle size distribution at No Load using TEM

like characteristics of the NOC particles result in a spread when they are dropped on the TEM grid. Zhao et al. (2007) [19] assumed a ratio of height to projected diameter of 0.1 as a result of the spread. A similar assumption of the ratio results in an agreement of the particle size from DLS and TEM. The present experiment measures the particulates by sampling from the muffler at the end of the exhaust manifold. Therefore, the exact size of the particulates formed during the combustion process could not be exactly predicted from the results. However, earlier studies by Sgro et al. (2003) [14] and Lanzuolo et al. (2008) [20] showed that the coagulation rate of the particulates below 5 nm range is very low because of the weak van der Waals pairwise interaction [21]. Taking this into account, it can be concluded that as the particulates in the exhaust are in the size range below 5 nm, the coagulation in the exhaust line is negligible.

In order to chemically characterize the structures of the NOC particles, we have analyzed the optical band gap energy using the absorbance results (shown in Fig. 2). The band gap energy is known to be a powerful indicator of the chemical characterization of aromatic structures [9]. In solid state physics, band gap energy represents the energy level difference between the highest occupied valence band and lowest unoccupied conduction band. The absorbance (α) can be correlated with the optical band gap energy (E_g) using the Tauc equation [7, 9], as given in equation no. (1).

$$\sqrt{\alpha E} = B\left(E - E_g\right) \tag{1}$$

where, E is the energy of the incident photon and B is a constant. The photon energy can be computed from the wavelength of the incident photon using the velocity of light in the medium (in this case water). The optical band gap energy can be obtained as the intercept on the abscissa by fitting a linear plot between E (on the abscissa) and $\sqrt{\alpha E}$ (on the ordinate). When different kinds of particles are present in the sample the above plot does not identify single band gap energy. In such cases, different band gap energy is evaluated from the plot obtained using the data of the absorption spectrum of engine reported in Fig. 2 up to a wavelength of 400 nm.

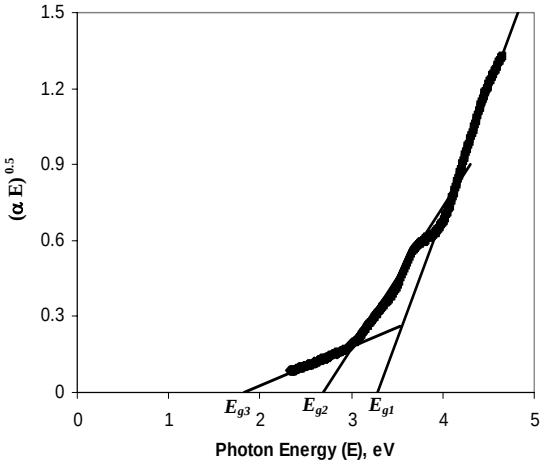

Fig 6. Tauc plot of the NOC particles collected from gasoline engine exhaust

We could evaluate three different band gap energies by fitting the best linear fits in three segments of photon energy data. The band gap energy values are found out to be 3.28 eV, 2.7 eV and 1.81 eV, respectively. The highest band gap energy is for data in the wavelength range of 200 to 244 nm, the middle one is for data in the range of 244 to 306 nm and the lowest one is for the range in 306 to 400 nm. As the absorbance continually goes down to low value beyond 300 nm (Fig. 2), we refrain from paying much attention to the lowest band gap energy value obtained from Fig. 6.

Earlier studies reported that the band gap energy of carbonaceous structures in the range of 2 – 4 eV involves π-π^* transition of sp^2 hybridization [7, 9]. Further it was noted that the band gap energy decreases with the increase in the number of aromatic clusters in the atomic structure. Robertson and O'Reilly (1987) [22] presented that in a sp^2 cluster, the band gap energy (E_g) varies more or less inversely with the cluster size as,

$$E_g = \frac{6}{M^{1/2}}, \tag{2}$$

where, M is the number of aromatic rings in the cluster. According to equation (2) the band gap energies of 3.28 eV and 2.7 eV correspond to aromatic structures having three and five aromatic rings. Therefore, band gap energy analysis clearly indicates the NOC particulates as chemical structures with small number of aromatic rings in them. These flame generated structures in the gasoline engine exhaust postulates that the soot formation processes initiates even in these engines, though they cannot be extended up to the fully grown soot as the fuel-air mixture equivalence ratio remains within the sooting threshold.

In order to have an idea about the amount of nano-organic carbon particulate emitted from the gasoline engine exhaust we have calculated the number concentration and the mass concentration of the particles using the data from the absorption and DLS measurements. An exhaust gas flow rate of 0.045 lpm has been maintained for this purpose. A complex

refractive index of (1.35-*i*0.09) at a wavelength of 266 nm [8] has been considered for the NOC particles, while the density of the soot precursor particle has been considered to be 1.0 g/cm^3 [8]. A well known combined Beer-Lambert law has been used to find out the particle number concentration as follows:

$$\log\left(\frac{I_0}{I}\right) = \alpha_{ext}(\lambda)l \tag{3}$$

Where, I_0 is the intensity of the incident light (or the light intensity passing through a reference cell) I is the light transmitted through the sample solution, and $\alpha_{ext}(\lambda)$ is the extinction coefficient [7] expressed as:

$$\alpha_{ext}(\lambda) = -M_{total} \times \frac{6\pi}{\rho_p \lambda} \times \mathrm{Im}\left(\frac{m_p^2 - 1}{m_p^2 + 2}\right) \tag{4}$$

$$M_{total} = N_p \times \frac{\rho_p \pi d_p^3}{6} \tag{5}$$

Where, N_p, cm^{-3}, is the number concentration of the molecules or the particles and $m_p(\lambda) = n_p(\lambda) + ik_p(\lambda)$ is the complex refractive index of the particles, as given before. Here for calculating the number and mass concentration the mass mean diameter (d_p) of the particles has been considered. The number concentration of the particles in the exhaust gas has been found out to be 3.02×10^{12} cm^{-3} considering a mass mean diameter of 2.4 nm obtained from the DLS results. The corresponding mass concentration and emission index at the same condition has been found out to be 2.19×10^{-8} g/cm^3 and 0.27 g/kg of fuel. The number and mass concentration data in this range has also been measured by Borghese et al. (1998) [11] and Sgro et al. (2003) [14] from the water trapped sample of gasoline exhaust.

4. CONCLUSIONS

The emission of NOC particles at the exhaust of small non-road gasoline engine has been confirmed with the help of UV-absorption and fluorescence spectroscopy results as both the spectra show peaks which are typical to the nano-sized organic carbon particles. The particle size at the exhaust has been found to be below 5 nm by using DLS as well as TEM study. The chemical analyses of the sample show that the particles consist of three to five aromatic ring structures. The particle number concentration at the exhaust has been measured to be 3.02×10^{12} cm^{-3} considering a mass mean diameter evaluated from the size distribution. Such high concentration of ultrafine particles at the engine exhaust can be a matter of concern. This is more so as these extremely fine particulates remain undetected by the commercially available particle sizing instruments.

ACKNOWLEDGEMENT

One of the authors (B. Paul) gratefully acknowledges the support from Council of Scientific and Industrial Research (CSIR), Govt. of India (Grant No. 9/96(0622)2K10-EMR-I) for conducting this research. The authors wish to record their sincere gratitude to UGC-DAE Consortium for Scientific Research, Kolkata Centre, for their support to perform this work. The TEM measurement has been performed at SINP TEM facility.

5. REFERENCES

1. Oberdorster, G., Gelein, R. M., Ferin, J. and Weiss, B., 1995, "Association of particulate air pollution and acute mortality: involvement of ultrafine particles", Inhalation Toxicology, 7:111-124.
2. Lighty, J. S., Veranth, J. M. and Sarofim, A. F., 2000, "Combustion aerosols: Factors governing their size and composition and implications to human health", J. Air Waste Manage. Assoc., 50:1565-1618.
3. Sgro, L.A., Simonelli, A., Pascarella, L., Minutolo, P., Guarnieri, D., Sannolo, N., Netti, P. and D'Anna, A., 2009, "Toxicological Properties of Nanoparticles of Organic Compounds (NOC) from Flames and Vehicle Exhausts", Environ. Sci. Technol., 43: 2608–2613.
4. Novakov, T., Penner, J.E., 1993, "Large contribution of organic aerosols to cloud-condensation-nuclei concentrations", Nature, 365: 823–826.
5. D'Annaa, A., Rolando, A., Allouis, C., Minutolo, P., D'Alessio, A., 2005, "Nano-organic carbon and soot particle measurements in a laminar ethylene diffusion flame", Proceedings of the Combustion Institute, 30:1449–1456.
6. Bruno, A., de Lisio, C., Minutolo, P., D'Alessio, A., 2007, "Evidence of fluorescent carbon nanoparticles produced in premixed flames by time-resolved fluorescence polarization anisotropy", Combustion and Flame, 151:472– 481.
7. D'Alessio, A., D'Anna, A., Gambi, G., Minutolo, P., 1998, "The spectroscopic characterization of UV absorbing nanoparticles in fuel rich soot forming flames", J. Aerosol Science, 29 (4):397-409.
8. Cecere, D., Sgro, L.A., Basile, G., D'Alessio, A., D'Anna, A., Minutolo, P., 2002, "Evidence and characterization of nanoparticles produced in nonsooting premixed flames", Combust. Sci. Tech., 174:377–398.
9. Minutolo, P., Gambi, G., D'Alessio, A., 1996, "The optical band gap model in the interpretation of the UV-visible absorption spectra of rich premixed flames", Proc. Combust. Inst., 26:951–957.
10. Paul, B., Datta, A., Datta, A., Saha, A., 2009, "Occurrence and characterization of carbon nanoparticles below the soot laden zone of a partially premixed flame", Combustion and Flame, 156:2319-2327.
11. Borghese, A., Merola, S. S., 1998, "Detection of extremely fine carbonaceous particles in the exhausts of diesel and sparkignited internal combustion engines by means of broad-band extinction and scattering spectroscopy in the ultraviolet band 190 nm - 400 nm", Proc. Combust. Inst., 27: 2101–2109.
12. Merola, S.S., Gambi, G., Allouis, C., Beretta, F.,

Borghese, A., D'Alessio, A., 2001, “Analysis of exhausts emitted by i.c. engines and stationary burners, by means of u.v. extinction and fluorescence spectroscopy”, Chemosphere, 42: 827-834.
13. Bruno, A., de Lisio, C., Minutolo, P., D'Alessio, A., 2006, “Characterization of ultrafast fluorescence from nanometric carbon particles”, J. Opt. A: Pure Appl. Opt., 8:S578–S584.
14. Sgro, L.A., Basile, G., Barone, A.C., D’Anna, A., Minutolo, P., Borghese, A., D’Alessio, A., 2003, “Detection of combustion formed nanoparticles”, Chemosphere, 51: 1079–1090.
15. Sgro, L. A., Borghese, A., Speranza, L., Barone, A., Minutolo, P., Bruno, A., D’Anna, A., D’Alessio, A., 2008, “Measurement of nanoparticles of organic carbon and soot in flames and vehicle exhausts”, Environ. Sci. Technol., 42: 859–863.
16. Grotheer, H.H., Hoffmann, K., Wolf, K., Kanjarkar, S., Wahl, C., Aigner, M., 2009, “Study of carbonaceous nanoparticles in premixed C_2H_4–air flames and behind a spark ignition engine”, Combustion and Flame, 156:791–800.
17. United States Environment Protect Agency Regulatory Announcement, September, 2008, EPA420-F-08-013. http://www.epa.gov/nonroad/marinesi-equipld/420f08013.pdf
18. Berlman, I.B., 1971. *Handbook of Fluorescence Spectra of Aromatic Molecules*. Academic Press, New York.
19. Zhao, B., Uchikawa, K., Wang, H., 2007, “A comparative study of nanoparticles in premixed flames by scanning mobility particle sizer, small angle neutron scattering, and transmission electron microscopy”, Proceedings of the Combustion Institute, 31:851–860.
20. Lanzuolo, G., Sgro, L. A., De Filippo, A., Barone, A. C., Borghese, A., D’Alessio, A., 2008, “Coagulation of organic carbon nanoparticles in exhaust conditions”, Environmental Engineering Science, 25:1365–1377.
21. Narsimhan, G., Ruckenstein, E., 1985, “The Brownian coagulation of aerosols over the entire range of Knudsen numbers: connection between the sticking probability and the interaction forces”, J. Colloid Int. Sci., 104:344–369.
22. Robertson, J., O'Reilly E. P., 1987, “Electronic and atomic structure of amorphous carbon”, Phys. Rev. B, 35:2946 - 2957.

6. MAILING ADDRESS

Bireswar Paul
Research Scholar, Department of Power Engineering,
Jadavpur University Salt Lake Campus,
Kolkata 700 098, West Bengal, India
E-mail: paulbireswar@yahoo.co.in