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A Spectroscopic Study of the Nano-Organic Carbon Particles from ISO-Octane  
Flame and Gasoline Engine

**Bireswar Paul<sup>a</sup>, Amitava Datta<sup>a</sup>, Aparna Datta<sup>b</sup>, Abhijit Saha<sup>b</sup>**

<sup>a</sup>**Dept. of Power Engineering, Jadavpur University, Salt Lake Campus,  
Kolkata – 700 098, India**

<sup>b</sup>**UGC-DAE Consortium for Scientific Research, Kolkata Centre, India**

**Contact Information: paulbireswar@yahoo.co.in, amdatta\_ju@yahoo.com**

Existence of nano-sized organic carbon particles, of size less than 10 nm, have been reported in the exhaust of gasoline engines in some earlier works [1-2]. However, uncertainties exist regarding the origin of these particles, and various alternative sources for these particles have been proposed, e.g. dilution and cooling of the unburned fuel vapour or evaporated lube oil and combustion front in the engine cylinder [3-4]. The present research compares different spectroscopic results of samples taken from a gasoline engine exhaust and from the surface of a partially premixed iso-octane flame, burning in hot air, in order to establish an association between the nano-organic carbon particulates emitted from the engine with the in-cylinder combustion process.

In order to establish the objective, a small gasoline engine has been operated at no load condition and a laboratory iso-octane flame (Equivalence ratio 2.27) has been established on a co-flow burner. Two hot air streams are fed into the burner. The primary and secondary air streams have been maintained at temperatures of 145°C and 160°C, respectively, to ensure a complete vaporization of the iso-octane fuel. The fuel is injected into the inner primary air stream by using a microinfusion pump (LP 50 BW). The flow passage after the fuel injection point upto the burner has been maintained at the specified temperature by using a strip heater. The secondary air temperature is maintained to keep the burner hot so that the fuel vapor does not get condensed. The flame has a double flame structure having inner rich premixed flame and an outer non-premixed flame. The sample from the inner flame surface has been extracted by using a quartz microprobe having a tip opening of 0.25 mm. The sample from the flame surface is made to pass through de-ionized (DI) water kept in a test tube by using a vacuum pump. This type of sampling method has been used previously by many researchers [5] and works as a sort of fractionation of the materials dissolving only the NOC particles while the gaseous substances pass through. Sample for the engine study has been collected by the same procedure from the centre of the exhaust manifold at no load condition. For both the cases dichloromethane has been used as the solvent for collecting the sample for the Fourier transformed infrared (FTIR) spectroscopy study.

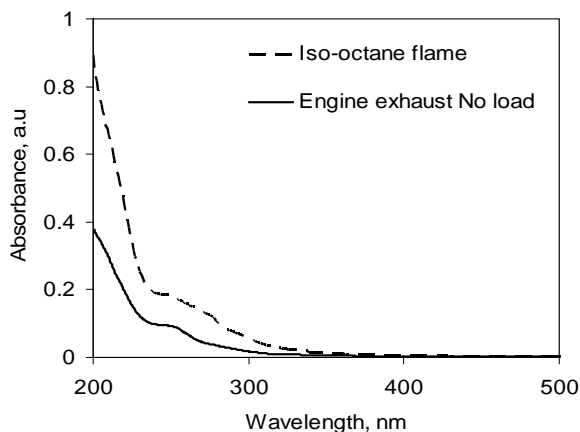
Hydrosols of the samples have been degasified by nitrogen gas to ensure complete evaporation of the dissolved volatile compounds in water. UV absorption spectroscopy and dynamic light scattering (DLS) have been used to confirm the existence of NOC particles in the hydrosol samples. UV absorption of the samples from both the sources shows similar spectra (Figure 1), with the absorbance decreasing from its value at 200 nm to become

negligible beyond 350 nm. Such a UV absorption spectrum is typical of NOC particles and is unlikely of soot, which shows a broad absorption spectrum extending from UV to visible range. The DLS size measurements demonstrate the particulate nature of the sample and confirm them to be finer than 10 nm in both flame and engine exhaust (Figure 2). Fourier Transform Infrared (FTIR) spectroscopy (Figures 3 and 4) of the sampled materials from the two sources compares their bond structures. The presence of C-H aliphatic functional groups in the NOC structures is clearly evident in the two cases. The presence of carbonyl (C=O) functional groups, corresponding to a peak at around  $1720\text{ cm}^{-1}$ , has also been confirmed for both the cases. On the other hand, though the existence of C-C and C-H plane deformation of condensed aromatic groups, shown by peaks in the range of  $1000\text{--}1300\text{ cm}^{-1}$ , are observed in the engine FTIR spectra, such functional groups is not apparent in the flame spectra.

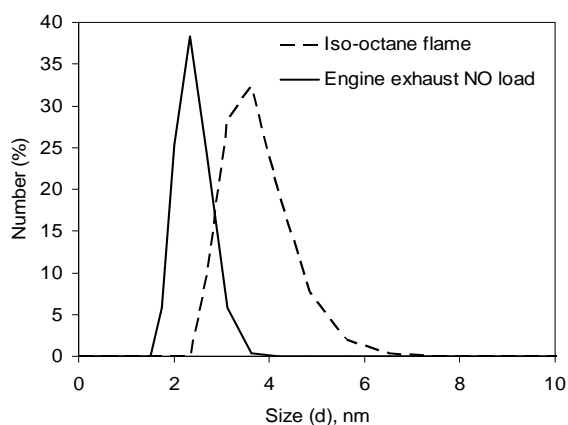
Thus the spectroscopic results show that very fine NOC particles emitted from the engine exhaust have many structural and physical similarities with similar particles existing in the flame environment of similar fuel. It indicates that in-cylinder combustion is the origin of these NOC particles in the engine exhaust. Few structural dissimilarities observed among the particles from the two sources may be attributed to the different combustion conditions existing in the two cases.

### References:

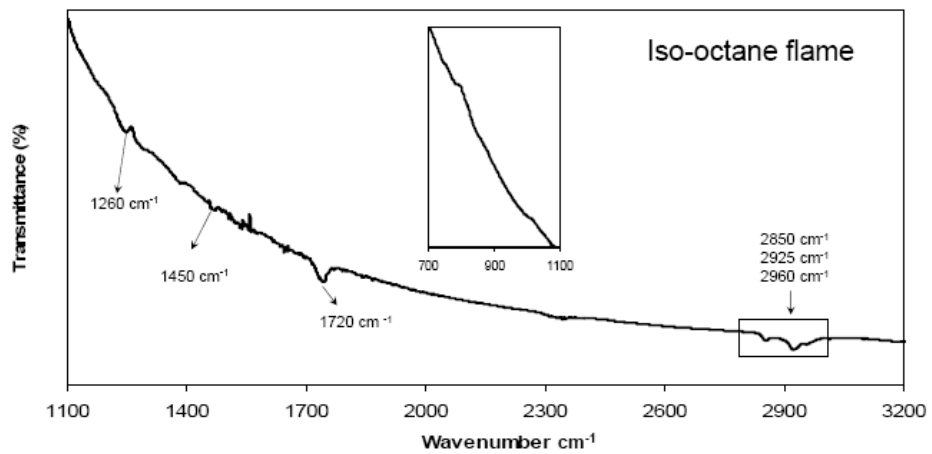
- [1] L.A. Sgro, A. Borghese. Measurements of Nanoparticles of Organic Carbon and Soot in Flames and Vehicle Exhausts. *Environ. Sci. Technol.*, 2008, 42, 859–863.
- [2] H.H. Grotheer, K. Hoffmann, K. Wolf, S. Kanjarkar, C. Wahl, M. Aigner. Study of carbonaceous nanoparticles in premixed C<sub>2</sub>H<sub>4</sub>–air flames and behind a spark ignition engine. *Combustion and Flame*, 2009, 156, 791–800.
- [3] D.B. Kittelson. Engines and nanoparticles: A review. *J. Aerosol Sci.*, 1998, 29(5/6), 575–588.
- [4] A. D’Anna. Combustion-formed nanoparticles. *Proceedings of the Combustion Institute*, 2009, 32, 593–613.
- [5] B. Paul, A. Datta, A. Datta, A. Saha. Occurrence and characterization of carbon nanoparticles below the soot laden zone of a partially premixed flame. *Combustion and Flame*, 2009, 156, 2319–2327.



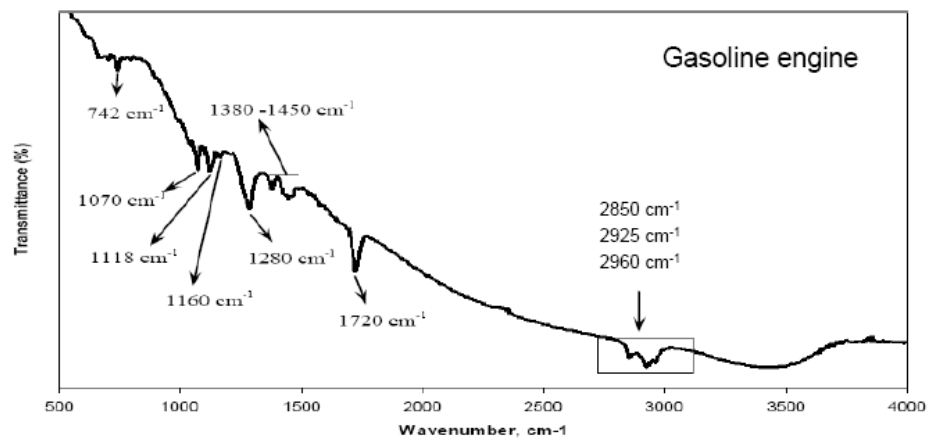
**Figure 1:** Absorption spectra of the sample from iso-octane flame and gasoline engine exhaust.



**Figure 2:** DLS size distribution of the NOC particles in the iso-octane flame and gasoline engine exhaust.



**Figure 3:** FTIR spectra of the sampled material from the Iso-octane flame.



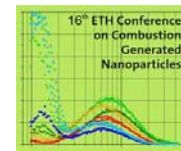
**Figure 4:** FTIR spectra of the sampled material from the gasoline engine exhaust at No load.



# A Spectroscopic Study of the Nano-Organic Carbon Particles from Iso-Octane Flame and Gasoline Engine

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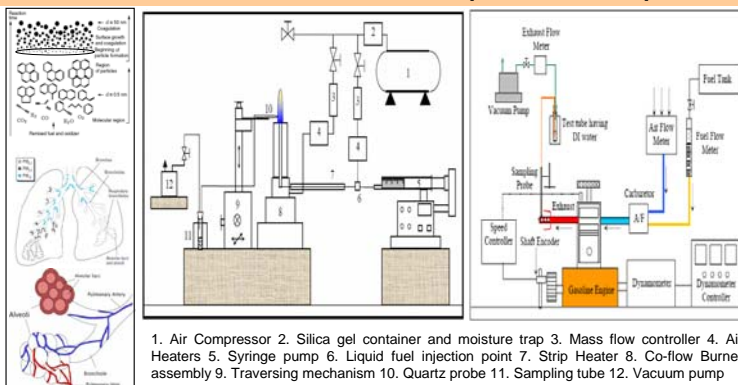
<sup>a</sup>Dept. of Power Engineering, Jadavpur University, Salt Lake, Kolkata – 700 098, India  
<sup>b</sup>UGC-DAE Consortium for Scientific Research, Kolkata Centre, Kolkata - 700 098, India  
Contact Information: paulbireswar@yahoo.co.in, amdatta\_ju@yahoo.com



## Background of the study

- > Nano-organic carbon (NOC) particles are ultrafine precursor soot particles below the size range of 10 nm. These particles fall in the transition zone between individual atoms or molecules and the corresponding bulk material
- > The research interest on these particles stems from their adverse effects on the human health and environment as well as from the chemistry of soot formation process
- > NOC particles can penetrate deep into the lung and can cause pulmonary inflammation and other lung diseases; can act as cloud condensation nuclei and alter earth's radiation balance
- > Existence of these particles have been reported in the exhaust of gasoline engines in some of the literatures.
- > However, uncertainties exist regarding the origin of these particles, and various alternative sources for these particles have been proposed, e.g. dilution and cooling of the unburned fuel vapour or evaporated lube oil and combustion front in the engine cylinder

## Schematic of the Experimental Setup



## Objective

To compare the different spectroscopic results of the samples from gasoline engine exhaust and surface of a partially premixed Iso-octane flame in order to establish the origin of the NOC particles in the engine exhaust.

## Flame setup parameters

**Flame parameters:**  
 Fuel type: Iso-octane  
 Flame type: Partially premixed flame with equivalence ratio 2.27. Double flame structure.  
 Inner rich premixed flame & outer diffusion flame.  
 Primary air heater temperature: 145°C  
 Secondary air heater temperature: 160 °C  
 Sampling location: Inner flame front at 15 mm HAB.



## Engine specification and operating condition

**Specification of the engine:**  
 Engine model: MK 25 HSP  
 No of cylinder: 1 (One)  
 Engine type: 4-stroke gasoline engine  
 Displacement Volume: 256.7 ml  
 Rated output: 2.5 kW at 3600 rpm

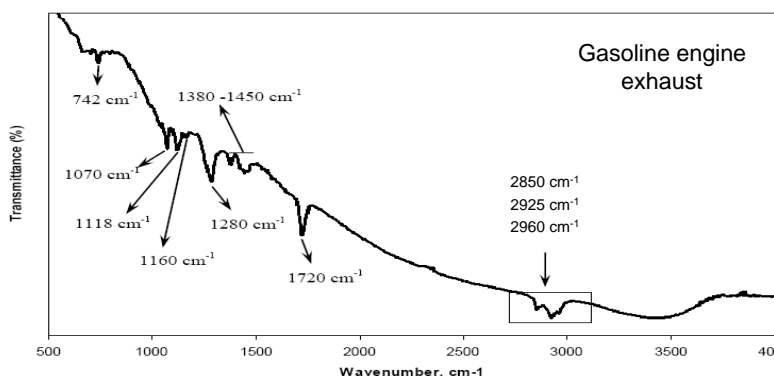
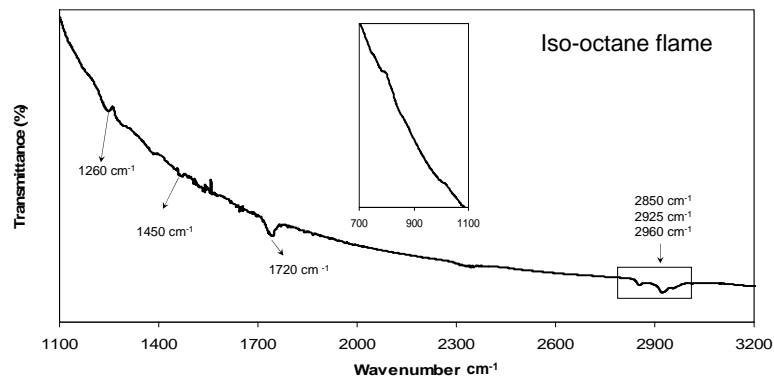


**Operating Condition:**  
 CR: 4.67  
 Engine speed: 3000 rpm  
 Engine load: No load Condition

## Sample preparation

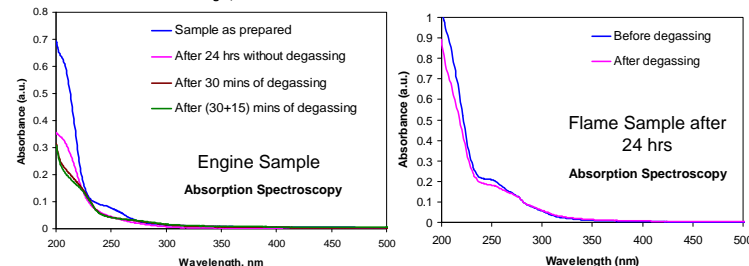
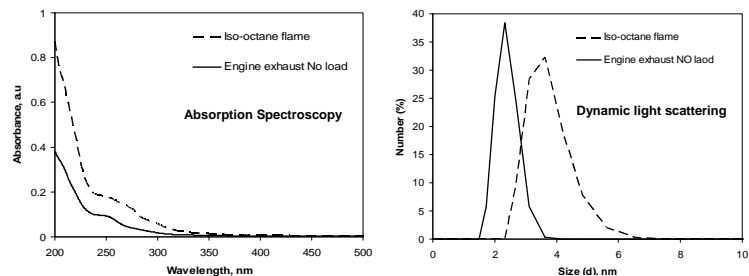
- **Solvent** : De-ionized (DI) water (10 ml), **Sampling time** : 15 mins (for engine), 45 mins (for ISO-octane flame), **Sample degassing** : By purging nitrogen gas through the sample for sufficient length of time to remove unwanted dissolved gases,
- **Sampling for FTIR** : Samples have been collected in dichloromethane (volatile) and doped in KBr salt pellet

## Results: FTIR Spectroscopy



Absorption Peaks (cm <sup>-1</sup> )	Assigned functional groups
2960–2925–2850	Asymmetric and symmetric C–H stretching of CH <sub>3</sub> , CH <sub>2</sub> aliphatic groups, respectively
1720	Carbonyl C=O stretching
1450–1380	Asymmetric CH <sub>3</sub> and scissor CH <sub>2</sub> deformations, Symmetric CH <sub>3</sub> deformation and cyclic CH <sub>2</sub>
1300–1000	C–C and C–H plane deformation of aromatic groups and ether C–O–C stretching

## Absorption Spectroscopy and Dynamic light scattering



## Discussion

- Degassing removes dissolved volatile organic compounds from the sample as evident from the absorption spectra.
- No absorption in the visible spectral range indicate absence of fully grown soot.
- Similar absorption spectra from flame and engine indicate towards combustion origin of the particles in the engine exhaust.
- Size less than 10 nm evident from the DLS is inconformity with the reported NOC size in the literature.
- FTIR spectroscopy of the samples reports certain structural similarities.

## Conclusions

✓ The spectroscopic results show that very fine NOC particles emitted from the engine exhaust has much structural and physical similarities with such particles existing in the flame environment of similar fuel. It indicates that in-cylinder combustion is the origin of these NOC particles in the engine exhaust. Few structural dissimilarities observed among the particles from the two sources may be attributed to the different combustion conditions existing in the two cases.

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- References:** [1] L.A. Sgro, A. Borghese. Measurements of Nanoparticles of Organic Carbon and Soot in Flames and Vehicle Exhausts. Environ. Sci. Technol., 2006, 42, 859–863.  
[2] H.H. Grotteer, K. Hoffmann, K. Wolf, S. Kanjarkar, C. Wahl, M. Aigner. Study of carbonaceous nanoparticles in premixed C2H4-air flames and behind a spark ignition engine. Combustion and Flame, 2009, 156, 791–800.  
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