Final Scientific Report
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Host Institution: National Research Council Canada – Measurements Science and Standards

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Title of the project: **Laser-Induced Incandescence of Black Carbon-loaded filters** (Incandescenza indotta da laser per l'analisi quantitativa di Black Carbon campionato su filtro)

Period: 05/02/2018-25/02/2018

Introduction

Black Carbon (BC) is well known for its adverse health effects and has been identified as the second most significant positive climate forcing agent next to carbon dioxide. BC is an ubiquitous component of particulate matter. It is produced both naturally and by human activities as a result of the incomplete combustion of fossil fuels, biofuels, and biomass.

The need to measure, characterize and monitor BC particles emission triggered the interest for the development of advanced diagnostic techniques based either on their thermal or optical properties.

A common practice in ambient aerosol measurements is to accumulate particles on a filter before optical analysis. This allows concentration of the particulate and desensitization to gas phase artifacts, both allowing lower BC detection limits. However scattering artifacts introduced by the filter media and accumulated particles can impact the quantitative accuracy of such method. Laser-induced Incandescence (LII) is a measurement method developed for aerosol BC measurements which reaches limit of detection for moderately clean ambient air. Noting that the method is not impacted by light scattering, the applicability of the technique to BC loaded filter could represent a great advancement of technology for BC measurements in air.

Objective

The main objective of the present project is to apply the LII technique to BC-loaded filters with the goal of extending the measurements sensitivity and assessing the degree to which the limit of detection can be extended. Moreover, the study of BC particles attached to filters will allow a deeper physical study of the impact of rapid laser heating on BC internal structure.

Work Plan

Being LII usually applied to aerosol phase measurements, the research activity within this project is focused on the design of the experimental set-up and the definition of the experimental conditions (laser energy density, laser shots, etc.) for LII measurement on a solid surface, such as a quartz-fiber filter.

The effect of the filter loading and the response of different types of BC particles will also be investigated.

Results

At the beginning of the research activity at NRC laboratories some efforts were spent for designing the experimental apparatus for LII measurements on quartz-fiber filter. The experimental apparatus developed by NRC group for in-flame LII measurements[1] has been modified in order to fit the BC-loaded filters and to continuously monitoring the laser energy density. The experimental apparatus is shown in Figure 1.

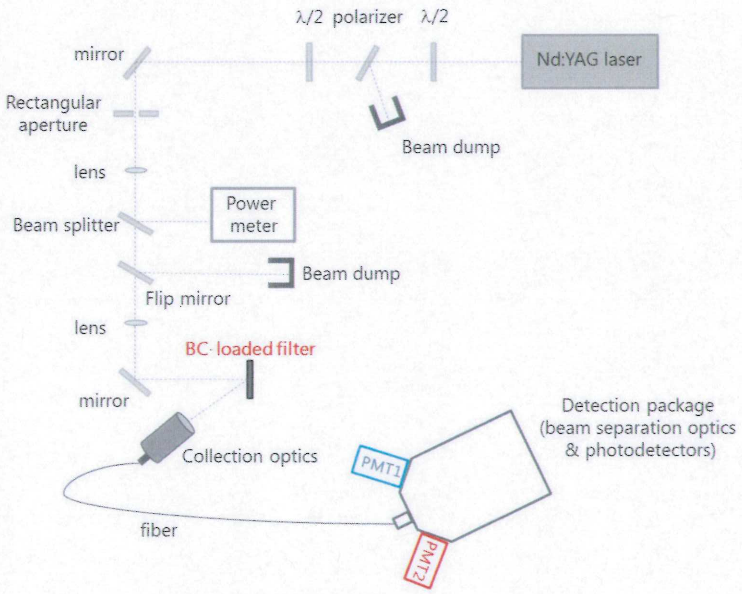

Fig. 1 Experimental apparatus

The fundamental beam (1064 nm) of a Nd:YAG laser (Big Sky Ultra CFR, 50 mJ, 7 ns FWHM), firing at 5 Hz, was used as a light source. A variable attenuator consisting of two half-wave plates and a polarizer was used to adjust the laser fluence. A rectangular aperture was inserted into the laser beam and imaged (1:1) at the measurement location to avoid diffraction effects and to generate a 1064-nm beam with a more uniform energy distribution across a rectangular profile 2 mm wide and 2.5 mm high at the probe volume focal point. A beam splitter has been positioned into the beam path in order to continuously monitor the laser energy by means of a power meter, as reported in Figure 1. Also a flip mirror has been placed into the laser beam in order to stop the laser beam while moving the filter to a fresh measurement spot.

[1] D.R. Snelling, G.J. Smallwood, F. Liu, Ö.I. Gulder, W.D. Bachalo, Appl Opt 44(31), 6773 (2005)

The LII radiation was focused into a 1.0 mm core fiber and transferred to the LII detection package were the LII signal was spectrally separated onto two fast photomultipliers (PMT 1 and PMT2) that records signal with center wavelength at 450 and 750 nm via a combination of dichroic mirrors and band-pass filters. The LII detection system consisting of the collection optics, the core fiber and the detection package has been optically calibrated by means of a large-area Sphere-Optics radiance calibration source. This allows the evaluation of BC temperature and volume fraction via two-color pyrometry. The signals from the two photomultipliers were digitized using a fast oscilloscope and acquired by a Labview program.

It is well know from the literature that LII signals increase with laser fluences in aerosol phase measurements. No indication about the behavior of the LII signal is reported for solid phase measurements. Therefore, in order to define the optimal experimental condition for this kind of experiment, LII measurements were carried out varying the laser fluence from 0.15 to 1.2 mJ/mm^2, which are typical laser fluences for aerosol phase LII measurements. For each laser fluence single shot measurements were performed with a maximum of 100 laser shots for each measurements spot. In order to reduce the signal to noise ratio three different spots on the filter were analyzed for each laser fluence. This also allowed us to check for the filter load uniformity.

A blank quarz-fiber filter was tested for undesired background signal. Fortunately no background signal was detected on both LII channels.

Different type of BC coming from different combustion sources, namely inverted flame, mini-cast burner and helicopter engine, were investigated. Those sources produce BC particles characterized by a different content of Elemental and Organic Carbon, EC and OC respectively. Most of the filter investigated have already been punched for thermal-optical analysis. The correlation between the LII data and the EC/OC data could give insight on the sensitivity of the LII technique to the nature of the BC particles under analysis and it will also allow the validation of the LII technique on filter as a quantitative type of analysis.

All the investigated BC-loaded filters show a similar behavior with laser fluence. As an example, Figure 2 reports the results obtained for a filter loaded with BC particle collected at the exhaust of an inverted flame burner at different laser fluences. At low laser fluence (0.15 mJ/mm^2, Fig. 2a) LII signals increase during the initial 20 laser shots then they seem to be plateauing. The initial LII signal rise turns into a signal fall while increasing the laser fluence (Fig. 2b and c). Surprisingly, the signal plateau after the initial 20 laser shots is always present at all the laser fluences. This is probably due to BC particles trapped into the filter fibers. However, more work is needed to precisely address such phenomenon. The immediate signal drop at intermediate and high laser fluences suggests the occurrence of a sublimation process and therefore it would not be recommend to work at such laser fluences.

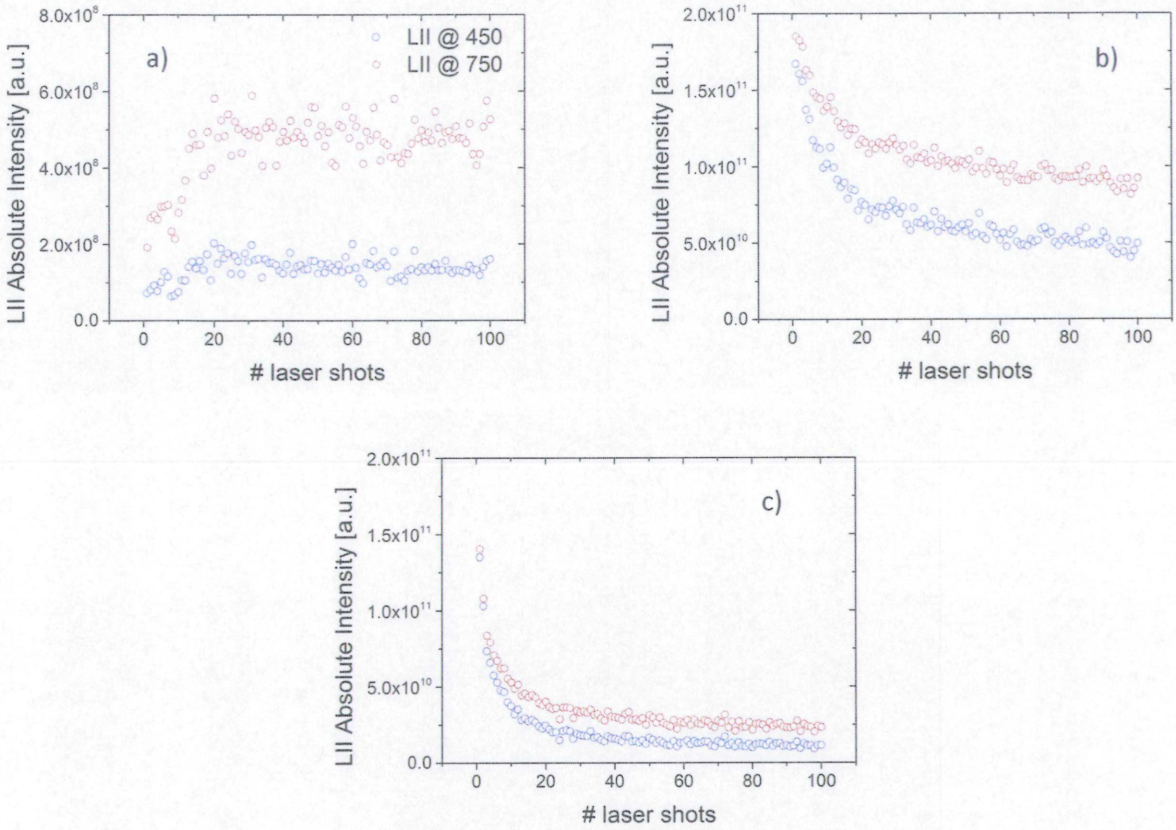

Fig. 2 LII signal behavior with laser shots at different laser fluences: 0.15mJ/mm^2 (a), 0.6 mJ/mm^2 (b) and 1.2 mJ/mm^2 (c)

Another possible explanation for this behavior is that particles are coming off the filter when the laser beam hits the filter surface. In order to verify such hypothesis, a fast particle analyzer (DMS500, Cambustion) was placed just above the laser spot on the BC-loaded filter to capture any particle coming off the filter (Figure 3). In fact, the DMS500, combines electrical mobility measurements of particles with sensitive electrometer detectors, allowing generation of particle size/number distributions in real-time.

Fig.3 Image of the DMS500 sampling probe

Fast mobility spectra measurements show that for laser fluences higher than 0.5 mJ/mm^2, a consistent number of particles are coming off the filter. In particular, already the first laser shot creates ~100-200nm diameter particles from BC-loaded filters . Moreover, ~10nm diameter particles are also created by the first and subsequent shots at such laser fluence. Most likely, the 100nm mode reflects filter-sampled BC particles that are re-suspended by the high fluence light. On the other hand, nucleation of simultaneously-sublimed soot forms the 10nm mode. The two modes are shown in Figure 4. None of those modes was observed at low laser fluence.

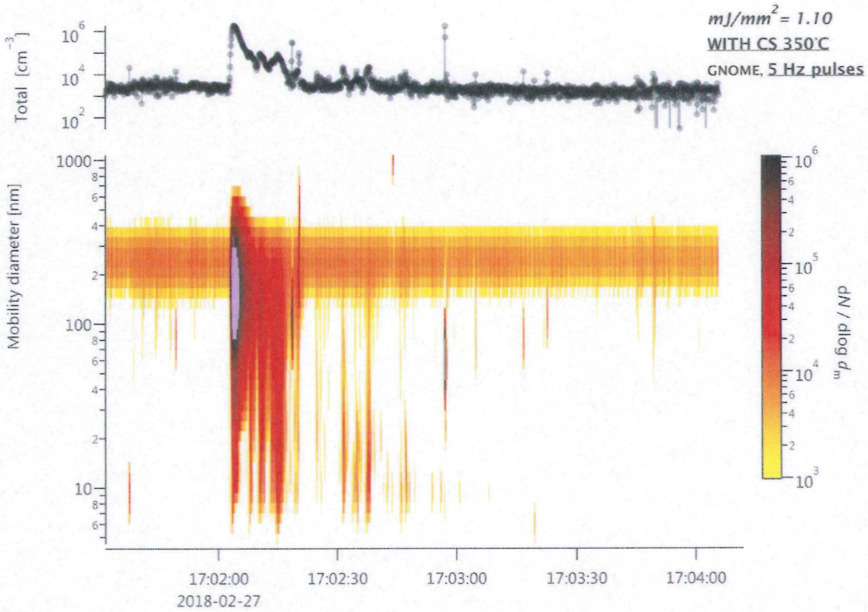

Fig. 4 Evidence of the ~150nm (typical soot mobility) and one ~10nm (typical freshly nucleated particles) modes

These results are very interesting and has to be taken into account in defining the operating condition for LII of BC-loaded filter. According to these results working at high laser fluence will strongly affect the quantitative BC measurements since a consistent number of particles are leaving the probe volume. Therefore, single shot LII measurements has to be performed.

Conclusions and future work

The STM program research activity represents a first attempt in applying LII technique to BC-loaded filters. Some effort was spent in defining the most appropriate operating condition (e.g. laser fluence and number of laser shots). Preliminary results are very promising but also suggest that particular care has to be taken when performing LII on filters. In fact, the LII signal strongly depends on the number of laser shots. Working at low laser fluence will not be ideal, since the LII signal is increasing with the first 20 laser shots, but it would probably help in address the nature of the BC particle. This approach will be investigated by combining the LII data with EC/OC data from thermal-optical analysis.

On the other hand, at intermediate and high laser fluence a consistent number of particles is leaving the filter surface already with the first laser shot, affecting the quantitative BC data. Therefore, in the coming month both laboratories (CNR-ICMATE and NRC-MMS) will work on a strategy to avoid particles loss and to calibrate the LII response for quantitative BC measurements.

Other type of filters, such as ceramic filters, will also be tested.

The two groups will continue to collaborate on this project exchanging filters from one lab to the other for further analysis. They will also jointly work on the processing and interpretation of the data.

Foreseen joint publications

The STM program has contribute to strengthen the collaboration between Dr Francesca Migliorini and Dr Lobo. Following the research visit Dr. Migliorini and Dr. Lobo will be jointly responsible for the preparation of a manuscript summarizing the results which will be submitted for publication in a peer-reviewed journal.

Milano, April 6, 2018

Dr Francesca Migliorini

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