LII INSTRUMENT FOR ENVIRONMETAL APPLICATION

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Abstract
In this work a portable instrument has been developed for the detection of carbonaceous particles for environmental applications. The instrument is essentially based on the two-color laser-induced incandescence (LII) technique and has been calibrated by using a cold soot source in order to derive the soot concentration from the LII signals. Then, particulate measurements have been carried out in different experimental conditions covering a wide range of concentration. For validation, these measurements have been also compared with results obtained with a commercial aethalometer. A good correlation between the two sets of results has been obtained.

Introduction

The study of combustion-generated particulate matter has received particular attention by the research community for different aspects such as the global climate change, environmental pollution and the effects on human health. The need to measure, characterise and monitor atmospheric particles emission triggered the interest for the development of advanced diagnostic techniques based either on their thermal or optical properties. Laser-Induced incandescence (LII) technique is a powerful technique able to measure concentration and size of carbonaceous particles. Many papers can be found in the literature on the development and application of this technique, but an exhaustive analysis of the potential of this diagnostic is far from being reached [1]. Instruments have been also developed and used in different experimental situations [2-3]. In particular the LII300 (Artium Technologies Inc., CA, USA) is able to measure soot concentration from 2 $\mu g/m^3$ up to 20 g/m^3 with primary particle size in the range of 10-100 nm. Therefore the pulsed LII technique exhibits a high dynamic range and can be used for the evaluation of carbonaceous particles content both at the exhaust of engines and in the environment.

Aim of this work is to further investigate the capability of the pulsed LII technique to be applied for environmental applications such as ambient air quality and source emission monitoring. Based on previous work [4] and on the use of an integrating sphere we have recently developed an experimental arrangement for high sensitivity carbonaceous particles measurements (Italian Patent ITRM20090617). Pulsed LII measurements have been performed in different experimental conditions and compared with the ones derived by using a commercial aethalometer. The

results confirm the possibility of using pulsed LII technique for environmental measurements.

Experimental

The main features of the implemented instrument are shown in Fig. 1. Soot particles are sampled using a stainless steel sucking probe, driven by a Dynamic Dilution Sampler (DDS, TCR Tecora, Milan, Italy) and send in a test cell, which is essentially a pyrex tubelet (I.D. = 6.7 mm, O.D.= 9 mm, 10 cm long) with two quartz windows at both ends. The IR beam of a Nd:YAG laser (Quantel, Big-Sky, CFR 400, 10 Hz) is properly aligned within the tubelet. The laser fluence is set to about 350 mJ/cm^2, assuring that sublimation effects can be considered negligible at the incandescence peak. The beam intensity distribution is checked and monitored with a Gentec Beamage Focus I. To avoid scattering from the tubelet walls a diaphragm (4 mm diameter) is used to limit the laser beam diameter. The test cell is placed inside an integrating sphere (Sphere Optics Hoffman LLC, Contoocook, NH). The integrating sphere has the aim of collecting the largest part of the signal generated inside the tubelet and emitted by the particles in every direction. Besides the two circular apertures used for allocating the tubelet, the sphere is provided with a further circular aperture placed perpendicular to the tubelet axis. This aperture is used to allocate the receiving optics for LII signal collection.

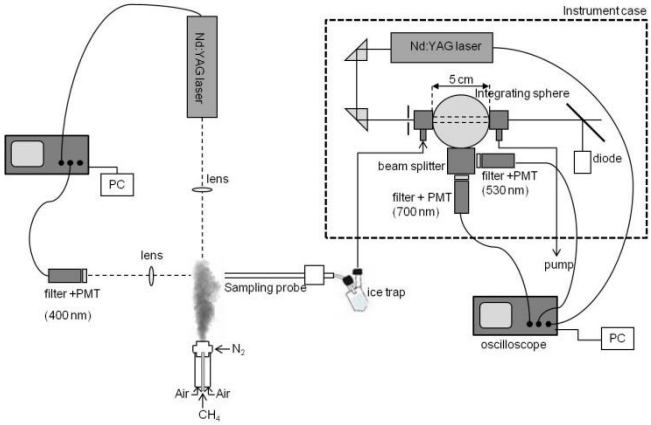

Figure 1. Experimental set-up

The overall LII signal is detected through a system of optical blocks (Hamamatsu) containing a short pass filter (CVI, $\lambda < 850$ nm), a dichroic mirror (660 nm) and two arms. Each arm consists of a band-pass filter and a PMT module (Hamamatsu H5783-20) powered by a power supply (Hamamatsu C7169). The two band-pass filters are centered at 530 nm (40 nm FWHM) and at 700 nm (60 nm FWHM).

A fast digital oscilloscope (Agilent, 1 GHz, 4Gs/s), triggered by the laser Q-switch pulse is used for data acquisition and storage. The two-color LII time-resolved curves are obtained with an average of about 500 acquisitions and processed using

a MATHCAD program. In order to evaluate the "prompt" signal value, the average over a 4 ns interval (1 ns before and 3 ns after) around the maximum of the LII curve is performed [5, 6]. Measurements are carried out using a sampling flow rate of 1 Nl/min and a laser beam frequency of 5 Hz.

Results and discussion

In order to derive the soot concentration from the LII signals, a calibration procedure is required. The calibration is carried out at the exhaust of a home-made soot generator by comparing LII measurements of soot sampled into the instruments with in-situ LII measurements, which are properly calibrated by means of a calibrated tungsten ribbon lamp. The home-made soot generator essentially consists of a quenched diffusion flame. As for in-situ LII, the IR beam of a Nd:YAG laser (Quanta System, SYL 202) is used and properly focused in the probe volume (Fig.1). To obtain particle concentration one-color incandescence signal is sufficient, once the incandescence temperature has been verified to be at the sublimation value in the plateau laser fluence regime. In this work the temperature has been checked to be 4000 ± 50 K, in consistency with previous measurements [5]. The incandescence signal is collected with an achromatic lens on a 1.8 mm diameter diaphragm positioned just before a photosensor (Hamamatsu) coupled with an interference filter (400 nm wavelength, 70 nm FWHM). The time-resolved LII signal is acquired and stored with a fast digital oscilloscope (Tektronix, 1GHz, 5 Gs/sec) triggered by the laser. The laser is running at 6 Hz and the LII curve integrated over 500 acquisitions. This allows us to perform in-situ measurements simultaneously with the LII instrument and over the same integration time. Concerning the LII instrument, the sampling probe has been positioned immediately above the probe volume of the in-situ measurements. In order to condense the water vapor coming from the combustion gases, an ice trap is placed upstream of the sampling line. Replacing the soot generator with the calibrated lamp, the emission radiation is detected in the same experimental conditions. The processing calibration procedure to derive soot concentration is then carried out as widely described in the literature [6].

In Fig. 2 the calibration curve is shown together with the corresponding linear fitting. In particular, the soot concentration measured with the in-situ LII is reported versus the prompt incandescence signal collected with the LII instrument at 530 nm wavelength. As it can be observed in the figure, a linear curve passing through the origin of the axes is obtained.

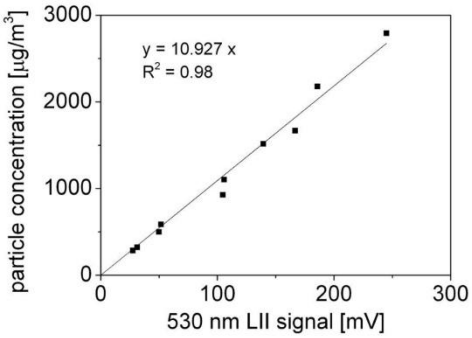

Figure 2. Instrument calibration curve

The LII instrument has then been tested in different environmental conditions in order to cover a range of carbonaceous particles load as wide as possible. Different ambient air (office, laboratory and parking lot), as well as the exhaust of the home-made soot generator and of gasoline- and diesel-fuelled (without DPF) cars have been monitored, collected and measured. In order to validate LII measurements, on-time concentration measurements of optically absorbing aerosol particles have been also carried out using a commercial aethalometer (microAeth AE51, MAGEE Scientific Co.; Berkeley, USA). Both measurements were carried out with almost the same integration time, which was fixed at one minute for the aethalometer and at 51 s for the LII instruments. The sampling probes of the two instruments have been placed in an adjacent position. An exception has been made for the measurements at the exhaust of the soot generator. Due to the presence of a high temperature of the combustion gas flow, and consequently the need to introduce an ice trap, the sampling procedure has been performed as follows. The gas flow after the ice trap, is sucked in a measuring cell and then sampled by the two instruments probes. It is important to stress that being the aethalometer an instrument for air monitoring, concentration on the order of $\mu g/m^3$ have to be produced in order to avoid the aethalometer filter saturation.

As an example, in Fig. 3 measurements performed in a parking lot (a) and at the exhaust of gasoline-fuelled (b) car are reported versus time. The aethalometer measurements have been collected every minute while the incandescence signal intensity has been detected every three minutes. In both cases, a significant change in the concentration allows us to verify the good overlapping of the two sets of measurements. The significant decrease of the concentration over time observed in the case of the measurements at the exhaust of the gasoline-fuelled car (Euro3) is due to the heat-up transient during the start-up regime. It is interesting to observe that in Fig. 4b (parking lot), the peak detected by the aethalometer is due to cigarette smoke and is not registered by the LII instruments. Cigarette smoke is essentially a liquid-like aerosol of a low molecular weight and a high hydrogen content. Being almost gas phase it is not detected by the incandescence. Such

observation allows us to stress that the concentration measurements obtained with the aethalometer, which are derived from extinction measurements, can be overestimated due to the contribution of the scattering signal.

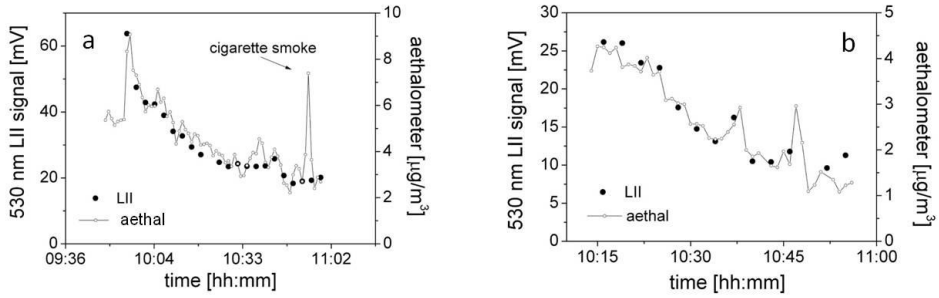

Figure 3. Comparison between LII and aethalometer measurements in different environments: (a) parking lot, (b) gasoline-fuelled car exhaust.

Taking into account the calibration, in Fig. 4 the particles concentration measured with the LII instrument is reported versus the values obtained from the aethalometer for all the environments investigated. As a wide concentration range is considered, a logarithmic scale is used for both axes. A good linear correlation is obtained for the two sets of measurements. It is interesting to observe that the data referring to the air monitoring are in the same range of values, while a wide spread is registered for measurements collected at the exhaust of the gasoline-fuelled car compare to the diesel-fuelled one.

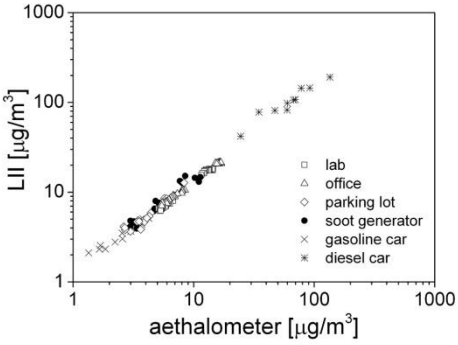

Figure 4. Particles concentration from LII signal instrument versus aethalometer measurements for different environmental conditions.

Directly comparing the particulate concentrations measured with the two instruments, the values obtained with LII instrument are about 25% higher than the aethalometer ones for every environmental condition tested. Taking into account that the two techniques are based on different phenomena, such difference can be considered acceptable.

Starting from the intensity of the LII signals, the limit of the detection of the developed LII instrument has been estimated to be in the range of 200 ng/m^3, which is sufficient for most of the environmental applications.

Conclusions

In this work a new instrument for carbonaceous particle detection and concentration measurement is presented in details. The instrument, which is based on the two-color LII technique, has been tested in different environmental conditions in order to have a range of carbonaceous particles load as wide as possible. The limit of the detection of the developed LII instrument has been estimated to be in the range of 200 ng/m^3. LII instrument measurements have been compared with concentration measurements carried out using a commercial aethalometer for validation. A good agreement in both the fluctuations over time and the absolute value of the concentration is obtained, which confirms the applicability and reliability of the LII instrument in a wide range of applications.

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