High sensitivity Laser-Induced Incandescence instrument for carbonaceous particles detection

F. Migliorini*, S. De Iuliis, S. Maffi, G. Zizak
CNR-IENI, Istituto per l'Energetica e le Interfasi, via Cozzi 53 – 20125 Milano

1. 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, characterize 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.

2. Apparatus

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. 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.

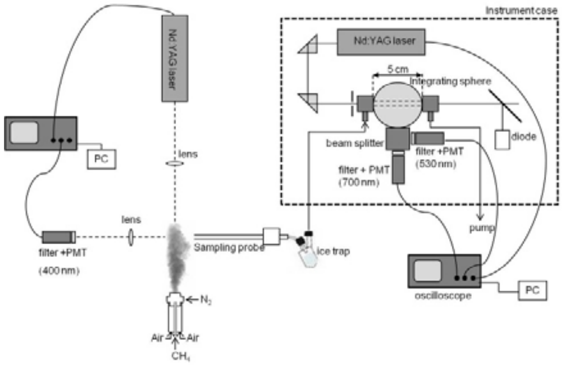


Figure 1: Experimental set-up

The overall LII signal is detected through a system of optical blocks (Hamamatsu) containing a short pass filter (CVI, λ < 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.

4. Results

The LII technique involves heating particles with a high-power pulsed laser of several nanosecond duration followed by cooling down until they reach thermal equilibrium with the surrounding environment [1]. The grey-body radiative emission from the hot particles increases in intensity during the laser pulse depending on the incandescence temperature up to a maximum value [Fig. 2]. The peak of the incandescence signal depends on the particles volume fraction, while the decay time is related to the particle size [7]. The two-color version of the LII technique, being essentially based on the two-color pyrometry, allows performing absolute soot volume fraction measurements. Typical incandescence time decay curves at 530 and 700 nm are reported in Fig. 2. By rationing the LII intensity at the two detection wavelengths, and by taking into account the calibration procedure, soot volume fraction and incandescence temperature are derived. LII signals strongly depend on different parameters, such as optical and heat-exchange properties of the particles as well as the laser fluence (pulse energy/ cm2) [8]. Therefore, in order to investigate the nature of the detected particles, LII measurements at different fluences have been performed. In particular, carbonaceous particles collected in our laboratory and at the exhaust of a soot generator fuelled with methane and ethylene have been measured. Figure 3 shows the ratio of the incandescence signals (related to the incandescence temperature) at 530 nm and 700 nm versus the laser fluence for the different kinds of particles investigated.

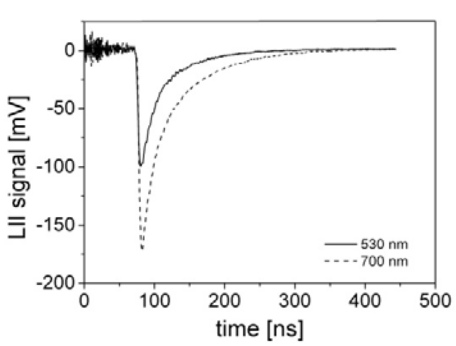


Figure 2: Typical LII time decay curves.

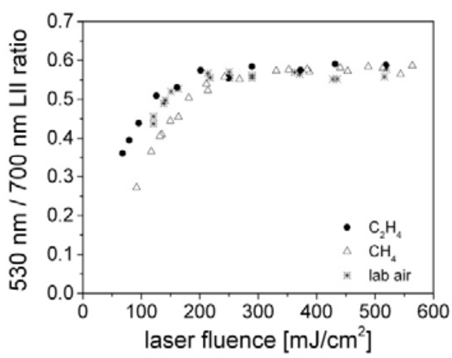


Figure 3: Incandescence ratio versus laser fluence.

As it can be observed, in all cases the ratio increases with the laser fluence up to a threshold level of about 300 mJ/cm^2. Above this value the ratio, , remains quite constant, meaning that the incandescence temperature is constant as well, close to the sublimation temperature (4000 K). Before reaching the plateau the three curves show a different behavior though, suggesting that the particles under investigation present different optical and heat-exchange properties. Therefore to ensure the independency of the LII intensity from the nature of the investigated particles measurements have been performed in the plateau regime at 350 mJ/cm^2.
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 derive the soot concentration from the LII signals, the instrument has been properly calibrated. 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) for validation purposes. 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. It is important to stress that being the aethalometer an instrument for air monitoring, concentration on the order of μg/m^3 have to be produced in order to avoid the aethalometer filter saturation.
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.

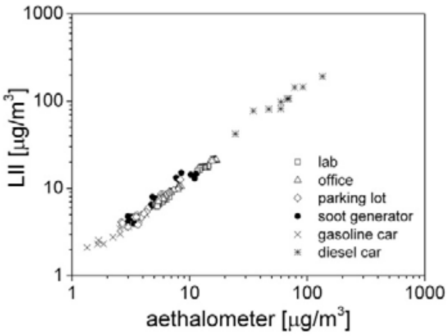


Figure 4. **LII signal instrument versus aethalometer measurements for different environmental conditions.**

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.

5. Summary

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.

6. References

[1] C. Schulz, B.F. Kock, M. Hoffmann, M. Michelsen, S. Will, B. Bougie, R. Suntz, G. Smallwood, *Appl. Phys. B* 83(2006): 333-354.
[2] S. Dankers, A. Leipertz, S. Will, J. Arndt, K. Vogel, S. Schraml, A. Hemm, *Chem. Eng. Technol.* 26 (2003): 966-969.
[3] J. Liggio, M. Gordon, G. Smallwood, S-M. Li, C. Stroud, R. Staebler, G. Lu, P. Lee, B. Taylor, J.R. Brook, *Environ. Sci. Technol.* 46 (2012): 4819-4828.
[4] S. De Iuliis, F. Cignoli, S. Maffi, G. Zizak, *Appl. Phys. B* 104 (2011): 321- 330.
[5] S. De Iuliis, F. Migliorini, F. Cignoli, G. Zizak, *Appl. Phys. B* 83 (2006): 397-402.
[6] S. De Iuliis, F. Cignoli, G. Zizak, *Appl. Opt.* 44 (2005) : 7414-7423.
[7] L.A. Melton, *Appl. Opt.* 23 (1984) :2201-2208.
[8] S. Maffi, S. De Iuliis, F. Cignoli, G. Zizak, *Appl. Phys. B* 104 (2011): 357-366.

High sensitivity Laser-induced Incandescence instrument for carbonaceous particles detection

F. Migliorini, S. De Iuliis, S. Maffi, G. Zizak

CNR-IENI, Istituto per l'Energetica e le Interfasi, Milano, ITALY

Contact : migliorini@ieni.cnr.it

Objectives

- ✓ Development and testing of an experimental apparatus based on LII technique for high sensitivity carbonaceous particles measurements in different experimental conditions.
- ✓ Investigation of the extension of the LII technique to environmental application
- ✓ Comparison of the results with a commercial aethalometer

What is LII and what does it do ?

The Laser-induced incandescence technique involves heating particles with a high-power pulsed laser of several nanosecond duration followed by cooling down until they reach thermal equilibrium with the surrounding environment.

Quantitative measurements for refractory materials, such as soot:

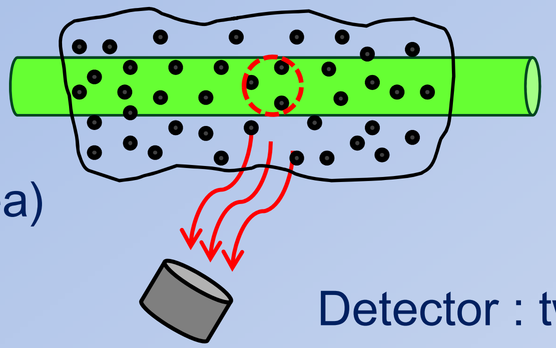
- concentration

  0.01 ppt- 10 ppm volume; 20 ng/m^3- 20g/m^3 mass
- primary particle diameter

  typically 5-50 nm
- number density of primary particles

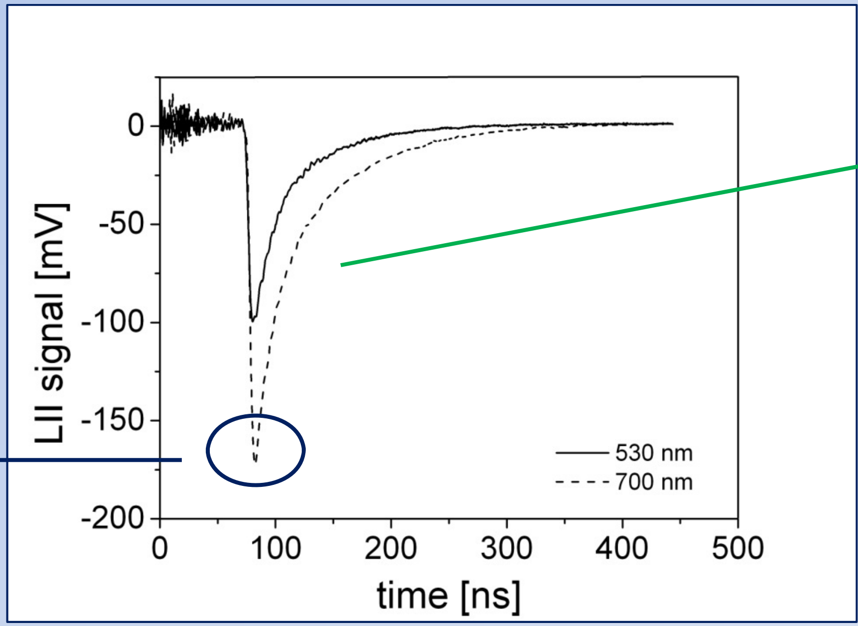
What is LII and what does it do ?

Laser:
- λ_{exc} = 1064 nm
- Fluence (Energy/area)
- Top-hat laser profile



Detector : two $\lambda \rightarrow$ 2C-LII

LII signal



prompt LII $\propto f_V$

Decay curve
⇩
Time-resolved LII
⇩
d_p

LII- based instruments

LII 300

Artium Technologies Inc.

National Research Council Canada / Conseil national de recherches Canada

Sandia National Laboratories

Single particle soot photometer

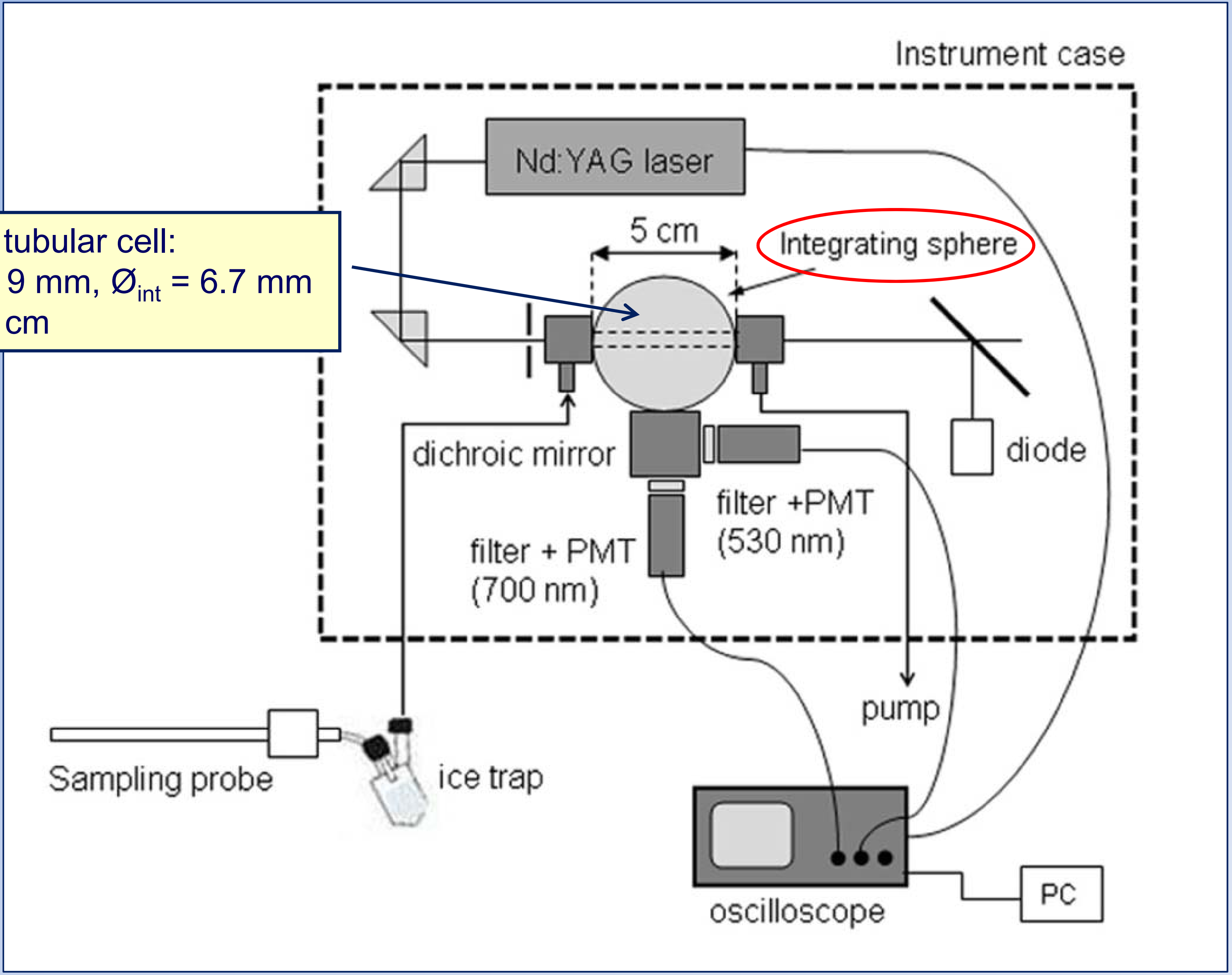
DROPLET MEASUREMENT TECHNOLOGIES

- ✓ soot concentration: 2 μg/m^3-20 g/m^3
- ✓ primary particle size: 10-100 nm

- ✓ Low detection limit: 10 ng/m^3
- ✓ mass equivalent diameter: 70-500 nm
- ✓ counting rate: 0-8000 particles/cm^3

LII INSTRUMENT

pyrex tubular cell:
Ø$_{ext}$ = 9 mm, Ø$_{int}$ = 6.7 mm
l = 10 cm



Aethalometer

- ✓ The instrument provides a real-time optical measurement of light absorbing carbonaceous aerosols (mainly black carbon)
- ✓ The principle of the Aethalometer is to measure the attenuation (ATN) of a beam of light (800 nm wavelength) transmitted through a quartz fiber filter, while the filter is continuously collecting an aerosol sample at controlled flows.

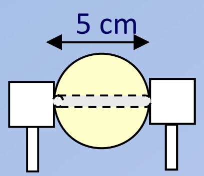
sampling rate = 100 ml/min;

time-resolution = 1 min;

particle concentration ng/m^3

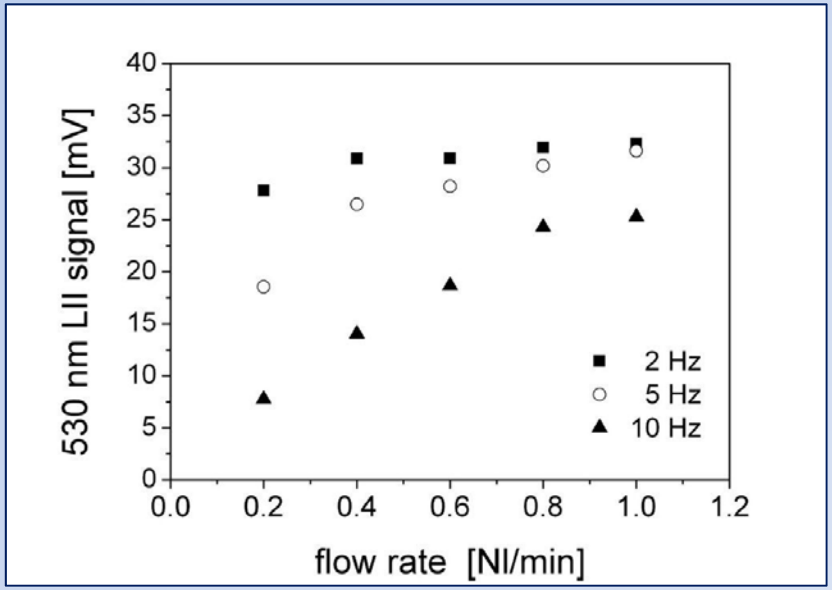
Experimental conditions

Laser frequency & sampling rate



Tube volume = 1.76 cm^3 = 1.76 * 10^{-3} liter

Sampling rate [l/min]	Residence time [s]	# laser pulses at 2 Hz	# laser pulses at 5 Hz	# laser pulses at 10 Hz
1	0.11	0.21	0.53	1.06
0.8	0.13	0.26	0.66	1.32
0.6	0.18	0.35	0.88	1.76
0.4	0.26	0.53	1.32	2.64
0.2.	0.53	1.06	2.64	5.28



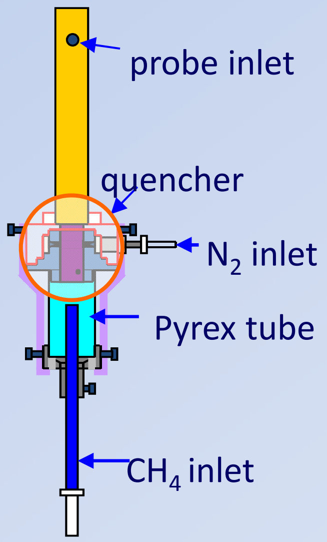
Aethalometer time resolution = 60 s ⇨ LII signal is collected with an average over 256 curves and laser running at 5 Hz

LII signal collected with 1 l/min sampling rate and f = 5 Hz

Experimental conditions

The LII instrument has been tested in different environmental conditions in order to cover a range of carbonaceous particles load as wide as possible:

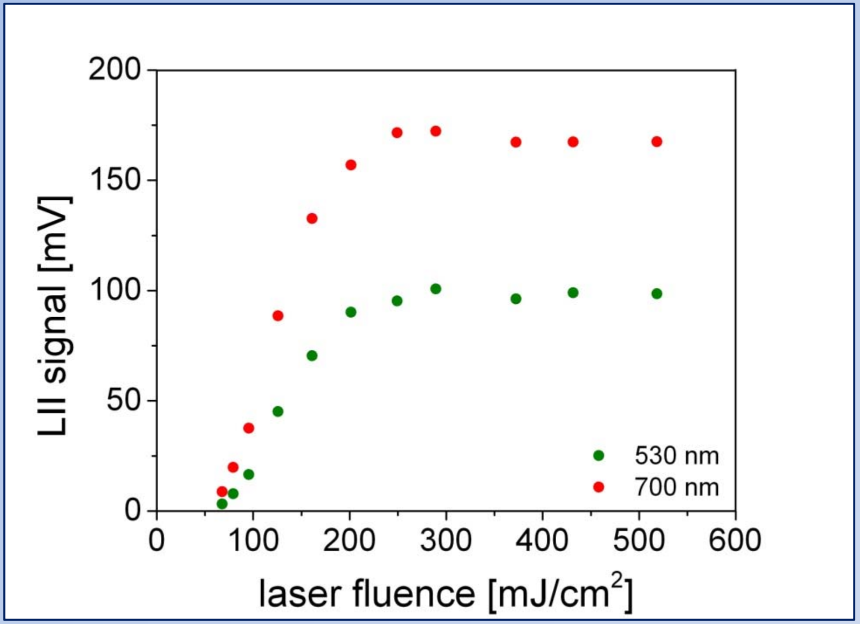
- laboratory
- office
- parking lot
- gasoline and diesel cars' exhaust
- home-made soot generator

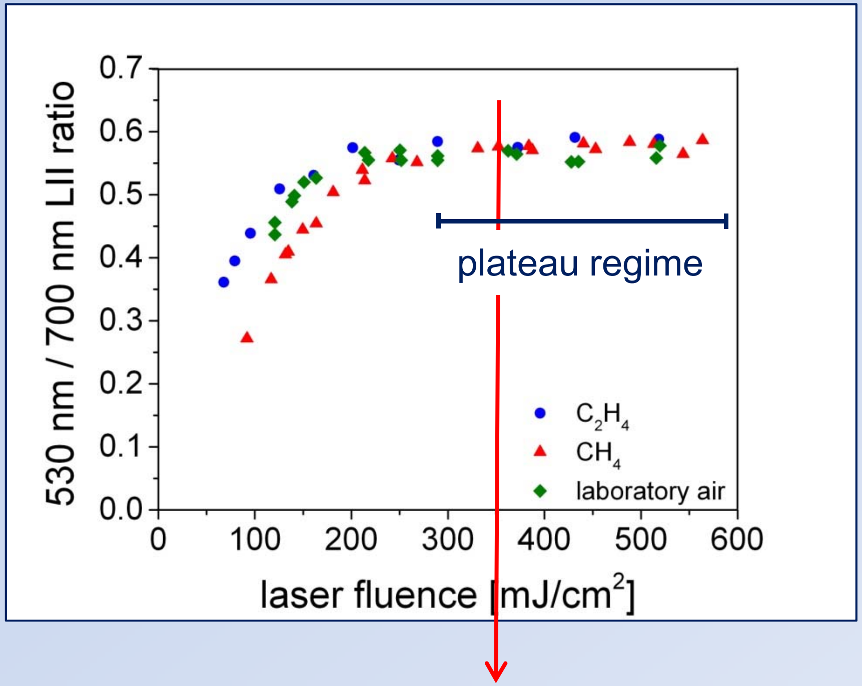


LII signal *vs* laser fluence

LII signal strongly depends on:

- ✓ particle optical properties
- ✓ particle heat-exchange properties
- ✓ laser fluence (pulse energy/area)



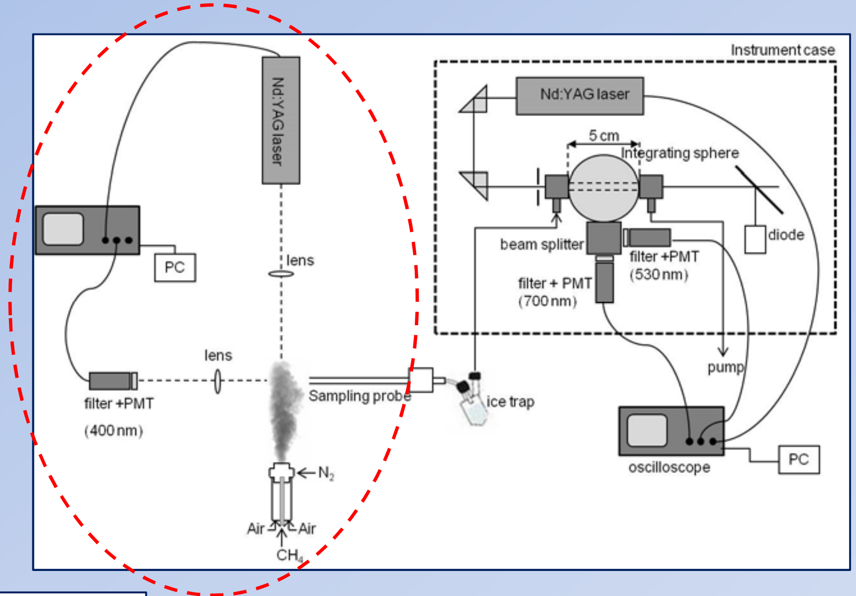


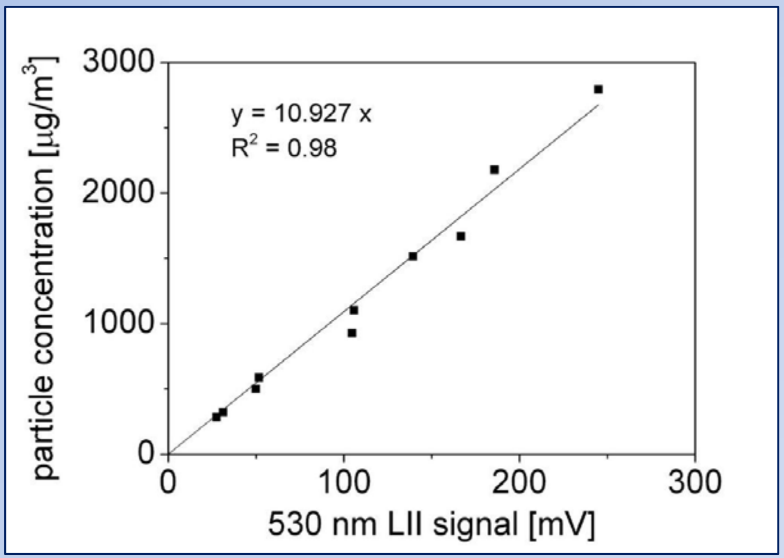
laser fluence = 350 mJ/cm^2

Instrument calibration

In-situ LII in a quenched CH_4 diffusion flame

- particle concentration changed by dilution
- λ_{exc}= 1064 nm
- 350 mJ/cm^2
- λ_{det}= 400 nm
- lamp calibration ⇨ µg/m^3



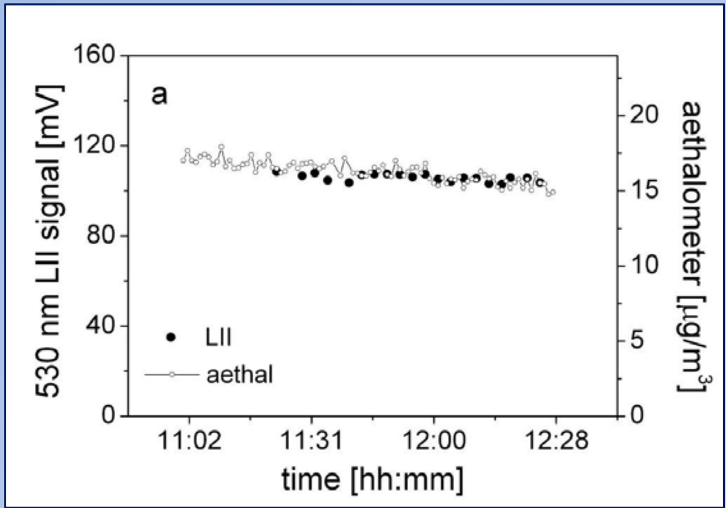


✓ Good linear correlation

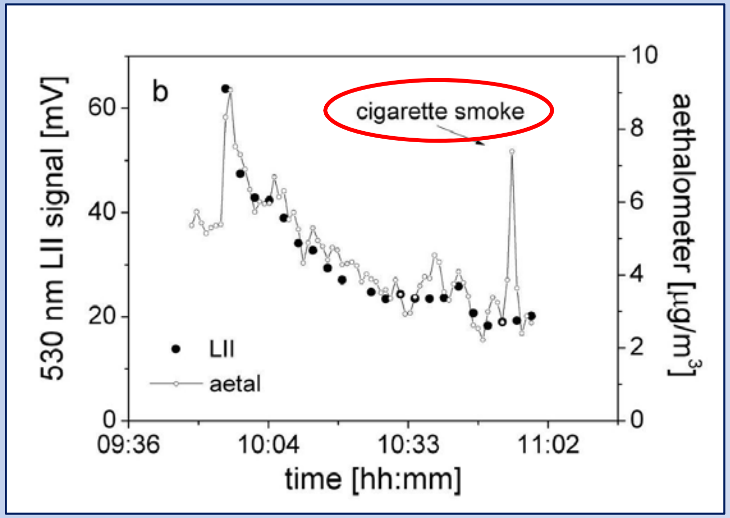
✓ Low Detection limit ~ 200 ng/m^3

Results

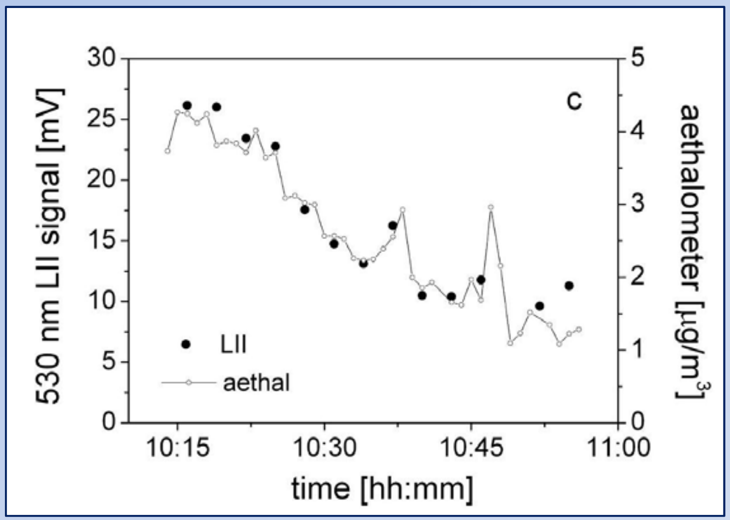
laboratory



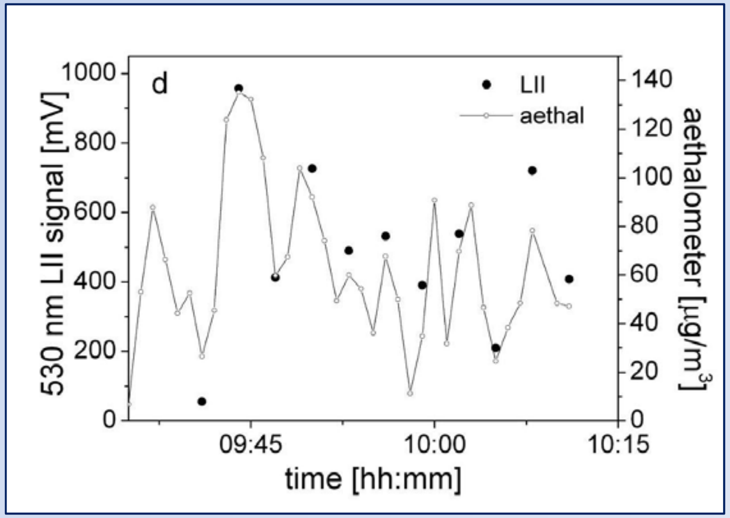
parking lot



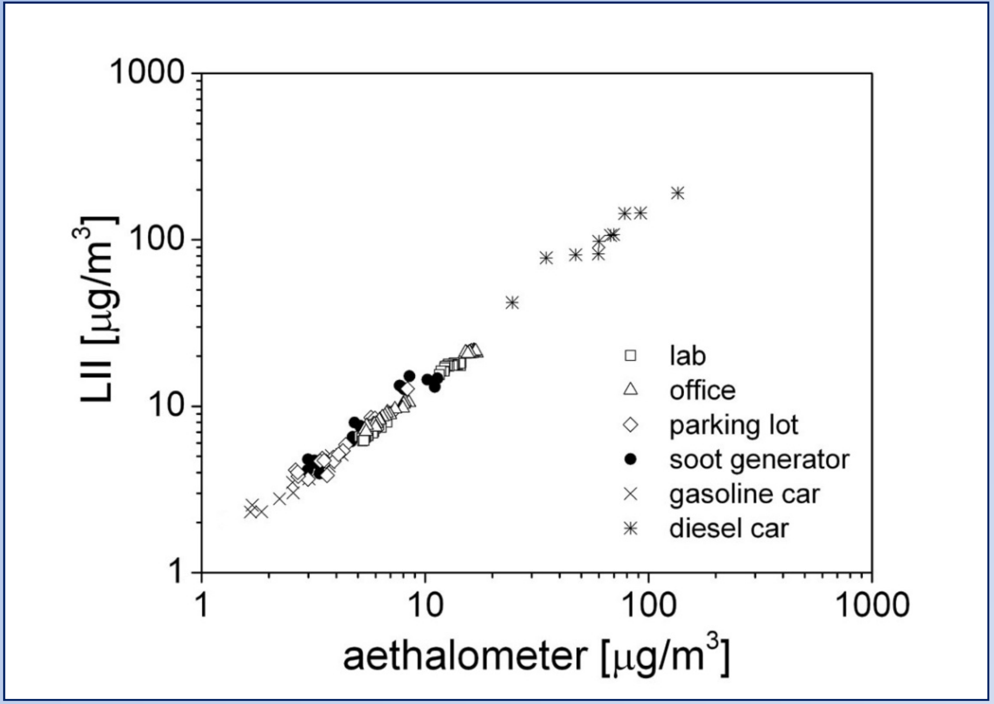
Gasoline car's exhaust



Diesel car's exhaust



LII vs AETHALOMETER



- ✓ Good linear correlation
- ✓ The values obtained with the LII instrument are about 25% higher than the aethalometer ones for every environmental condition tested

Conclusions

- ✓ Presentation of a new portable instrument for carbonaceous particles detection based on the 2C-LII technique.
- ✓ The instrument has been tested in different environmental conditions in order to have a range of carbonaceous particles load as wide as possible.
- ✓ Good agreement with measurements carried out using a commercial aethalometer.
- ✓ The limit of the detection of the developed LII instrument has been estimated to be about 200 ng/m^3.

Future work

- ✓ Increase the sensitivity by increasing the band pass filters and enlarging the laser beam diameter.
- ✓ Couple the two-color LII technique with elastic light scattering to derive the soot aggregate size.
- ✓ Comparison with instruments based on non-optical techniques.

Acknowledgments

The authors would like to acknowledge support for this project from the Ministero dello Sviluppo Economico (MSE)

Thank you for your attention !