LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR ELEMENTAL COMPOSITION ANALYSIS OF AEROSOLS

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Abstract
Laser-induced Breakdown spectroscopy was applied for the elemental analysis of aerosols. Particular care has been taken in optimizing the time resolution of the LIBS spectra and the detection limit of the technique has been evaluated for Na, Ca and Mg atoms. The applicability of the technique has been extended to the case of fly ash generated from coal combustion.

Introduction
The analysis of aerosol particles may involve a wide range of applications such as monitoring of combustion processes and effluent waste streams, particulate air pollution control and atmospheric sciences. Several aerosol measurement techniques have been devised encompassing a broad range of operating principles. In particular laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique that utilizes a laser-induced microplasma which functions as both the sample volume and the excitation source [1]. A pulsed laser beam is tightly focused in a particle source flow. The resulting optical breakdown decomposes and excites all species within the plasma volume. The light emission is characterized by a continuum spectrum containing discrete atomic emission lines. These lines, both neutral (I) and ionic (II) and the continuum emission decay with time, but persist strongly on the order of tens of microseconds. In general the continuum spectrum decay faster than the atomic lines allowing the possibility of detecting atomic lines with a good signal-to-noise ratio by adjusting the delay and the integration time of the detector gate. However from an analytical point of view all the quantitative aspects of LIBS are still under study to better understand the complex nature of the laser-sample and plasma-particle interaction processes which depend on the laser pulse characteristics, sample properties, space and time [2]. Applications of the LIBS technique cover a wide range of species and compounds indicating that nearly all elements of interest in aerosol analysis are readily accessible with LIBS.

Fly ashes are the mayor combustion residues produced during the combustion of pulverized coal in thermoelectric power plants. It is a fine-grained, powdery particulate material that is carried off in the flue gas and usually collected by means of electrostatic precipitators and baghouses. However fine particulate can escape
the collecting devices. Due to the strong signal intensity and relative simplicity of the LIBS apparatus, some applications of the LIBS technique for the analysis of the emissions of burning coal have been recently presented [3-4].

In this work, Laser-induced Breakdown Spectroscopy has been implemented for the detection of low concentration of elements of aerosols in air. Aerosols of sodium, calcium and magnesium were used for the optimization of the LIBS experimental set-up. Fly ashes analysis was used as practical application of the technique.

**Experimental set-up**

A LIBS experimental apparatus typically consists of a pulsed laser, optics, and a detection unit, mainly composed by a spectrometer and a detector. In the present work, a pulsed Nd:YAG laser (Quanta system, $\lambda=1064$ nm, 7 ns FWHM, 6Hz) was used to create the plasma by means of a 165-mm focal length lens. The plasma spectral emission was collected perpendicularly to the incident laser beam onto a fiber optic coupled to the detection unit. Two different detection units with different spectral resolution were implemented. A low resolution spectrograph (JY UFS 200) coupled with a gateable, intensified 1024 elements diode array (Tracor Northern, TN-6130-1) with related control unit (Tracor Northern, TN-1710) was used to record spectra from 231 nm to 847 nm. This allows to get an overview of the atomic emission over a wide range of wavelengths, but the lack in resolution limits the fine analysis of the atomic lines of the element of interest. Therefore, a high resolution spectrometer (Spex 1681 C, 1200 groove/nm, 0.2-nm resolution) coupled with an intensified CCD camera (Princeton EEV, 1152 x 298) was also employed. The intensified CCD detector was synchronized to the laser Q-switch in order to test different detector gates (delay and integration width).

For each experimental condition 250 signals, each one made by an accumulation of 10 laser shots, were averaged in order to improve the signal to noise ratio.

Particle source stream were generated using a typical pneumatic-type medical nebulizer. Aqueous solutions of NaCl, CaCl$_2$ and MgCl$_2$ were nebulized and introduced into an air flow to facilitate droplets vaporization and to produce a fine dispersion of metallic salt. For each element a range of solution concentrations (0.001-0.1M) has been tested in order to evaluate the detection limits of the technique. The atomic emission lines at 588.9 nm and 589.6 nm (Na), 393.6 nm and 396.8 nm (Ca) and 279.5 nm and 280.2 nm (Mg) have been investigated. Cl lines are out of the spectral range of our spectrometer.

**Results**

A typical LIBS spectrum of sodium recorded on time with the plasma emission is shown in Fig.1. As it can be observed, an intense continuum background due to the major Bremsstrahlung emission mechanism predominates, especially in the ultraviolet region. Strongest elemental spectral lines can be observed over this background. In the figure sodium atomic line at 588 nm is shown, together with the
hydrogen $\alpha$ and $\beta$ lines at 486 nm and 656 nm, the nitrogen triplet ($742,744,746$ nm), overlapped due to the low resolution of the detector, and the oxygen line at 777 nm.

![Figure 1. Typical LIBS spectra of sodium plus plasma emission](image)

For the evaluation of the elemental spectral line, a subtraction of the plasma-produced emission is required, which can cause, especially if the element is present only in traces, serious issues in the signal-to-noise ratio. It is important to remind that both continuum signal and the elemental ones decay with time, with the atomic lines persisting longer than the background. The adjustment of the delay of the detection gate with respect to the laser pulse and the related integration time are parameters to be controlled and analyzed in order to maximize the signal-to-noise ratio. Both parameters strongly depend on the nature of the species under investigation. Consequently an experimental analysis has been performed for each atomic element: having the gate width at 2 $\mu$s, the effect of the delay time has been studied. To this purpose the high resolution detection unit has been preferred.

![Figure 2. LIBS spectra for Na(I) (a) and Mg (b) at different delay times](image)
In Fig. 2 the effect of the delay time has been shown for the cases of sodium (a) and magnesium (b). As for sodium, an intense background emission is observed from 0 (on time) to 3 μs delay time. Therefore a delay time equal or higher than 5 μs is recommended for this element. Similar behavior has been observed also for calcium (here not reported). In the case of magnesium, instead, the atomic emission signal is significantly intense compared to the background even at low delay time. Then, in this case, for an optimal signal-to-noise ratio a delay of 4 μs has been chosen.

As vaporization, atomization and ionization of the aerosol particles in the sample volume strictly depend on the laser energy, the atomic emission line has been investigated as a function of the laser energy itself. In these analysis, since all the investigated elements present doublet of atomic lines, the area of both peaks has been considered as LIBS signal. In Fig. 3 signal intensity is reported versus the pulse energy, for the case of sodium. An almost linear trend of the curve is observed over the investigated range of laser energy (70-240 mJ).

![Figure 3. LIBS signal intensity variation of Na lines with laser energy](image)

Nevertheless, increasing the laser energy an increase of the background emission is observed as well. Therefore, an intermediate laser energy of 150 mJ has been chosen as optimal working condition. The same behavior has been observed for Ca and Mg.

In order to investigate the detection limit of the system, measurements at different solution concentration (0.001-0.1 M) have been performed. Figure 4 shows the behavior of LIBS signal versus the solution concentration for all the elements.

A linear dependence is observed in the range 0.001-0.05 M, while a slight saturation effect appears at higher concentration probably due to the inability of the plasma to excite all the atoms present at higher delays.
The lowest detectable concentration ($10^{-3}$ mol/L) obtained with our arrangement corresponds to a minimum detection limit of 80-100 μg/m$^3$ for each element. The use of a high resolution detection unit and known atomic elements in the probe sample allowed to define the optimal working conditions and tested the detection limit of the technique. For a practical application to systems of environmental interest, where the composition of the sample is unknown, a wider (even with low resolution) spectral region needs to be explored in order to simultaneously detect all the species present in the sample. As an example, LIBS measurements have been carried out on fly ashes by using the low resolution detection unit. In Fig. 5 the resulting spectrum is shown, obtained with a delay time and a gate with of 5 μs. In this condition well defined atomic lines can be observed over a negligible background emission. In particular, lines of Mg and Ca can be appreciated together with the atomic line of carbon (247.8 nm). Therefore, the technique has been proved to be suitable for environmental analysis. Further work needs to be done for the application to an unknown sample and especially for the improvement of the detection limits.

![Figure 4. LIBS signal intensity versus element concentration.](image)

![Figure 5. LIBS spectrum of fly ashes.](image)
Conclusions
An experimental set-up for the implementation of Laser-induced Breakdown Spectroscopy (LIBS) has been developed for the detection of low concentration of elements in air. The system has been optimized in terms of laser energy, width and delay time of the detection gate. The detection limit of the system is around 80-100 μg/m³. A test of practical interest has been performed on fly ashes showing the applicability of the technique for the detection of pollutants in ambient air. Further work will be devoted to improve the sensitivity of the system and to extend the technique to other elements of environmental interest such as heavy metals.

Acknowledgment
The authors would like to acknowledge support for this project from the Ministero dello Sviluppo Economico (MSE) and the technical assistance of Mr. Enio Fantin.

References