



Application of a laser-induced breakdown spectroscopy handheld instrument to the diagnostic analysis of stone monuments

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ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) has been in use for decades, but only recently the technique has progressed so to allow the construction of efficient handheld, self-contained commercial instruments featuring a large range of capabilities. In particular, the development of portable handheld instruments able to perform non-invasive, spatially resolved, multielement, *in-situ* analysis has provided an impressive impulse to the scientific investigation of cultural heritage materials. In this work, the design of a handheld LIBS instrument and the first test measurements performed on a fragment of a sedimentary rock monument are presented. A full broadband LIBS emission spectrum with a point and shoot operation was recorded directly within few seconds, so providing information on the elements present in the weathered layer in comparison to the stone surface. Further, the Calibration Free (CF)-LIBS approach was used to test the possibility to obtain a suitable quantitative composition of the main elements present in the sample.

1. Introduction

Typical problems encountered in the study of monument building stones consist in their outdoor location and their being portions of large structures. Thus, very often the object has to be moved indoors for laboratory analysis, but this procedure is generally in conflict with classical conservation ethics. Over the last few years, to avoid the removal of cultural heritage objects located outdoors and that cannot be moved indoors, portable and handheld instruments have been developed and improved to allow the performance of trustable *in-situ*, contactless, fast, sensitive, multi-elemental, non-invasive, non-destructive or micro-destructive analysis having a minimum impact on the art objects. Thus, sampling and any alteration of the physical and chemical integrity of materials can be avoided and the risk of accidental damage and related insurance costs are reduced (Vandenabeele and Donais, 2016). This result has been achieved by miniaturization of components, more compact designs and improvements of detector technology, instrument-computer interfacing, focusing optics and radiation sources suitable for use in various parts of the spectrum (Vandenabeele and Donais, 2016). For example, mobile instrumentation has been used for direct object analysis in archaeological sites or geological outcrops, in the exhibition room of museums and of wall paintings and rock art. Analysis was finalized not only to the conservation and restoration treatments, but also focused on the materials and the technique used to build the

artwork, in order to obtain chronological and geological information (Vandenabeele and Donais, 2016).

The mobile analytical instruments most frequently used are based on X-ray fluorescence (XRF) and Raman spectroscopy (Vandenabeele and Donais, 2016). Although XRF is a non-invasive technique, its main disadvantage consists in the difficulty to measure in air elements with atomic number below 13, such as Na, Mg and Al. The main advantages of Raman spectroscopy are non-invasiveness, reliability and sensitivity, whereas the main disadvantages are the fluorescence emission, which renders difficult the acquisition of Raman spectra, and the interference of external light (Chalmers et al., 2012).

In the last decades laser-induced breakdown spectroscopy (LIBS) has been increasingly employed in studies of historical and archaeological objects, monuments and artworks (Anglos, 2001; Giakoumaki et al., 2007; Spizzichino and Fantoni, 2014; Anglos et al., 2014). Repeated laser pulses were also shown to be able to remove dust coatings and analyze the weathering layers, thus allowing detailed investigation of rock varnish features and underlying pristine rock composition (Gobernado-Mitre et al., 1997; Mavelaki-Kalaitzaki et al., 2001; Lazic et al., 2004; Ortiz et al., 2010; Kiros et al., 2013; Senesi et al., 2016, 2017). With respect to other analytical techniques such as scanning electron microscopy - energy dispersive X-ray, secondary ion mass spectroscopy, XRF spectroscopy and particle-induced X-ray emission, LIBS offers a number of competitive features for the analysis of cultural

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heritage objects. These include simultaneous multielement analysis under atmospheric conditions in a very short time, microinvasiveness, simplicity of instrumentation, almost no sample preparation, and no restriction of sample shape and size (Creemers and Radziemski, 2006). Further, several mobile LIBS instruments have been developed which allow *in-situ* measurements at museums and outdoors at excavation sites and historical monuments (Cuñat et al., 2005; Bertolini et al., 2006; Ferretti et al., 2007; Fortes et al., 2007; Agresti et al., 2009; Gaona et al., 2013). The level of mobility of a LIBS apparatus depends on several factors, such as weight, size and robustness of the instrument, and its degree of independence of resources (e.g., electrical power, cooling water, gases, etc.).

Similar to Raman instrumentation (Smith, 2003), LIBS instruments can be distinguished in “portable” and “transportable” based on whether the instrument is “portable” by a single person fitting in a suitcase or backpack and is battery-operated, or “transportable” by more persons often with the aid of cars or vans and requiring some installation work. In particular, handheld instruments are typically “portable” because they feature no moving parts, which enhance robustness, and can be operated while being held in the hand of the operator in the appropriate position during the relatively short measurement time. Within the last five years several commercial handheld LIBS instruments have become available, some of which feature capabilities that rival traditional bench-top LIBS instruments. These include good resolution, spectral ranges from vacuum ultraviolet (UV) to near-infrared (NIR), argon purging, rastering and portability, which enable LIBS field applications that were heretofore impossible (Connors et al., 2016).

The aim of this study was to test for the first time a portable, handheld LIBS analyzer in atmospheric air with the purpose of simulating real conditions expected for on site measurements to obtain the direct, real-time elemental identification in a stone building monument, and allow the comparison and discrimination between two different portions (the weathered layer and the rock surface) of the same sample. This, by impinging a few laser pulses on the same sample spot, so obtaining specific spectra allowing to track rapidly elements such as Al, C, Ca, Fe, K, Mg, Na and Si present on the weathered layer *i.e.*, the black crust, and the stone surface. Further, the Calibration Free (CF)-LIBS approach, which has the main advantage of being independent of matrix effects, was used to attempt to evaluate the quantitative elemental composition of the two portions.

2. Principles of the LIBS technique and methodologies supporting quantitative analysis

Due to its reliable, compact and highly focused power density, the typical benchtop LIBS system for most applications consists of a Nd-doped yttrium/aluminum garnet (Nd:YAG) pulsed laser operating at the fundamental wavelength of 1064 nm. The laser energy is focused on the sample by a lens placed at a few centimeters from the laser source. The laser blasts the sample surface by one or more laser pulses of energy in the range from 1 to 150 mJ, each lasting about 5–20 ns, which removes/ablates an amount of sample in the range of few hundreds of ng to μg . A wide variety of phenomena occur during this process, including rapid local heating, melting and intense evaporation, which produce an overall electrically neutral plasma composed by molecular fragments, atoms, ions and free electrons. When a local balance of the elementary processes occurring between these species is reached, the system is considered to be in a Local Thermodynamic Equilibrium (LTE) state (Hahn and Omenetto, 2010). A few μsec after the laser pulse the plasma decays or cools so that excited atoms in the plasma emit radiation of characteristic wavelengths, which is focused by a lens into a fiber-optic system that transfers it to a spectrometer. The spectrum so obtained is composed by a number of individual peaks that are diagnostic of the elements present in the sample and feature three main parameters, *i.e.* wavelength, intensity, and shape, which depend on the type, amount and surrounding environment of the emitting elements. The main

objective of quantitative LIBS analysis is to obtain an optically thin plasma in the LTE state, the elemental composition of which is equivalent to that in the sample, *i.e.* to realize a stoichiometric ablation, so that the spectral line intensities would result directly related to the actual element concentrations in the sample (Creemers and Radziemski, 2006).

The quantitative evaluation of elements in a sample can be achieved by using the CF-LIBS approach that is based on a plasma physics model and is able to overcome sample matrix effects, *i.e.* to reduce the quantitative statistical uncertainty, thus avoiding the cumbersome use of calibration standards and the generation of calibration curves (Creemers and Radziemski, 2006; Ciucci et al., 1999). The CF-LIBS model is based on the assumptions that the plasma is optically thin and in the LTE state, its chemical composition is the same as that of the sample, and its temperature, as described by the LTE model, can be accurately extracted from the spectrum (Creemers and Radziemski, 2006). Thus, the integrated emission peak intensity can be calculated assuming that a Boltzmann distribution is held at the LTE temperature. Further, the plasma parameters, *i.e.* electron excitation temperature, T_e , and electron density, N_e , can be calculated. The first, from each emission line considered by using the Saha-Boltzmann plot methodology, and the second from the average of the Stark broadening values obtained from the different emission lines or from the Stark broadening of the $H\alpha$ emission line usually present in LIBS spectra acquired in air. By principle, the CF algorithm would allow to calculate the concentration of all elements present in the sample down to the detection limit of the method.

3. Materials and methods

The sample used in this work is a limestone fragment from a block of the masonry of Castello Svevo, Bari, Italy, which shows a surface degradation featuring a black crust layer. The fragment is the same analyzed in a previous works by benchtop LIBS (Senesi et al., 2016, 2017).

In this work, a portable, handheld LIBS instrument named NanoLIBS (B&W Tek, Newark, DE, USA) was used to perform the measurements. The instrument consisted of a miniature-diode-pumped, solid-state, short-pulsed laser emitting at a wavelength of 1064 nm with a maximum output of 300 mW, a pulse duration of 500 ps and a maximum pulse energy of 150 μJ , and operating at a high repetition rate, *i.e.* between 1 and 5 kHz. A compact spectrometer allowed to record the spectra in the non-gated mode in a wavelength acquisition range from 180 to 800 nm, *i.e.* from UV to visible, with an overall resolution of 0.4 nm for the entire spectral range. However, the actual resolution of the spectrometer is wavelength dependent, resulting higher in the UV range than in the visible range of the spectrum.

The whole setup was enveloped in a lightweight handheld body (Fig. 1), with a mass and dimensions of approximately 1.8 kg and $26 \times 10 \times 30$ cm, respectively. A liquid crystal display (LCD) touch screen panel allowed to control the spectrometer and the acquisition settings. For safety reasons, a sensor installed in the analytical head allowed to control automatically the laser output, so that the laser could operate only when the analytical head was in contact with the sample (Fig. 2, left).

LIBS measurements were performed by placing the nose of the instrument against the sample and then starting the analysis via a trigger, *i.e.* a screen icon on the analyzer. In this experiment, the integration time of the spectrometer was set at 4 ms that corresponds to twelve laser pulses for a 1 kHz laser. The system featured a rastering beam that covered an area with a diameter of about 300 μm . In each measurement lasting about 6 s a total of 150 spectra were averaged, which corresponds to about 1800 laser pulses. Three measurements were averaged for each data point, and each portion of the sample was analyzed in ten different positions by the same procedure to obtain a single average spectrum.

For field operations the NanoLIBS was provided with a rechargeable

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