



Laser Induced Breakdown Spectroscopy methodology for the analysis of copper-based-alloys used in ancient artworks[☆]

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ABSTRACT

In this paper Laser Induced Breakdown Spectroscopy has been applied for determining the elemental composition of a set of ancient bronze artworks coming from archaeological site of Minervino Murge – Southern of Italy (dated around VII b.C.). Before carrying on the analysis of the archaeological samples, the characterization of the analytical technique has been accomplished by investigating the trueness of the typical assumptions adopted in LIBS, such as Local Thermodynamic Equilibrium, congruent ablation and plasma homogeneity. With this purpose, two different laser pulse durations, 7 ns and 350 fs, have been used. We have focused our attention on LIBS analysis of bronze standards by considering and discussing the bases of both methodology and analytical approach to be followed for the analysis of ancient copper-based-alloy samples. Unexpectedly, regardless from the laser pulse duration, the LIBS technique has shown, by considering an adequate approach on the emitting plasma features, that its peculiarities are anyway preserved so that a fast analysis of ancient copper-based-alloys can be achieved. After verifying the suitability of the methodology, it has been possible to fulfill the typical assumptions considered for the LIBS calibration curves method and use it for ancient bronze artworks analysis.

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1. Introduction

Several works, discussing the potentiality of Laser Induced Breakdown Spectroscopy (LIBS) as an analytical tool for the determination of the elemental composition of solid targets, point out its numerous advantages. They include fast response and high sensitivity (generally ppm), extremely wide range of materials that can be investigated without any need of an analytical chamber, possibility of performing the analysis without sampling or surface treatment, and flexibility of the experimental set-up configuration [1]. The huge range of applications, that LIBS can be employed for, has led to a good understanding of the fundamental questions at various experimental conditions. It has been established that the species distribution among their excited states in the plasma depends on the expanding fluidynamics of the ablated particles and on the balancing of the elementary processes [2–6]. The LIBS analytical peculiarities and the deep knowledge developed on laser induced plasma characteristics clearly suggest the benefits from LIBS methodology for automatic and fast analysis requirements. In this scenario the possibility of applying LIBS technique for the analysis of

ancient artworks is an important question in those countries, such as Italy, where the number of archaeological findings is so huge that conventional time-consuming analytical techniques are not suitable enough. Indeed, the massive quantity of findings, that lay in museums, require fast analytical tools able to reduce the costs and increase the rate of operation. In this context, LIBS technology can play a really important role because of its immediate response and negligible damage induced onto the investigated sample. The LIBS analysis of bronze samples has already been studied by other authors [7–9] who discussed its advantages as well as calibration problems occurring in copper-based-alloys laser induced plasmas. Several works [10,11], discussing the properties of the copper-based material emission plasmas, have been published although some contradictions arise [12]. Prior to the analysis of the ancient artworks, a deep characterization of the methodology has been carried on in order to check the trueness of the typical assumptions of the LIBS calibration curves method. It is known that, for relative low density of energies, a thermal vaporization mechanism characterizes ns laser ablation leading towards fractionation effects. On the other hand, since thermal mechanisms scarcely contribute to ultra-short laser ablation processes, for which laser energy densities are slightly above the threshold, a stoichiometric material sampling can be supposed when using fs pulses [11,13–15]. For these reasons, two different laser pulse durations, 7 ns and 350 fs, have been used in order to establish if fractionation processes can be neglected and if the same approach can be

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followed for both plasma regimes, so that the calibration curves method can be anyhow applied. Finally, we have focused our attention on the LIBS analysis of bronze artworks and discussed, from a fundamental point of view, which methodology and analytical approach should be used.

2. Experimental set-up

The instrumental set-up consists of a laser source, a spectroscopic system, pulse generators and a target holder allowing micrometric adjustment of target position as described in previous works [16]. Two different laser sources with pulse duration of 7 ns or 350 fs have been employed. The ns laser source provides pulses, with a repetition rate of 10 Hz and a fixed fluence of 5.0 J cm^{-2} at 532 nm. The ultra-short pulses are provided by a Twinkle Light Conversion Nd:Glass laser ($\lambda = 527 \text{ nm}$), running a 10 Hz repetition rate, an energy of 3.0 mJ and a relative fluence of 4.2 J cm^{-2} . In order to get these working fluences, either a 250 mm or a 100 mm focal length lens has been employed for the ns or the fs laser beam, respectively. The spectroscopic system consists of a monochromator TRIAX 550 Jobin Yvon with a 1800 g/mm grating and an ICCD i3000 Jobin Yvon and a pulse generator Stanford inc. DG 535 for selecting the delay time and the gate width of the detector. The plasma emission is collected by a fused silica 7.5 cm focal length biconvex lens directly on the monochromator slit. According to the specific experimental needs, the ICCD can be programmed to work with the photodiode column signals integration to give a single spectrum or detecting separately the signal by each photodiode, in order to realize a spectral resolved image. In the latter case the spectral resolution depends on the slit aperture and each array corresponds to the spectrum of a $26 \mu\text{m}$ portion of plasma.

In order to collect the emission signal exactly in the same way for all the standards and samples, and to avoid target surface displacement with respect to the laser focus, spectral resolved imaging has been applied for the fine alignment of the received signal. Adjustments of target position have been performed by a micrometric step, so that the emission of the investigated spectral lines always reach the same ICCD matrix area. The spectral response of the whole detection system and the wavelength calibration have been performed by means of reference lamps. The employed copper alloys certified standards (Tech Lab-Metz-France) cover the following range of weight percentages: 0.25–6.12% for Pb, 0.26–12.96% for Sn, 0.57–3.19% for Ni, 0.02–0.36% for Fe, 1.22–32.70% for Zn, 0.01–3.72% for Si and 0.05–0.20% for Sb; whereas the Cu amount is always higher than 65%. All the spectroscopic data for the investigated emission lines have been provided by NIST [17] and Kurucz [18] databases.

3. Results and discussion

3.1. Qualification of LIBS technique for the elemental chemical analysis of bronze samples

The most important assumption for analyzing plasma composition by any diagnostic method is based on the hypothesis that all the detected plasma volume is homogeneous. In the case of LIP the elemental partial pressure decreases from the internal hot core to the external border as well as with the time delay from the laser pulse [2,16], but, if chemical reactions contribution can be neglected, there is no reason to suppose any change in composition within the plasma itself. In previous works, it has been established that during the ablation of conductive materials in air, chemical reactions take place at long delay times and at plasma edges [19,20]. When the composition is determined by optical emission spectroscopy it is important that self-absorption, if involved, can be considered negligible during the detection of the considered emission lines. Finally, if the plasma is locally homogeneous and optically thin, the concentration value obtained by species emission lines should keep constant the determined value in all the examined portions of the plasma. To prove these arguments, spectral resolved imaging experiments, as shown in Fig. 1, have been performed. The spectral resolved image of Fig. 1 shows the spectrum of the central slice of the plasma along the propagation direction Z-axis. The ratio of Pb and Sn intensities with respect to Cu is reported in Fig. 2 as a function of the distance from the target at a delay time of 800 ns and a gate width of $5 \mu\text{s}$. By the inspection of Fig. 2, it can be observed that, for a bronze sample, the intensities of Pb I at 283.30 nm and of Sn I at 284.00 nm normalized with respect to the Cu I emission line at 282.44 nm, hold a constant value for the most the sampled plasma volume. Conversely, where non homogeneity occurs, as a consequence of the plasma border interaction with air, the absolute emission contribution is at least one order of magnitude lower than from the homogeneous zone. Although this observation is one of the main fundamentals to be addressed for the analytical use of LIBS, some more evaluations should be made. Among these, it should be surveyed the dependence of analytical results on theoretical assumptions since the observed emission lines are directly correlated to the species energy distributions in the expanding plasma instead of the investigated sample species concentrations [2]. In relation to this set of experiments has been devoted to check the validity of using, for bronze samples, the calibration curves method where the main component operates as the internal standard. It is

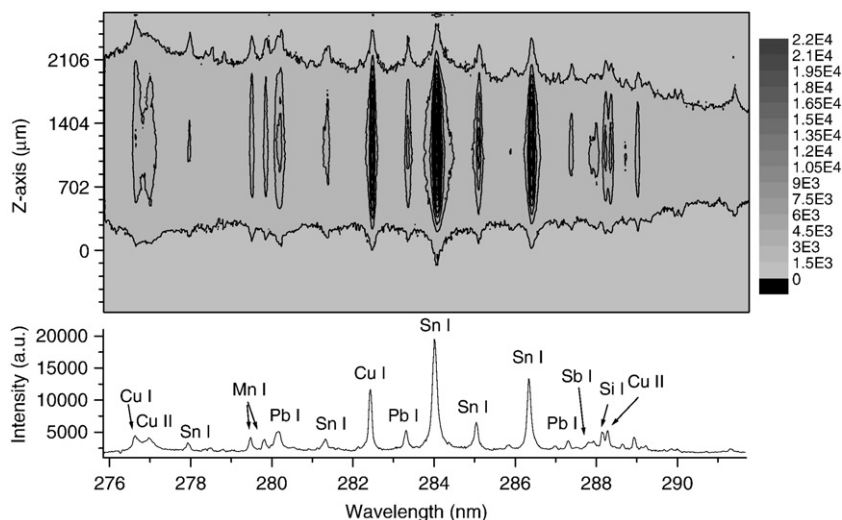


Fig. 1. Typical spectrally resolved image of a selected section of bronze spectrum between 276 and 292 nm.

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