

LIBS Calibration Curves and Determination of Limits of Detection (LOD) in Single and Double Pulse Configuration for Quantitative LIBS Analysis of Bronzes

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The LIBS technique has been utilized for a long time in the Cultural Heritage field. However, the potential of this technique for accurate quantitative analysis could be greatly improved using an innovative experimental setup based on the use of two laser pulses suitably retarded. On the basis of the analyses performed on a set of certified bronze samples, reference curves were built and Limits of Detection (LOD) were calculated. The detection limits for the elements of interest were calculated under the optimum conditions for the double-pulse configuration and compared with those obtained under the optimum conditions for single-pulse configuration. Significantly improved detection limits were achieved, for all the elements investigated.

Keywords: LIBS, Bronzes, Quantitative Analysis, Calibration Curves

1. INTRODUCTION

Laser Induced Breakdown Spectroscopy (LIBS), also named Laser Induced Plasma Spectroscopy (LIPS) or Laser Ablation Spectroscopy (LAS), is a technique based on the spectral analysis of the radiation emitted by a plasma generated by focusing an intense laser pulse on the sample surface.

The intense laser pulse focalized on the sample surface causes evaporation, atomization and ionization of the material and produces a plasma which expands and cools very rapidly. In typical LIBS conditions the ablation process is stoichiometric: analyzing the atomic and ionic lines emitted by the plasma provides the identification of the species present in the sample and their quantification.

The intrinsic simplicity, robustness and quickness of LIBS make it particularly appropriate for in-situ analysis even in hostile environment. In recent years, a number of applications of LIBS technique have been proposed in the field of Materials Science, Industrial Processes Control, Environmental Protection and Cultural Heritage conservation and study [1].

It is generally agreed among the scientific community that poor detection limits are the most important limitation of the LIBS technique, compared to other consolidated analytical techniques. Therefore, several research groups have investigated possible ways to improve the

LIBS Limit of detection (LOD) [2,3]. One of the most promising approaches to solve this problem is the combined use of a pair of laser pulses to ablate the material and further excite the resulting plasma. Spectral analysis of laser-induced plasmas for surface ablation has demonstrated the possibility of analyte signal enhancement with dual pulse configurations as compared with traditional single-pulse LIBS. It was found that both the ionic and atomic emission lines intensities are considerably enhanced with respect to single pulse. Thanks to the recent introduction of the first mobile dual-pulse instrument for LIBS analysis (Modi), double pulse measurements on archaeological artefacts can now be performed in a few minutes and in situ, without sampling or any kind of pre-treatment of the sample [4].

To demonstrate the feasibility of LIBS analysis for such kind of objects, in the present work we performed a systematic study which lead us to building proper calibration curves for major and trace elements in bronze alloys that simulate real archaeological artifacts, at atmospheric pressure in air using single and collinear double pulse configurations of laser-induced breakdown spectroscopy. Calibration plots were constructed for Sn, Pb, Zn and Cu and the corresponding limits of detection (LOD) were determined.

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2. EXPERIMENTAL SETUP

The measurements were performed at Applied Laser Spectroscopy Laboratory in Pisa, using the MOBILE Dual-pulse Instrument (Modi) [2] for LIBS analysis produced by Marwan Technology s.r.l. (See fig.1).



Figure 1 - The MOBILE Dual-pulse Instrument (Modi) used for LIBS analysis

The instrument integrates a dual-pulse Nd-YAG laser ($\lambda=1064$ nm), which emits two collinear laser pulses with energy variable between 50 and 150 mJ per pulse (12 ns Full Width at Half Maximum) at a maximum repetition rate of 10 Hz and a reciprocal delay which can be set from 0 to 60 μ s. The LIBS measurements can be performed on small samples inside a closed experimental chamber, equipped with a motorised table for exact positioning of the sample at the focus of the laser beams. A laser pointer and an optical microscope allow the control of the region of the sample under analysis. Alternatively, for direct measurements on the large objects an articulated 5-joints arm allows the focusing of the laser outside the instrument and the collection of the spectral signal.

The LIBS signal is collected through an optical fibre and sent to a compact Echelle spectrometer coupled with an intensified CCD camera for spectral acquisition.

The operations of the instrument are controlled by an integrated personal computer which manages the sample visualization and positioning, the experimental settings of the laser (energy of the beams, delay between the pulses, repetition rate) and the spectral acquisition parameters (number of spectra averaged, acquisition delay, CCD measurement gate and gain).

The emission spectrum is characteristic for each emitting element in the plasma, which allows qualitative and quantitative multi-elemental analysis. The LIBS spectra,

after acquisition and storage, are qualitatively and quantitatively analysed using the proprietary software LIBS++.

A typical analysis can take between one and five minutes, according to the complexity of the LIBS spectrum produced.

3. QUANTITATIVE ANALYSIS USING CALIBRATION CURVES

The classical definition of LIBS intensity considers the peak value of the emission line; however, an equally legitimate definition of LIBS intensity could be formulated in terms of the integral of the emission line. As we will see in the following, there are several reasons that would suggest the latter choice. The most obvious is the fact that the line integral is calculated over a number of points, therefore the effect of the detector electronic noise is somewhat reduced in the evaluation of the integral, while it fully affects the peak value of the line (see discussion below). Moreover, all the causes of line broadening produce a spatial ‘spreading’ of the line on the surface of the detector. The integral emission, being proportional to the number of photons emitted at the transition of interest, remains the same, while the peak value of the emission line is influenced by the broadening. Since the line integral scales as (Peak value) x (Width), an increase of the line width corresponds to a decrease of the peak value of the line, and vice versa.

A calibration curve built using the integral values of the emission line is also less sensitive to self-absorption, with respect to the same curve built using the peak values of the line. In fact, it has been demonstrated [4] that for a given optical opacity of the line considered, the ratio of the peak value in the presence of self-absorption (I) with the same value that would be obtained if self-absorption would be not present (I_0) is equal to

$$\frac{(I)_{peak}}{(I_0)_{peak}} = \frac{(1 - e^{-\kappa(\lambda_0)l})}{\kappa(\lambda_0)l} \tag{1}$$

while for the integral line intensity the ratio scales approximately as the same quantity

$$\frac{(I)_{int}}{(I_0)_{int}} \approx \left[\frac{(1 - e^{-\kappa(\lambda_0)l})}{\kappa(\lambda_0)l} \right]^\beta \tag{2}$$

with $\beta=0.46$. This is due to the fact that, in the presence of self-absorption, the peak intensity decreases as in eq. (1) but, at the same time, the line width increases as

$$\frac{(\Delta\lambda)_{int}}{(\Delta\lambda_0)_{int}} \approx \left[\frac{(1 - e^{-\kappa(\lambda_0)l})}{\kappa(\lambda_0)l} \right]^\alpha \tag{3}$$

with $\alpha=-0.54 = \beta - 1$.

According to the current definition, the LOD is the lowest analyte concentration, if actually present in the sample, that will be detected and can be identified [2,3]. To determine the limit of detection, the suggest-

ed procedure requires taking ten measurements at ten different locations on a blank sample; the limit of detection is then given as

$$LOD = 3s/b \quad (4)$$

where s is the standard deviation of the spectroscopic signals of the ten measurements on the blank sample and b is the slope of the linear calibration curve. It can be pointed out that the limit of detection, which practically represents the lowest analyte concentration which is measurable against the (noisy) background, is only one of the possible quantities that can also be defined, such as the Limit of Quantitation (LOQ) (the lowest analyte concentration that can be measured with acceptable reproducibility and precision) [2,3].

The definition of LOD requires some considerations. First of all, it is assumed that the calibration curve is linear around zero analyte concentration and that the calibration curve would be exactly zero at zero analyte concentration (more exactly, the calibration curve at zero analyte concentration must coincide with the average value of n independent measurements on a blank sample, with $n \gg 1$). However, when the calibration curve is obtained as a result of a best fitting procedure on real experimental data, its intercept at zero analyte concentration is always different from zero, unless this condition is imposed *a priori*.

In fact, in real LIBS applications, the calibration curves are often built using a limited number of samples (usually less than 10); moreover, it can be difficult to obtain a reliable blank for the analyte corresponding to the same matrix considered in the measurement, and the range of concentration span in most cases makes the non-linearity of the calibration curve, evident.

Although from the point of view of quantification of an unknown sample, there is no need for the calibration curve to be linear, or for the curve to pass by zero at zero analyte concentration, the proper definition of LOD requires all of these conditions.

Let us explain better this concept considering the case of Gaussian electronic noise, with a given statistical amplitude s , superimposed to the signal. The definition of the variance of the signal on the blank sample, in case of a calibration curve built using the peak value of the line is straightforward ($s = \sigma$). Given a slope b of the calibration curve, the resulting limit of detection would be

$$LOD_{peak} = 3s/b \quad (5)$$

On the contrary, using the line integral as definition of the LIBS intensity, it seems quite obvious that we should also use the integral of the electronic noise as a measurement of the signal variability on the blank. In principle, the line integral should be evaluated over the whole spectral range available; in practice, the integral of the line is measured in a narrow spectral region around the line maximum. The same interval must be chosen for evaluating the variance of the integral of the noise on the blank sample; if the experimental line width is DI , for both the calculation of the line integral and the evaluation of the 'noise' on the blank sample, we can, for example, consider

a spectral region between $\lambda_0 - 3\Delta\lambda$ and $\lambda_0 + 3\Delta\lambda$. In our experimental conditions, this spectral interval would correspond to n ($n > 1$) channels on the detector, so that the integral of the noise would show a variance

$$s = \sigma \cdot \Delta\lambda / \sqrt{n}.$$

At the same time, the slope of the calibration curve built using the line integral would be $b = b \cdot \Delta\lambda$.

Therefore

$$LOD_{int} = 3s/\bar{b} = 3 \cdot (\sigma \Delta\lambda / \sqrt{n}) / (b \cdot \Delta\lambda) = LOD_{peak} / \sqrt{n} \quad (6)$$

In our experimental conditions, taking into account the instrumental width, $n \sim 5$. The use of a calibration curve based on the line integral, therefore, gives more than a factor of 2 improvement in the limit of detection, with respect to the definition based on peak intensity.

What happens if the measurements at zero analyte concentration are not possible, because for example a reliable blank sample is not available? An alternative definition of the LOD in this case allows to identify the variability of the signal at zero analyte concentration with the same variability measured at the lowest non-zero point of the calibration curve [2,3]. The above definition is correct, as soon as the variability of the signal considered is only due to the noise; all the variation associated with the nature itself of the signal, such as fluctuations of plasma temperature and electron density, as well as of the ablated mass, add to the variation of the signal, but surely they cannot be considered as 'noise'. For being more clear, at zero analyte concentration the typical variation in temperature and electron density observed in the plasma are practically not influent on the statistic of the signal, while they can produce large variations on the line signal (peak or integral) when it is present. The use of the lowest concentration LIBS signal fluctuations as a measure of the noise on the blank might be therefore misleading, unless the variations of the signal due to other factors are negligible.

This discussion brings immediately the consideration that the definition of Limit of Detection in terms of the noise statistics and curve slope is conceptually valid only when the indetermination on the slope and intercept of the calibration curve at zero analyte concentration are negligible. In real measurements, the uncertainties on the calibration curve should be considered while evaluating the limit of detection. Long and Wineforder [3] in 1983 proposed the use of the Propagation of Error Method for the calculation of the Limit of Detection, obtaining

$$LOD = \frac{3\sqrt{s^2 + s_a^2 + (a/b)^2 * s_b^2}}{b} \quad (7)$$

where a is the intercept of the calibration curve at zero analyte concentration, s_a is the standard deviation on the intercept and s_b is the indetermination on the slope of the calibration curve.

It is clear that the above definition preserves the meaning of LOD as the minimum concentration of the analyte that can be detected with reasonable certainty by LIBS,

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while maintaining the intrinsic simplicity of the original definition.

It should also be considered that, while calculating the Limit of Detection, only the points in the linear region of the curve must be considered. However, in many real applications, the non-linearity of the calibration curve may be masked by the fluctuations of the plasma parameters, the electronic noise of the detector, etc. Moreover, in many cases the lower concentration zone of the calibration curve may be difficult to probe because of the lack of suitable standards; at low concentrations of the analyte in the sample, the error associated with the measurements is also higher. All these effects concur in deteriorating the Limit of Detection, according to the above discussion.

One of the methods most applied for compensating for the calibration curve dependence on the plasma parameters is the normalization of the analyte LIBS signal with a line of the matrix [2]. The requirements for an effective normalization are rather stringent: for reducing the effects of electron density fluctuations, both the line of the analyte spectrum and the normalization line should be in the same ionization stages; moreover, for minimizing the effects of temperature fluctuations both the upper level energies of the transition considered and the ionization energies of the elements should be very similar. When spectrometers with limited spectral band are used, it is also necessary to have the reference line in the spectrum close to the one of analyte.

4. EXPERIMENTAL RESULTS

Twelve bronze certified samples (see Table 1 for their composition) were analysed with single- and double-pulse LIBS technique, in order to build calibration curves for the main elements of the bronze alloys, i.e. Cu, Sn, Pb, e Zn.

The acquisition gate was set to 2 μs, with a delay of 2 μs after the (second) laser pulse. The delay between the laser pulses was set to 0 (single pulse configuration) or 2 μs (double pulse configuration). The procedure used for acquiring the LIBS spectra involved a few cleaning laser shots on the same spot, followed by the average of further five LIBS signals. The measurements were repeated on two different spots of the same sample.

Sample	Cu (%)	Zn (%)	Pb (%)	Sn (%)
S1	80.0	-	15.0	5.0
S2	90.0	-	4.0	6.0
S3	92.3	-	0.2	7.5
S4	82.5	14.0	0.5	3.0
S5	87.3	3.7	2.7	6.3
S6	83.82	4.5	5.66	5.48
S160	85.0	2	6.5	6.5
S161	86.0	6	4.0	4.0
S162	93.0	-	2.0	5.0
S163	92.5	-	0.6	6.9
S164	88.0	8.0	2.0	2.0
S165	90.8	3.14	2.36	3.7

Table 1 - Certified composition of the samples

The following emission lines were considered for building the calibration curves:

SPECIES	λ (nm)	E _i (eV)	E _k (eV)
Cu I	296.12	1.12x10 ⁴	4.49x10 ⁴
Sn I	317.51	3.43x10 ³	3.49x10 ⁴
Pb I	363.97	7.81x10 ³	3.52x10 ⁴
Zn I	472.24	3.25x10 ⁴	5.37x10 ⁴

Table 2 - Emission lines used for building the calibration curves

The electron density of the laser-induced plasmas was measured using the method described in ref. [5], involving the determination of the FWHM of the H_α Balmer line at 653.3 nm. The distribution of the electron density values for single- (left) and double-pulse (right) measurements is shown in figure 2. The lower end of the box accounts for the lower quartile, the upper one for the upper quartile, the line inside for the median, the whiskers account for the minimum and maximum values within a distance of 1.5 box heights from the box end.

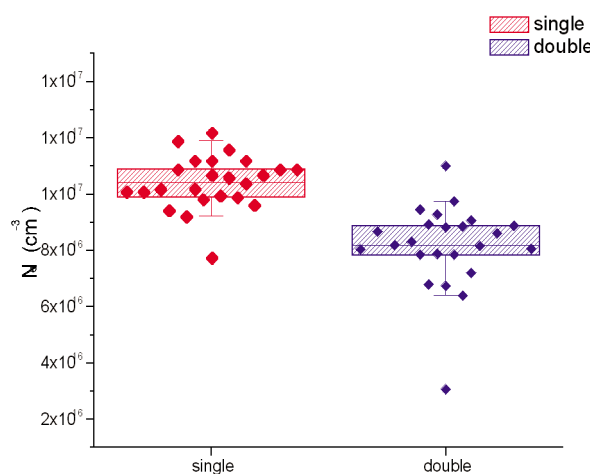


Figure 2 - Boxchart of the electron densities in single- and double-pulse LIBS configurations

As already reported in the literature, the electron densities measured in double-pulse LIBS configuration are definitely lower than the same values obtained in single-pulse configuration. The observed variability of the measured values is in part due to the experimental uncertainties, in part to the matrix effect which is unavoidable when using different standards which spans a large range of different concentrations.

The calibration curves for Cu, Pb, Sn and Zn are shown in figures (3-6); the curves corresponding to a confidence limit of 80% on the linear fitting of the experimental data are also shown in the figures.

The first thing which is worth discussing about these curves is the ‘anomalous’ behaviour of the Cu calibration curve (an increase in Cu concentration corresponds to a

decrease of the LIBS signal). This effect was already observed by Borisov et al. [6] in Cu-Zn binary alloys. It is related to the change in the physical characteristics of the samples occurring when the Cu concentration in the standards is varied, and it is one of the most convincing examples of the occurrence of matrix effects in these kind of samples. Obviously, although it is possible to use this calibration curve for estimating the Cu concentration of unknown samples, the accuracy of these measurements would not be very good. The second thing that appear clearly from the measurements is the improvement in the quality of the calibration curves obtained using the double-pulse LIBS configuration. This consideration is supported by the comparison of the Limits of Detection for Pb, Sn and Zn calculated in both the configurations, according to eq. (7). Note that, due to the particular matrix effect present for the Cu calibration curve, it makes no sense the extrapolation at zero concentration of this

curve and thus, it is not possible calculating from the present data the LOD for this element.

	SINGLE	DOUBLE
Pb	0.3 %	0.08 %
Sn	0.2 %	0.09 %
Zn	0.4 %	0.1 %

Table 3 - LOD for the considered elements

The LODs obtained using double-pulse configuration is a factor 2-4 better that the ones obtained in single-pulse configuration. In general, the values of these LODs are higher than the ones usually reported in the literature. However, the optimization of the calibration curves for enhancing the LODs requires the use of standards at very low concentrations, which is not the case when the goal of the measurements is the quantitative analysis of sample showing these elements in the percent range.

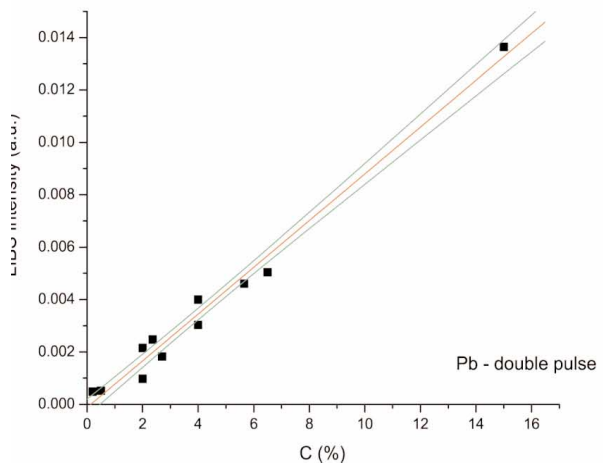
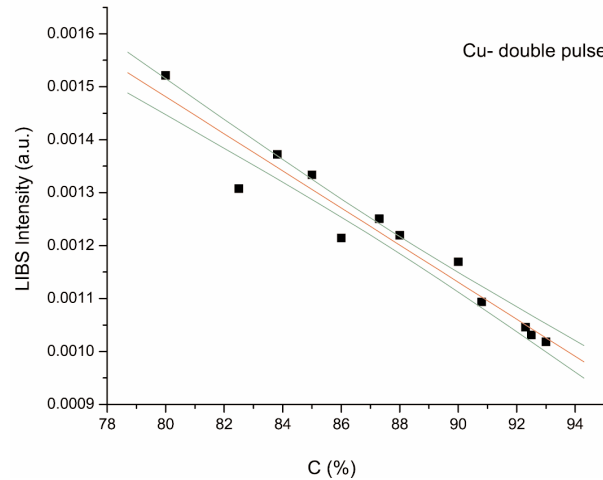
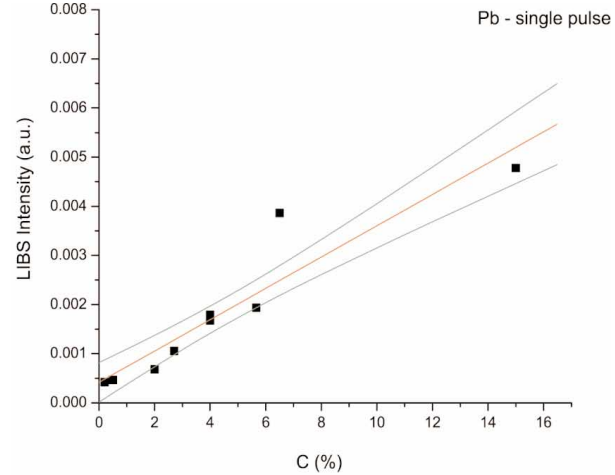
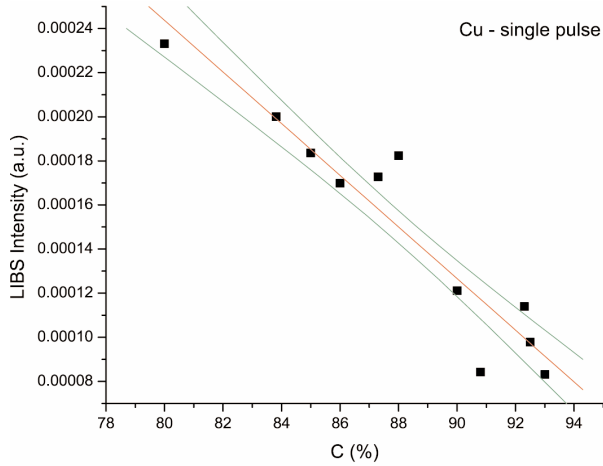


Figure 3 - Calibration curve for Cu (top: single pulse, bottom: double-pulse)

Figure 4 - Calibration curve for Pb (top: single pulse, bottom: double-pulse)

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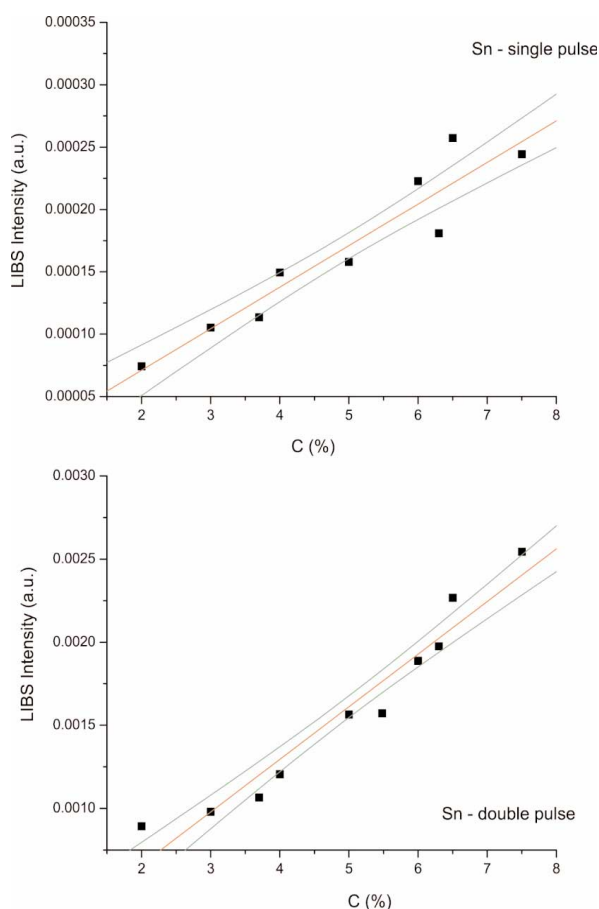


Figure 5 - Calibration curve for Sn
(top: single pulse, bottom: double-pulse)

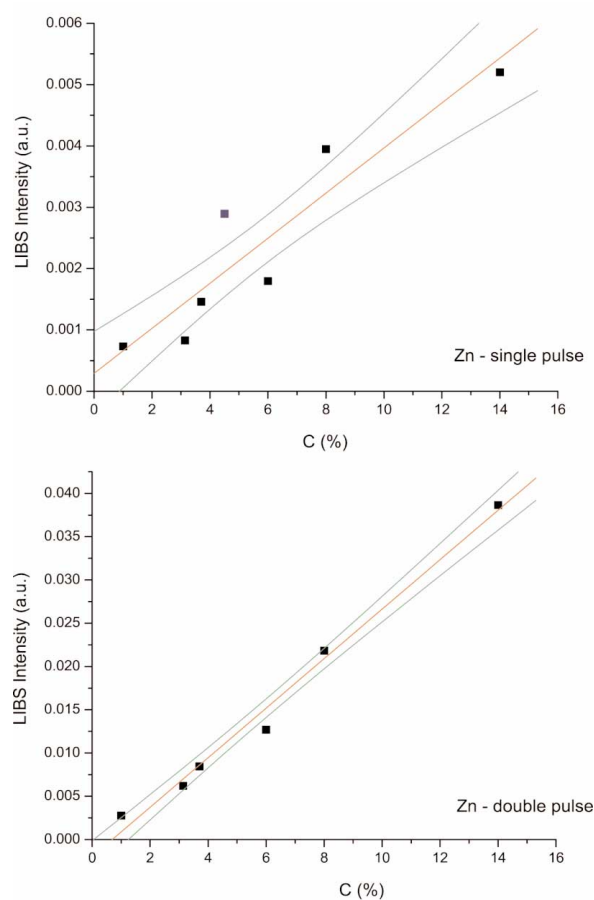


Figure 6 - Calibration curve for Zn
(top: single pulse, bottom: double-pulse)

5. CONCLUSION

The results reported in this paper evidenced the feasibility of quantitative analysis on bronze artefacts of archaeological interest, using mobile instrumentation for double-pulse LIBS analysis. The analytical results obtained using such configuration are characterised by better Limits of Detection and better accuracies than the corresponding results obtained in 'classical' single-pulse LIBS.

This fact, associated to the recent commercial availability of mobile instrumentation for double-pulse LIBS analysis (Modi), opens new and encouraging perspective for the fast and non-invasive in situ analysis of archaeological indoor collections.

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