Comparison of LIBS and μ-XRF measurements on bronze alloys for monitoring plasma effects

M F Alberghina, R Barraco, M Brai, T Schillaci* and L Tranchina
Dipartimento di Fisica e Tecnologie Relative, Università di Palermo, Viale delle Scienze Ed. 18, 90128 Palermo (Italy)

Abstract. The laser-induced breakdown spectroscopy (LIBS) technique is often used as atomic spectroscopic technique for elemental analysis of materials. However, it presents some drawbacks that make an accurate quantitative analysis difficult. Since the plasma properties, such as spatial inhomogeneity and plume stoichiometry strongly depend on the experimental conditions, the measurements are less reproducible. In order to evaluate the measurement fluctuations, we propose to use the more established micro X-Ray fluorescence (μ-XRF) technique for validating LIBS data. In particular, the quantitative data, obtained by varying the laser fluence, the shot numbers and the temporal acquisition parameters, were compared with those obtained by μ-XRF on laboratory made samples of binary, ternary and quaternary bronze alloys. For LIBS measurements a mobile double pulse laser instrument equipped with an high resolution Echelle type monochromator coupled to an intensified CCD camera was used. μ-XRF analyses were performed with a portable instrument that uses a micro collimated X-Ray beam and it is equipped with an high resolution detector. The LIBS results show a strong dependence both on the instrumental set up and the chemical-physical properties of the sample. With our findings we could identify the most suitable parameters to be used in the investigation of the different bronze alloys. The possibility to carry out a quantitative analysis by using the LIBS technique was checked through the comparison with related μ-XRF data. In particular in this paper we identified a set of reliable LIBS parameters for the quantitative analysis of copper, tin and zinc. Further analyses will be necessary to reach this goal also for the minor constituents as lead.

Keywords: Plasma features, LIBS parameters, μ-XRF, bronze alloys, quantitative analysis.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a spectroscopic technique based on laser-induced formation of a plasma above the sample surface, followed by time-resolved analysis of the optical emission associated to atomic and molecular transitions. In the past two decades, LIBS has developed rapidly as an analytical approach to elemental analysis, especially in process-analytical applications, microanalysis and remote sensing [1-3]. The reliability and refinement of LIBS as an analytical tool was made possible by a continuous improvement in instrumentation, such as the intensified charge couple device (ICCD) array detector and more mature and more reliable laser sources. The array detectors are very important since they allow the capture of multiple emission lines from a single LIBS event. The advancement in the development of broadband high resolution spectrometers, including Echelle and multi-spectrometers design made the detection and the simultaneous analysis of multiple key elements of the target material possible. Up to now this technique has mainly been employed for
the qualitative analysis. The quantitative applications are difficulty due to several factors that affect the measurements leading to the instability of the laser-induced plasma. Main parameters affecting the analytical performance of LIBS are the laser properties (wavelength, energy, pulse duration, shot-to-shot power fluctuation), the ambient conditions, the thermo-physical properties of the sample, the detection window (delay time and gate width) and the geometrical set-up of the collecting optics [4]. These problems have renewed the need for qualitatively and quantitatively understanding the laser-interaction process in order to determine the optimal experimental conditions for analytical measurements [5]. The initiation, formation and decay of the plasma are complex mechanisms. As the laser plasma is the excitation source of LIBS measurements, the properties of the laser can influence the analytical qualities of the LIBS analysis. After the laser pulse has terminated, the plasma decay over an interval from few hundred nanoseconds up to several microseconds, depending on the laser energy deposited and on the material composition [6]. At higher laser fluences, different mechanisms come into play because, for subsequent pulses, the laser energy hits the melted and recondensed matter. The elements of the original sample may have been selectively evaporated so that the redeposited material no longer exhibit the original composition [7]. The spectra observed change as the plasma evolves temporally and the goal of retaining the composition of the sample after ablation into the plasma is an important issue. Moreover, for an accurate chemical analysis, the ablated mass composition must be the same as the sample composition [6, 7].

When the plasma is in local thermal equilibrium (LTE), local gradient of plasma properties (temperature, density, thermal conductivity) is low enough to let a particle in the plasma to reach the equilibrium: diffusion time must be similar or higher than the time necessary to the particle to achieve the equilibrium [8]. LTE of the plasma is a condition that maximizes the analytical ability of the plasma as source of a quantitative physical technique. On the basis of the above considerations, an investigation approach to made the experimental conditions similar to the LTE is to set the LIBS parameters in a way to reduce the statistical fluctuations and to have an experimental mean value of the relative intensity ratio of two spectral lines, arising from the same upper level, closest to the theoretical value. In this way a quantitative analysis could be feasible. On the other hand, we have to consider also the temporal evolution of the plasma that is related to the thermo-physical properties of the element present in the sample. In particular, due to the boiling temperature and to the heat of vaporization, the pressure vapor of each element in the sample could assume different values and different decay times. This makes the stoichiometric composition of the plasma different from that of the original sample [7]. Then, in order to optimize the LIBS measurement procedure it is necessary to verify that the LTE condition is satisfied and to evaluate the detection delay time for each element to be investigated. For this purpose we studied copper-base alloys, difficult to analyse by LIBS because of their large dissimilarity in the chemical-physical properties of the elemental constituents which strongly affect the stoichiometric ratios with respect to the original evaporated surface [7-10]. Nevertheless, the LIBS technique, applied as quantitatively analytical analysis needs to be checked from a more routinary and well established technique such as the XRF [11-13]. Then, the LIBS data were compared with those obtained by XRF in order to verify the reliability of the quantitative LIBS analysis. On the basis of our findings, we will propose to extend this methodological approach to other kinds of materials such as stones, glasses, biological samples and so on.

2. Experimental

Five laboratory made metal samples containing binary, ternary and quaternary alloys were analyzed. The nominal composition of the samples is reported in Tab. 1 as weight percentage. The samples were mechanically lapped on a surface by a swing-frame grinder and chemically finished by using abrasive paste in order to obtain a mirror surface. This was subsequently polished by repetitive ultrasound washing processes.
Table 1. Nominal composition of the bronze samples.

| Sample label | Cu (%) | Sn (%) | Pb (%) | Zn (%) |
|--------------|--------|--------|--------|--------|
| DFT 1        | 85.0   | 15.0   | –      | –      |
| DFT 2        | 95.0   | 5.0    | –      | –      |
| DFT 3        | 97.0   | 3.0    | –      | –      |
| DFT 4        | 92.3   | 7.5    | 0.2    | –      |
| DFT 5        | 82.3   | 3.0    | 0.5    | 14.0   |

LIBS analysis was carried out with a portable double-pulse instrument (Marwan Technologies, mod. Modì). Laser ablation of the samples was obtained by means of a double Q-Switched Nd:YAG laser (Lotis TII, mod. 2131 DM). LIBS measurements were performed on the samples located inside a closed experimental chamber, equipped with a motorized table for the exact positioning of the sample into the focus of the two laser beams used for sample positioning. An optical microscope allowed to monitor the region of the sample under analysis.

The LIBS instrument integrates a Nd:YAG dual-pulse laser that emits two collinear laser pulses at 1064 nm with a maximum repetition rate of 10 Hz. The reciprocal delay is adjustable from 0 to 80 µs with a laser duration of about 10 ns. In our investigation, the flash lamp energy was set in the range 9.5 - 23 J with an output laser energy per pulse of 5 - 120 mJ. The laser beam was focused on the sample by using a Plano-convex lens. Plasma emission is collected to an angle of about 30° respect to the laser beam axis and carried by an Y bundle optical-fiber. One fiber end is linked to the entrance slit of a compact Mechelle spectrometer (Andor, mod. 5000), whereas the other end to a gated ICCD (Andor, mod. iStar). The gate aperture of the intensified CCD was synchronized with the laser burst. Mechelle spectrometer, coupled to the gated ICCD, allows the simultaneous spectral recording in the range 200 - 950 nm with a resolving power ($\lambda/\Delta\lambda$) of 5000. LIBS instrument is controlled via an integrated personal computer which manages 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, gate pulse delay (GPD), gate pulse width (GPW) and multi channel plate (MCP) gain. The experimental set-up values used for the laser source and for the Mechelle spectrometer were chosen with the aim to enhance the signal-to-noise ratio (SNR). In order to evaluate the dependence of crater features (diameter, morphology and fusion state of the metal) on laser energy, LIBS acquisitions were performed at different laser energy values in the range 5 - 120 mJ per pulse, with one or five double laser shot accumulations, setting the ICCD setup gater GPD and GPW to 500 ns and 2.0 m s respectively. SEM images on the craters were acquired in high vacuum modality by using a Quanta 200 F (FEI Company) microscope. The set up instrument were 15 kV for the electron gun, 300× magnification, and a chamber pressure of 7.87 $10^{-5}$ mbar. Crater images were also acquired by optical microscopy (OPTEK) with a magnification of 50×. Moreover, LIBS acquisitions were performed by setting the laser energy value at 15, 30 and 70 mJ, the ICCD setup gater GPD variable in the range 0.5 - 10 µs and GPW in the range 1.5 - 3.5 µs. All the measurement were performed with a delay time between two laser pulses of 1 µs and setting the delay time of the first Q-Switch laser pulse to 135 µs. The MCP gain of the ICCD was setting to 230. A calibration of the Mechelle Spectrometer was performed before each set of measurement by using an Hg-Ar calibration lamp (Ocean Optics). LIBS spectra, after acquisition and storage, are qualitatively and quantitatively analyzed using a dedicated software (LIBS++). The calibration-free method [14], implemented by LIBS++, was not used because it is based on the assumption that the plasma is in LTE, condition that instead we intend to verify. Thus, measurements of the peak intensity areas were performed for each spectral line characterizing the elements from the LIBS spectra. The peak emission lines used were 510,5 nm,
515.3 nm and 521.8 nm for Cu (I), 468.0 nm, 472.2 nm and 481.0 nm for Zn(I), 364.0 and 368.3 nm for Pb(I), 283.9 nm and 286.3 nm for Sn(I). The more intense peak emission lines have been considered for the evaluation of the transition probability ratios. In particular, 515.3 nm and 521.8 nm for copper, 283.9 nm and 286.3 nm for tin and 472.2 nm and 481.0 nm for zinc.

XRF analyses were performed by using a portable X-ray fluorescence (XRF) instrument ArtTAX 200 (Bruker AXS). The ArtTAX is equipped with a low-power X-Ray tube with a molybdenum anode. A pinhole system, in the X-ray source, provides collimated beam in the sample making available the instrument to perform spatially resolved multi-elemental analysis on three-dimensional structures. The X-ray fluorescence is detected by a XFlash detector (silicon drift detector) with high speed and low noise electronics with an energy resolution <145 eV at 5.9 keV. ArtTAX is equipped with a helium flow system that allows to detect the lighter elements up to sodium. The helium flow on the detection path reduces the photoelectric absorption of characteristic X-rays emitted by the sample due to air molecules. The experimental XRF settings was chosen in order to optimize the SNR and we used: for the molybdenum anode voltage and current, 40 kV and 600 µA; an acquisition time of 300 sec and a helium flow rate of 1.6 l/min.

3. Results and discussions

In order to evaluate the dependence of crater features (diameter, morphology and fusion state of the metal) we present in Fig. 2, the SEM images of the sample craters related to four values of the flash lamp energy (9.5 J, 11.5 J, 13.5 J and 23 J). The comparison of the SEM images shows that the sample DFT 1 presents a more regular circular shape and a complete melting process of the material. This fact is due to the thermo-physical properties and relative concentrations of copper and tin present in DFT 1 alloy. Table 2 reports the thermo-physical properties of all elements contained in the samples. In particular, the lowest melting heat of tin and the highest thermal conductivity of copper are the main factors that affect the crater features. The first one causes a decreasing of alloy melting temperature, the second one a faster heat loss, both factors lead to a more homogeneous fusion state and shape.

Table 2. Thermo-physical properties of the elements present in samples.

|          | Pb   | Sn   | Zn   | Cu   |
|----------|------|------|------|------|
| Atomic mass | 207.2| 118.71| 65.39| 63.546|
| Thermal conductivity (Wm⁻¹K⁻¹) | 35.3 | 66.6 | 116 | 401 |
| Melting temperature (K) | 600.5 | 504.9 | 692.5 | 1357.6 |
| Boiling temperature (K) | 2032 | 2865 | 1180 | 2835 |
| Heat of melting (KJ mol⁻¹) | 5.121 | 7.2 | 6.67 | 13 |
| Heat of vaporization (KJ mol⁻¹) | 177.8 | 296.2 | 114.2 | 306.7 |
| Specific heat capacity (J/kg/K) | 130 | 210(α) 220(β) | 390 | 386 |

On the basis of the optical images, the area evaluation of the laser crater for DFT 1 sample, shown in Fig. 3 as function of the laser energy has been obtained using ImageJ, a Java-based image processing software [15]. The plot evidences the linear trend of the areas with increasing laser energy. Moreover this tendency is noticeable also in other samples, even if due to the above reasons, it is affected by larger statistical error. These facts can be correlated with the peculiar thermal properties of the different compositional matrix of the samples. In fact, samples DFT 1, 2 and 3 are binary Cu-Sn alloys, DFT 4 and DFT 5 are ternary and quaternary alloys, respectively. A typical LIBS spectrum, is showed in Fig. 4, that displays two wavelength ranges of the same LIBS acquisition on DFT 5 sample. In this figure are underlined the spectral lines considered in this work. In
order to highlight the lower spectral line intensities corresponding to Sn (I) and Pb(I) respect to Zn(I) and Cu(I) which are ten times more intense, the intensity scales on the figures were settled to different values. Focusing our attention on DFT 1 sample, the behaviour of the peak intensity values of copper neutral atom Cu (I) emission lines at 515.3 nm and 521.8 nm and tin neutral atom Sn (I) emission lines at 283.9 nm and 286.3 nm as function of the laser flash lamp energy values are shown in Fig. 5 respectively.

![Figure 2. SEM images of sample craters related to four laser flash lamp energy values](image-url)
Figure 3. The crater area as a function of laser flash lamp energy.

Figure 4. LIBS spectrum of DFT 5 sample. On the left the wavelength region with evidenced the Sn (I) and Pb(I) spectral lines and on the right the spectral range for Zn(I) and Cu(I).

The choice of the suitable laser energy is conditioned by the need to have the best SNR and to minimize the LIBS micro destructive aspects, mandatory for particular applications where it is necessary to guarantee the integrity of objects to be investigated. The flash lamp energy values that satisfy the above requirements are in the rage of $10.5 \div 12.5 \, \text{J}$ within we selected out the mean value of 11.5 J, evidenced as red in Fig. 5.

Figure 5. Line intensities as a function of the laser flash lamp energy for Cu (I) (spectral lines 510.5 nm, 515.3 nm and 521.8 nm) and Sn (I) (spectral lines 283.9 nm and 286.3 nm).
In order to optimize the temporal ICCD parameters, GPW and GPD, different measurements were carried out with the chosen 11.5 J laser flash lamp energy value. The optimal GPW value of the Mechelle spectrometer for detecting copper in the samples, relatively to transition probabilities of Cu \((3d^{10} 1S 4d \ ^2D_{3/2} \rightarrow 3d^{10} 1S 4p \ ^2P_{1/2}\) and \(3d^{10} 1S 4d \ ^2D_{5/2} \rightarrow 3d^{10} 1S 4p \ ^2P_{3/2}\), corresponding to Cu(I) emission lines at 515.3 nm and 521.8 nm), has been determined, using the relative line intensity ratio of two spectral lines arising from the same upper level. The relative intensity ratio can be calculated by [16]

\[
\frac{I_1}{I_2}_{th} = \frac{A_1 \frac{g_1 \lambda_2}{g_2 \lambda_1}}
\]

where \(A_{1,2}\) indicates the transition probability between the state two state, \(g_{1,2}\) the statistical weight and \(\lambda_{1,2}\) the corresponding wavelength. The theoretical relative intensity ratio, 1.75 for Cu [17,18], has been compared with the average value of the experimentally obtained transition probability ratios. These are reported in table 3 for the samples that have the lowest copper concentration as the DFT 1 and the DFT 5. In table 3, \(\sigma\) corresponds to the standard deviation.

The variation of the transition probability ratios were calculated at different delay times. Table 3 shows also the relative deviation \(\Delta\) defined by equation (2). \(\Delta\) measures the adherence of the mean value to the theoretical one.

\[
\Delta = I - \frac{(I_1/I_2)_{meas}}{(I_1/I_2)_{th}}
\]

The value of \(\Delta\), optimal for both samples, allowed us to select 2.5 \(\mu s\) as the more suitable value of GPW for copper.

**Table 3. Transition probability ratios of Cu (I) lines.**

| GPW [\(\mu s\)] | \((I_1/I_2)_{meas.} \pm \sigma\) | \(|\Delta|\) | \((I_1/I_2)_{meas.} \pm \sigma\) | \(|\Delta|\) |
|-----------------|-------------------------------|----------|-------------------------------|----------|
| 1.5             | 1.96 ± 0.09                   | -0.12    | 2.13 ± 0.23                   | -0.21    |
| 2.0             | 1.97 ± 0.15                   | -0.13    | 2.29 ± 0.20                   | -0.30    |
| 2.5             | 2.04 ± 0.17                   | -0.16    | 1.59 ± 0.26                   | 0.09     |
| 3.0             | 2.52 ± 0.31                   | -0.44    | 1.69 ± 0.13                   | 0.04     |
| 3.5             | 2.79 ± 0.49                   | -0.59    | 1.53 ± 0.19                   | 0.13     |

In order to identify the optimal value of GPW of the Mechelle spectrometer to detect the tin (present only in the DFT 5 sample), the relative transition probabilities of Zn triplet \((4s5s \ ^3S_1 \rightarrow 4s4p \ ^3P_{0,1,2}\) has been determined, using the same above criteria. The theoretical relative intensity ratios, 1.50, 4.39 and 2.93 for Zn [18], have been compared with the average value of the experimentally obtained transition probability ratios. The results are given in table 4 for the DFT 5 sample. The value of \(\Delta\) allowed us to select 2.5 \(\mu s\) as more suitable value of GPW for Zn, in accordance also with the possibility to reveal with the same ICCD parameters copper and zinc present in the bronze alloys.
Table 4. Transition probability ratios of Zn (I) lines.

| GPW [μs] | \( \Delta (I_1/I_2)_{\text{meas.}} \pm \sigma \) | \( \Delta \) | \( (I_1/I_2)_{\text{meas.}} \pm \sigma \) | \( \Delta \) | \( (I_1/I_2)_{\text{meas.}} \pm \sigma \) | \( \Delta \) |
|---------|----------------------------------|---------|----------------------------------|---------|----------------------------------|---------|
| 1.5     | 2.05 ± 0.54                      | -0.36   | 4.35 ± 0.64                      | 0.01    | 2.18 ± 0.35                      | 0.26    |
| 2.0     | 1.92 ± 0.19                      | -0.28   | 4.59 ± 0.67                      | -0.04   | 2.39 ± 0.26                      | 0.18    |
| 2.5     | 1.69 ± 0.18                      | -0.12   | 4.30 ± 0.71                      | 0.02    | 2.57 ± 0.44                      | 0.12    |
| 3.0     | 1.71 ± 0.25                      | -0.14   | 3.83 ± 0.77                      | 0.13    | 2.34 ± 0.37                      | 0.23    |
| 3.5     | 1.65 ± 0.11                      | -0.10   | 4.54 ± 1.07                      | -0.03   | 2.75 ± 0.56                      | 0.06    |

The variations of the spectral line intensities of Cu doublet (3d\(^{10}\)1S \( \rightarrow \) 3d\(^{10}\)1S 4d \(^2\)D \(_{3/2} \rightarrow \) 3d\(^{10}\)1S 4d \(^2\)D \(_{3/2} \rightarrow \) 3d\(^{10}\)1S 4d \(^2\)D \(_{3/2} \rightarrow \) 3d\(^{10}\)1S 4p \(^2\)P \(_{1/2} \) and 3d\(^{10}\)1S 4d \(^3\)D \(_{3/2} \rightarrow \) 3d\(^{10}\)1S 4p \(^3\)P \(_{3/2} \)) and Zn triplet (4s5s \(^1\)S \(_1 \rightarrow \) 4s4p \(^3\)P \(_{0,1,2} \)) with the GPD times are shown in Fig. 6 relatively to the DFT 5 sample.

Figure 6. Variations of the line intensities of Cu (I) and Zn(I) as a function of the GPD times.

The average value of the experimental transition probability ratios for the copper doublet and the zinc triplet are given in table 4, whereas its variation with the delay time is shown if Fig. 7.

Table 4. Transition probability ratios of Cu (I) and Zn (I) lines.

| Element | Wavelength (nm) | Experimental | Theoretical (NIST [18]) |
|---------|-----------------|--------------|-------------------------|
| Cu (I)  | 521.8/515.3     | 1.59 ± 0.26  | 1.75 ± 0.44             |
|         | 481.05/472.2    | 1.69 ± 0.18  | 1.50 ± 0.38             |
| Zn (I)  | 481.05/468.01   | 4.30 ± 0.71  | 4.39 ± 1.10             |
|         | 472.2/468.01    | 2.57 ± 0.44  | 2.93 ± 0.73             |

For sake of clarity, in Fig. 7 are reported only the transition probability ratios of the zinc spectral lines 472.20 nm on 468.01 nm and 481.05 on 472.2 nm. GPW value was settled to 2.5 μs.
Evaluation of tin and lead was not possible with the chosen set up parameters. In fact, different partial vapor pressure values as a function of the time delay of the elements present in alloy, may lead to the plasma non-stoichiometry. In particular, the partial vapor pressure of tin and lead, which have a lower boiling temperature than copper [7], reaches a value less than two order of magnitude respect to copper. The temporal evolution of both elements has a similar behaviour with a decay time of the order of few tens ns. Therefore, for revealing lead and tin, it is necessary to reduce the GPD time in order to detect the largest amount of the signal emitted from the plasma, but on the other hand, this reduction on GPD value leads to a decrease in the SNR. To overcome this problem, a compromise was reached by carrying out measurements with a greater number of LIBS acquisitions and increasing the laser energy value. Consequently, five laser shots were accumulated, setting the laser flash lamp energy to 16.5 J, the GPD to 1.5 μs and the GPW to 2.5 μs.

In Fig. 8 are reported the LIBS calibration curves for tin and copper. The plots report the peak intensity ratio as a function of tin and copper weight concentration relatively. In Fig. 8 on the right, the first value of the calibration curve of copper and related to the DFT 5 sample, suffer from the fact that the partial pressure vapour of zinc has a decay time faster than the other elements present in the alloy and of the order of five times greater. This means that the concentration of zinc detected in the plasma is over estimated in comparison to the real concentration on the sample.

Fig. 9 shows the analytical copper peak intensity normalized to tin peak intensity, as a function of the element concentration ratio in the samples. Experimental data were well fitted by a linear equation
relatively to binary and ternary bronze alloys, being the data of the quaternary alloy, as before mentioned, influenced from the non stoichiometric composition of the plasma due to the large differences in melting and boiling point of constituent elements, associated to the longer resident time of Zn in the plasma. XRF calibration curves for tin and copper are well linear fitted. Consequently also the graph corresponding to copper peak intensity normalized to tin peak intensity, as a function of the element concentration ratio in the samples shows a linear fit with a residual value of the same order for each of the calibration curves. Therefore, in order to compare LIBS results with the calibration curves obtained by XRF analyses, Fig. 10 shows the LIBS analytical copper peak intensity normalized to tin peak intensity, as a function of XRF intensity ratio of the same elements in the samples.

The results were in a very well good agreement. Moreover, μ-XRF analysis were carried out on the shot laser point before and after the laser ablation to verify the sample composition. Variations in the composition were not found.

4. Conclusions

The results are highly sensible to the settings of the LIBS experiment, the element to be analyzed, its concentration and the compositional matrix. For what concerns the stability of the shape, morphology and fusion features of the crater on material, the DFT 1 sample has showed a more stable behaviour referable to own thermal-physical features such as heat conductivity, melting and boiling values. The investigations carried out on copper and zinc have allowed to identify the optimal values of the laser pulse energy, the GPW and the GPD time in order to maintain a condition of greater stability in the plasma. Unfortunately, the high fluctuations found in the results related to tin and lead did not permit an optimal assessment of these parameters. It seems appropriate for this purpose, to increase the energy range and the number of spectra accumulated in order to improve the SNR. All these facts lead to the conclusion that, both the adjust of the energy range and the increase of the number of acquisitions could be possible solutions. Nevertheless both involve different problems. The first one causes an increasing of the noise and the second one not is applicable in the cases where it is mandatory to use a non-invasive analytical technique. Then, it is necessary to reach a compromise of both aimed to each particular case study. In order to simultaneously reveal tin and lead and to avoid the above shortcomings, it necessary to reduce the GPD because of the shorter decay life time and to the lower partial vapor pressure of these elements in the plasma. LIBS analytical data relatively to...
copper peak intensity normalized to tin peak intensity, as a function of the element concentration ratio in the samples, shown a perfect agreement. In particular they are in good accordance with the analytical data obtained by a well established analytical technique as μ-XRF.

The results presented in this paper, represent our endeavour in order to optimize the best LIBS parameters to be used case by case, in particular taking in consideration applications where the use of micro invasive techniques it’s mandatory. Further studies shall be directed to extend our research to other metal alloys, considering also the study of the processes that lead to corrosion phenomena in metals. Moreover, with the scope to better validate the results presented in this paper, our intention will be to apply the Calibration-Free procedure applicable when the LTE conditions are satisfied.

5. Acknowledgments

The authors wish to thank Mr. Marcello Mirabello for their appreciable technical support and Dr. Paolo Guerra for SEM image acquisitions. This research has been carried out within the PRIN 2007 project “Optimization of integrated physical techniques of X-ray spectrometry, laser and electron spin for the study of corrosion processes on surface and volume of metals and alloys”, funded by Italian Ministry for University and Scientific Research.

References

[1] Cremers A and Radziemski L J 2006 Handbook of Laser-Induced Breakdown Spectroscopy (John Wiley & Sons, Ltd, West Sussex, England)
[2] Miziolek A W, Palleschi V and Schechter I 2006 Laser Induced Breakdown Spectroscopy (LIBS): Fundamentals and Applications (Cambridge University Press: Cambridge, UK)
[3] Demtroder W 2008 Laser Spectroscopy Volume 1 Basic principles (Springer-Verlag Brinl Heidelberg, Germany)
[4] Tognoni E, palleschi V, Corsi M and Cristoforetti G 2002 Spectrochimica Acta part B 57 1115
[5] Cristoforetti G, Lorenzetti G, Benedetti P A, Tognoni E, Legnaioli S and Palleschi V 2009 J. Phys. D: Appl. Phys. 42 1
[6] Borisov O V, Mao X and Russo R 2000 Spectrochimica Acta part B 55 1693
[7] Fornarini L, Colao F, Fantoni R, Lazic V and Spizzichino V 2005 Spectrochimica Acta Part B 60 1186
[8] Shaikh N M 2006 Plasma diagnostics of Zn, Cd and Hg using Laser-Induced Breakdown Spectroscopy, PhD thesis in Physics, Department of Physics, Quaid-I-Azam University, Islamabad, Pakistan
[9] Borisov O V, Mao X L, Fernandez A, Caetano M and Russo R E 1999 Spectrochimica Acta Part B 54 1351
[10] Gagean M and Mermet J M 1998 Spectrochimica Acta Part B 53 581
[11] Yoonyeol Y, Taesam K, Myeongkwon Y, Kilyong L and Gaeho L 2001 Microchemical Journal 68 251
[12] Pérez-Seredilla J A, Jurado-López A and Luque de Castro M D 2007 Talanta 71 97
[13] Brai M, Gennaro G, Schillaci T and Tranchina L 2009 Spectrochimica Acta Part B 64 1119
[14] Tognoni E, Cristoforetti G, Legnaioli S and Palleschi V 2010 Spectrochimica Acta Part B 65 1
[15] Collins T J 2007 Image J for microscopy BioTechniques 43 25
[16] Griem H R 1964 Plasma Spectroscopy Mc Graw Hill Inc.
[17] Reader J and Corlis C H 1980 Part. I Wavelengths – Wiesse W L and Martin G A Part. II Transition Probabilities in Wavelengths and Transition Probabilities for atoms and atomic ions, National Standard Reference Data System-National Bureau of Standards (Washington, USA)
[18] Handbook of basic Atomic Spectroscopic data, NIST http://www.physics.nist.gov