Quantitative determination of antimony in archaeological bronze artefacts by laser-induced breakdown spectroscopy

V Tankova¹, V Mihailov¹, G Malcheva¹, P Penkova² and L Leshtakov²

¹ Acad. G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria
² National Archaeological Institute with Museum, Bulgarian Academy of Sciences, 2 Saborna Str., 1000 Sofia, Bulgaria

E-mail: vtankova@issp.bas.bg

Abstract. Laser-induced breakdown spectroscopy (LIBS) is a reliable, fast and micro-destructive diagnostic method for qualitative and quantitative analysis of a variety of materials. In this paper, we report the results of quantitative determination of antimony in four archaeological bronze artefacts analyzed by means of LIBS. For the purpose of this study, an approach of multi-elemental quantitative LIBS analysis is proposed, based on the use of an element with known concentration as an internal standard and measurement of the spectral lines intensities of the internal standard and the element with unknown concentration. An important plasma parameter which is included in the quantitative analysis is the excitation temperature as determined by the Boltzmann plot method. The quantity of antimony in the bronze artefacts obtained by means of the proposed LIBS approach is between 1.49% and 3.13%.

1. Introduction

The laser induced breakdown spectroscopy (LIBS) technique is a form of atomic emission spectroscopy which has evolved as an effective analytical tool for elemental analysis. Its principle is based on irradiation of a material (solid, liquid or gas) with a laser beam focused on the sample surface which results in plasma formation. The spectrum of the light emitted by the plasma plume provides analytical information about the elemental composition of the target material [1].

When the objects investigated are archaeological artefacts, it is essential to avoid damaging the sample. One of the advantages that make LIBS preferred in the field of archaeometry is its micro-destructive nature. The elemental composition of ancient materials provides valuable information about the origin and use of archaeological artefacts, as well as about the manufacturing technologies.

The aim of this work is to determine the quantity of antimony in four bronze archaeological artefacts (socketed axes and spearheads) using LIBS. All objects are dated from the Late Bronze Age and Early Iron Age (14th – 10th century BC). The antimony concentration in these items is of particular interest, since depending on the amount of this element an assumption about the provenance of the artefacts can be made. According to the shape and decoration, most of the artefacts are typical for the eastern part of Central Europe and differ significantly from the ones used by the Thracians during the Late Bronze Age on the Balkan Peninsula. In this period, the addition of antimony above 1% to the bronze alloy has been typical in the eastern part of Central Europe and has not been practiced in the Balkans [2]. Accurate determination of high concentrations of antimony using standard calibration methods is not possible,
because the amount of this element in the available standards is as a trace element. This is why, we applied the approach of multi-elemental quantitative LIBS analysis with the use of an internal standard.

2. Experimental methods
The schematic diagram of the experimental system used for LIBS analyses in this work is shown in figure 1.

Figure 1. Schematic diagram of LIBS setup used in the research.

To ablate the material, a Q-switched Nd:YAG laser (Quanta Ray GCR-3) was used operating at the fundamental wavelength of 1064 nm with a pulse energy of 8 mJ and pulse duration of 10 ns. The ablation was performed in ambient air at atmospheric pressure. The laser beam was focused normally to the surface of the sample by means of a lens with a focal length $f$ of 170 mm. The radiation emitted from the plasma was collected and transferred to an echelle spectrometer (Mechelle 5000, Andor Technology, with a grating of 52 grooves/mm and a reverse linear dispersion of 1 – 4 nm/mm) via an optical fiber (diameter 50 μm). The spectrum was recorded by an ICCD camera (DH734-18F-03, Andor Technology, having 1024×1024 pixels). The Q-switched Nd:YAG laser and the detection system were synchronized through a pulse/delay generator (type G5–56). All the spectra were registered at the delay time of 1 μs after the laser pulse and a gate of 1 μs. The spectrometer covers the spectral range of 220 – 850 nm and was calibrated by means of a Hg/Ar standard lamp for wavelength and by a deuterium-halogen light source standard lamp for intensity.

The experimental apparatus has the capability to acquire spectra in a “kinetic series” mode, which means registering a series of spectra each of them accumulated and averaged from an equal number of laser pulses. The study was performed by applying five series each consisting of 50 successive laser shots at the same spot. In order to remove the layer affected by patina, 100 cleansing pulses were first applied.

In this work, the internal standard used was tin. Its amount in the artefacts was determined by means of X-Ray Fluorescence (XRF) by an EDX–720 EDXRF spectrometer (Shimadzu, Japan). The measurement was performed in air with a 1-mm collimator, 50 kV for 100 s. The elements in the samples were identified based on the characteristic X-ray lines in the energy range 0 – 40 keV. The instrument chamber size (30 cm in diameter and 15 cm high) is large enough to allow an artefact to fit in without necessity of sampling.

3. Results and discussions
LIBS has demonstrated its great potential as a sensitive tool for qualitative elemental determination, but the situation is more complicated when it comes to quantitative analysis. Quantitative LIBS analysis can be achieved either by a calibration-based method or by a calibration free one. In calibration-based methods, calibration curves are constructed of emission line intensity versus elemental concentration using matrix-matched standards with known composition and appropriate dominant element. Then the elemental concentrations of the unknown sample are determined by comparing the spectral line
intensities with those obtained from the calibration curves [3]. As an alternative method, which eliminates the need for calibration curves, the approach of multi-elemental quantitative LIBS analysis has been proposed. It is based on measuring the experimentally obtained spectral line intensities and evaluating the excitation temperature. When the concentration of one of the constituents is known (internal standard), the unknown concentration of other element can be deduced using the relationship between the observed line intensities of these elements. In our case, the internal standard was tin and the element with unknown concentration was antimony:

\[
\frac{I_{m_n}^{Sn}}{I_{k_l}^{Sn}} = \frac{C^{Sn}}{C^{sb}} \frac{(A_{k_l}g_k)^{Sn}}{(A_{m_n}g_m)^{sb}} \frac{U(T)^{sb}}{U(T)^{sn}} \exp \left( \frac{E_{E_m} - E_{E_n}}{k_BT} \right)
\]

where, \(I_{k_l}\) and \(I_{m_n}\) are the spectral line intensities emitted from transitions between the upper energy level \(E_k\) and the lower energy level \(E_l\) (eV) and between the upper energy level \(E_m\) and the lower energy level \(E_n\), respectively. \(C (\text{cm}^{-1})\) is the density of the emitting species, \(A_{k_l}\) and \(A_{m_n}\) (s\(^{-1}\)) are the transition probabilities for \(k\rightarrow l\) and \(m\rightarrow n\) transitions, respectively. \(g_k\) and \(g_m\) are degeneracies of the upper energy levels, \(U(T)\) is the partition function which depends on the excitation temperature \(T\) and \(k_B\) is the Boltzmann constant. The concentration of tin in the investigated objects was determined by means of XRF, so that tin was selected as an internal standard in the LIBS measurements.

To evaluate the electron density, the Stark spectral line broadening can be used. The full width at half maximum (FWHM) intensity of a Stark broadened spectral line is related to the electron density in plasma through the relation [4-6]:

\[
N_e = \frac{\Delta \lambda}{2\omega} \times 10^{16},
\]

where, \(\Delta \lambda\) is FWHM of a Stark broadened spectral line and \(\omega\) is the Stark broadening parameter, which depends on the wavelength and the plasma temperature and can be found in the literature [7]. The experimentally measured spectral line is broadened by the Stark effect, which has a Lorentzian profile, and by the instrumental broadening, which has a Gaussian profile, so that the line shape has a Voigt profile, which is a convolution of a Lorentzian profile and a Gaussian profile (figure 2). The Stark broadened spectral line shape represents a deconvolution of a Voigt profile and a Gaussian profile [8]. To determine the electron number density, the spectral line of Sn I at 326.23 nm was selected. The Stark broadening parameter \(\omega\) for that line and for the estimated temperature is 0.04 Å. Thus, \(\Delta \lambda\) was determined to be 0.016 nm and \(N_e\) was calculated to be 2×10\(^{16}\) cm\(^{-3}\).

![Figure 2. Experimentally measured spectral line of Sn (I) at 326.23 nm and instrumental broadening (laser line). The dots are experimental data points and the red line represents the Voigt fit. The asterisks are the apparatus function data points and the green line represents the Gauss fit.](image)

The quantitative LIBS analysis relies on the assumptions of optically thin plasma, stoichiometric ablation and a plasma condition known as local thermodynamic equilibrium (LTE). Stoichiometric ablation guarantees that the plasma composition represents exactly the material composition. The optically thin plasma condition ensures that the unfavorable effect called self-absorption is neglected. In the presence of LTE in the plasma, the collisions with electrons prevail over the radiative processes,
for which a huge number of free electrons is needed [9, 10]. The minimum electron density required for satisfying this condition, and which represents the basic criterion used to check how close the plasma is to LTE is given by the McWhirt criterion [11, 8]:

$$N_e \geq 1.6 \times 10^{12}\sqrt{T}(\Delta E)^3,$$  \hspace{1cm} (3)

where $N_e$ (cm$^{-3}$) is the electron density, $T$ (eV) is the plasma temperature and $\Delta E$ is the maximum energy difference between the upper and lower energy level. The value of $2 \times 10^{16}$ cm$^{-3}$ for the electron number density in the plasma, which we obtained, satisfies the above mentioned criterion.

Under the condition of LTE, the population of the excited levels of each species is described by the Boltzmann distribution and the spectral line intensity can be associated with the concentration of the emitting species by [12, 13]:

$$I_{ki} = FC\frac{A_{ki}g_{ki}}{U(T)} \exp\left(-\frac{E_{ki}}{k_BT}\right),$$  \hspace{1cm} (4)

where $F$ is an experimental factor taking into account the optical efficiency of the collecting system and is associated with the ablated mass and plasma volume. Taking natural logarithm of equation (4) is obtained:

$$\ln\left(\frac{I_{ki}}{A_{ki}g_{ki}}\right) = \ln\left(\frac{FC}{U}\right) - \frac{E_{ki}}{k_BT}.$$  \hspace{1cm} (5)

A Boltzmann plot is constructed by plotting the left-hand side of equation (5) on the y-axis against $E_{ki}$ on the x-axis for at least two spectral lines of the element (figure 3). The intensity of each spectral line is represented as a point in the Boltzmann plane. The temperature is derived from the slope of the Boltzmann plot which is $-E_{ki}/k_BT$.

![Boltzmann plot](image)

**Figure 3.** Boltzmann plot of Cu (I) spectral lines constructed for one of the investigated bronze artefacts.

To construct the Boltzmann plot and to determine the plasma temperature in the current study, a set of 15 spectral lines of the major element Cu (I) in the bronze alloy were used. The excitation temperature was estimated to be $T = 10000$ K (0.86 eV).

For the purpose of the quantitative determination of antimony in the artefacts, appropriate spectral lines (figure 4) of tin (Sn I 277.98 nm) and antimony (Sb I 252.85 nm) were chosen. The transition probabilities of these spectral lines are $A_{Sn}^{Sb}=1.77 \times 10^8$ s$^{-1}$ and $A_{Sn}^{Sb}=1.8 \times 10^7$ s$^{-1}$, the degeneracy and energy of the upper energy levels are $g^{Sn}_k = 7, E_{Sn}^{k} = 5.527$ eV and $g^{Sb}_m = 4, E_{Sb}^{m} = 6.124$ eV were taken from the NIST database [14]. The partition functions for Sn (I) and Sb (I) at the estimated temperature ($T = 0.86$ eV) are $U^{Sn} = 8.36$ and $U^{Sb} = 7.20$ [14].
The above listed values of the parameters are substituted in equation (1) and thus the antimony concentration is calculated.

![Figure 4](image.png)

**Figure 4.** Two sections of the spectrum representing spectral lines of Sb (I) 252.85 nm and Sn (I) 277.98 nm used for quantitative determination of Sb in bronze artefacts obtained for one of the investigated objects.

With the procedure described above the antimony concentration in all four archaeological bronze artefacts was determined.

In order to validate the proposed method, the antimony quantity in the investigated bronze artefacts was also determined by XRF and the results are compared with those from the LIBS analysis (table 1). The results from the quantitative determination of antimony by LIBS show a satisfactory agreement with the results from XRF. This demonstrates the applicability of the proposed method for quantitative LIBS analysis of antimony in a bronze alloy.

| Sample number | XRF Sn concentration | XRF Sb concentration | LIBS Sb concentration |
|---------------|----------------------|----------------------|-----------------------|
| 263           | 11.5                 | 1.96                 | 1.7                   |
| 284           | 10.5                 | 1.139                | 1.54                  |
| 422           | 8.2                  | 1.026                | 1.49                  |
| 423           | 14.8                 | 4.273                | 3.13                  |

**Table 1.** Results obtained from quantitative LIBS and XRF analysis for antimony in archaeological bronze samples (wt %).

4. Conclusion

In the present study, we performed a quantitative determination of antimony in a set of four bronze archaeological artefacts. The method we applied is based on the use of an element with known concentration as an internal standard and the assumption that the plasma is optically thin, stoichiometric and in LTE. The LTE condition was checked through the McWhirter criterion, which gives the minimum electron density required for LTE establishment. The electron density was determined by the Stark broadening of a selected spectral line of Sn (I) at 326.23 nm and it was estimated to be $2 \times 10^{16}$ cm$^{-3}$. One of the plasma parameters involved in the quantitative analysis (excitation temperature) was estimated. The temperature was determined by the Boltzmann plot method and was estimated to be 0.86 eV. The amount of antimony determined by LIBS in the investigated objects is between 1.49% and 3.13%.

According to the results obtained from the quantitative LIBS analysis of the bronze artefacts, the antimony concentration in all of the objects is more than 1%; it can therefore be assumed that it is additionally included to the alloy. This fact, together with the decoration and shape of the objects, may be considered as a confirmation of the assumption that these artifacts were produced in the eastern part of Central Europe. From this assumption, conclusions can be drawn about possible trade relations or connections between the peoples inhabiting the eastern parts of Central Europe and the territory of today’s Bulgaria during the Late Bronze and Early Iron Ages.

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