Qualitative and quantitative laser-induced breakdown spectroscopy of bronze objects

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Abstract. Laser-induced breakdown spectroscopy (LIBS) is an analytical technique for qualitative and quantitative elemental analysis of solids, liquids and gases. In this work, the method was applied for investigation of archaeological bronze objects. The analytical information obtained by LIBS was used for qualitative determination of the elements in the material used for manufacturing of the objects under study. Quantitative chemical analysis was also performed after generating calibration curves with standard samples of similar matrix composition. Quantitative estimation of the elemental concentration of the bulk of the samples was performed, together with investigation of the surface layer of the objects. The results of the quantitative analyses gave indications about the manufacturing process of the investigated objects.

1. Introduction
During the last twenty years, the increasing popularity of the LIBS method has been due mainly to the relative simplicity and versatility of the experimental setup for investigating different types of objects – inorganic and organic, solids and fluids, located in various environment – air, gas or liquid. Compared to the traditional techniques for analysis, LIBS has a number of advantages: this technique is almost non-destructive and the study can be performed over the whole piece in air at room temperature without preparation or fragmentation requirements. There are no requirements about the shape and the size of the investigated object. The possibility of focusing the laser beam on a microscopic spot allows spatial characterization of the object on the surface and in depth as well. These advantages are of decisive importance when the investigated objects are archaeological artefacts [1, 2, 8].

During the last years, the laser-induced breakdown spectroscopy has demonstrated its possibilities as a promising instrument for spectral analysis of the elemental content of different materials [1, 2]. Since then LIBS has found application in various areas of industry and science. Recently, this analytical method demonstrated the prospects of the technique to become a useful analytical tool in art and archaeology [3-7].

In this work, a set of ancient bronze objects discovered in the North-West part of Bulgaria was...
investigated by LIBS. Analytical information obtained from the LIBS measurements was used in order to investigate the surface layer of the objects and to determine the elemental composition of the alloy. A comparison of the results obtained by LIBS and X-ray fluorescence was performed.

2. Experimental

2.1. Samples
In this work we present results from a study of ten bronze finds from the Late Bronze Age (2000 years B.C.). The archaeological samples investigated are part of a bigger collection of various bronze objects that has been discovered in a prehistoric settlement situated in the North-West part of Bulgaria. In figure 1, some of the bronze archaeological samples under study are presented.

![Sample 237](image1)
![Sample 452](image2)
![Sample 285](image3)
![Sample 748](image4)

**Figure 1.** Photographs of some of the analyzed archaeological bronze objects.

2.2. Experimental set-up
In the present study, a nanosecond Q-switched Nd:YAG laser (Quanta Ray GC3) was used operating at the fundamental wavelength 1064 nm, with pulse duration 10 ns, pulse repetition rate 10 Hz and energy 750 mJ per pulse. The energy of the laser was reduced to 5-10 mJ using a variable attenuator. The laser beam was focused by a lens ($f = 170$ mm) on the surface of the sample thus creating a plasma plume. The emitted light was collected by an optical fiber (with diameter 10 μm) and analyzed by an Eschelle spectrometer (type Mechelle 5000, with a grating of 52 grooves/mm and a reverse linear dispersion of 1-4 nm/mm); the spectra were recorded via an intensified charge coupled device (ICCD) detector (DH734-18F-03, Andor Technology) having 1024 × 1024 pixels. The detector was gated by means of a delay/pulse generator type Г5-56. In order to discriminate the atomic and ionic emission from the continuum background of the plasma emission, the delay time of 1μs and gate 1μs were used in the measurements. The spectrometer covers the spectral range 220-850 nm and was calibrated by W/De and Hg/Ar standard lamps for intensity and wavelength, respectively. During the experiments, every sample was placed on a translatable stage and the measurements were carried out within 1 mm from the focal point of the lens, so that a high spatial resolution was achieved. The sample surface was held in a vertical position and the laser beam was focused horizontally at a right angle onto the surface. The experimental parameters were optimized in order to obtain a good signal-to-noise ratio, ensure the best measurements reproducibility and, at the same time, to avoid damaging of the samples.

For surface investigations, emission spectra were recorded for a single laser pulse while for depth profiling measurements spectra were collected and averaged for several successive laser shots.

X-ray fluorescence analysis was performed in order to verify the qualitative and quantitative results obtained by LIBS. For this purpose, a Rayny – EDX-720 spectrometer (Simadzu) was used.

3. Results and discussion

3.1. Qualitative analysis
The main materials used in the Bronze Age have been copper and bronze (copper-tin alloys). Addition of tin to copper at a level of 5-10 % by weight was found to produce a slightly harder alloy, which was easier to cast. Other metals used included lead (Pb) and tin (Sn). The first important analytical
The question is to identify the type of alloy and then to determine the quantity of the metals and trace elements contained in order to make a complete characterization of the investigated objects [9].

The typical LIBS spectrum from the archaeological finds analyzed is shown in figure 2. During the experiments, the signal from 10 laser shots on a single position of the sample was accumulated and averaged. All of the samples were found to contain copper (Cu), tin (Sn) and lead (Pb) as main elements. Other elements, such as iron (Fe), nickel (Ni), manganese (Mn), arsenic (As), silicon (Si), calcium (Ca) and phosphorus (P) were also detected as minor and trace elements. The elements like silicon and calcium originate from the soil, where the objects have remained for 4000 years.

The results from the qualitative LIBS measurements were confirmed by the XRF analysis.

3.2. Quantitative analysis

The plasma composition depends not only on the composition of the sample, but also on the laser parameters, sample surface conditions, as well as on the optical and thermal properties of the investigated object. These are known as matrix effects and affect the intensity of the spectral lines of the elements contained in a particular matrix.

In our work, for quantitative determination of the elements in the investigated artefacts, 4 copper alloy reference samples of similar elemental composition with a suitable dominant element were used. In this way, the plasma emission is almost the same for all the samples.

The investigation of the composition of the surface layer was performed using the first several laser pulses applied on the same point on the surface of the sample. In our experiments, in order to reach the pure metal, the surface of the artefacts was mechanically cleaned and after that 100 laser shots were applied before starting the measurements. The concentrations of Sn and Pb in the archaeological objects were obtained adopting the plotted calibration curves for certified bronze alloys (figures 3 and 4).

![Figure 2. Typical LIBS spectrum obtained for one of the investigated bronze archaeological samples.](image)

![Figure 3. Calibration curve for tin (Sn).](image)

![Figure 4. Calibration curve for lead (Pb).](image)
For good statistics, a kinetic series of 10 spectra accumulated for 10 laser pulses were made for bronze archaeological objects and the standard samples.

The results obtained by quantitative LIBS and XRF analyses in the bulk of the samples are shown in table 1. For two of the samples (748, 404), Pb was not observed by XRF because the concentration is close to the detection limit of the experimental system. For some of the results, obtained by LIBS analysis, the error bars are bigger, which could be explained by the sensitivity of this method to the inhomogeneity of the material.

Table 1. Concentrations of tin and lead in the bulk of the samples obtained by LIBS and XRF.

| Sample | Concentration of Sn, % | Concentration of Pb, % |
|--------|------------------------|------------------------|
|        | LIBS                   | XRF                    | LIBS                   | XRF                    |
| 748    | 7.8±3.1                | 10.5±0.1               | 0.06±0.01              | -                      |
| 404    | 8.2±0.8                | 11.5±0.1               | 0.17±0.03              | -                      |
| 285    | 8.5±4.7                | 13±0.1                 | 0.9±0.1                | 0.9±0.2               |
| 409    | 9.5±0.5                | -                      | 0.05±0.01              | -                      |
| 779    | 10.8±1.7               | 9.8±0.1                | 3.6±0.4                | 3.3±0.2               |
| 237    | 12.1±9.3               | 14.5±0.1               | 0.05±0.01              | 0.6±0.2               |
| 318    | 12.7±1.3               | 11.5±0.1               | 0.5±0.1                | 1.5±0.2               |
| 520    | 13.1±3.4               | 16±0.1                 | 0.11±0.02              | 0.7±0.2               |
| 492    | 15.3±6.0               | -                      | 1.54±0.15              | -                      |
| 452    | 17±3.0                 | 19.5±0.1               | 2.3±0.2                | 1.5±0.2               |

The quantitative LIBS analysis of the surface content of tin in the bronze samples investigated shows high tin concentration for some of the objects (around 80% tin). This could be an indication of surface treatment of these artefacts during the manufacturing process. For these samples (404, 285, 237, 520, 748), the XRF analysis shows a higher concentration of Sn in the bulk, compared to the LIBS results. The probable reason for this discrepancy is that for the LIBS analysis the surface of the samples was cleaned by 100 laser pulses before the measurements.

The samples 409 and 492 are not analyzed by XRF, and for samples 748 and 404 lead is not detected by XRF.

The results obtained for the Sn and Pb concentrations show that most of the archaeological bronze samples under study contain these elements in concentrations that are typical for the Late Bronze Age [9]. Two of the objects contain more Sn (up to 20%) and Pb and one is with the highest Pb content (about 4%) (figure 5).

The higher lead and tin concentration might be explained as additionally added for improving the casting properties of the alloy, or might be a result of the process of recycling other metal objects.
4. Conclusions
The results from the analyses show that the measured tin concentration is between 9 % and 20 % in the analyzed samples, which is typical for the Late Bronze Age. A high tin content on the surface, compared to the main body of the objects, was measured for some of the samples. The higher lead and tin content of some of the finds might be an indication of different manufacturing processes. The LIBS results were checked and confirmed by XRF measurements.

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