Investigation of archaeological metal artefacts by laser-induced breakdown spectroscopy (LIBS)

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Abstract. In this work, laser-induced breakdown spectroscopy was applied to determining the elemental composition of a set of ancient bronze artefacts dated from the Late Bronze Age and Early Iron Age (14th – 10th century BC). We used a Nd:YAG laser at 1064 nm with pulse duration of 10 ns and energy of 10 mJ and determined the elemental composition of the bronze alloy that was used in manufacturing the samples under study. The concentrations of tin and lead in the bulk of the examined materials was estimated after generating calibration curves for a set of four standard samples. The preliminary results of the analysis will provide information on the artefacts provenance and on the production process.

1. Introduction

The analysis of ancient artefacts provides archaeologists and restorers with valuable information about the use and origin of archaeological objects as well as on the materials that were used. Metal objects have been made and used by people since very ancient times. Their making, style and context of use constitute indicators of technology, culture and trade activities. That is why the identification of compositional materials in metal findings discovered on a particular site is very important.

The laser-induced breakdown spectroscopy (LIBS) is a spectroscopic analysis of the plasma formed as a result of the interaction of a focused light pulse from a high-power laser with a material. Atomic (or ionic) spectral emissions of the plasma thus generated can be used for real-time multi-element analysis of different type of materials – gaseous, liquid or solid [1, 2]. A large number of papers have been published concerning both the LIBS fundamentals and the application of LIBS to material analysis [3–6]. In general, a large number of elemental analysis techniques are well established in the field of material science and quite a few of them have enjoyed recognition in archaeometry and artwork analysis (SEM, XRF, PIXE, ICP-MC etc.). The number of analytical applications of LIBS has been continuously growing thanks to its intrinsic conceptual simplicity and versatility compared to the conventional techniques for analysis.

LIBS has features which make it a useful tool for real-time measurements. These include multi-element analysis, micro-destructiveness, instrumentation portability, non-contact optical nature of the measurements regardless of the material to be analyzed, high measuring speed, and no sample


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preparation. LIBS measurements are generally carried out in ambient air at atmospheric pressure. The possibilities of making qualitative and quantitative analysis by LIBS and depth analysis provide useful information on the composition of the investigated materials. These advantages are of decisive importance when the objects examined are archaeological artefacts.

In this work, we applied LIBS to studying a set of ancient bronze objects belonging to the museum collection of the National Institute of Archaeology with Museum at the Bulgarian Academy of Sciences. The analytical information obtained from the LIBS measurements was used in order to determine the elemental composition of the alloy and to investigate the provenance of the objects under study.

2. Experimental

2.1. Samples

We present results from a study of five bronze finds dated from Late Bronze Age and Early Iron Age (14th – 10th century BC). The artefacts are spearheads and socketed axes. Figure 1 presents sketches of two of the objects under study.

![Sample 263](image1)
![Sample 421](image2)
![Sample 422](image3)

![Sample 284](image4)
![Sample 269](image5)

**Figure 1.** Analyzed archaeological bronze objects.

2.2. Experimental set-up

The laser beam of a nanosecond Q-switched Nd:YAG laser (Quanta Ray GC3) operating at the fundamental wavelength (1064 nm, pulse duration 10 ns, pulse energy 8 mJ) was focused onto the target by a lens with a focal length of 170 mm). The ablation took place in air at atmospheric
pressure. The plasma emission was collected using an optical fiber (with diameter 50 μm) and analyzed in an Echelle spectrometer (type Mechelle 5000, with a grating with 52 grooves/mm and a reverse linear dispersion of 1-4 nm/mm). The LIBS spectrum was recorded by an intensified charge coupled device (ICCD) detector (DH734-18F-03, Andor Technology) having 1024×1024 pixels. The detector was gated by a delay/pulse generator type Г5-56. In order to separate the atomic and ionic emissions from the continuum background of the plasma emission, delay time of 1 μs and gate of 1 μs were used. This equipment offers a large spectral range – from 220 nm to 850 nm; the spectrometer was calibrated by W/De and Hg/Ar standard lamps for intensity and wave-length, respectively.

The experimental parameters were optimized in order to obtain a good signal – to - noise ratio, to ensure the best measurements reproducibility and, at the same time, to avoid damaging the samples. In depth profiling measurements, the emission spectra were collected and averaged for several successive laser shots. A schematic drawing of the experimental set-up is presented in figure 2.

3. Results and discussion

3.1. Qualitative analysis

Bronze is a metal alloy consisting primarily of copper (85-95%); commonly the remainder is tin, often with the addition of other metals (such as lead, manganese, nickel or zinc) and sometimes non-metals (such as arsenic, phosphorus, silicon) present in small amounts. Bronze is harder than copper as a result of alloying this metal with tin or other metals. During the Bronze Age, two distinct forms of bronze were commonly used: “classic bronze” (which contained about 10% tin and was used in casting) and “mild bronze” (about 6% tin, hammered into sheets from ingots).

During the experiments, the signals from 30 successive laser shots at a single position of the sample were accumulated and averaged. Before the measurements, 100 laser shots were directed at the same point in order to clean the surface and reach the pure metal.

A selected LIBS spectrum is shown in figure 3. As seen by the characteristic emission lines marked in the spectrum, the bronze alloy contains copper (Cu), tin (Sn) and lead (Pb) as main elements. Other elements, namely, iron (Fe), nickel (Ni), titanium (Ti), zinc (Zn), aluminium (Al) and antimony (Sb) were also detected. One of the aims of this work was to investigate the provenance of the finds. In view of the shape and decoration of the artefacts, it is assumed that they are more typical for Central Europe in this time period, being different from those Thracians were using during the Late Bronze Age. The concentration of antimony in the alloy could provide useful information about the origin of the artefacts. The copper-antimony alloys (usually containing between 2-12% Sb) were first discovered in the archaeological record during 1890’s, primarily

![Figure 2. Experimental set-up.](image)

![Figure 3. Typical spectrally resolved LIBS spectrum.](image)
from Late Bronze Age/Early Iron Age Hungarian contexts (Urnfield period) [7]. In the present experiment, we did find antimony in the objects (figure 4), but further experiments are needed to estimate the antimony concentration.

3.2. Quantitative analysis

We attempted to determine the tin and lead concentrations in the material used for manufacturing of the artefacts, because these elements define the mechanical properties of the alloy.

The elemental composition of the metal object can be affected by corrosion, which leads to material deterioration and a possible change of the weight ratio of certain elements, thus affecting the reliability of the results of the quantitative elemental analyses. This is why, in our experiments we applied 100 successive laser shots to reach the pure metal surface before recording the spectra of the alloy itself.

Four standard samples with a similar elemental composition and a suitable dominant element were used for quantitative determination of tin and lead in the artefacts. The sample properties were thus defined, bearing in mind that the matrix effects and the plasma emission are almost the same for all samples. The quantity of tin and lead in the real objects was established after plotting calibration curves (figures 5 and 6). The selected spectral lines used for the calibration of the elements were chosen so as to minimize the spectral interferences and the self-absorption. For good statistics, kinetic series of 10 spectra accumulated for 30 laser pulses were registered for the bronze artefacts and the standard samples. The results of the quantitative LIBS analysis are shown in table 1. According to the preliminary results for the tin and lead concentrations, in all samples (except for sample 263) the tin and lead concentrations are very high, the reason being the influence of the corrosion layer. Therefore, the surface of the artefacts should be cleaned mechanically.

![Figure 4. Detected Sb spectral line.](image)

Figure 5. Calibration curve for tin (Sn).

![Figure 6. Calibration curve for lead (Pb).](image)

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

| Sample |
|--------|
| Sn     | Pb    |
| 263    | 18.3±4.8 | 0.03±0.006 |
| 269    | 47.2±10.9 | 7.26±0.7  |
| 284    | 37.5±3.7  | 0.9±0.09   |
| 421    | 55±11     | 1.7±0.3    |
| 422    | 31.7±6.6  | 4.3±0.6    |

From Late Bronze Age/Early Iron Age Hungarian contexts (Urnfield period) [7]. In the present experiment, we did find antimony in the objects (figure 4), but further experiments are needed to estimate the antimony concentration.
to remove the corrosion layer before starting the experiments. For Sample 263, the concentrations of tin and lead are typical for the Late Bronze Age.

4. Conclusions
We present preliminary results of a study of five metal artefacts from the Late Bronze Age and the Iron Age. The quantitative analysis shows that the results obtained for tin and lead concentrations are affected by the thick corrosion layer, so that further experiments are planned.

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