Portable LIBS system for determining the composition of multilayer structures on objects of cultural value

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Abstract. This study presents the use of a portable Laser Induced Breakdown Spectroscopy (LIBS) prototype for determining the elemental composition of a metal jug. The system includes emission from a multiuse Q-switched Nd:YAG laser. By sampling at different points, the surface composition is determined. Furthermore, the presence of two layers of Pb and Cu and their thicknesses are determined through in-depth analysis.

1. Introduction
In recent decades, advances in analytical science and instrumentation have led to the increased use of analysis techniques in the field of conservation, art history and archeology [1-3].

Preservation, integrity and aesthetic value are of prime importance in the analysis of important cultural objects. Sampling is often strictly limited due to the possibility of damaging the object. In addition, it is not always possible to move objects to the laboratory because of their size or regulations. Therefore, it is necessary to develop and apply techniques that are nondestructive and applicable in situ.

Characterization techniques based on X-rays and ion beams, such as scanning electron microscopy coupled with X-ray microanalysis (SEM-EDX), proton-induced X-ray emission (PIXE), and X-ray diffractometry (laser ablation) inductively coupled mass spectrometry (LA-ICP-MS), allow for the reliable qualitative and quantitative analysis of the material. However, difficulties in on-site analysis and the need for the extraction of sample material interfere with their use in heritage and archaeological settings [4-8]. The LIBS device is a potential alternative due to its portability, its ability to analyze samples without pretreatment, its ability to determine the sample depth and its analysis speed. There are previous reports that confirm these benefits and place LIBS as a promising technique in this field [9].

This study presents the use of a prototype LIBS system to determine the elemental composition of multilayer structures in cultural objects. A one-of-a-kind Japanese jug from the mid-twentieth century, belonging to a private collection and having a high current value, was chosen as a sample. The piece was highly deteriorated due to environmental damage. The LIBS technique was used as part of a

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historical investigation that required the determination of the material employed because of its ability to perform the analysis without introducing additional damage. One aspect of particular interest was the determination of the possible presence of layers of different materials.

2. Experimental

Figure 1 shows the LIBS prototype and its schematic. The prototype consists of a Q-switched Nd:YAG laser operating at its fundamental wavelength (1064 nm). The laser emits in a multipulse regime with a 700-µs total duration and a 20-µs micropulse duration, with pulses separated by 10 µs. The total pulse energy is 60 mJ (measured by PM300E of Thorlabs). The laser beam is focused onto the sample, which located at a distance of 50 mm from the lens. The sample is aligned optically with the stereoscope, through which it is possible to view the analysis area. The signal is collected through an optical fiber and analyzed by an Ocean Optics USB2000 spectrometer with a measurement range of 350-1000 nm and an optical resolution of 0.35 nm. The integration time of the analyzed plasma was 50 ms.

Figure 1. a) Portable LIBS prototype, b) outline of the experimental installation.

Figure 2 shows the jug, which is selectively sampled at different points on the surface using the stereoscope. A wide spectral window, covering approximately 420 nm and centered at 590 nm, was selected to identify as many elements as possible, including those arising from environmental factors (e.g., Ca, Mg, Si, Al, Na, and K). The composition of the jug is completely unknown, making its identification necessary. Given the deterioration caused by environmental conditions, the ideal type restoration, mainly from a chemical point of view, will be determined.

Figure 2. Japanese jug from the twentieth century.
Each laser pulse constitutes a LIBS measurement. The data obtained in each measurement were analyzed using the database of atomic spectra published by the National Institute of Standards and Technology (NIST) [10] and the spectral patterns obtained from the LIBS prototype.

3. Results and discussion

Figure 3 shows the characteristic standardized spectrum and determined elements of the four sampled surface points of the jug. Similar spectra were obtained for the remaining three points. The characteristic lines of the determined elements correspond to Ca (II) (393.36 nm), Pb (I) (405.78 nm), O (II) (464.18 nm), N (II) (500.51 nm), Cu (I) (521.82 nm), Si (II) (546.68 nm), Si (II) (566.95 nm), Na (I) (588.99 nm) and K (I) (766.48 nm). Cu is the fundamental component, having a higher proportion in relation to the others. Smaller-scale elements such as Ca, Si, Na and K were found with marked relative differences between their intensities, which indicate changes in their concentrations. These elements are attributed to the deposition of dirt and impurities on the sample surface. Another specific element is Pb, which also has lower intensity values than Cu. Finally, O and N have essentially the same behavior in all measurements, and their presence is mainly caused by the combustion process during the laser-matter interaction with the atmosphere.

Each time a laser pulse impacts the jar surface, it removes a portion of the material and generates plasma. If the laser hits the same site repeatedly, it will perforate the material. To obtain the composition profile and identify different elements and layers present in the jar, a multi-spectral analysis was performed from the plasma generated by each laser shot. The layer determination procedure consists of recording pulse-to-pulse intensity variations of emission lines characteristic of maximum-amplitude surface elements, obtaining Ca (II) at 393.36 nm, Pb (I) at 405.78 nm, Cu (I) at 521.82 nm, Si (II) at 546.68 nm, Na (I) at 588.99 nm and K (I) at 766.48 nm. Figure 4 shows the intensity of these elements as a function of the number of pulses. It is important to note that these data are only the most easily distinguishable lines in the obtained spectrum. In principle, one could find a much larger number of lines. However, the lines shown here are sufficient for the purposes of determining the types of materials present in this jar.
As the number of pulses and thus the degree of penetration increases, the amount of Ca, Si, Na and K decreases. The slight variation in intensity after pulse 4 indicates that the elements have virtually disappeared. The non-zero intensity is justified by the presence of a background signal with different values depending on the region of the spectrum where they are located. The low levels in the intensities of these elements compared to Cu imply small concentrations in the object. The above analysis supports the idea that these elements result from the deposition of dirt and impurities on the jar surface.

Figure 4. History of the elemental composition of the jar as a function of depth: Ca (II) (393.36 nm), Pb (I) (405.78 nm), Cu (I) (521.82 nm), Si (II) (546.68 nm), Na (I) (588.99 nm) and K (I) (766.48 nm).

During the first pulses (1-3), the Cu shows increasingly high intensity values, constituting the main element on and, to some degree, into the jar surface (pulse 1). Pb initially (pulse 1) has very small intensity levels, which increase linearly until reaching a maximum value after pulse 4. After this pulse, the intensity of Cu gradually decreases to almost zero. However, the intensity of Pb is stable during the following pulses. After pulse 13, virtually all elements have disappeared, with Pb being the main element in the composition of the jar. Figure 5 shows the jug spectrum superposed with a Pb spectrum pattern (purity 99.999%, certified by Kurt J. Lesker) after pulse 13, showing a perfect match. Therefore, the presence of two phases or layers, one consisting primarily of Cu and the other consisting primarily of Pb, is evident.

In Figure 6, the behavior between the intensity ratio Cu / Pb and Pb reveals the Cu-Pb interface, which occurs during pulse 4. Pb promptly reaches its maximum value and the Cu / Pb ratio becomes less than one, which, in the following pulses, tends linearly to zero. Although two layers were determined in the depth profile of the jug, Figure 4 shows that Pb, in addition to Ca, Si, Na and K, is present in the Cu layer. This result derives from the thickness of the Cu layer and the laser energy. The energy was selected within an optimum work area, and, given the thickness of the Cu layer, it remains relatively sufficient for interaction with the following layer (Pb) and to produce laser ablation. Figure 4 also shows the presence of Cu in the Pb layer, which is due to the distribution of the laser energy.
The distribution of pulse energy is not perfectly homogeneous (it is lower at the edges than in the center), so the amount of material removed from the irradiated region is lower in the edges than in the center. Thus, there may be remnants of the previous layers as the depth increases. [11]

![Graph](image1)

**Figure 5.** Comparison between the spectra of the metal jug and standard Pb.

![Graph](image2)

**Figure 6.** Detailed behavior of the Cu/Pb rate and Pb relative intensity.

As a result of the laser-ablation interaction between the laser and the jug, a crater is made on its surface. Figure 7 shows the crater produced by 13 laser pulses corresponding to the compositional history of the jar, obtained through a 60x magnifying microscope. The image was captured in perspective of the surface. Because of contrast effects, the upper dark region corresponds to the crater.
rim and the lower dark region (circular) corresponds to the base. It is possible to determine its approximate depth using the scale of the image. Thus, a penetration factor of 6.8 µm/pulse is obtained for a total of 13 laser pulses and a depth of 88 µm. Thus, if the layer is fully penetrated after pulse 4, the thickness of the Cu layer is estimated at 27 µm.

**Figure 7.** Contrast image of the laser-treated zone captured by optical microscopy.

4. Conclusions

Using the LIBS technique, the composition of the jug was identified as containing two basic materials: Cu and Pb. These materials are arranged in layers, with Cu being the surface element with an estimated 27-µm thickness. Given the presence of a Cu surface coating, the use of acidic solutions (citric acid, acetic acid, sulfuric acid, nitric acid, formic acid) and alkaline solutions (ammonia water, alkaline Rochelle salt, sodium hexametaphosphate, ammonium carbonate) is suggested for chemical restoration. The elements Ca, Si, Na and K are impurities due to dirt and the environment that influences the object's surface.

The portable LIBS prototype used in this study confirms the known benefits of LIBS. In particular, thanks to its portability, it is possible to perform quick, in-situ analyses without the removal of valuable pieces.

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