

LIBS as an advanced tool in the chronocultural study of archaeometallurgical objects

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In this work, the capability of LIBS for the characterization of cultural heritage samples has been presented. Metallic objects investigated included archaeological specimens such as ancient Alexandrian coins and copper based alloys from Bronze Age and Iron Age. To characterize and catalogue these metallic objects different analytical methods such as intensity peak ratios, statistical tools and calibration curves were established. In the case of copper-based alloys, arsenic concentration has been found as a key factor for distinguishing between Bronze Age and Iron Age objects, allowing the chronocultural sorting of each piece. The results demonstrate that the chronological sorting carried out by LIBS matches agreeably with archaeological dating criteria.

Keywords: Laser-induced breakdown spectrometry, archaeometallurgy, chemometric methods, chronocultural sorting and quantitative analysis

1. INTRODUCTION

From a historical point of view, the knowledge of archaeometallurgy is of great importance in order to study the technology, the origin and the progressive evolution of civilizations. The chemical information extracted from the raw material used in the past and the technology employed in the production of archaeological objects is fundamental in the understanding of ancient events [1]. Recently, the development of modern analytical methods has contributed to the compositional study of archaeological objects [2]. The application of these methods [3-8] in the cultural heritage area has provided data about the structure of the materials, the origin of the objects, their usage and the level of degradation in the artworks. The chemical analysis by laser-induced breakdown spectrometry (LIBS) of ancient artefacts involved several steps. Visual inspection is the first step in the analysis which offers general information about the physical constitution of the object (origin, the raw material and the metallurgy employed) and also a global vision concerning to the heterogeneities and surface oxidation. The second step is based on the chemical study and characterization of ancient objects by LIBS. In this sense, spectral analysis of ancient artifacts can be carried out in two procedures: a surface (lateral and in-depth) analysis in order to examine the environmental elements such as Ca, Mg, Si, Al, Na and K present in the sample, and a chemical assessment of the metal alloy. Finally, the last stage in this methodological procedure is the chronocultural sorting [9] of the ancient objects. Metallic objects under investigation included ancient Alexandrian coins and copper based alloys used for weapons, home utensils, jewellery and decoration. In these samples, recognition and quanti-

tative analysis of alloying elements is an important point to consider because it could be used as a chronological indicator. Nevertheless, the recycling of bronzes in the ancient metallurgy is a limiting factor for establishing a relationship between the chemical composition and the age, metallurgy and the origin of the object.

In this work, different analytical methods such as intensity peak ratios, statistical tools and calibration curves will be discussed in order to characterize and catalogue archaeometallurgical objects.

2. EXPERIMENTAL SET-UP

The experimental set-up presented in this work has been described elsewhere [9]. A schematic detail of the LIBS experimental set-up is shown in Fig. 1. Briefly, this consists of a pulsed Q-Switched Nd:YAG laser operating in the second harmonic (532 nm) with homogeneous energy along the beam cross section (Spectron, model SL 284, pulse width 5 ns).

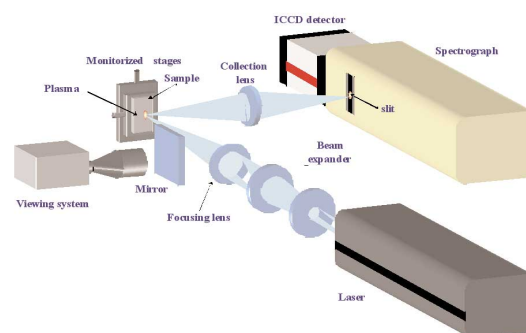


Figure 1 - Schematic drawing of a typical LIBS set up

The microplasma was generated on the sample surface in air at atmospheric pressure. The laser pulse energy was set to 12-15 mJ for all the studied samples. The beam was 3x expanded and then focused onto the sample surface with 50 mm focal length BK7 lens. With this configuration the spot diameter was less than 60 μm so the effect on the appearance of the object was virtually negligible (Fig. 2). Plasma emission was collected at right angle by a plano-convex glass lens (BK7, diameter = 25.4 mm) with a focal length of 100 mm onto the entrance slit of a 0.5-m focal length Czerny-Turner imaging spectrograph (Chromex, model 500 IS, f-number 8, fitted with indexable gratings of 300, 1200 and 2400 grooves mm⁻¹). Spectral emission was detected by an intensified charge-coupled device (ICCD, Stanford Computer Optics, model 4Quik 05) with 768 x 512 pixels, each 7.8 x 8.7 μm². This configuration provides a spectral window of ~ 15 nm and a spectral resolution of 0.02 nm pixel⁻¹ using an entrance slit width of 50 μm and the grating of 2400 grooves mm⁻¹. Operation of the detector was controlled with 4Spec software. Experimental conditions for all the samples were 500 ns delay time, 500 ns acquisition time and 750 MCP voltage. The sample was positioned on two crossed motorized stages (Physik Instrumente) for both X and Y displacement and was placed approximately 200 mm away from the collection lens, with the distance from the entrance slit to the lens being 200 mm. Thus, the optical magnification was approximately 1. A viewing system for assisting in examination and sample positioning was used.

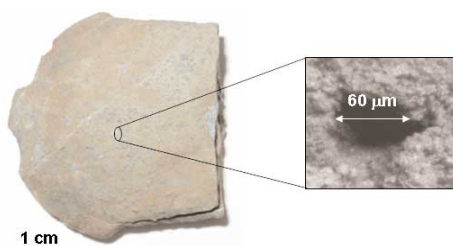


Figure 2 - Ancient bronze from Early Bronze Age showing the diameter of the crater

3. RESULTS AND DISCUSSION

3.1 Spectral characterization and effect of sample morphology on LIBS signal

For the present work, a single spectral window covering approximately 15 nm and centered at 242 nm was chosen since all elements constituents of copper based alloy and others metallic objects compose of silver could be measured simultaneously, ensuring the minimum damage to the sample by laser ablation. Two typical LIB spectra of standard bronze samples containing arsenic, tin, lead and iron as minor components is shown in Fig. 3. However, it should be noted that during characterization of the samples other elements such as calcium, sodium, magnesium and silicon could be found. These elements are attributed to dirt deposition and impurities on the surface of the sample.

On the other hand, archaeological metallic objects often present heterogeneities and surface oxidation derived from heat treatment during manufacturing and environmental degradation of the object during its history. This fact produces variations in the morphology and the elemental composition of ancient metal alloys which can affect the reliability of the analysis. For this reason, lateral and in-depth analysis would be conducted in order to obtain accuracy information about chemical composition and consequently a precise logging of the studied object.

3.2 Use of LIBS analysis and chemometric methods for chronocultural sorting of ancient objects

In order to evaluate the capability of chemometric methods based on LIBS for characterize and sort of ancient objects a set of twenty-six Alexandrian coins has been studied.

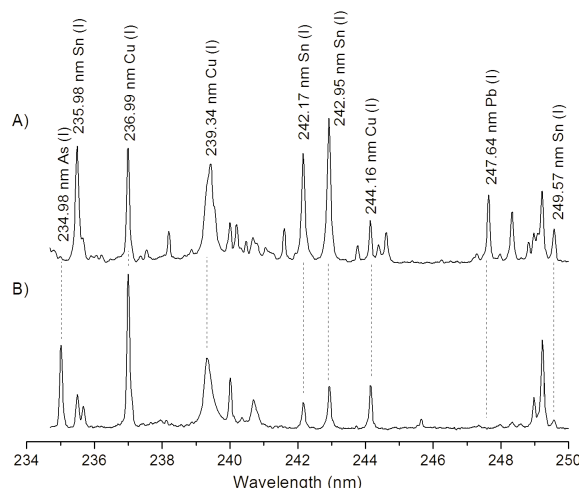


Figure 3 - Typical LIB spectra obtained from two certified bronze samples (A) and (B) which present an arsenic composition of 0.2 and 3 %, respectively.

The selected samples (Fig. 4) belong to different periods (Nero, Antoninus Pius, Probus, Diocletianus and Maximianus). The ancient coins are copper based alloys and the elements identified by LIBS were Ag (I) at 237.57 nm, Cu (I) at 249.29 nm, Sn (I) at 248.41 nm, Pb (I) at 247.64 nm and Fe (I) at 250.19 nm.

Chemometric analysis involves the use of mathematical and statistical tools to improve the performance of the analytic process, ensure the quality of the results and also to extract more information from the data. In the course of this statistical study, ancient coins were sorted in based on their rationed intensities calculated for Pb/Cu, Sn/Cu, Fe/Cu and Ag/Cu. One of these statistical tools is the analysis of the variance (ANOVA). This mathematical approach demonstrated that only the Pb/Cu intensity ratio presents significant differences within the average values. In this case, the p-value for the F-test was smaller than 0.05, indicating that there is a significant difference be-

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tween the averages of Pb/Cu from one emperor to another with 95% confidence. The ANOVA representation for Pb/Cu intensity ratio component is presented in Fig. 5. As shown, the Pb/Cu average is distinct for all the cases studied. This fact could erroneously classify the eras in five different emperors, however, by applying the minimum significant difference method of Fisher (LSD) it is possible to recognize only four homogeneous assemblies (Table I). This can be attributed to the similar chemical composition and consequently an in-existent significant difference between Nero and Pius coins. Consequently, other chemometric methods as the principal component analysis (PCA), discriminating linear analysis (DLA) and binary diagram were tested.

The PCA analysis consists of reducing the number of variables to a minimum of independent variables, i.e. principal components (PC), which are a linear combination of the original variables. For this set of samples, only a unique principal component corresponding to Pb/Cu with an eigenvalue bigger than 1.0 were found. This value explains the 57.82 % of the total variance from the original data, while Fe/Cu and Sn/Cu intensity ratios only explain the 25.52% and 16.63% of the total variance, respectively.

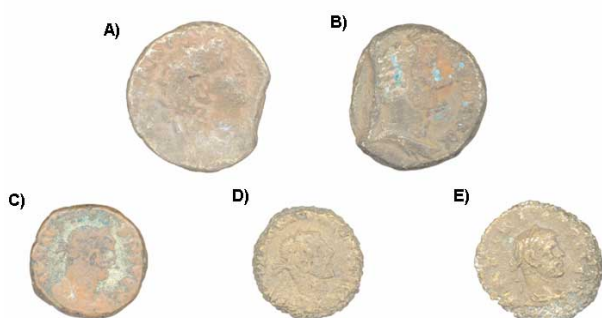


Figure 4 - Photographic detail of selected ancient coins characterized by LIBS: A) Nero, B) Antoninus Pius, C) Probus, D) Diocletianus and E) Maximianus coins

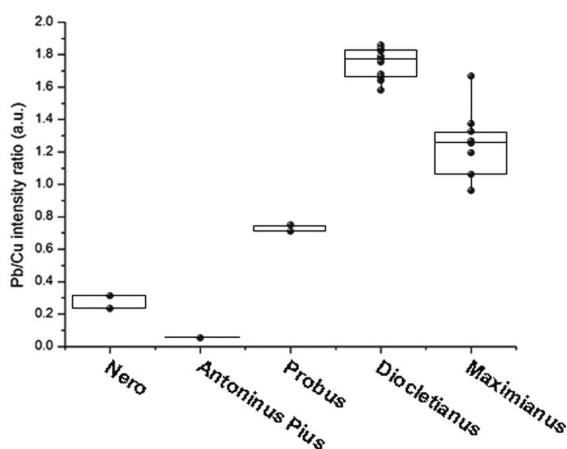


Figure 5 - ANOVA plot for Pb/Cu intensity ratio values corresponding to the different emporium.

For this reason, others multivariate methods of analysis such as binary analysis and DLA were assessed. Similar results were obtained in both statistical procedures so only a brief description of this binary analysis has been discussed in this article. Fig. 6 illustrates the Pb/Cu versus Sn/Cu intensity ratios. From this figure, the first assembly exhibits a very low Pb/Cu ratio, lower than 0.05 and the set could be assigned as belonging to era of Antoninus Pius, 149-150 A.D. The next cluster of data presents a Pb/Cu intensity ratio from 0.2 to 0.4. These pieces could be assumed to belong to the reign of Nero, 64-66 A.D. The coins of Probus, 280-282 A.D. constitute a third group with a Pb/Cu ratio from 0.7 to 0.8. In addition, it is possible to distinguish two more assembly of Alexandrian coins with a higher Pb/Cu intensity ratio value, larger than 1.0, which could be indicate they belong to the period of the Tetrarchy (Diocletianus and Maximianus). It should be noted that in this last cluster of data, the Maximianus coins usually presents Pb/Cu ratios around 1.0-1.4, while in the Diocletianus eras the Pb/Cu values go from 1.6 to 1.9

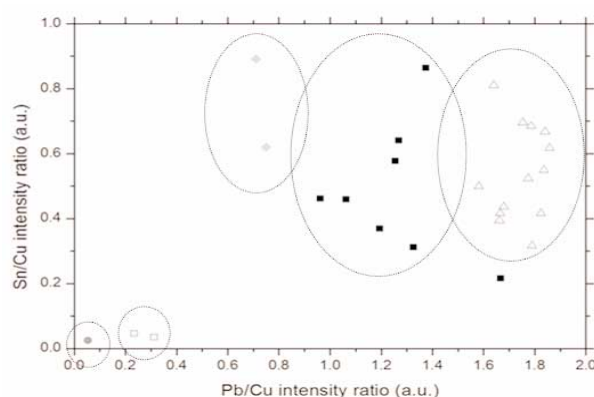


Figure 6 - Pb/Cu intensity vs. Sn/Cu intensity for Nero (□), Antonino Pius (●), Probus (◆), Diocletianus (Δ) and Maximianus (■) imperial reign.

Table I - Multiple range tests for ancient coins belong to different Emperor indicating the homogeneous groups.

Emperor	N° samples	Intensity ratio mean	Homogeneous groups
Nero	2	0.27358	X
Antoninus Pius	1	0.05307	X
Probus	2	0.73025	X
Diocletianus	8	1.26348	X
Maximianus	13	1.74528	X

It is a well known fact that the mint of Alexandria was established up in four different mint shops during the period of the Tetrarchy. From this result, it is important to emphasize that although these two groups of coins were struck during the same era and circulated by the same mint, they possess statistically significant differences among them in their Pb/Cu ratio values. This finding could indi-

cate that these two assemblies were circulated by different mint shops so that the foundries of the metal would also be located in distinct sites, however this conclusion should be confirmed with further archaeological evidences.

3.3 Use of quantitative analysis for chronocultural sorting of archaeological metallic objects

This section discusses the potential of quantitative analysis using LIBS for cataloging a set of 37 metallic objects belonging to the Bronze Age and the Iron Age (including bracelets, chisels, daggers, fibulae, rings and seals, among others) [9]. Photographs of a selection of these metallic objects are shown in Fig. 7.

In this study, the arsenic concentration in metallic objects was used as a key factor for distinguishing between Bronze and Iron Ages objects, allowing the chronocultural sorting of each piece. For example, the arsenic content in bronze based alloys was relative large in the Early Bronze Age. However, this element was substituted first by tin in Middle Bronze Age, by tin-lead alloys in the Final Bronze Age and finally by iron in the Iron Age.

The analytical figures of merit for the five elements of interest (Cu, As, Sn, Pb and Fe) of reference standard samples calculated by LIBS are summarized in Table II. Data were obtained by accumulating three laser shots at each sample position after ten laser shots used for cleaning purposes. Each certified reference standard was measured ten times.

As shown, the linearity of calibrations curves for the five elements studied was excellent with R^2 values better than 0.98 and the LIBS precision (expressed as relative standard deviation, RSD (%)) varied from 1.6 % to 28.5 %, which are within the typical reproducibility levels provided by LIBS. However, this value increased as the elemental concentration decreased. On the other hand, RSD values of background were better than 17 %. The limits of detection (LOD) were 10, 0.20, 2.7, 0.25 and 0.15 mg g^{-1} for Cu, As, Sn, Pb and Fe, respectively. In the case of Cu and Sn, LOD values were higher than expected; and were due to the use

of weak lines which prevent self-absorption effects. In spite of this, those values are in good agreement with the needs of archaeological analysis.

After construction of the calibration curves for each element, and to ensure the quality of the results in the quantitative analysis, a minimum of five different positions in the samples were analyzed to avoid the lateral heterogeneity present in the surface of the piece. Furthermore, the viewing system described in the experimental section of this work was used to select a clean zone in the sample. The averaged concentration of each element was thus determined.

In a second step, the quantitative analysis was carried out with the objective of realizing the chronocultural sorting of this set of samples. For this purpose and as the arsenic was used like key factor to search for possible differences between samples, a binary diagram copper versus arsenic composition was constructed (Fig. 8). From this figure, it distinguishes two large clusters of data. One assembly of ancient bronzes with a higher As concentration in the range 1.3-1.9 %. In these samples (rank # 3, 4, 16, 35) the content of other minor elements is negligible and the set could be assigned as belonging to the Early Bronze Age. Another cluster of data exhibited an arsenic content below 0.2 %, while other alloying elements such as Sn, Pb and Fe present an average composition of 5.2, 1.2 and 0.8 %, respectively. These pieces could be assumed to belong to the Iron Age.

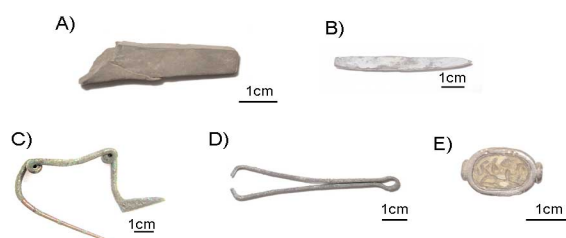


Figure 7 - Photographs of selected archaeological objects characterized by LIBS including: (A) metal chisel, (B) metal chisel, (C) metal fibulae, (D) metal tweezers and (E) metal seal

Table II - Analytical figures of merit of the LIBS method for the five elements of interest

Element	Spectral line (nm)	Correlation coefficient (R^2)	Upper limit (%)	RSD ^a (%)	RSD ^b (%)	C_{LOD}^c (mg g^{-1})
Copper	244.16	0.9922	96.7	1.6	10.0	10
Arsenic	234.98	0.9987	2.9	7.6	8.0	0.20
Tin	249.57	0.9810	14.7	11.5	17.0	2.70
Lead	247.64	0.9997	11.2	18.7	12.0	0.25
Iron	234.83	0.9926	0.42	28.5	5.0	0.15

^a Precision expressed as RSD (%) of the line intensity.

^b Precision expressed as RSD (%) of the background signal either side of the spectral line at the concentration used in the C_{LOD} .

^c Limit of detection calculated from equation:

$$C_{LOD} = \frac{(3 \cdot C \cdot RSD_b)}{S/B}$$

In this last assembly it was possible to identify a disperse set of eight samples (rank # 5, 6, 8, 21, 23-25, 31) with an arsenic content between 0.2 and 0.5 % which could indicate

they belong to the Middle or Final Bronze Ages. In this case, according to archaeological criteria, to the calculated concentration of minor elements (As, Sn and Pb) and to the

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context where the samples were found, these ancient bronzes could be catalogued as belonging to the Iron Age. Finally, to verify the presence of other compositional groups, a cluster analysis was conducted by correlating the concentration ratios of As/Cu, Sn/Cu, Pb/Cu and Fe/Cu and calculating the Euclidean distance between each sample (Fig. 9). In this dendrogram, it is possible to corroborate the presence of a first group of four samples (rank # 3, 4, 16, 35) belonging to the Bronze Age, of a second group of thirty one specimens (rank 1, 2, 5-11, 13-15, 17-32, 34, 36, 37) belonging to the Iron Age and finally, two outliers (rank 12, 33) that do not cluster together with any of the groups. It should be noted that no correlation was found between samples of the same category, i.e., fibulae and rings. This fact could indicate similar samples have different origins or manufacturers.

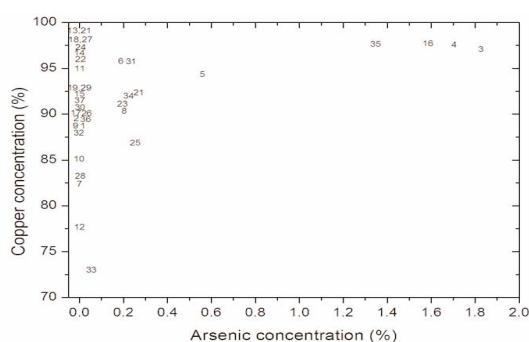


Figure 8 - Binary diagram of copper versus arsenic concentration obtained by LIBS for the set of 37 archaeological samples.

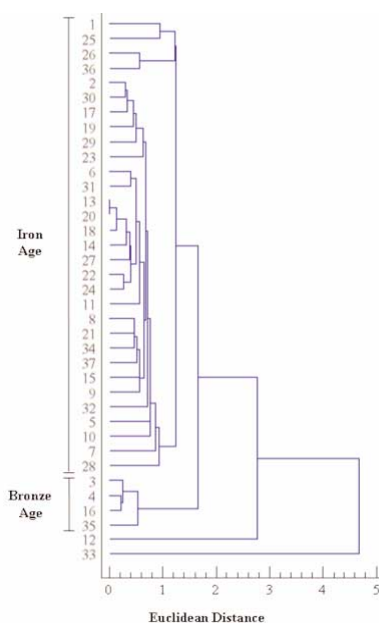


Figure 9 - Dendrogram of Euclidean distance for archaeological samples calculated on As/Cu, Sn/Cu, Pb/Cu and Fe/Cu showing the two cluster belonging to Bronze Age and Iron Age.

4. CONCLUSIONS

In this work, laser induced breakdown spectroscopy

has been demonstrated as an adequate analytical technique for the analysis of cultural heritage samples without limit of size and shape. Capabilities of LIBS in terms of spatial resolution, fast analysis and limits of detections (analytical figures of merit) aims to achieve the maximum information on the level of degradation, the age and the raw material employed in their production.

The sensitivity and versatility of LIBS make it ideal for distinguishing samples belonging to different epoch on the basis elemental composition. For this objective, different methods including statistical procedure and quantitative analysis have been purposed. Characterization and cataloging of ancient objects belonging to different archaeological sites has been carried out by LIBS. However, one of the main problems in cultural heritage analysis is related to the difficulties to find appropriate standard reference materials to perform a quantitative analysis. In this sense, mathematical methods have been applied in order to chronocultural sorting of ancient coins without the need of quantitative analysis.

In all the archaeometallurgical objects studied, the results are well correlated with the archaeological criteria used for dating.

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