

Handheld laser-induced breakdown spectroscopy, portable energy dispersive X-ray fluorescence spectroscopy and Graph Clustering applied to the identification and inner stratigraphy of archaeological metallic artifacts

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Abstract – Two advanced analytical techniques, i.e., non-destructive portable Energy Dispersive X-Ray Fluorescence (pED-XRF) and micro-destructive handheld laser-induced breakdown spectroscopy (hLIBS) supported by a Graph Clustering method have been applied to identify the elemental composition and inner stratigraphy of five copper and two iron alloy artifacts originated from various ancient graves in the area of Minervino Murge (Barletta, Andria, Trani - BAT), Apulia, Italy. The main elements detected by both techniques were Cu, Sn and Pb in copper alloys and Fe with minor amounts of Cu and Pb in iron ones, together with Al, Ca, Si, Mg and K feasibly originated from soil contamination, and the trace elements Sb and Zn. The pED-XRF spectra were distributed in three distinct clusters, whereas LIBS spectra were classified in four clusters.

These instruments have proved to be able to provide reproducible quantitative data in agreement with literature data, thus representing powerful means in outdoor archaeology and archaeometry campaigns.

I. INTRODUCTION

Metals have played a crucial role in human history, influencing its technological, socio-economic and political development over the last 6,000 years. In particular, the study of metallic archaeological artifacts is fundamental for the reconstruction of the origins and progressive evolution of human technologies and to track

the trades of raw materials. When selecting investigative techniques to obtain maximum information about objects, it is important to prioritize a minimal damage to the artifact and preservation of its legibility.

In this context, handheld instruments such as Energy Dispersive X-Ray Fluorescence (ED-XRF) and Laser-Induced Breakdown Spectroscopy (LIBS) find successful application. The main advantages of these techniques are: the analytical rapidity and the availability of handheld/portable instruments that makes it possible their use in situ, either in the open field or inside museums, which allows to preserve the artifact with no need to take it to the analytical laboratory and/or treat the surface [1,2].

The objective of this research was to assess the performance of handheld (h) LIBS and portable (p) ED-XRF coupled with the Graph Clustering method, in identifying and determining the elemental composition, evaluating the inner stratigraphy and establishing correlations between the compositional data and the technological features of a number of copper and iron alloy artifacts collected from various ancient graves in the Minervino Murge area (BAT), Apulia, Italy.

II. MATERIALS AND METHODS

The samples used in this work were seven artworks dated to the VI century B.C. and collected in an Iron age necropolis of Minervino Murge (BAT), Apulia, Italy. The copper alloy objects were: a belt (A), a basin (B), a fibula (C), a helm (D), a pendant (E) (Figure 1), whereas the

iron alloy objects were a dagger/knife (F) and a spatula (G).

The XRF spectra were acquired by the pED-XRF, SciAps X-200 (Woburn, MA, USA) set to Alloy mode. This setup allowed a quantitative acquisition of data using specific reference libraries. Two beams were used for the detection of the elements, i.e., 40 kV for heavy elements and 10 kV for light ones, in 30s of time.

The LIBS spectra were acquired with a Z-903 (SciAps, Inc., Woburn, MA, USA) LIBS instrument, having dimensions of 27 x 22 x 7 cm and weight of 1.97 kg and powered by an on board Li-ion battery. This instrument employs a Class 3B 1064 nm Nd:YAG diode-pumped solid-state pulsed laser producing a 100- μ m focused beam that delivers a 5–6 mJ pulse to the sample at the 1-ns pulse duration for a firing rate between 1 and 50 Hz. This instrument can record a broad range of plasma light emission, i.e., from 190 to 950 nm, a spectral range over which every element has at least one emission line. The spectral data were collected at a 650-nsec delay time over the 1-msec integration time. The elemental depth profiles of samples were collected on two samples area at a laser-firing rate of 10 Hz employing 128 laser shots after one cleaning shot. An average of ten measurements were taken on different points of each sample to obtain its representative composition. Due to the corrosion of artifacts surfaces and the impossibility of removing the corroded layers, the analyses were performed with high accuracy in order to preserve the integrity of the pieces.

The pED-XRF and hLIBS spectra were classified using the Graph Clustering method, which was introduced for the classification of samples based on their LIBS spectra and then also successfully applied to the classification of samples from their XRF spectra [3]. In particular, this method is applied to distinguish and classify objects, each one represented by a cluster that is more or less scattered according to its surface conditions. The method uses a parameter based on the degree of similarity in the spectra, which is mathematically expressed by the normalized scalar product between the two vectors representing the intensity of the XRF signal at different energies [4]. Thus, independently on the data points dispersion, it is always possible to state that two objects are different if the corresponding clusters can be distinguished from each other. The associated graph was visually represented utilizing the Gephi software (version 0.8.2, employing the Force Atlas Layout).

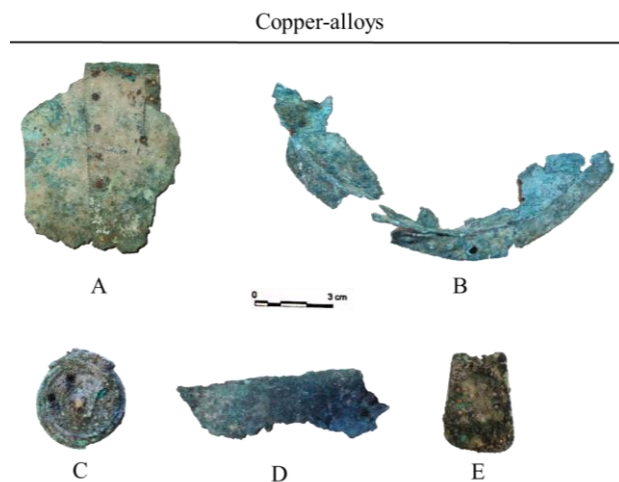


Figure 1: The copper alloy artifacts analysed (with the permission of the Soprintendenza Archeologia, Belle Arti e Paesaggio per le Province di Barletta - Andria - Trani e Foggia).

III. RESULTS AND DISCUSSION

The main elements detected in different proportions by pED-XRF were: Cu, Sn and Pb in copper alloys and mostly Fe in iron, whereas extraneous elements such as Ca, Si and K were also detected but not considered for classification and analysis (Fig. 2).

The quantitative analysis of the alloys (Table 1) was achieved using the reference standards included in the instrument database. The amount of Sn was less than 10% in all copper alloys, which suggested that they were constructed by a cold hammer technique. A higher amount of Sn would be present in a brittle alloy [5]. Furthermore, sample E exhibited a high Pb content, likely attributable to the presence of an oxidation patina. It is well-documented that Pb is subjected to a surface enrichment phenomenon [6].

	A (belt)	B (basin)	C (fibula)	D (helm)	E (Pendant)	F (dagger/knife)	G (spatula)
Al	1.655	1.587	1.489	2.388	3.007	0.134	
Si	15.068	9.796	16.298	6.932	15.238	2.416	1.163
Ti		0.131	0.073	0.063	0.150		
V	0.198		0.153		0.261		
Fe	0.895	0.387	7.288	0.224	1.828	96.941	98.280
Ni	0.103				0.070	0.056	
Cu	73.346	80.596	66.739	82.279	46.950	0.225	0.220
Mo						0.010	0.015
Sn	5.394	6.259	5.816	6.520	6.163		
Pb	2.998	0.277	1.478	0.288	24.143	0.050	0.048
Bi	0.085				0.215		
Sb			0.258		0.425		
P	0.525	1.006	0.618	1.216	1.372	0.143	0.055
S						0.114	0.181

Table 1: Average concentration (wt%) of the main elements identified by pED-XRF.

The graph clustering classification of pED-XRF spectra

(Fig. 3) allowed to distinguish three clusters of which the biggest one grouped all copper alloys objects (labelled T) with the exception of the belt sample that was represented in a second cluster (labelled U), and a third cluster (labelled V) that included the two iron alloys. Thus, the use of only pED-XRF spectra did not provide enough details to differentiate in class the copper alloy artifacts.

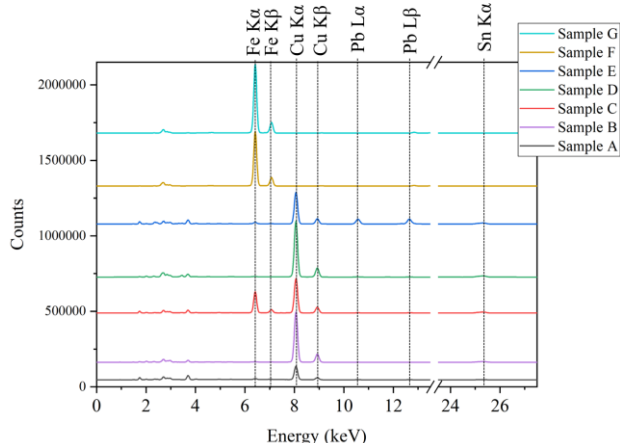


Figure 2: pED-XRF spectra of the samples analysed. The dashed lines indicate the main peaks of Fe, Pb, Sn and Cu.

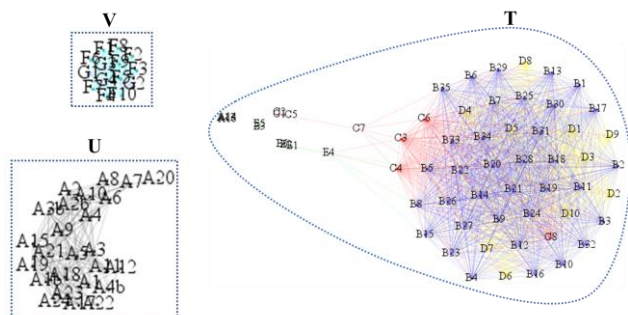


Figure 3: Graph clustering of pED-XRF spectra of the samples analysed.

The main elements detected in the full LIBS spectra (Fig. 4) were Sn, Cu and Pb in copper alloys and mainly Fe and minor contents of Cu and Pb in iron alloys. Other elements detected in the samples oxidation coating were Al, Ca, Si and Mg, which originated from soil contamination. Furthermore, the trace elements Sb and Zn were identified. Copper-alloy objects showed similar emissions lines with Cu being the major component, and the main difference being the strong emission of Sn. Similarly to pED-XRF quantitative analysis, sample A showed the greatest inhomogeneity of Sn and Pb at the various measuring points on the foil/lamina. As expected, the iron-alloy objects F and G showed a predominance of Fe emission lines in their spectra and minor amounts of Cu and Pb (less than 1 wt%).

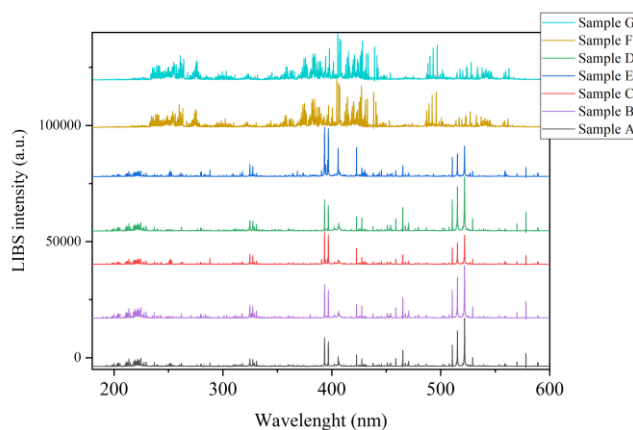


Figure 4: LIBS spectra of the samples analysed.

The graph clustering classification of LIBS spectra allowed to discover differences between spectra that were not apparent from immediate data interpretation. In particular, four clusters could be identified (Fig. 5), i.e., a cluster labelled W, which included the iron alloy artifacts, two clusters labelled X and Y, which included, respectively, the copper alloy samples C and E and the biggest one labelled Z, which included the other copper alloy objects.

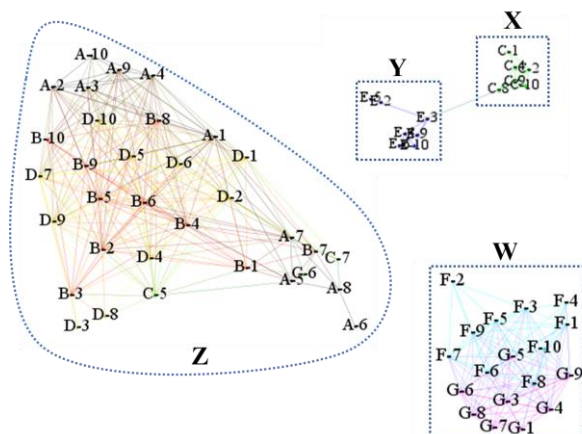


Figure 5: Graph clustering of LIBS spectra of the samples analysed.

The comparison of the cluster plots obtained by the two techniques, shows differences in the classification of the samples. In particular, the cluster labelled U, which includes the pXRF spectra of sample A, moves away from the cluster of copper-alloy objects due to the absence of Ti in these spectra. In the case of hLIBS spectra classification, a clear separation of sample A is not visible, but it is possible to notice a separation of the spectra within the point cloud of the cluster Z due to the inhomogeneous composition of the sample. The classification based on hLIBS spectra allows the objects to be distinguished in more groups due to the greater number of minor and trace elements that the technique is able to identify. In particular, samples C and

E, respectively, grouped in clusters X and Y, move away from the main cluster of copper-alloys Z due to the presence of more intense Ca, Si, K and Na peaks in the spectra. Furthermore, the proximity between these two clusters is due to the presence of Sb in both samples, while the clear separation is due to the high amount of Pb in sample E.

The above classification of artifacts in various clusters allowed to choose the most interesting ones to be further subjected to an in-depth study using the depth profiles measured with hLIBS. The analysis of depth profiles could provide relevant information on the sample composition below the corrosion layer and on the processing method used to construct the object. The depth profiles were measured by LIBS at depths of 10 μm after each laser shot in areas where the objects appeared more inhomogeneous in composition. In particular, three reference emission lines were selected, i.e., Cu I (465.11), Sn I (283.99), Pb I (368.34), and fitted in Gaussian curves whose normalized peak areas were related to the number of laser shots.

The decrease of the LIBS signal of Cu, Pb and Sn measured after about 60-80 shots for all the copper alloy samples suggested the removal of the surface layer of the patina which allowed the laser to reach the intact metal layer. Sample A (belt) was the most interesting sample examined, and resulted to be composed by three different pieces of metal connected each other by small nails/tacks/pins (Fig. 6a). The composition of the two laminas appeared different in the amount of main elements. In particular, the presence of Sn was not detected in any analysis point (Figs. 6b and 6c). The difference in composition of the two laminas suggested that either they were produced at different times and connected to each other after the object was repaired or a confinement of Sn occurred in the innermost layers of the alloy due to hammering.

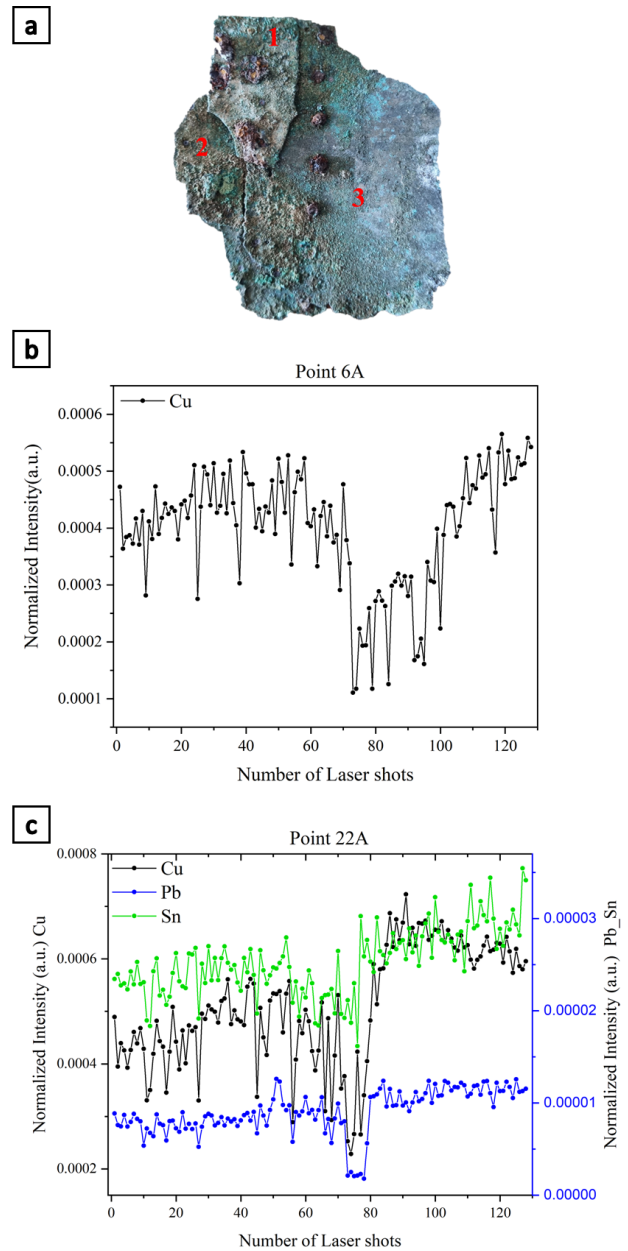


Figure 6: Depth profile LIBS spectra of the sample A: a) backside of sample A, where the three different laminas connected each other by small nails can be observed. The numbers stand for the three different pieces of metal; b) profile of lamina 3; c) profile of lamina 2.

IV. CONCLUSIONS

The preliminary study of the archaeological objects considered in this work confirms that the two spectroscopic techniques used are suitable for the characterization of metal alloy artifacts. Furthermore, handheld instruments appear to feature a good compromise between resolution and dimension, thus making them an excellent choice in the case of outdoor

campaigns or for measurements in inaccessible places. These instruments have proved to be stable in measurements even over time, showing excellent reproducibility, especially in the case of pED-XRF. Furthermore, the quantification of elements achieved is in agreement with literature information on ancient metal-alloy artifacts.

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