

# **LIBS as an identification and documentation tool in the conservation process: applications at the W.D.E. Coulson Conservation Laboratory, INSTAP-SCEC**

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Laser Induced Breakdown Spectroscopy (LIBS), is applied on a regular basis for the analysis of metal objects that are kept in the storage of INSTAP-SCEC and occasionally for objects from other institutions or museums of the broader region of Eastern Crete. The analysis is carried out at the W.D.E. Coulson Conservation Laboratory using LMNTI, a transportable LIBS instrument specially designed and constructed at IESL-FORTH for the needs of non-sampling analysis of ancient artefacts. LMNTI provides information about the qualitative and semi quantitative composition of metal objects which contributes to the accurate identification and documentation of the metal artefacts, the choice of the appropriate remedial and/or preventive conservation treatment and the study of their technological characteristics.

Keywords: LIBS, non-sampling analysis, qualitative/semi quantitative composition, archaeological conservation

## **1. INTRODUCTION**

The successful application of scientific methods of analysis, over the last two decades, for the illumination of archaeological questions and the study of the deterioration processes of archaeological materials, has resulted in the increased interest of the archaeological community in the development of portable instrumentation for the application of non-destructive or non-invasive analytical techniques in the conservation laboratory, the museum or the archaeological site, for the study of a wide range of materials.

The Institute of Electronic Structure and Laser (IESL-FORTH) in collaboration with the Institute for Aegean Prehistory-Study Center for East Crete (INSTAP-SCEC) have worked on the development of a compact, transportable Laser-Induced Breakdown Spectroscopy (LIBS) instrument that can serve the needs of analysis in the conservation laboratory.

The instrument that derived from this collaboration, LMNTI (el-em-ent-one) (Fig.1), currently belongs to the INSTAP-SCEC, where it is used in the W.D.E. Conservation Laboratory in routine analysis of ancient artefacts [1].

The INSTAP-Study Centre for East Crete, is located in a quite isolated area of the island of East Crete at the village of Pachia Ammos, and hosts material from several American and Greek-American archaeological projects. The main focus of the institute is the excavation, study and publication of prehistoric sites in the broader area of

East Crete. Furthermore, it assists in the publication of several archaeological projects in the Aegean.

The Study Centre is far from Universities or other institutions with analytical facilities. Moreover, strict regulations by the Greek archaeological authorities make very difficult if not impossible the transfer of archaeological objects to Herakleion or Athens for analysis which is one of the reasons that have directed the research of Greek scientists towards the development of portable or transportable analytical instruments and the main reason for the collaboration of Institute for Aegean Prehistory with IESL for the development of LMNTI.

The aim of this publication is to bring the conservator closer to this technology by presenting the analytical capabilities and the practical application of LMNTI in the conservation laboratory for the clarification of fundamental questions starting with the identification of the metal or metal alloys that were used for the production of prehistoric and historic metal artefacts which the conservators are called to treat and/or to provide the appropriate measures for their long term preservation.

## **2. INSTRUMENTATION**

The basic principles and analytical capabilities of the LIBS as well as the main features and operation of LMNTI have been already discussed in the bibliography [1-4] and therefore they will be only briefly mentioned here.

LMNTI (Fig. 1), is an independent bench-type instru-

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ment on wheels (H: 90 cm, W: 80 cm, D: 65 cm) and can be easily moved in the laboratory or to other rooms in the same building. It can also be transported to other locations on a small van.



Figure 1 - Front view of LMNTI

The main components of LMNTI include: a) compact Q-switched Nd:YAG laser (with power supply), producing 10 ns pulses at 1064 nm with energy up to 50 mJ; b) 0.19 m imaging spectrograph with two diffraction gratings offering spectral resolution of 0.5 nm and 1 nm respectively; c) quartz optical fiber (0.6 mm) for collecting the plume emission into the spectrograph; d) intensified CCD detector and a pulse generating unit to provide proper gating; e) platform on a XYZ translation stage for mounting and positioning objects and samples; f) small color CCD camera for accurate sample viewing and aiming; and g) a personal computer for instrument control and data analysis.

The laser beam guiding optics and the viewing camera are housed in a sub-unit that is mounted on the top surface of the instrument along with the sample holder. The PC monitor and keyboard are also placed on the top surface while the PC tower and the rest of the components are housed in the main case of the instrument.

All functions and parameters of the instrument as

well as the measurements are controlled through unified user-friendly software, which also provides an automated interpretation of the data based on a reference data base that is gradually being updated and improved.

Emission spectra are recorded following irradiation of the sample with a single laser pulse. Elements are identified on the basis of the characteristic wavelength values of the emission lines [1].

### 3. ADVANTAGES AND DISADVANTAGES

LIBS, is a well known, practically non-destructive technique which can provide quick and reliable elemental analysis of archaeological materials. It has been used for the analysis of pigments in easel paintings, icons, polychromes, pottery, glass and metal objects and the results have demonstrated that it is a very useful analytical tool with various applications in art and archaeology [5-12].

The advantages of LMNTI specifically, as an identification and documentation tool in the conservation process, can be summarised as follows:

- The technique does not require sampling.
- Moreover, it is one of the few techniques that can be applied to archaeological material without any formal approval or special permit from the General Directorate of Conservation, Ministry of Culture. Given the difficulty in the approval of sampling or non-sampling analysis permits, this alone makes LMNTI an indispensable tool for quick and low cost survey of metal or other archaeological materials.
- It provides qualitative and semi-quantitative elemental analysis.
- It can perform multiple spot analyses.
- It allows clear observation of the object, selection and accurate aiming of spots for analysis through the built-in camera. Focusing is facilitated by the capability of the sample holder to move in three axes (Fig. 2).



Figure 2 - Bench-top working surface with monitor where we can view the artefacts and focus on the desired spot

- The instrument is supplied with a user friendly interface and can be operated by conservators after basic training.

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- The software includes a reference library and provides an option of automated interpretation of the spectra. It also provides the option of overlaying the acquired spectra with reference ones. The reference library is being continually supplemented with new data as the analysis of objects proceeds. Data of reference samples is also added when available. However, interpretation is largely depended on the experience of the user as happens with all analytical techniques.
- It allows the stratigraphic study of corrosion layers by gradual in depth analysis. This however is subject to the experience and the expertise of the user.
- It allows the photographic documentation of spots during all stages of analysis (before, after the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> etc. pulse and after the end of analysis). Documentation images are stored in folders along with the data that is obtained from the analysis. Therefore, when a depth profiling study is carried out, spectra are acquired separately for each one of several successive laser pulses and are stored along with the images for thorough comparative study and interpretation.

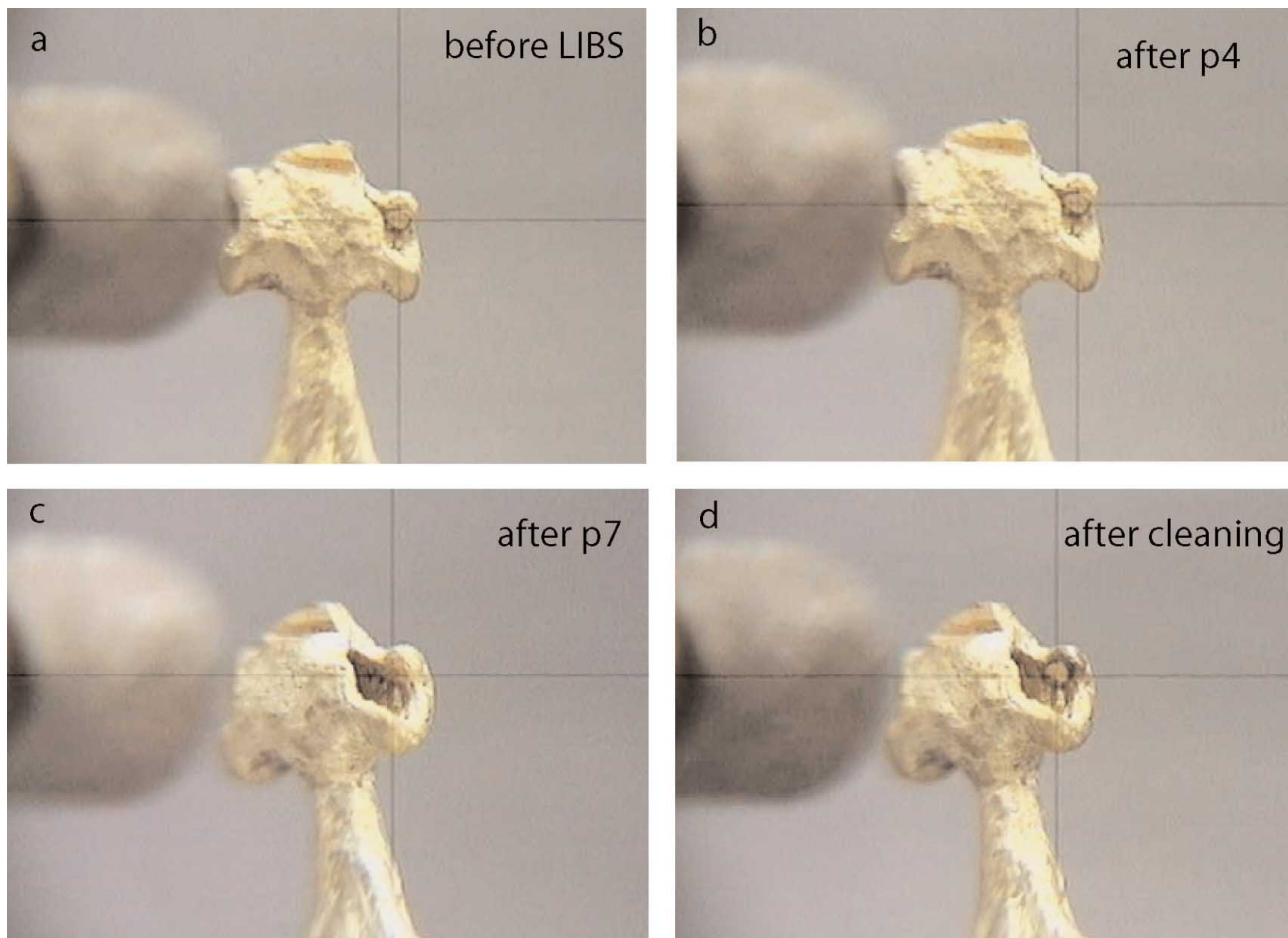


Figure 3 - Macroscopic effect on the spot of analysis (200µm), before and following the analysis, with 4 and 7 laser pulses and after cleaning of the dark spot with ethanol.

Apart from the above mentioned advantages there are also a couple of disadvantages that should be mentioned; namely the non quantitative analysis and the minor removal of the patina on the spot of analysis in the scale of a few µm (ca. 100-200 mm diameter).

As regards the first concern, we should note that some work has already been done on this direction using proper reference standards and therefore there is potential for quantitative analysis based on calibration curves. More specifically, quantitative analysis tests have focused, up to now, on the determination of the amount of tin (Sn) in bronze objects. A series of reference bronze samples with

tin concentration in the range of 0.5-13% by weight have been analyzed by LIBS in order to construct a calibration curve, which is used for the quantitative analysis of bronze objects [1]. On the basis of this calibration curve a few Minoan bronze objects were analysed and found to contain tin in the range of 5-11% by weight. More work is currently in progress to compare LIBS analysis results in archaeological bronze objects against the actual alloy composition obtained with a standard technique and in addition to assess the reliability of the Cu-Sn reference samples used as models of the ancient bronze alloys [1]. It is noted that the progress of this work is relying on the

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availability of proper reference standards that represent realistically the composition of ancient bronzes.

An additional factor that has to be carefully considered is the extended corrosion of bronze, which leads to material alteration and possible loss of certain metals in the form of soluble salts thus affecting the reliability of the analysis. In order to diminish this effect one has to choose the areas with minimum corrosion and to remove the surface layers with few pulses before acquiring spectra for quantitative analysis.

As regards the second concern, a minor removal of the patina, we should clarify that the spot where the surface is superficially ablated is hardly visible to the naked eye, especially when examining corroded surfaces, but can be visible as a brighter spot on gold or silver alloy surfaces (Fig. 3b)

A dark stain that is occasionally observed on un-corroded metal surfaces, around the spot (Fig. 3c), is produced by the ablation of the material and can be easily removed by ethanol swabs (Fig. 3d)

The patina is gradually restored but we still need to monitor and document this self-healing process. In general it is recommended to observe the spot after every pulse and to stop the analysis as soon as clear spectra, that provide the answers to the questions that have been defined beforehand, are obtained. A few more pulses can usually give a better spectrum for presentation but should be avoided if not absolutely necessary.

**4. CASE STUDIES**

The results of analysis of a number of metal objects from two different assemblages, the first dating to the historic and the second to the prehistoric era have been chosen as the most representative ones in order to demonstrate the practical aspects of the analysis, the diagnostic capability of LMNTI and its contribution in the archaeological and conservation process. In both cases the metal objects were examined in order to obtain information about their elemental composition which can be then used in the following stages of work

- Identification/characterisation of the metal alloys and therefore accurate documentation of the collections
- Identification of surface depositions
- Identification and characterisation of the corrosion layers
- Understanding of the object and assessment of the state of preservation (the extent and type of corrosion present on the surface).
- Consideration of all the above information for the choice of the methods and materials that are best suited for the preventive or remedial conservation of the artefacts.

**4.1 Examination of historic metal artefacts**

The first assemblage to be discussed includes a group of ten Byzantine and Post Byzantine metal objects from

the Historical Museum of Herakleion. The Collection was brought to the W.D.E. Coulson Conservation Laboratory by one of the associate conservators of the Lab (K. Zervaki) in order to conserve them and then return them back to the museum for display.

All these objects consisted of white metal alloys which are often quite difficult, even to conservation professionals to identify. The white metal alloys of zinc, tin, lead or silver can be very similar macroscopically. Especially lead, tin and zinc are all soft and low melting point metals which show considerable similarities in their macroscopic characteristics particularly when they are covered by atmospheric corrosion layers. Although they possess good corrosion resistance in a range of environments, archaeological and historical objects are usually covered by corrosion products. Most of these corrosion products are white, thus preventing visual distinction between the metals or their alloys.

The objects of this assemblage, for example, were all identified and registered in the Museum records as lead objects. However, the results obtained with LMNTI showed that lead is the main component of one object only (Medieval Calendar, Cat. No 2229) and is present in another two in relatively low quantity. Overall, the main elements that were detected were tin, zinc, lead, copper and silver (Table 1).

Catalogue Number	Museum Description	LIBS Analysis
232	Lead / pendant	<b>Sn, Cu, Ag, Pb</b>
245	Gilded lead / lady's figurine	<b>Sn, Cu</b>
247	Lead / boy's figurine	<b>Zn</b>
258	Lead / woman's figurine	<b>Cu, Zn</b>
1262	Lead / gondola	<b>Cu, Pb</b>
1376	Gilded lead / figurine of sitting child	<b>Cu, Zn, Ag</b>
1645	Lead / ring with nativity scene	<b>Sn, Zn, Pb</b>
1673	Lead / Athena's head	<b>Zn, Cu</b>
1699	Lead / dog's figurine	<b>Zn</b>
2229	Lead / calendar	<b>Pb, Ag, Cu</b>

Table 1 - Identification of metal artefacts from the Historical Museum of Herakleion, before and after LIBS analysis. The major elements determined are written bold.

Some of the objects consist only of zinc (Cat.No 247 and 1699) which appears to be quite an unusual case, while others consist of a tin-lead alloy that is very rich in tin (Cat. No 1645, 232 and 245).

Multiple spot analyses on the "statuette of Athena" (Cat. No 1673) showed that the main body consists of zinc (Fig. 4a, b) while the surface was probably copper plated. This suggestion is based on the analysis of the black areas on the surface where significant amount of copper is detected (Fig. 4c, d).

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Variations in the quantitative composition of the alloy that was used as soldering material for the joins of parts were also detected.

One of the figurines (Cat. No 258), which was covered by a greyish encrustation with selective occurrence of green corrosion products, consisted of copper with significant amount of zinc and therefore it can be characterised as brass. In some areas yellowish shine spots were visible which explain the initial description of the object as gilded lead. Analysis on these spots showed the same composition as the rest of the body. A low content of magnesium is also detected that is usually attributed to environmental depositions.

Similarly, zinc and copper were also the main elements that were identified in the figurine of the sitting

child (Cat. No 1376), which had been registered in the museum records as a gold plated lead.

In this figurine however, multiple spot analyses on the spots which showed a yellowish shine, detected the major peaks of silver and not gold.

It is apparent that the information that was obtained by LIBS with LMNTI played a major role in the choice of the methodology and the materials that were used for the conservation of these artefacts as their composition was proved to be, in most cases, completely different from.

Moreover, the LIBS analysis data was incorporated in the old museum records, the characterisation of the objects was corrected and the artefacts were in general re-considered with regard to the new data.

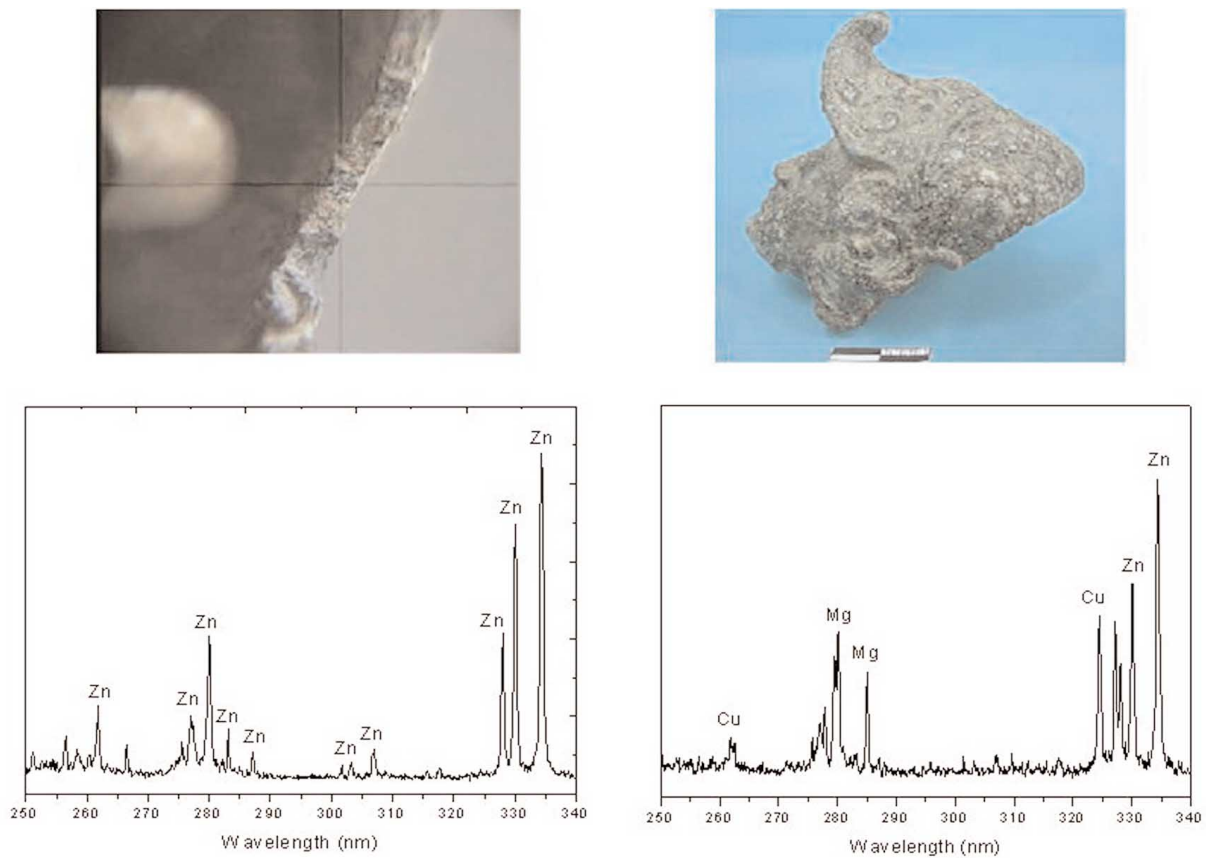


Figure 4 - Analysis on the main body of 1673 (Statuette of Athina) showed pure zinc (left), while with multiple spot analyses on the black patina apart from zinc a considerable amount of copper and magnesium were detected (right).

**4.2 Examination of prehistoric artefacts**

The second assemblage that will be discussed here includes prehistoric metal objects, from the recent excavations of an Early Minoan cemetery at Petras on East Crete. This newly excavated and still unpublished assemblage is most important as very few cemeteries of such an early period have been excavated on Crete up to now and therefore any information that can be extracted from these metals can make a significant contribution to the study of the Early Minoan metallurgy. The metal objects

that were examined, mostly jewellery, were offerings associated with the human skeletal remains placed in the graves. The analyses were carried out before conservation and in most cases even before cleaning the soil off the surface. The gold-based artefacts showed a quite consistent composition with a considerable amount of silver and a very small amount of copper. This composition seems to be a deliberate one. Gold-silver alloys are quite common since the Early Bronze Age. It seems that silver is added to gold in order to: a) increase the hardness of

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the alloy b) reduce the amount of gold in use while still producing an object of precious metal or c) as some scholars believe, for aesthetic purposes in order to achieve a lighter and brighter colour. A quite remarkable observation here is that the gold-silver alloy shows a consistency in the relative proportion of the two metals; most of the spectra look exactly the same especially after the first few pulses when surface depositions are removed. On both cleaned and un-cleaned objects the spectra from the first few pulses detect magnesium, silicon, aluminium and calcium which originate from the burial depositions (alumino-silicates). After few pulses usually 2 or 3 the

surface depositions are removed and we get almost clear spectra of gold-silver alloy. Therefore, as the analysis proceeds we get information first about the nature of the surface depositions and then about the elemental composition of the alloy (Fig. 5).

The silver-based artefacts vary in their elemental composition, silver being the dominant component. Most of the silver jewellery contains a small amount of copper while in other miscellaneous silver offerings copper is not detected at all. In general, silver rivets which are attached on tweezers and needed to be harder contain more copper than the jewellery and the other offerings.

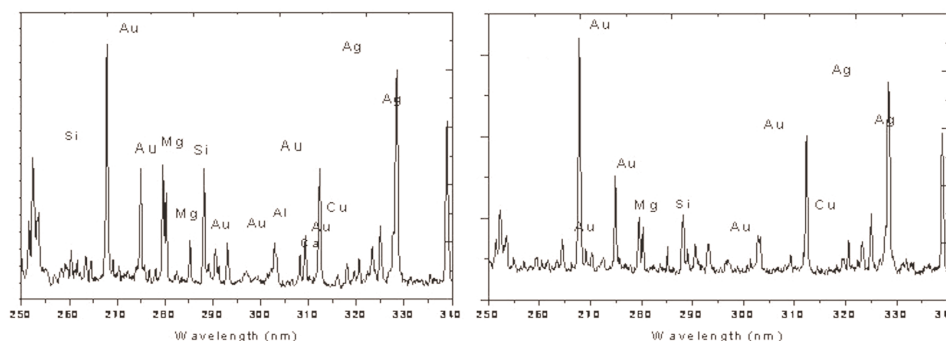


Figure 5 - LIBS spectra of gold-silver alloy from the third (left) and the seventh (right) pulse on the same spot. The alumino-silicates are gradually removed in a few pulses.

One single lead object that was examined consisted of pure lead or at least we can say that no other metal was detected with this method.

As regards the copper alloys, several metallurgical studies in the Aegean point out that the use of Bronze appears in the beginning of the Middle Minoan Period. This argument is often used as a criterion for dating objects with considerable amount of tin to the Middle Minoan period. This suggestion is in good agreement with the results of the

analysis of the copper ornaments that were examined on the course of this study. However, the tweezers that were examined, although they come from a clearly Early Minoan context, show a substantial amount of tin and a small amount of lead (Fig. 6.). This can be a very significant technological observation that invites for thorough analysis of all the bronzes that are contained in this context and if possible of other contexts of the same period.

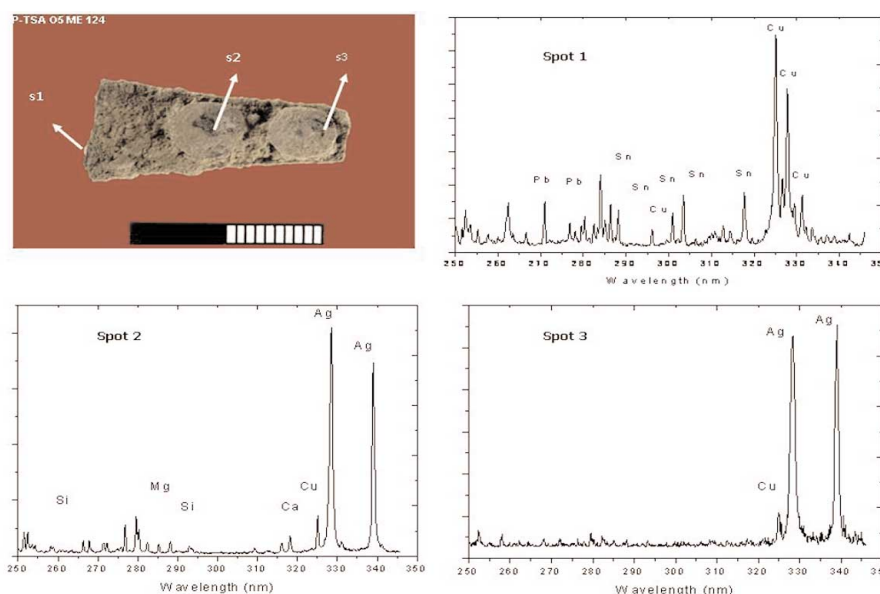


Figure.6 - Multiple spot analyses on EM Bronze tweezers (spot1) with silver rivet (spots 2 and 3).

## 5. CONCLUSION

LIBS analysis with LMNTI has up to now proved to be an effective and satisfactory method for a quick and low cost study of archaeological and historical metal collections.

Its applications in the conservation laboratory include:

- Identification and characterization of metal alloys
- Stratigraphic study of corrosion layers
- Nature of burial depositions
- Clues on ancient technology and raw material selection
- Clarification of archaeological questions and selection of the objects that should be further analysed with other techniques which could also provide quantitative data.
- Screening process to get some quick answers to basic questions before going into more complicated methods of analysis that might require sampling. Thus, the use of LIBS as a survey or screening tool can minimise the number of samples for further analysis.

All the above information contributes to the choice of the most appropriate preventive and/or remedial methods and materials for the conservation of archaeological and historical metal objects aiming at their long term protection.

Future work focuses on the development of a data base with the results of our analysis in order to be able to proceed into the comparative study of several contexts which will ultimately allow us to have statistical results and to add some new contributions to the study of the Bronze Age Metallurgy.

Moreover, we hope that LMNTI will be calibrated in the future for quantitative analysis as well, which will expand greatly its analytical capabilities and consequently its applications.

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