

# ***In situ* LIBS and XRF analysis of the Porticello bronze statues at National Museum of Magna Grecia in Reggio Calabria (Italy)**

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Since long elemental analysis is a means of studying archaeological and historical materials with respect to such aspects as provenance, fabrication technology, deterioration mechanisms, etc. However, most of the applications reported in the literature refer to laboratory analysis, which in general implies the transfer of the object to the laboratory and/or sampling. This procedure may have important disadvantages: according to the circumstances, the artistic relevance of the object may forbid sampling, whereas its fragility and/or its dimensions may forbid transportation. The use of portable, non-destructive instrumentation for *in situ* micro-analysis appears to be the most straightforward solution to the above mentioned problems. Using such methods, the objects can be analyzed without removing them from the exhibition, thus minimizing the inconvenience for the public; moreover, the non-destructive character of the analysis, along with the short measurement times, allows for a meaningful statistical approach; as the time available is the only limitation here, large numbers of measurements are easily achievable, which is particularly important in the case of highly inhomogeneous or deteriorated objects. X-Ray Florescence (XRF) and Laser-Induced Breakdown Spectroscopy (LIBS) seem to be suitable techniques for this kind of analysis on indoor collections. Both these techniques are in fact characterized by easy portability of the instrumentation, they are non-destructive as they do not require sampling and analytical information is provided in very short measurement times.

Keywords: LIBS, XRF, Bronze Statues, Indoor Collections

## **1. INTRODUCTION**

Elemental analysis is widely applied as a mean of classification and determination of fabrication technology, deterioration mechanisms, and identification of the point of origin of archaeological findings [1,2]. However, most of the applications reported in the literature refer to laboratory analysis of the artefacts, which in general implies the transfer of the object to the laboratory and/or the sampling of some material from it. This procedure can be difficult for the analysis of indoor collections, since removal of the objects from the exhibition and transportation to an external laboratory is often problematic; on the other hand, sampling of the artefacts for the analysis can be inappropriate in case of high value objects, or at least impractical for very small objects.

The use of portable, non destructive instrumentation for *in situ* micro-analysis appears as a solution to the above mentioned problems. Using techniques such as LIBS [3] and XRF [4], the objects can be analysed without removing them from the exhibition. Moreover, the non-destructive

character of the analysis, along with the short time associated with the measurements, allows for a statistical approach (several different points can be measured on the same sample, which is particularly important in the case of highly inhomogeneous or degraded objects) which can be essential for a proper classification of typologically similar objects on the basis of their elemental composition.

This paper is organized in the form of a critical discussion on current activities and results for LIBS and XRF analysis of indoor collections. Up to now, the practical application of LIBS and XRF analysis to 'real life' situation has been strongly limited by the unavailability of reliable LIBS mobile instrumentation. An interesting measurement campaign, involving LIBS and XRF measurements, was performed in year 2002 by the Applied Laser Spectroscopy group in an important Italian museum. However, although the possibility of making analytical measurements on objects at exhibition was demonstrated, the experimental campaign involved the movement of heavy and bulky instrumentation within the museum, with all the associated problems that can be easily imagined.

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In order to overcome these difficulties and build the first fully integrated mobile LIBS instrument, a joint project was developed by the Applied Laser Spectroscopy (ALS) Laboratory and Marwan Technology srl. The first prototype – now commercially available - was called Mod™ (MOBILE Double-pulse Instrument for LIBS analysis) [5]. The goal of the project was to take the LIBS technique from the laboratory to the museum. The main features of the instrument we developed are the use of double-pulse LIBS and the capability of standardless quantitative analysis [6]. In the following paper we will give a description of the instrument and will show some practical examples of its use.

## 2. EXPERIMENTAL SETUP AND STRATEGY

A picture of our LIBS mobile instrument (Modi) is shown in fig.1 (the head of the XRF instrument is also visible)



Figure 1 – The Modi LIBS instrument during the measurements at Museum of Magna Grecia

The instrument integrates a dual-pulse laser, which emits two collinear laser pulses at 1064 nm with energy variable between 50 and 120 mJ per pulse at a maximum repetition rate of 10 Hz and a reciprocal delay which can be set from 0 to 60  $\mu$ s. The LIBS measurements can be performed on small samples inside a closed experimental chamber, equipped with a motorised table for exact positioning of the sample at the focus of the laser beams. A laser pointer and an optical microscope allow the control of the region of the sample under analysis. Alternatively, for direct measurements on large objects an articulated 5-joints arm allows the focusing of the laser outside the instrument and the collection of the spectral signal. The LIBS signal, either produced inside the experimental chamber or directly on the artefact, is collected through an optical fibre and sent to a compact Echelle spectrometer coupled with an intensified CCD camera for spectral acquisition. The operations of the instrument are controlled by an integrated personal computer which man-

ages the sample visualization and positioning, the experimental settings of the laser (energy of the beams, delay between the pulses, repetition rate) and the spectral acquisition parameters (number of spectra averaged, acquisition delay, CCD measurement gate and gain). The LIBS spectra, after acquisition and storage, are qualitatively and quantitatively analysed using a proprietary software (LIBS++). A typical analysis can take between one and five minutes, according to the complexity of the LIBS spectrum produced.

As an example of the joint use of LIBS and XRF techniques for analysis of indoor collections, the case study is presented of a measurement campaign recently performed at the National Museum of Magna Grecia in Reggio Calabria (Italy), in the framework of a collaboration which involved the Applied Laser Spectroscopy Laboratory, the Institute for Technologies Applied to Cultural Heritage and a small private enterprise operating in southern Italy (TEA s.a.s.).

The portable X-Ray Fluorescence spectrometer used for the measurements in Reggio Calabria is a highly performing device developed at the Institute for Technologies Applied to Cultural Heritage of the Italian National Research Council by Dr. Marco Ferretti. The system is equipped with a water cooled x-ray tube, usually working at 60 kV, 1.5 mA (here the tube was operated at 45 kV, to reduce the intensity of the Sn  $K_{\alpha}$  line); the spot diameter at the measurement point is about 6 mm. The detector is a Peltier-cooled Si-Drift produced by Ketek (area 10 mm<sup>2</sup>, FWHM = 165 eV at 5.9 keV, Zr internal collimator). In the usual working conditions of the tube (60 kV, 1.5 mA), the detection limits are about 30 ppm for Ag, Sn and Sb and 200 ppm for Pb and Bi at 95% confidence level; these figures are referred to a copper matrix and a measuring time of 120 s [7].

Portable X-Ray Fluorescence (XRF) and Laser-Induced Breakdown Spectroscopy (LIBS) instrumentation allowed in situ analysis of several bronze pieces belonging to the group of the so-called *Porticello Bronzes* [8-12]. The find was recovered in the sea off the village of Porticello (Reggio Calabria) in 1969 and consists of a number of fragments, including a bearded head (see figure 2), pertaining to at least two statues. The use of X-Ray Fluorescence and Laser-Induced Breakdown Spectroscopy techniques allowed for a classification of the fragments according to their elemental composition. The fragments appear to belong to at least two different statues; although, in general, the compositional classification agrees well with the stylistic analysis of the fragments, significant improvements with respect to previous achievements emerge from the joint results of the two techniques used.

X-Ray Fluorescence (XRF) [15] and Laser-Induced Breakdown Spectroscopy (LIBS) [16] were used at the same time to analyse the Porticello bronzes. Both these techniques are (almost) non-destructive as they do not require sampling, and are able to provide quantitative

analytical information in very short measurement times. All these features were indeed extremely important for the in situ measurements at the National Museum in Reggio Calabria, where the Porticello statues are at exhibition.



Figure 2 - The Porticello ‘philosopher head’

It has to be pointed out that, though suitable to compare materials, such quantitative information may not coincide with the absolute bulk composition, that, in principle, is what one is looking for; in fact, it is well known that the presence of surface deterioration layers affects both LIBS and XRF measurements and prevents a reliable achievement of the absolute composition.

The Porticello samples measurements were performed in double-pulse regime (60 + 60 mJ with an interpulse delay of 1 μs), 1 ms after the second laser pulse, using a gate time of 2 μs. This choice provided a good signal to noise ratio, necessary for a precise measurement of the spectral line widths, at the same time guaranteeing, at least at relatively long delays, that the plasma parameters (particle density, temperature and electron density) would remain quasi-stationary during the measurement time window [3]. Ten different measurements on the same spot were averaged for obtaining the LIBS spectra; moreover, different points on the same samples were considered for obtaining statistically significant information.

Given the deeply corroded surface of the Porticello fragments (the pieces were found underwater) and the impossibility of removing these corrosion layers, no attempt was made to measure the absolute concentration of the alloys main components. Rather, thanks to the high sensitivity of both XRF and LIBS, it was possible to classify the alloys on the base of minor and trace elements, thus achieving the aim of the investigation that is, distinguishing the alloys used for different statues. The method relies on a significant number of measurements taken on different points of the same object; if the data points are then plotted in the space of the count-rates, each object will be represented by a cluster, more or less scattered according to its surface conditions. Independently on the data points dispersion, it is always possible to state that two alloys are different if the corresponding clusters can be distin-

guished from each other. Once more it has to be remarked that this method does not measure the absolute composition, but rather it compositionally compares the alloys. Given the strict requirement of non-destructivity that characterizes the investigation this was the only possible approach.

3. EXPERIMENTAL RESULTS

Five XRF measurements were carried out for each object; besides the main components of the alloy (Cu, Sn), minor elements such as Fe, As, Ag, Sb, Pb and Bi were detected. Similarly, the LIBS measurements evidenced, besides the surface contaminants possibly from the sea environment (Mg, K, Na, Ca, Sr, Si, Al, etc.) and the main components of the alloy, also the presence of Fe, Ag, Pb and Bi. As and Sb lines are not clearly detectable in the LIBS spectra, so that these elements were not considered for the classification of the fragments.

With respect to Bi a clear bimodal distribution could be observed in XRF measurements: in some pieces it is below detection limits, whereas in others it is unusually high [13] (see Fig.3). The same bimodal distribution of the Bi signal (integral intensity of the Bi I line at 306.77 nm) was observed in LIBS measurements

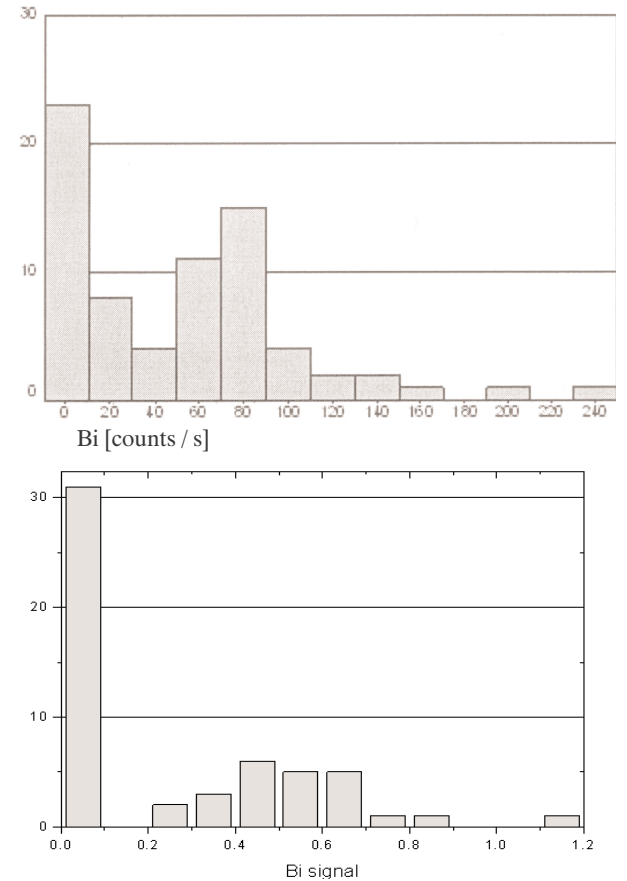


Figure 3 – Histogram of the count-rates showing the bimodal distribution of Bi in XRF (top) and LIBS (bottom) measurements

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It was also observed that all the pieces certainly attributed to the male nude(s) belong to the first group and those attributed to the “philosopher” to the second one. Consequently, we attributed all the pieces of uncertain pertinence according to the Bi level, and realized that also Pb and Ag, more or less clearly, had the same distribution; the boxplot of the count-rates shown in Fig.5 summarises the distribution of Bi, Pb and Ag for the two groups, here identified as the “philosopher” and the “male nude”.

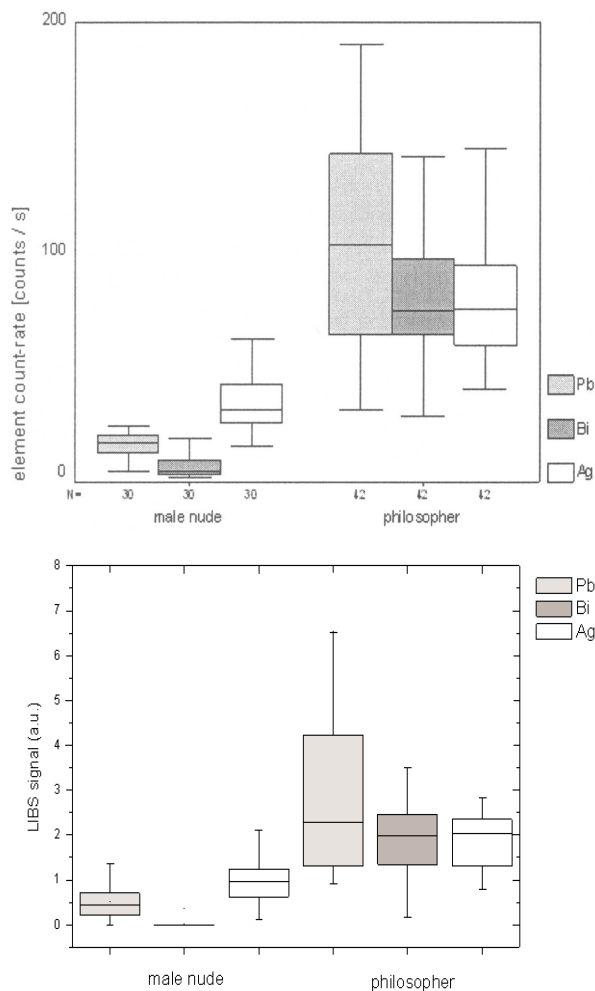


Figure 4 – Boxplot of the count-rates of Pb, Bi and Ag for the ‘male nude’ and the ‘philosopher’ in XRF (top) and LIBS (bottom) measurements. The lower end of the box accounts for the 25th percentile, the upper one for the 75th percentile, the line inside for the median, the whiskers account for the minimum and maximum values within a distance of 1.5 box heights from the box end.

The clustering of the fragments pertinent to the philosopher and to the male nude statues is evident from the plot of the points in the space of the LIBS signals (Bi, Ag, Pb).

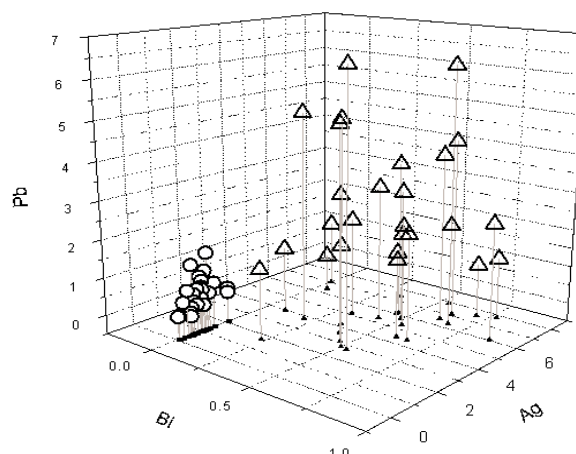


Figure 5 – Classification of the fragments in the space of the LIBS signals (Bi,Ag,Pb). The circles corresponds to the fragments pertinent to the male nude, while the triangles corresponds to the philosopher.

Similar results are obtained with the XRF measurements. In view of the results presented, it is thus possible to classify the fragments analysed as reported in Table I (inventory numbers of the fragments are quoted).

<i>Philosopher</i>	<i>Male nude</i>
17076- Fragment	17071- Fragment
17079- Vest	17072- Fragment
17082- Leg+vest	17073- Fragment
17091- Arm+vest	17074- Fragment
17093- Right foot	17080- Fragment
17094- Left hand	17081- Fragment
17095- Vest	17087- Gluteus B
17096- Head	17088- Gluteus A
17075- Fragment	17090- Phallus
19149- Vest	17092- Left foot

Table I – Classification of the Porticello bronze fragments

**4. CONCLUSIONS**

The joint use of XRF and LIBS to investigate the Porticello Bronzes has shown that both techniques can be fruitfully used to compositionally compare copper alloys and highlight possible differences in materials sources and fabrication contexts. Despite of the deep corrosion that affects the pieces and the different analytical volumes, the measurements are in good agreement and suggest that a full integration of the two techniques is at hand. Deeply corroded bronzes such as those of Porticello may require to protract ablation to reach the bulk, which would result in a higher damage of the piece. However, the correlation observed between LIBS and XRF intensities actually proves that the Bi, Pb and Ag trace elements are distributed more or less homogeneously from the surface towards the bulk and thus discrimination patterns can be revealed based on the presented XRF/LIBS semi-quantita-

tive data. If the trace elements were preferentially enriched or depleted from the surface, that it might be true for other corroded surfaces of metal alloys, XRF and LIBS intensities would not be any longer correlated. In general, if a portable XRF spectrometer is used as a non-destructive sniffer to drive the choice of LIBS measurement points, the overall number of ablations can be significantly reduced and consequently the impact on the piece will be reduced as well.

The detection of a higher number of elements showed compositional peculiarities that were not observed in past investigations and produced further knowledge on the Porticello Bronzes. This work shows that the fragments can be classified in two classes, the first characterized by the presence of bismuth and relatively high signals of Ag and Pb, possibly connected with the use of argentiferous lead (the 'philosopher'); the second with bismuth below detection limits and relatively low signals of Ag and Pb (the 'athlete'). The fact that the statues are at least two is consistent with past investigations, but the differences in the concentration of both deliberately used elements, such as lead, and minor elements, such as bismuth and silver, lead to conclude that probably they were not made in the same workshop, as conversely stated by Fiorentino et al. [11]. Furthermore the feet are not from the same statue: the right foot (inventory number 17093) has high Bi and therefore belongs to the 'philosopher', whereas the left foot (inventory number 17092), supposedly from the 'philosopher' as well, actually belongs to the 'athlete' from a compositional point of view.

Finally the high bismuth, silver and lead signals associated to the left hand (inventory number 17094) are consistent with its assignation to the 'philosopher', despite the recently raised objections that it seems too small in comparison with the head.

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