A COMPOSITIONAL STUDY OF THE PORTICELLO BRONZES BY PORTABLE X-RAY FLUORESCENCE AND LASER-INDUCED BREAKDOWN SPECTROSCOPY

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ABSTRACT

In this paper we report the results of a measurement campaign performed at the National Museum of Magna Grecia in Reggio Calabria (Italy). Portable X-Ray Fluorescence and Laser-Induced Breakdown Spectroscopy instrumentation allowed in situ analysis of several bronze fragments found on an ancient Greek ship sank at Porticello (Reggio Calabria). The joint 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 at least to two different statues; although, in general, the compositional classification agrees well with the morphological analysis of the fragments, significant improvements with respect to previous classification emerge from the joint results of the two techniques used.

KEYWORDS

Archaeometry, Cultural Heritage, XRF, LIBS, Bronze

INTRODUCTION

Elemental analysis is widely diffused as a mean for identification of the point of origin of archaeological findings [1-4]. 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 the removal of some material from it. This procedure can 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 the objects for the analysis can be inappropriate in case of high value manufacts, or at least impractical for very small samples.

The use of portable, non destructive instrumentation for in situ micro-analysis appears as a solution to the above mentioned problems. Using such methods, the objects can be analysed 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 time associated with the measurements, allows for a meaningful 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.

The results reported in this paper refer to a measurement campaign performed at the National Museums of Magna Grecia in Reggio Calabria (Italy) on the bronze fragments found in a Greek

ship, sunk in V century B.C. in the straits of Messina, in front of the village of Porticello (Reggio Calabria).
The campaign has been promoted by T.E.A. sas, private enterprise operating in southern Italy, in the ambit of the MESSIAH project, funded by Regione Calabria, in collaboration with the Applied Laser Spectroscopy of Institute for Chemical and Physical Processes (Pisa) and the Institute for Technologies Applied to Cultural Heritage (Rome), both of Italian National Research Council.
According to preceding studies, the fragments belong to at least two life-sized bronze statues [5,6].
Indubitably, the most interesting object from the wreck is the bearded head commonly known as the "Philosopher head" (see Figure 1).

Philosopher head | Left foot
Leg with vest | Right foot
Gluteus A | Left hand

Fig. 1 – Some samples analyzed

A previous typological study also attributed to the 'philosopher' other parts, including fragments of a vest, the left hand an two feet. On the other hands, several other fragments surely belonging to at least another different statue (a young male nude figure, probably an athlete) where found in the Porticello wreck [6]. Apart from a few distinctive fragments which can be associated to the nude statue, many other smaller parts cannot be easily associated to one or the other statue [8]. Early compositional analysis on some of the Porticello fragments, performed in 1976 by Frazzoli, Borrelli and Fiorentino [9], evidenced in fact a close similarity – considering the instrumentation available at that time - of the alloys used for the 'philosopher' and 'athlete' statues, a fact which led

Fiorentino, Marabelli and Micheli [10] to hypothesize that the two bronze statues where realized in the same foundry.
Thirty years after the first measurements by Frazzoli et al., the evolution of techniques and instrumentation in archaeometry allowed us to perform an extensive, non destructive measurements campaign on the Porticello statues which led to a clear differentiation of the alloys used in the ‘philosopher’ and ‘athlete’ statues and a consequent attribution to one or the other statue of the fragments.
The techniques used and the results obtained are described in the following sections.

EXPERIMENTAL TECHNIQUES

For the analysis of the Porticello fragments we jointly used X-Ray Florescence (XRF) [11] and Laser-Induced Breakdown Spectroscopy (LIBS) [12]. Both these techniques are characterised by easy transportability of the instrumentation, guarantee non-destructive measurements without sampling or previous treatment of the samples and are able to give quantitative information on the sample composition 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 were at exhibition. Figure 2 shows both systems during investigation of the Philosopher head.

Fig. 2 – The Modì instrument used for the LIBS measurements (right) and the XRF system (left) during investigation of the 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 instrumentation used for X-Ray Fluorescence measurements was developed at the Institute for Technologies Applied to Cultural Heritage of the Italian National Research Council [13].

The X-Ray source is a 45 kV, 1.5 mA water cooled X-Ray tube, producing a X-ray beam of about 6 mm transverse dimension on the sample, which allows to take advantage from both an intense primary beam and the possibility of exciting the K-lines of important intermediate elements as Ag, Cd, In, Sn and Sb. The fluorescence signal is detected with an energy-dispersive Peltier cooled 5mm^2 Ketek Si-Drift detector (175 eV resolution at 5.9 keV, Zr collimator) In the measurement conditions used for the Porticello fragment analysis, detection limits of 50 ppm for Ag, Sn and Sb amd about 200 ppm for Pb and Bi (confidence limit 95%) can be forecast, using a measurement time of 120 s [13]. For all the samples considered, the X-ray Fluorescence measurements have been repeated in five different points, for assessing homogeneity of the samples and reproducibility of the experimental results.
For the LIBS analysis, we used Modì (MObile Dual-pulse Instrument) [14], a double-pulse mobile LIBS system realized by the Applied Laser Spectroscopy group of IPCF-CNR in collaboration with Marwan Technology s.r.l. (Pisa). Modì uses a Nd-YAG Laser emitting two collinear pulses (with a reciprocal delay variable from 0 to 50 μs) at 1064 nm with 60 mJ energy per pulse and 12ns FWHM, coupled with an Echelle spectrometer (spectral resolving power $\lambda/\Delta\lambda$ = 7500) equipped with a iCCD for time-resolved LIBS measurements.
The Porticello samples measurements were performed in double-pulse regime (60 + 60 mJ with an interpulse delay of 1 μs), 1 μs after the second laser pulse, using a gate time of 2 μs. This choice which 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 [14]. Ten different measurements on the same spot were averaged for obtaining the LIBS spectra; also for LIBS measurements, and for the same reasons above mentioned, different points on the same samples were considered.

EXPERIMENTAL RESULTS

Both the XRF and LIBS technique can provide quantitative information on the elemental composition of the fragments analysed [15,16]. However, the high level of surface corrosion of the Porticello fragments (resulting from almost 2500 years of exposition to the attack of marine water) together with the impossibility of removing this corrosion layer without compromising the integrity of the samples, makes such information not significant.
On the other hand, the high sensitivity of both the techniques suggested a classification based on the minor and trace elements of the alloys. The XRF measurements clearly evidences, besides the main components of the bronze alloy (Cu, Sn) the presence in the alloys of Fe, As, Ag, Sb, Pb and Bi. Similarly, the LIBS measurements evidences, besides the main components of the alloy and the characteristic elements of the corrosion layer (Mg, K, Na, Ca, Sr, Si, Al, etc.), 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.
The first noticeable result of both the XRF and LIBS analysis is related to the distinct bimodal distribution of the Bi signal (proportional to the count rate in XRF measurements and to the integral intensity of the Bi I at 306.8 nm emission line for LIBS measurements) (see Figures 3a and 3b).

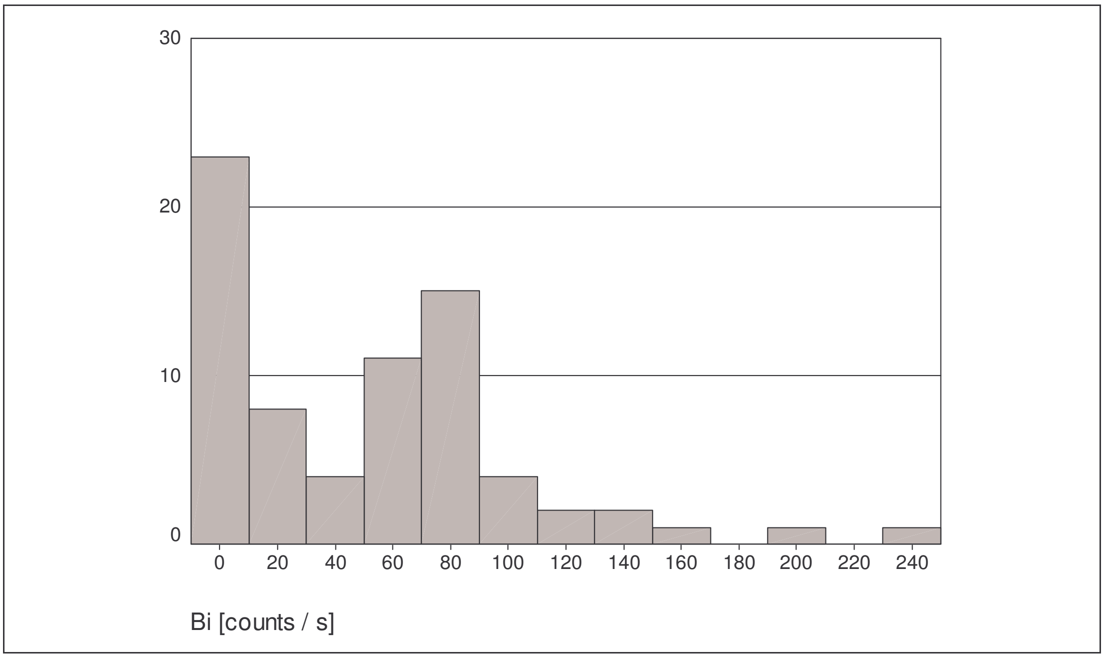

Fig. 3a – Distribution of Bi signals for the samples analyzed (XRF measurements)

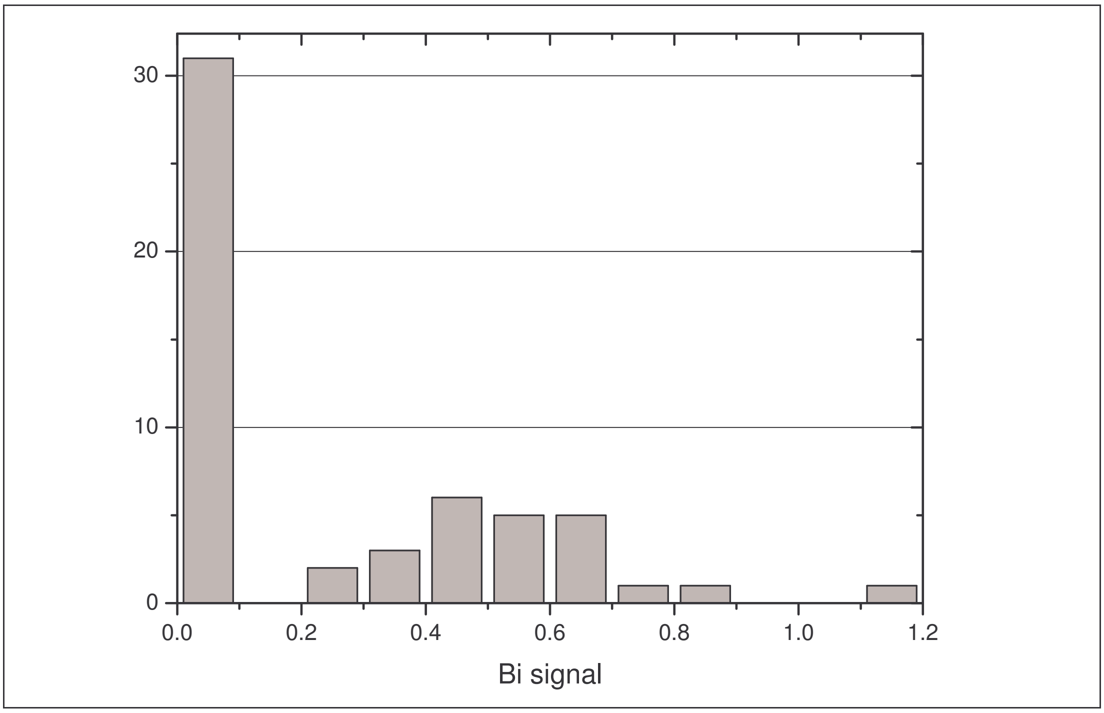

Fig. 3b - Distribution of Bi signals for the samples analyzed (LIBS measurements)

The presence of Bismuth in a copper alloy is not usual [17]; thus, this element can be considered for a possible classification of the bronze fragments under study.

Considering the distribution of XRF measurements it was 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. Accordingly 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 Figure 4 summarises the distribution of Bi, Pb and Ag for the two groups, here identified as the "philosopher" and the "male nude". Moreover Figure 5 shows the count-rates scatterplots Pb-Bi and Pb-Ag where each piece is identified by a different marker; the clustering of the data points is apparent and does not require further comments; the polygons have the only purpose of visually distinguishing the philosopher's points from those of the male nude(s).

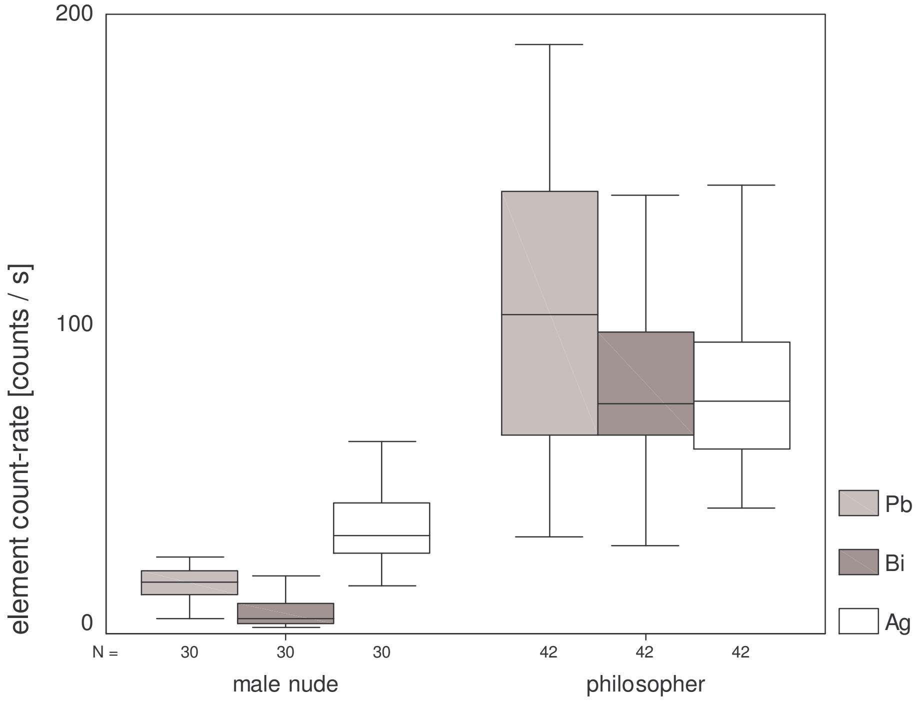

Figure 4 – XRF: boxplot of the count-rates of Pb, Bi and Ag for the male nude and the philosopher; the lower end of the box accounts for the 25th percentile, the upper one for the 75th percentile, the line inside for the median, the whiskers account for the minimum and maximum values within a distance of 1.5 box heights from the box end.

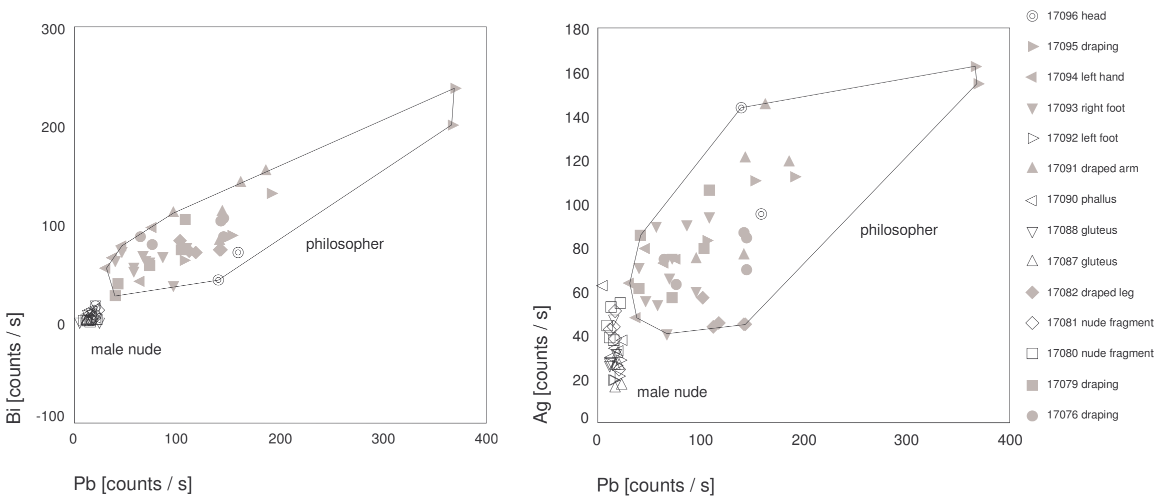

Figure 5 – XRF: Scatterplots of the count-rates Pb-Bi and Pb-Ag; the polygons are drawn with the only purpose of visually distinguishing the philosopher's data points from those of the male nude(s).

Similarly, the LIBS measurements evidence, 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.

The statistical distributions of Pb and Ag LIBS signals (integral intensities of the Pb I line at 405.78 nm and Ag I line at 338.29 nm, respectively) show significant differences between fragments pertaining to the 'male nude' and the 'philosopher' statues (see Figure 6).

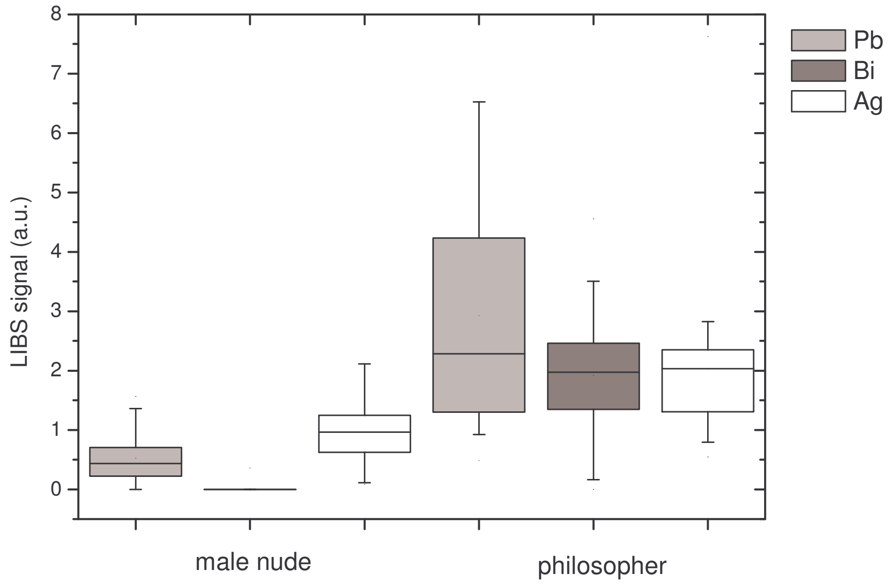

Figure 6 – LIBS: boxplot of the signals of Pb, Bi and Ag for the male nude and the philosopher; the lower end of the box accounts for the 25th percentile, the upper one for the 75th percentile, the line inside for the median, the whiskers account for the minimum and maximum values within a distance of 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).

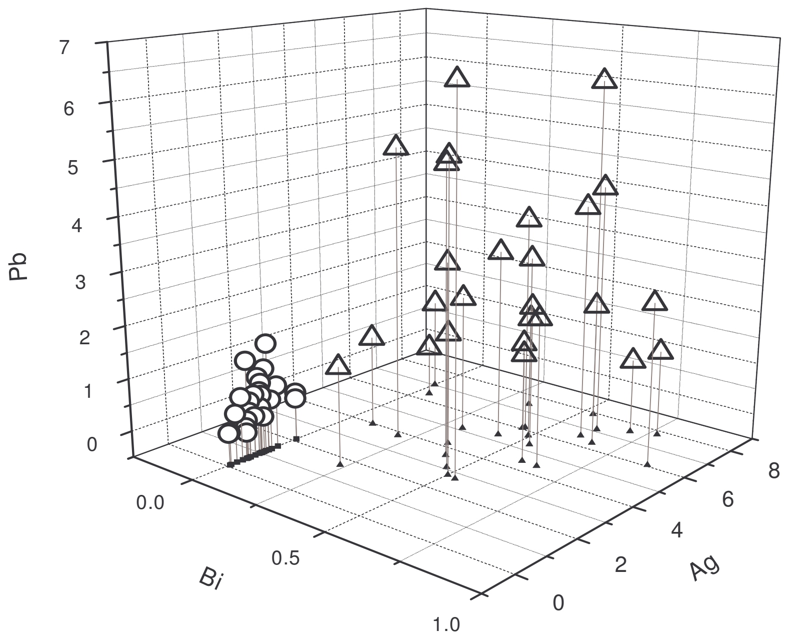

Fig. 7 – Classification of the fragments in the space of the LIBS signals (Bi,Ag,Pb). The circles corresponds to the fragments pertinent to the male nude, while the triangles corresponds to the philosopher.

In view of the results presented, it is thus possible a classification of the fragments analysed as reported in Table I.

Table I – Classification of the Bronze fragments according to XRF and LIBS measurements

Philosopher	*Male nude*
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

The numbers are the inventory numbers of the fragments

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. 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 (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. [10]. 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.

ACKNOWLEDGEMENTS

The authors acknowledge the collaboration and precious help of the scientific and technical personnel of the National Museum of Magna Grecia in Reggio Calabria. In particular we warmly thank Dr. Annalisa Zarattini, Superintendent for the Archaeological Heritage of Calabria, Dr. Pasquale Dapoto, Dr. Rossella Agostino and Dr. Irene Spuri.

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