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Abstract: This paper reports the results of a measurement campaign performed at the National Museum of Magna Grecia in Reggio Calabria (Italy). 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. The find occurred at sea, off the village of Porticello (Reggio Calabria) in 1969 and consists of a number of fragments, including a bearded head, 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.

Cover Letter

Carissimo Nico,
ti mando questo manoscritto per lo special isssue di Montreal, secondo me è un bel lavoretto anche dal punto di vista metodologico, con misure LIBS e XRF. Spero sia di interesse per i reviewers, almeno noi ci siamo divertiti abbastanza a fare queste misure, eravamo a due metri dai Bronzi di Riace, veramente una bella esperienza. Sono stato contento di aver coinvolto anche Marco Ferretti per l'XRF, è veramente una persona in gamba….
Ci sentiamo, un carissimo saluto da tutti
Vince

* Manuscript

In situ study of the *Porticello Bronzes* by portable X-Ray Fluorescence and Laser-Induced Breakdown Spectroscopy

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Abstract

This paper reports the results of a measurement campaign performed at the National Museum of Magna Grecia in Reggio Calabria (Italy). 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*. The find occurred at sea, off the village of Porticello (Reggio Calabria) in 1969 and consists of a number of fragments, including a bearded head, 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.

Keywords: Archaeological bronze statues, Elemental analysis, XRF, LIBS, Cultural Heritage.

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1. Introduction

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. [1-8]. 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 the most straightforward 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 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.

The results reported in this paper refer to a measurement campaign carried out at the National Museums of Magna Grecia in Reggio Calabria (Italy) on a number of bronze fragments found in an ancient ship sunk in the straits of Messina, in front of the village of Porticello (Reggio Calabria). According to previous studies, the fragments pertain to at least two life-sized bronze statues dated between the end of the V and the end of the IV century BC [9-14].

The most interesting piece of the group is the bearded head (see fig. 1) commonly known as the “philosopher head”.

A previous stylistic study also attributed to the ‘philosopher’ other parts, including fragments of a vest, the left hand and two feet. Further fragments belonging to at least one other statue (a young male nude, possibly an athlete) where found in the Porticello wreck [9]. Apart from a few distinctive fragments which can be clearly associated to the latter statue, the pertinence of many other smaller parts cannot be stated [13]. Early analyses on some of the Porticello fragments, performed in 1976 by Frazzoli, Borrelli and Fiorentino [14], highlighted in fact a close compositional similarity between the philosopher's and the athlete's alloys, a fact which led Fiorentino, Marabelli and Micheli [13] to hypothesize that the two bronze statues where made in the same foundry. In this regard it has to be noted that the analyses by Frazzoli et al. only account for the main components of the alloy (copper, tin and lead), no mention being made of the minor ones.

Thirty years after these measurements the availability of more advanced techniques and instrumentation allowed us to perform an extensive, non-destructive investigation on the Porticello statues which led to a clear differentiation of the alloys; it was therefore possible to distinguish the 'philosopher' from the 'athlete' and consequently attribute the uncertain fragments.

The techniques used and the results obtained are described in the sections below.

2. Equipment and methods

X-Ray Florescence (XRF) [15] and Laser-Induced Breakdown Spectroscopy (LIBS) [16] were used at the same time to analyse the Porticello bronzes. Both these techniques are characterised by easy transportability of the instrumentation, are 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.

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 portable X-Ray Fluorescence spectrometer is a highly performing device developed at the Institute for Technologies Applied to Cultural Heritage of the Italian National Research Council [17] (see figure 2).

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_{α} 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^2, 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 [17].

For the LIBS analysis, we used Modì (MObile Dual-pulse Instrument) [18], 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 (see figure 3).

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 [19]. 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 a statistically significant information.

Given the deeply corroded surface of the Porticello fragments (the pieces were found at sea) and the impossibility of removing these corrosion layers (our approach was strictly non-destructive), 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 distinguished from each other. Once more it has to be remarked that this method does not measure the absolute composition, rather it compositionally compares the alloys, that is all we can do, given the strict requirement of non-destructivity that characterizes the investigation.

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. With respect to Bi a clear bimodal distribution could be observed: in some pieces it is below detection limits, whereas in others it is unusually high [20] (see Fig.4).

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. Following this spontaneous behaviour, 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". Moreover Fig.6 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).

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.

As in the XRF measurements, also in the LIBS measurements a clear bimodal distribution of the Bi signal (integral intensity of the Bi I line at 306.77 nm) is visible (see figure 7)

Similarly, 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 8)

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)

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

In LIBS measurements, the only sample which does not seem to fit the classification in two groups of the fragments is sample 17089. Noticeably, this is also the only fragment showing a green surface patina (see figure 10, where it is shown besides other fragments showing the characteristic black patina). However, the absence of bismuth in the sample suggests a pertinence to the male nude statue or statues.

It is noticeable that the mean values of signals from Bi, Ag and Pb measured by XRF and LIBS show a good correlation (see figures 11a, 11b and 11c).

The correlation between Cu and Sn signals is less satisfactory (figures 12a and 12b), although well explainable considering the enrichment/depletion effects caused by the deep corrosion and the different analytical volumes of the two techniques.

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. 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. [13]. 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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Figure and Table Captions

Figure 1 – The Porticello 'philosopher head'

Figure 2 – The portable XRF spectrometer.

Figure 3 – The Modì instrument used for the LIBS measurements on the Porticello bronzes (the 'philosopher head' and the XRF spectrometer are also visible in the picture).

Figure 4 – XRF: histogram of the count-rates showing the bimodal distribution of Bi.

Figure 5 – 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 6 – 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).

Figure 7 - LIBS: histogram of the LIBS signals showing the bimodal distribution of Bi.

Figure 8 - 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.

Figure 9 – LIBS: 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.

Figure 10– Sample 17089. Note the different surface patina with respect to the other samples (fragment 17075 is shown for comparison)

Figure 11a - Correlation between XRF and LIBS average Bi signals for the fragments considered. The error bars of the experimental measurements represent the reproducibility of the measurements on the same sample. The line is the best linear fit of the data.

Figure 11b - Correlation between XRF and LIBS average Ag signals for the fragments considered. The error bars of the experimental measurements represent the reproducibility of the measurements on the same sample. The line is the best linear fit of the data.

Figure 11c - Correlation between XRF and LIBS average Pb signals for the fragments considered. The error bars of the experimental measurements represent the reproducibility of the measurements on the same sample. The line is the best linear fit of the data.

Figure 12a - Correlation between XRF and LIBS average Cu signals for the fragments considered. The error bars of the experimental measurements represent the reproducibility of the measurements on the same sample. The line is the best linear fit of the data.

Figure 12b - Correlation between XRF and LIBS average Sn signals for the fragments considered. The error bars of the experimental measurements represent the reproducibility of the measurements on the same sample. The line is the best linear fit of the data.

Table I – Classification of the Bronze fragments according to XRF and LIBS measurements. The numbers are the inventory numbers of the fragments

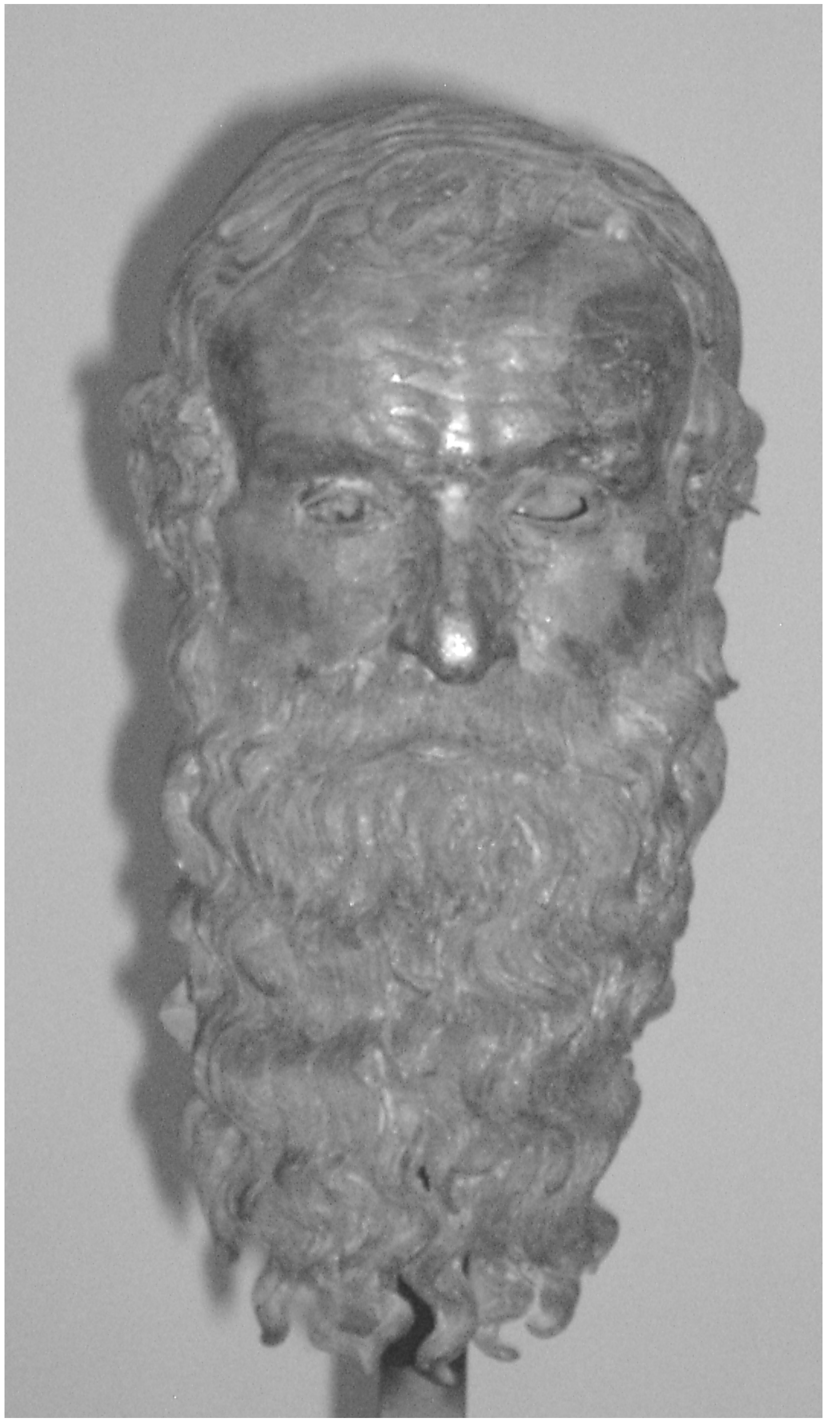
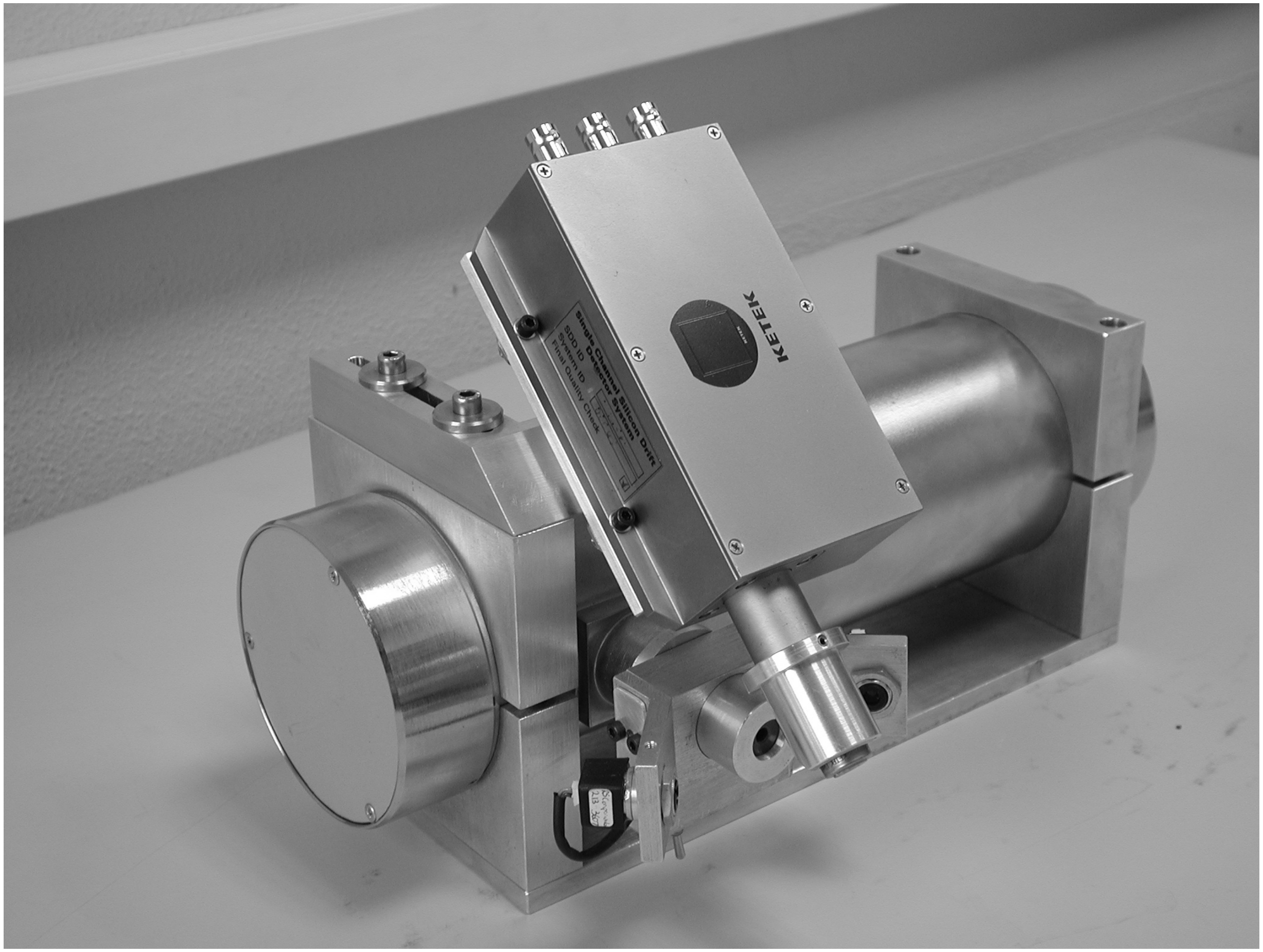


Figure 1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Single Channel Silicon Drift Detector System
SDD ID
System ID
Final Quality Check

Figure 2

Figure 3

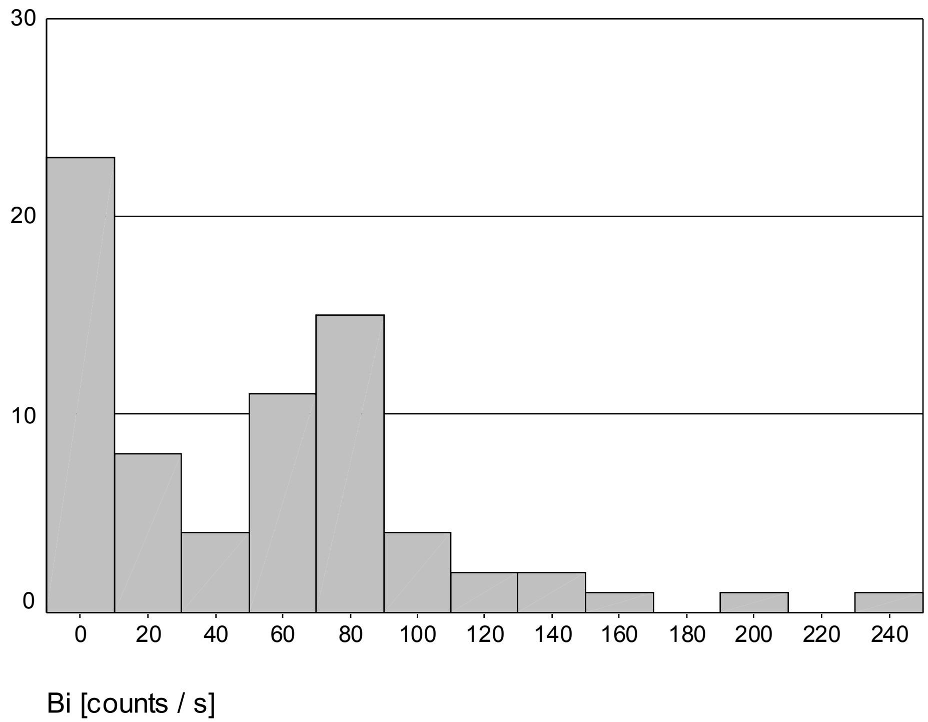


Figure 4

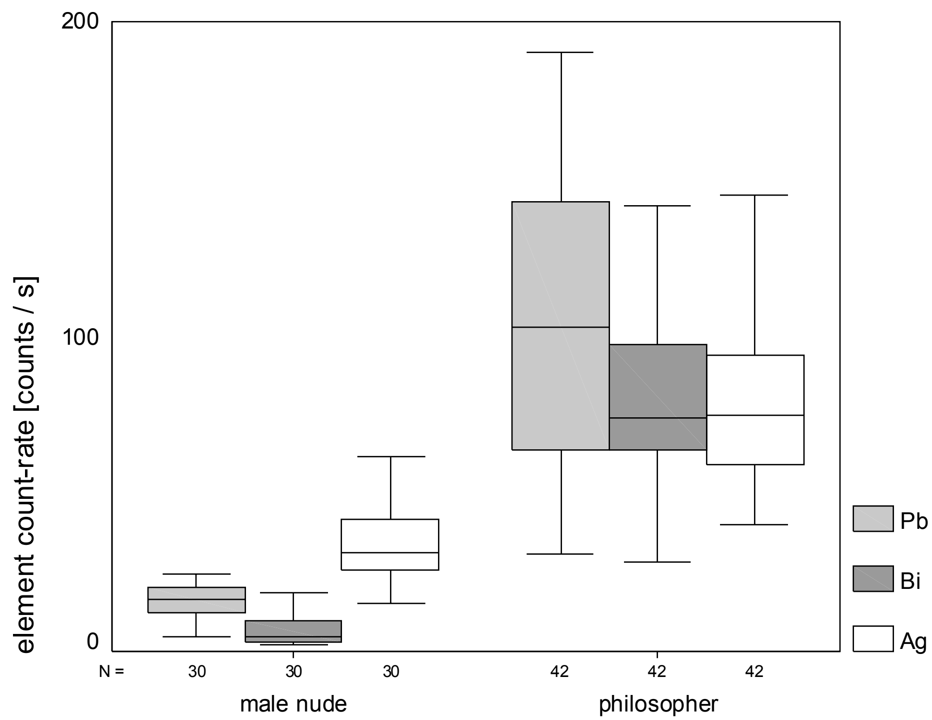
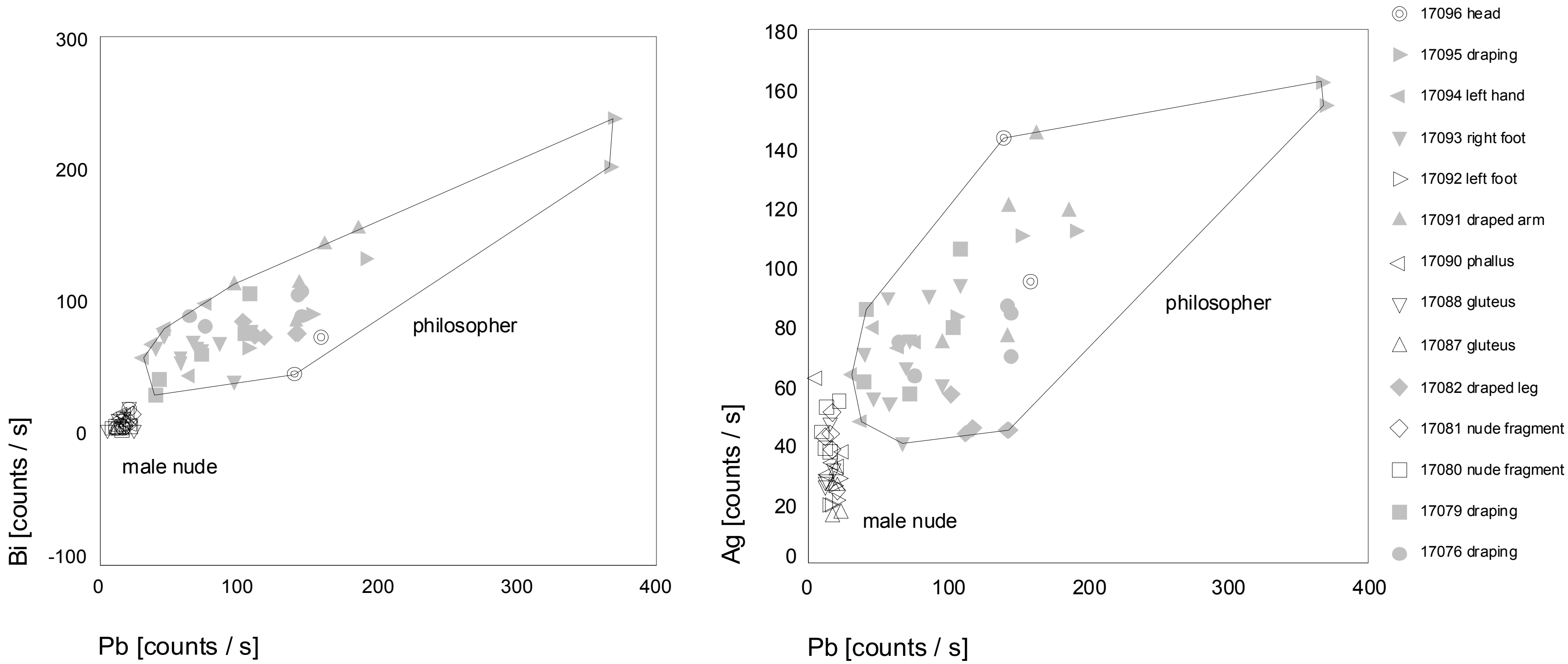

200
100
0
element count-rate [counts / s]
N =
30
30
30
42
42
42
male nude
philosopher
Pb
Bi
Ag

Figure 5


300
200
100
0
-100
Bi [counts / s]
0
100
200
300
400
Pb [counts / s]
philosopher
male nude
180
160
140
120
100
80
60
40
20
0
Ag [counts / s]
0
100
200
300
400
Pb [counts / s]
philosopher
male nude
17096 head
17095 draping
17094 left hand
17093 right foot
17092 left foot
17091 draped arm
17090 phallus
17088 gluteus
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17082 draped leg
17081 nude fragment
17080 nude fragment
17079 draping
17076 draping

Figure 6

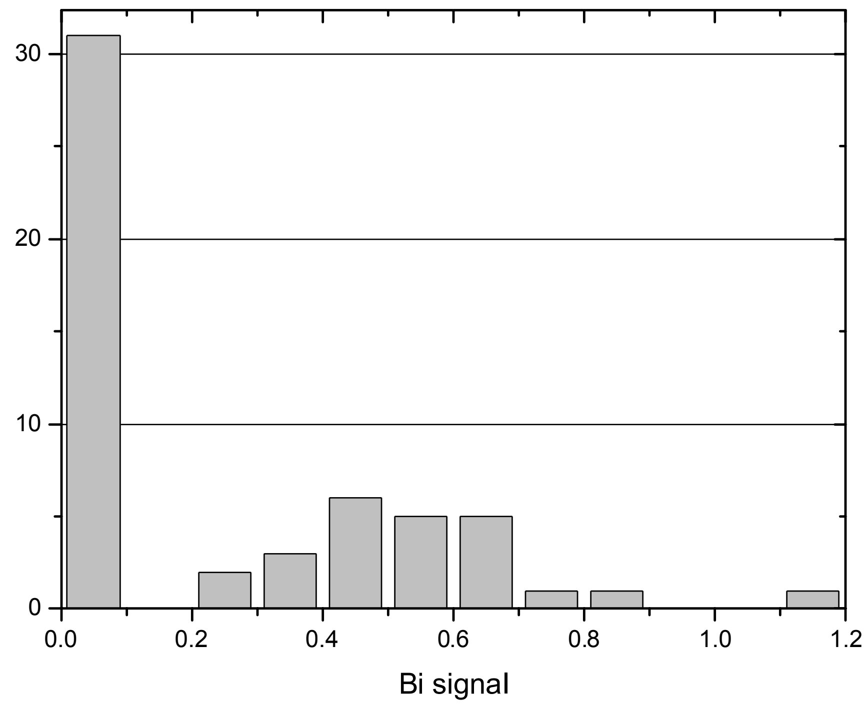
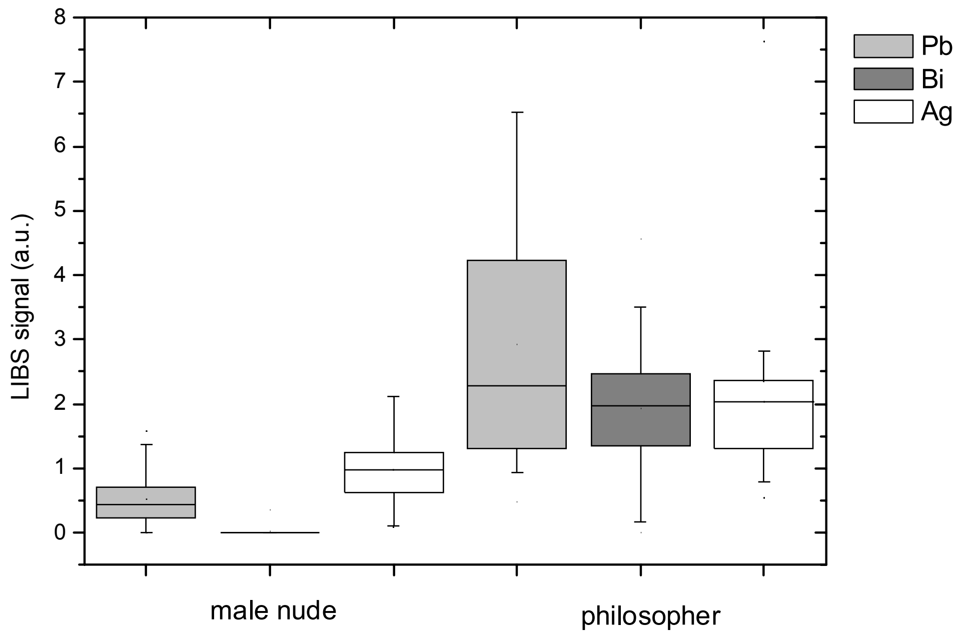


Figure 7



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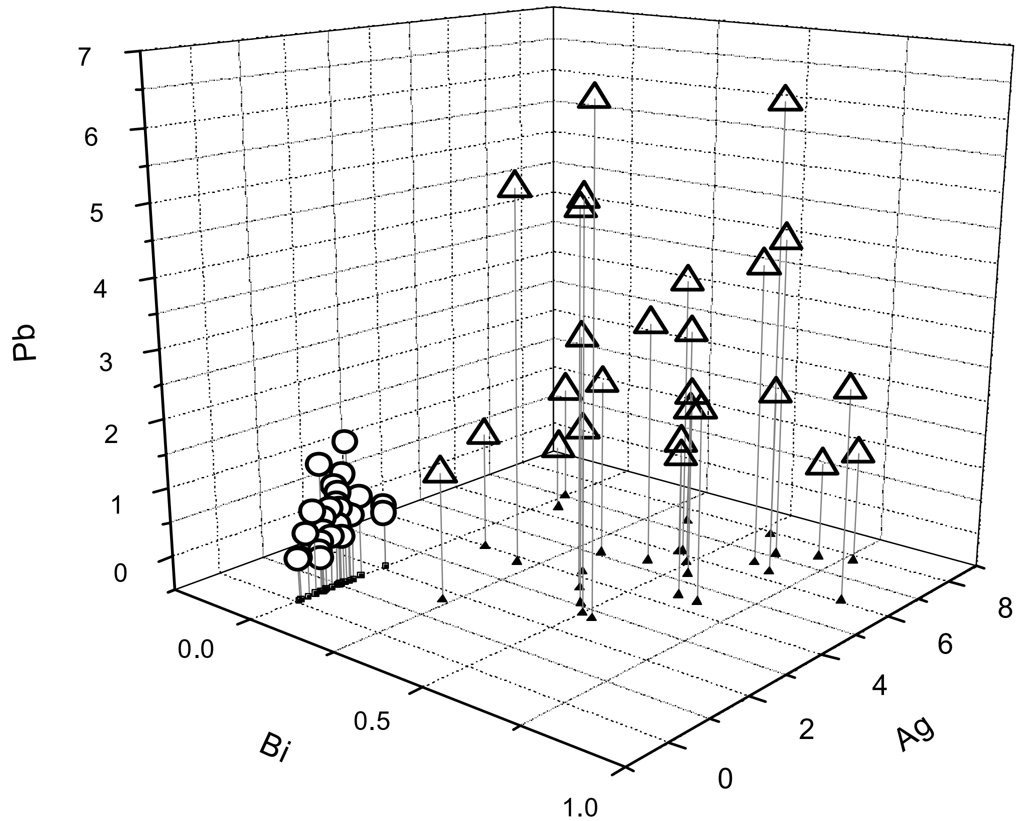

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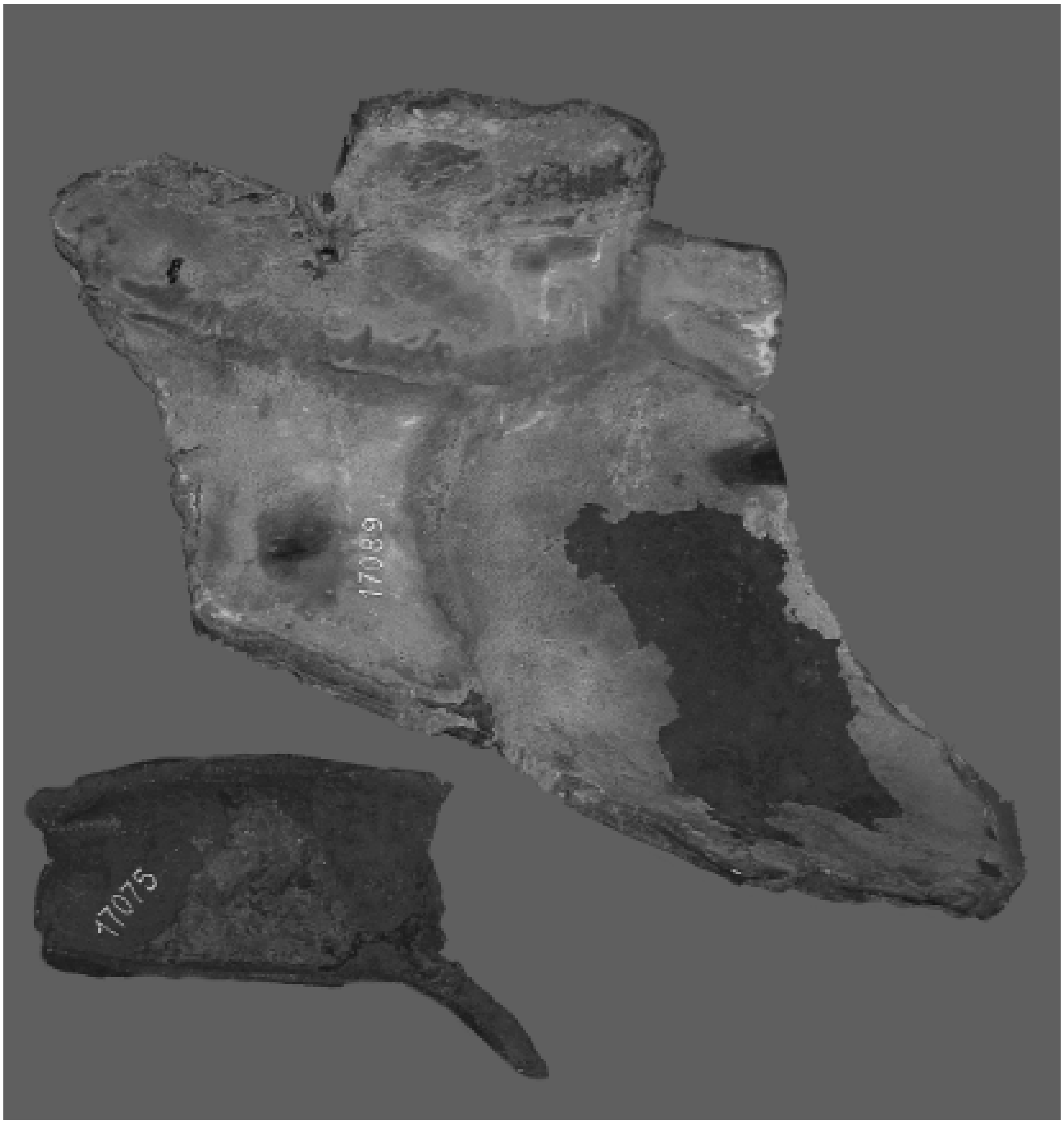


Figure 10

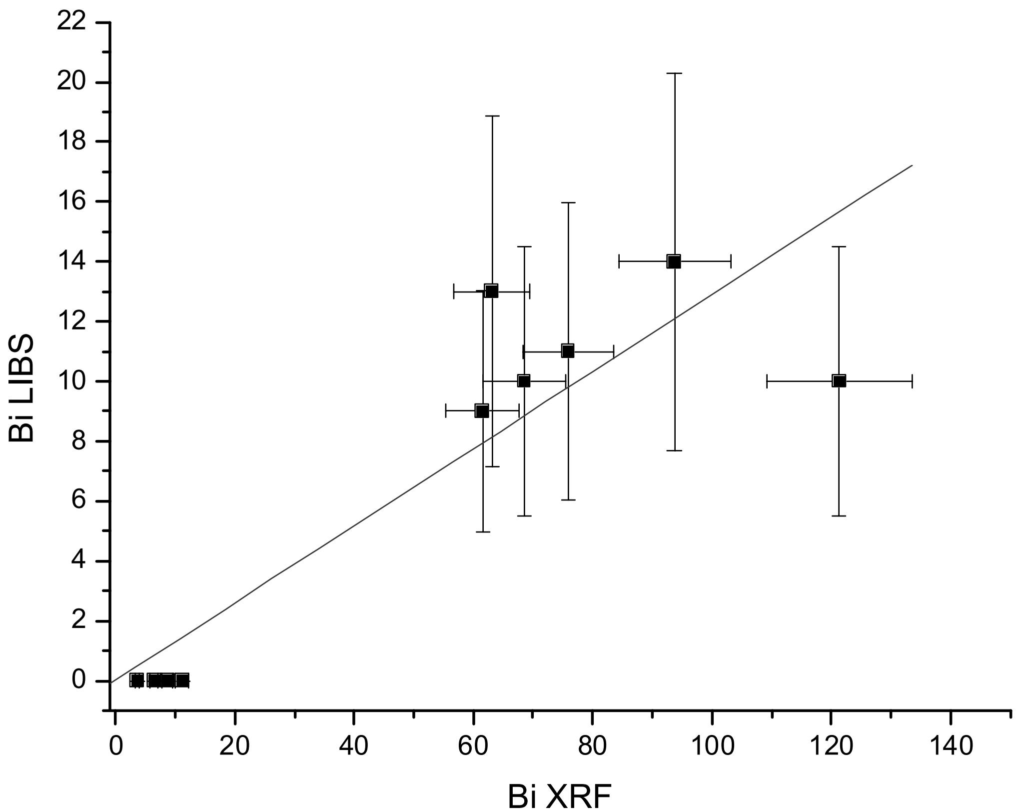


Figure 11a

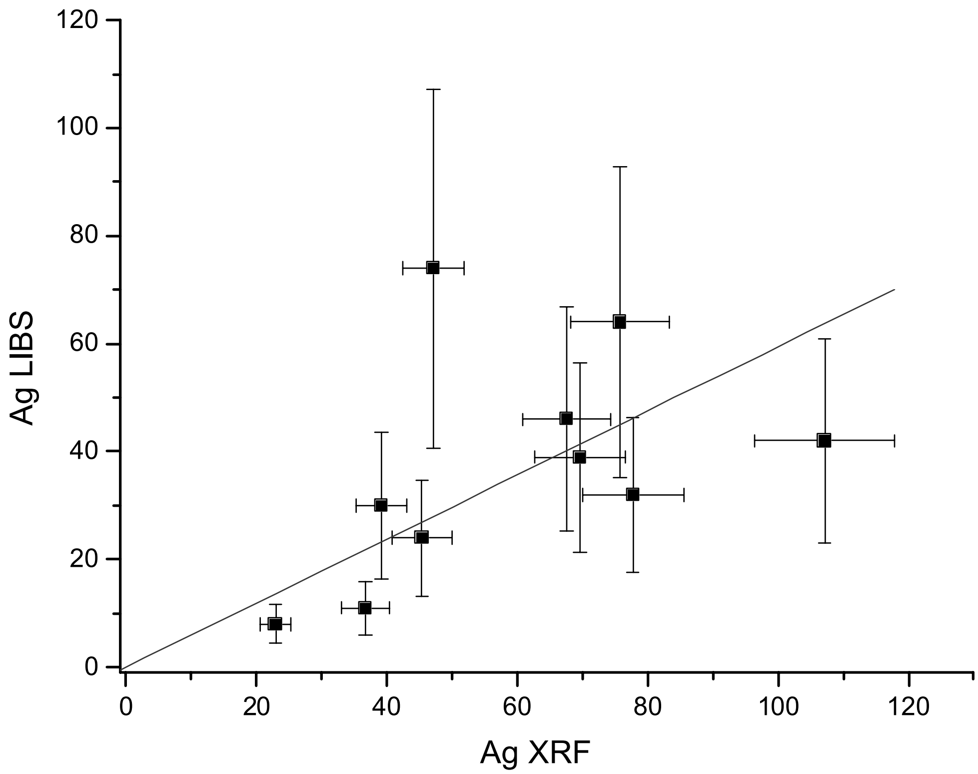
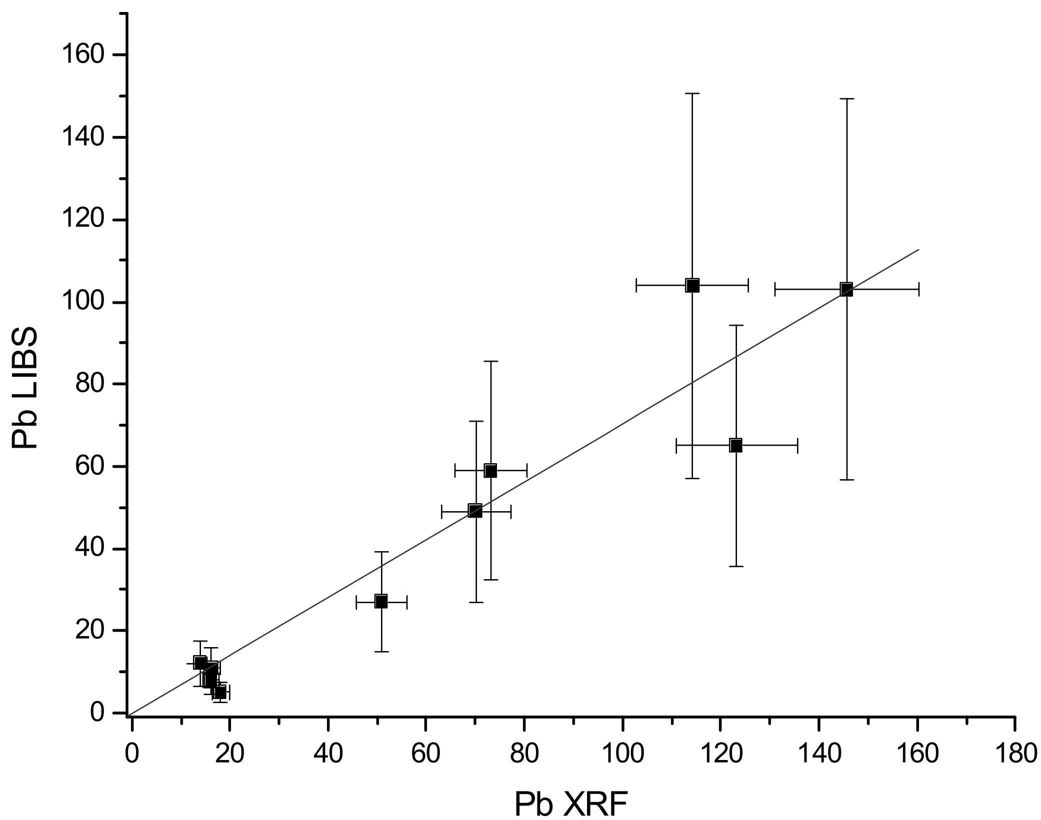


Figure 11b



Pb LIBS
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
160
180
Pb XRF

Figure 11c

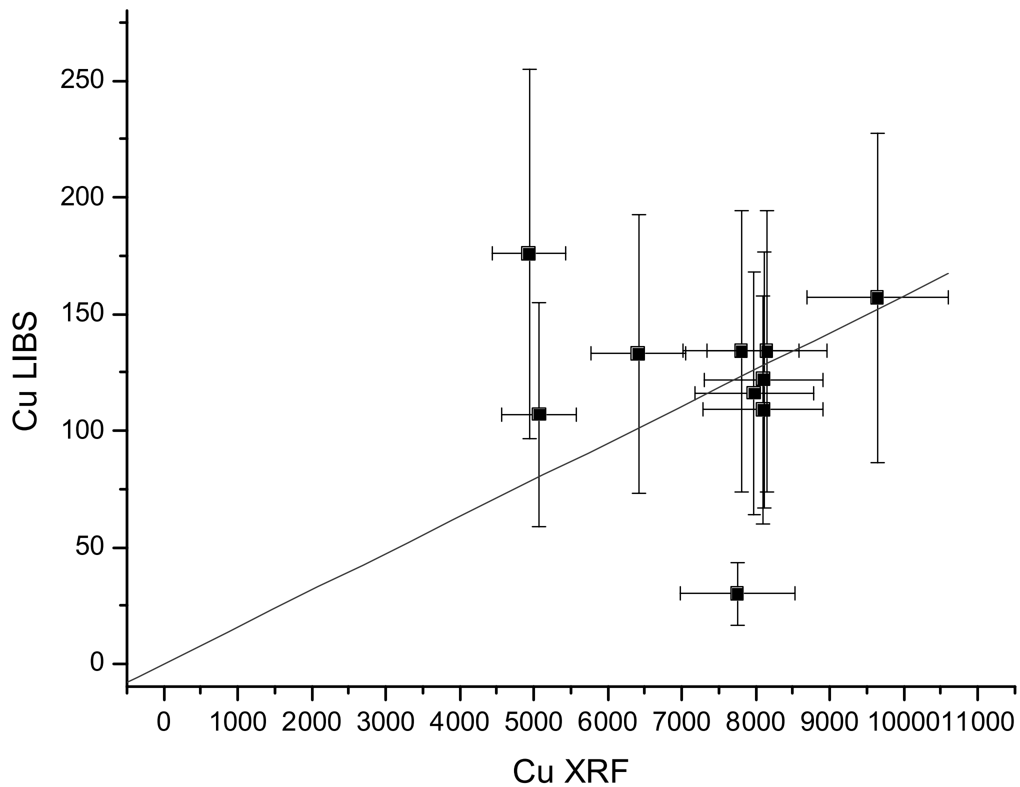

Cu LIBS
0
50
100
150
200
250
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
Cu XRF

Figure 12a

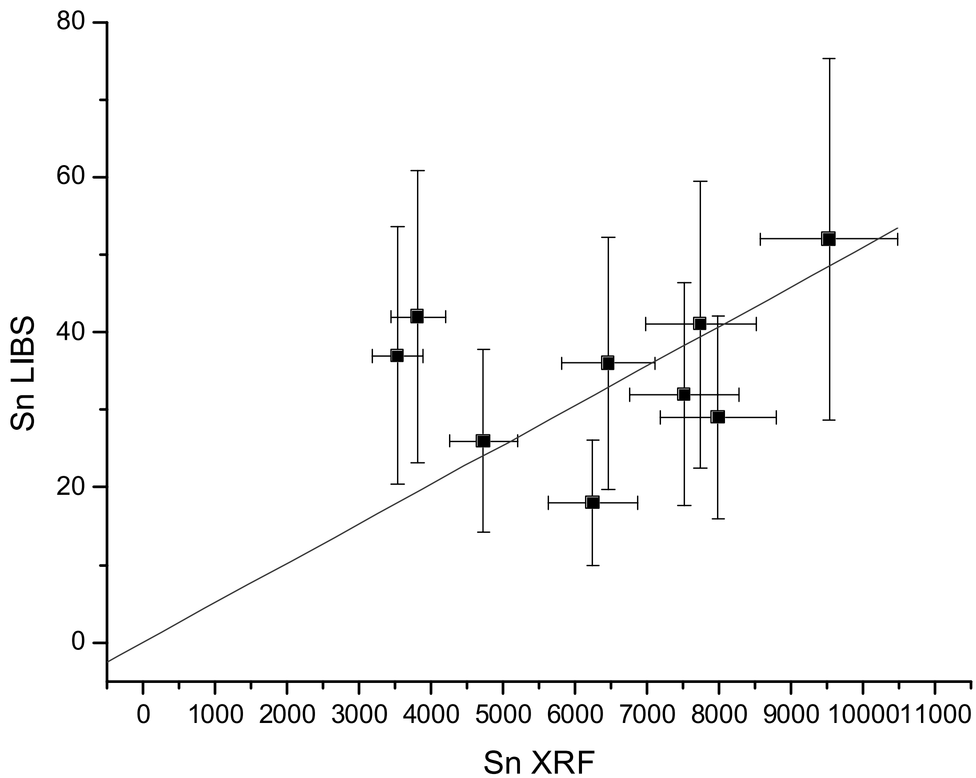

80
60
40
20
0
Sn LIBS
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
11000
Sn XRF

Figure 12b

Table I

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 19149- Vest	17090- Phallus 17092- Left foot