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SCIENCE FOR CULTURAL HERITAGE

Technological Innovation and Case Studies in Marine and Land Archaeology in the Adriatic Region and Inland

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CONTENTS

STUDY BY MOBILE NON DESTRUCTIVE TESTING OF THE BRONZE STATUE OF THE "SATIRO" OF MARSALA

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The bronze statue called the "il Satiro danzante" was found nnderwater in the Sicily channel in the 1997. The restoration at the Istituto Centrale per il Restauro was very long and eareful, assisted by diagnostics procedures in order to help the conservative choice in the consolidation of the artefact and to know the age and provenance of the statue. The results on the alloys composition and structure are reported in this paper.

Introduction

The study by means of destructive and non-destructive methods of investigation of the bronze statue of the "Satiro" had been possible because it was in restoration for a long period of time in the l'Istituto Centrale per il Restauro [1]. A complete diagnostic examination of a work under restoration is a practice becoming common, with some difficulties, in the conservative restoration of very relevant works [2]. The relative high cost of diagnostics limits, instead, the use in all cases, with remarkable risks and limitations overall for the aspects concerning the monitoring and maintenance of restored work.

An extended program of investigations hasn't, in fact, the only finality of conservation, but also of a better knowledge of restored work under the point of views of its material consistency and of a more precise historical identification [2]. In the case of a work, as the Satiro, accidentally recovered in the Sicily channel (outside by an historical context to which refer, then with a provenance and more uncertain historical context) the exams oriented toward the knowledge can have a greater importance then in other cases. This is the reason because in this paper the aspects of knowledge and identification of the work under study will be discussed in more details.

Among the different approaches to the study of ancient metals the use of in situ non invasive techniques is rather recent thank to the growing potentialities

of mobile systems of non destructive testing and to the possibility to perform metallographic exams in situ; this kind of exam allow to study the production technology and to identify the techniques used in the casting a big bronze statue [4]. The non destructive approach has been privileged, but it is not to be neglected to verify always the results with destructive tests, making microsapling in hinder parts of the artifact.
In the case of the Satiro the main open arcaeometric problems are: a) the age of the artefacts, b) its provenance, c) the casting techniques and the used surface treatments.

1. Measuring techniques and experimental apparatus

A short description of experimental methods and apparatus is given in the next paragraphs.

1.1. *In Field EDXRF spectrometer*

The Field Portable Energy Dispersive X-Ray Fluorescence (FP-EDXRF) technique is based on excitation of samples with X-rays and measurements of the energy of the secondary X-rays emitted by the samples themselves. The energy of secondary (also known as characteristic) X-rays depends on the chemical elements present in the sample being examined while the intensity of the energy is proportional to the abundance of the element under scrutiny.
These surveys may be carried out prior or during the restoration work; however, as the methodology is totally non-invasive, it may be applied for purely informative purposes, regardless of intervention. The penetration of X-rays varies from a mere few (as in the case of gold) to several hundred microns (as in the case of light-weight matrix elements, for example those containing relevant amounts of organic compounds).

The EDXRF examination is capable of detecting the composition of a metal alloy, in fact the high atomic numbers and the density of metal alloy facilitate the production of fluorescent X-rays of enough energy to be detected, even using a low intensity sources. The fluorescent lines emitted by all elements compounding the alloy appear within the spectrum, whereas low atomic-number elements are absent or minoritary in the matrix.

A typical EDXRF-system is composed of three parts: a) an X-ray tube; b) an X-ray detector with electronics; c) an acquisition system with a multichannel analyser.

The X-ray tube works at 30 kV and 0,1 mA. It is a light (air cooled) tube (less than 2 Kg of weight).

The detector used a Silicon Drift Detector (SDD) detector having a energy resolution of 139 eV at 6,4 keV. The detector is cooled with a Peltier build in circuit [5].

1.2. *Metallography*

Metallography is the technique of preparing a metal surface for analysis by grinding, polishing, and etching to reveal microstructual constituents. After preparation, the sample can easily be analyzed using optical or electron microscopy. A skilled technician is able to identify alloys and predict material properties, as well as processing conditions and corrosion process due to the exposition to the different environments [6].

Metallographic specimens were "mounted" using a hot compression thermosetting epoxy resin. Mounting a specimen provides a safe and ergonomic way to hold a sample during the grinding and polishing operations.

After mounting, the specimen is wet grounded to reveal the surface of the metal. The specimen is successively grounded with finer and finer grades of silicon carbide paper to remove damage from sectioning and then from each grinding step. After grinding the specimen was polished with a slurry of alumina, silica, or diamond on a napless cloth to produce a scratch-free mirror finish, free from smear, drag, or pull-outs and with minimal deformation remaining from the preparation process.

After polishing, certain microstructural constituents can be seen with the microscope, e.g., inclusions and nitrides. Finally in order to reveal crystal structure (apart the non-cubic ones) were used suitable chemical or electrolytic etchant.

2. Results and discussion

The starting point in the discussion on the obtained results is that, as is very common in the classic roman period, the statue is built soldering together different pieces. A careful examination during the restoration allow us to establish that a) head, b) chest, c) two legs, d) two arms are joint together by welding. The strong corrosion of the surface forbids the non destructive analysis of the alloys directly on the artefact after a scratching of the patina, that is a common practice on ancient bronzes that do not showing yet a thick degree of corrosion, as it is in the case of Satiro. It was chosen then to do few samples, however doing a mapping of the artefact surface with the aim to put in evidence superficial degradation phenomena of the alloy.

2.1. *Alloys composition*

In table I are shown the results obtained on the samples, obviously done on the different pieces compounding the Satiro, in figure 3 are shown the withdrawals points. Taking only into account the results to be refer to the six pieces the first observation is that the alloys shown a similar composition, all featuring a high lead concentration (14-21%) which, as will be confirmed following by the metallography, undergo a globular segregation. The head is constituted by high tin (11%) concentration alloy, in comparison with the other parts (4-6%), probably an intentional choice to obtain a better fluidity of the alloy. After all the hair alloy look similar, characterised only by lower lead concentration probably a liquefaction due to different behaviour during the melting and solidification phases. The first hair sample belongs to a piece melted apart. The lower iron concentration, the only marker allowing us to assess the purity of the row materials used, may suggest a greater care in the material selection, compared to that done for the other parts. The high artistic quality of the head, requiring a grater care, could therefore find verification.

Table I. Results of the EDXRF analysis on withdraw samples of the alloy from the Satiro.

Position of the withdrawals	Cu	Sn	Pb	Fe
head (rear inner folding in the right)	68,5	11,2	20,4	0,5
hair (inner side of the head)	76,6	9,8	13,6	0,4
hair (big piece detached)	73,8	9,3	16,9	0,4
left thigh (near the edge)	73,9	4,4	21,0	0,7
right thigh (external side)	70,4	6,4	21,7	1,4
left arm (inner side)	70,7	12,9	15,4	1,0
left arm (inner side)	72,2	12,7	14,1	1,0
right arm (external side)	69,1	8,7	21,1	1,1
right arm (inner side)	72,7	5,2	20,1	2,1
left leg (external side)	73,3	9,6	16,3	0,7
left arm (on the soldering)	49,5	7,4	42,5	0,6
right arm (on the soldering)	69,1	5,5	24,5	0,9

The sample taken from the welding show an increase of lead concentration, very evident in one of the two samples, pointing out the use of a copper alloy with a higher lead concentration.

The results of the metallographic study of the samples taken by the head (figure 1), the left arm and the left thigh clearly showed a crystalline microstructure constitute by a dendritic array tending to a polygonal shape with the evidence of sliding planes. All the samples show a much corroded surface; this corrosion goes deep into being of an inter-dendritic type. In the case of the head it is in the interval 300-500 micron and for the left arm reach the 800 micron. Lead rounded globes of variable size and inclusions of different kind are always present.

Table II shows the results of the analysis of the alloys obtained on the three metallographic samples; they are quite different from those on the withdraw samples. The superficial treatment of this sample could alter the results, for example for the presence of lead globe. The obtained result confirms however that the alloys of the Satiro have a high lead concentration and a tin one in the normal range for an artistic bronze.

Figure 1. Images of metallographic sample taken from the head, right 100 ×, left 200 ×.

Table II. Results of EDXRF analysis on the three metallographic samples.

Withdrawal position for metallography	Cu	Sn	Pb	Fe
Head (withdrawal from the nape)	80,7	8,2	10,9	0,2
Left arm	70,5	9,4	20,2	0,2
Left leg	71	8,5	20,5	0,2

Figure 2. Left an example of corrosion phenomenon (green patina), left an example of sea origin concretion.

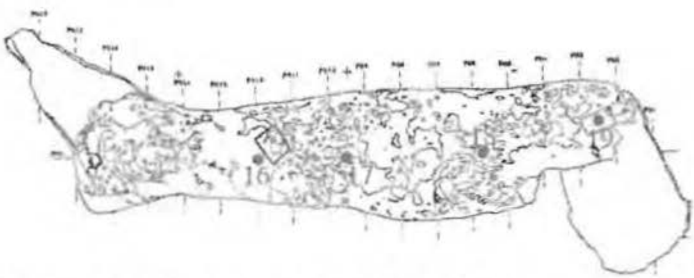

Figure 3. Position of some measuring points on the left leg of the Satiro.

2.2. *Results of the superficial mapping with a EDXRF spectrometer*

With the aim to characterise the different corrosion phenomena on the Satiro surface and, maybe, identify the hexogen material adhering to it, (figure 2), a systematic surface mapping was carried out. The points were chosen using the visible alterations and their colour with the help of the restorers. In the three following figures (figure 3-5) the position of 26 points is shown and in table III there is a short description of their visual aspect.

Figure 4. Position of some measuring point on the chest, head and back of the Satiro

There are several and useful results of the mapping that are not possible to include in this discussion. It was possible to identify particular alteration processes, such as that of point 18 (figure 6) in which the presence of iron and manganese allow to attribute the black colour to a digenesis phenomenon with minerals of the sandy floor.

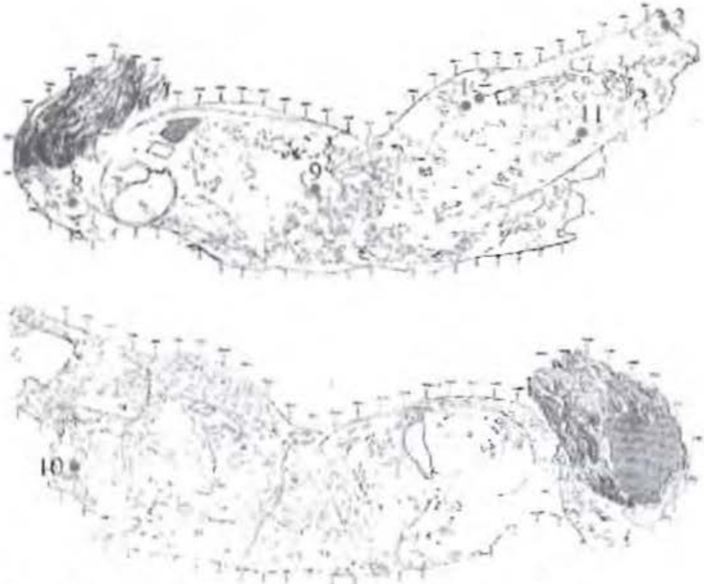

Figure 5. Position of some measuring points on the hip and thigh of the Satiro.

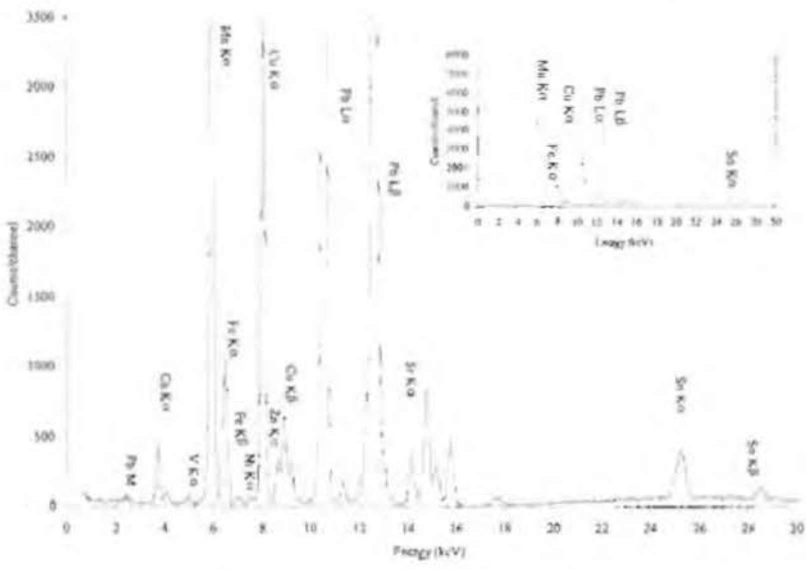

Figure 6. Two spectra of the left leg, point 18 colour dusty dark-black.

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Table III – Description of measuring points in the mapping on the Satiro surface

N°	Visual identification	Short description of obtained results
1	Near-white clear dusty green	Lead remarkable superficial enrichment
2	Green	Lead remarkable superficial enrichment
3	Near-white clear dusty green	Lead and zinc superficial enrichment
5	Nearly unpatinated iron grey	Lead remarkable superficial enrichment
6	Clear dusty green	Lead, iron and tin superficial enrichment
7	Blue-grey	Lead remarkable superficial enrichment
8	Grey-brown (clean spot)	Lead remarkable superficial enrichment, iron and vanadium
9	Clear brown	Iron and vanadium remarkable superficial enrichment
10	Thick emerald green	Lead, superficial enrichment, strontium, calcium, potassium and vanadium
11	Thick average green	Lead, superficial enrichment, iron, manganese and vanadium
12	Dark glossy green	Lead superficial enrichment
13	Blue-grey (below calcareous concretions)	Lead superficial enrichment
14	Olive-green	Lead superficial enrichment, calcium, manganese, iron and vanadium
16	Inner point	Lead, zinc, tin remarkable superficial enrichment
17	Dark-brown	Calcium, iron and strontium
18	Dusty dark-black	Lead remarkable superficial enrichment, calcium, potassium, manganese, iron, zinc and strontium
19	Remedial plug	Calcium, potassium, iron and strontium
20	Basin welding	Lead remarkable superficial enrichment
21	Cleaned area	Lead superficial enrichment, vanadium
22	Black point on the chin	Lead remarkable superficial enrichment, iron enrichment
23	Grey-brown point on the cheek	Lead and iron remarkable superficial enrichment, calcium, vanadium, strontium
24	Basin welding on the neck	Lead and iron remarkable superficial enrichment, zinc
25	Outer spot of the welding	Lead and iron remarkable superficial enrichment, zinc
26	Eye	Calcium, iron, strontium