The restoration of the *Colosso di Barletta*: EDXRF analysis

G. Buccolieri[1], V. Nassisi[1], D. Delle Side[1], E. Giuffreda[1], M. Marabelli[2], A. Buccolieri[3], V.N. Iacobellis[4], F. Paladini[1], F. Vona[5], A. Castellano[1]

[1] *Dipartimento di Matematica e Fisica, Università del Salento, INFN sez. di Lecce, SS. Lecce-Monteroni, 73100, Lecce, Italy; E-mail: giovanni.buccolieri@unisalento.it*
[2] *Istituto Superiore per la Conservazione e il Restauro, via di San Michele n. 23, 00153, Roma, Italy*
[3] *Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, SS. Lecce-Monteroni, 73100, Lecce, Italy*
[4] *Soprintendenza per i Beni Storici, Artistici ed Etnoantropologici della Puglia, via Pier l'Eremita 25, 70122, Bari, Italy*
[5] *Soprintendenza Speciale per il Patrimonio Storico, Artistico ed Etnoantropologico e per il Polo Museale della città di Napoli, via Tito Angelini 22, 80128, Napoli, Italy*

Abstract

The *Colosso di Barletta* is an imposing outdoor bronze statue, dating back the V century, located near the Basilica of "*Santo Sepolcro*" in Barletta (Apulia, Southern Italy). The monument underwent a structural restoration in 1981, during which the Central Institute of Restoration in Rome performed cleaning treatments and consolidation of the patinas.
Currently, the Laboratory of Archaeometry of the University of Salento is carrying on a campaign of non-destructive and *in situ* measurements by using energy dispersion X-ray fluorescence (EDXRF) in order to assess the chemical composition of the alloy and to study its patinas.

Introduction

Bronze is the alloy consisting primarily of copper and tin, which can often contain zinc and lead at different concentrations. It usually presents signs of corrosion, so that its colour normally ranges from light green to dark brown [1]. The most obvious result of this alteration is the appearance of a greenish thin layer called *patina* [2-3].
The aesthetic appearance and the integrity of an outdoor bronze monument can be altered by various environmental factors, natural and anthropogenic, such as changes of temperature, humidity variation, presence of contaminants and their concentration, marine aerosol (which contains mainly chlorine and sulphates) and bird droppings.
The evaluation and control of the durability of bronze monuments exposed outdoors in urban environments are technically complex topics and they are of fundamental interest for both corrosion scientists and conservators. In particular, in urban or industrial atmosphere, the main pollutants, once dissolved in the moisture film deposited on the metal, induce a very high acidity level.
The most frequently identified compounds in bronze corrosion are copper chlorides and cuprite (Cu_2O, copper(I) oxide), but most important are the four copper trihydroxychlorides, $Cu_2(OH)_3Cl$, (atacamite, paratacamite, botallackite and

clinoatacamite), which may occur as original corrosion compounds or as transformation products [4].

The *Colosso di Barletta* is an imposing outdoor bronze statue, 5.11 m high, dating back to the V century and placed near the Basilica of "*Santo Sepolcro*" in Barletta (Apulia, Southern Italy). This monument of Byzantine manufacture depicts a man of the apparent age of forty years, most likely Emperor Teodosio II, and it was probably built in 439 by Valentiniano III in Ravenna.

A legend tells it was thrown from a Venetian ship coming back from Byzantium after the sack of 1204, but the only certainty is that in 1309 the Dominican monks of Manfredonia obtained from Carlo II d'Angiò the permission to remove and merge the limbs of the statue, located at that time at the customs of Barletta, to forge the bells for their church.

The monument underwent a structural restoration in 1981, during which the Central Institute of Restoration in Rome performed cleaning treatments and consolidation of the patinas.

Moreover, during the same treatment, the *Colosso di Barletta* was fixed to a steel structure located within the statue.

The Laboratory of Archaeometry of the University of Salento is carrying on a campaign of non-destructive and *in situ* measurements by using energy dispersion X-ray fluorescence (EDXRF), in order to assess the chemical composition of the alloy and to study its patinas.

This investigation is particularly suitable because it allows to identify the chemical composition of the patinas, to perform a large number of acquisitions in a short time by realizing the mapping of the manufact and then restorers will intervene with awareness of the situation.

The attention has been focused both on the elements constituting the alloy (Cu, Sn, Pb, Fe, Zn and Mn) and on those that characterize the different patinas (S and Cl).

The experimental results obtained have allowed us to discriminate the various patinas, to classify them and to assume the genesis of some of them.

Materials and methods

The EDXRF portable apparatus is an instrument constituted by an X-ray tube constructed by MOXTEK (a beryllium window with thickness of 0.25 mm and diameter of 2 mm, an anode voltage of 4–40 kV, a current of 0–100 µA, an anode of palladium and cooled air), a detector Si(PIN) provided by AMPTEK model XR–100CR (with an energy resolution of 180 eV for photon at 5.9 keV, a window of beryllium of 25 µm, Peltier cooled) and a pocket multi-channel analyser constructed by AMPTEK model MCA8000, interfaced with a portable computer.

The investigations were performed on the following elements: S, Cl, Ca, Sn, Mn, Fe, Cu, Zn and Pb.

For each measuring point, two EDXRF spectra were acquired, both with acquisition time of 30 seconds and with a tube voltage of 6 kV (at 40 µA) or of 20 kV (at 3 µA). These values were sufficient to excite by Bremsstrahlung radiation the line S-K_α, Cl-K_α, Ca-K_α, Sn-L_α, Mn-K_α, Fe-K_α, Cu-K_α, Zn-K_α and Pb-L_α.

Calibration standards were prepared mixing copper sulfide (CuS), copper(I) chloride (CuCl), manganese oxide (MnO_2), iron, zinc, minium or lead tetroxide (Pb_3O_4), tin dioxide (SnO_2), copper(I) oxide (Cu_2O) and copper(II) carbonate basic ($CuCO_3 \cdot Cu(OH)_2$) in different weight percentages, in order to reproduce the chemical composition of bronze patina.

All chemical compounds were purchased from Sigma-Aldrich with analytical grade.

Chemicals compounds have been weighed by an analytical balance, subsequently mixed and homogenized in an agate mortar for ten minutes and finally compressed at 200 bar for ten minutes. The homogeneity of elements in the standard meets the requirements for the EDXRF quantitative analysis [5]. Moreover, the analyzed samples are supposed to infinite thickness and therefore the quantitative results are

expressed in terms of weight percentage (% wt).
The Microcal Origin Professional software has been used to elaborate the experimental data and to obtain the chemical compositions of the alloy and patinas.

Results

Figure 1 shows the measuring points, while table 1 and table 2 respectively show the descriptions of the analyzed regions and the concentration (% wt) of the elements investigated.
The concentrations of S, Mn and Zn were not reported since they were always below the limit of detection, respectively equal to 2 % wt, 1 % wt and 1 % wt.

Discussion

Table 2 shows that the bronze is rich of lead with concentration of nearly 50 % wt. In particular, in areas 3, 4, 5, 6, 7 and 13 (face and hand), the concentrations of lead are between 11.4 % wt and 225 % wt, while in regions 8, 10, 11, 14, 15, 16 and 17 (part of the bust and the skirt) lead concentrations are higher (36.5 – 50.8 %).
Then, the face, on the contrary of the bust, having a lower average concentration of lead, is richer in copper. This result indicates that the statue was made of different alloys of bronze: a richer in copper, used for the face and hands, and a richer in lead used for the bust.
The crown (regions 1 and 2) was forged with an alloy intermediate to the previous ones further containing tin: in particular in region 1, characterized by a reddish color, the concentration of tin is close to 20 % wt. It is very likely that the author aimed to get different color effects using different alloys.
Iron is absent in the alloy, and its presence in regions 9 and 17 is probably due to the casting of iron oxides from the nails of the support: before the current location, the different parts of the statue were held together by iron nails.
Chlorine, probably deposited as marine aerosol, is present in different regions of the bronze and in particular in those seldom exposed to rain (area 13). On the bronze is also present calcium, probably due to the deposition of powders of calcium carbonate ($CaCO_3$). This element was analyzed only qualitatively and its relative abundance is indicated with an asterisk (lower concentration) or more asterisks (higher concentration).

Conclusions

Non-destructive EDXRF analysis showed that the statue was made with different bronze alloys: an alloy richer in copper for the face and hands, a second alloy with high value of tin for the crown, and a third alloy with high value of lead for the bust.
Relatively to lower limbs, historians confirm that they are not coeval with the rest of the work.
The results on the chlorine concentration are also interesting: in fact, the presence of chlorine, probably due to the deposition of marine aerosol, should be certainly monitored. Chlorine is responsible of corrosion processes on bronze known as "*cancer of the bronze*". The mapping performed by EDXRF indicates regions where chlorine is most present and thus the EDXRF technique has revealed the regions where to perform future cleaning treatment.

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Figure 1: Measuring points

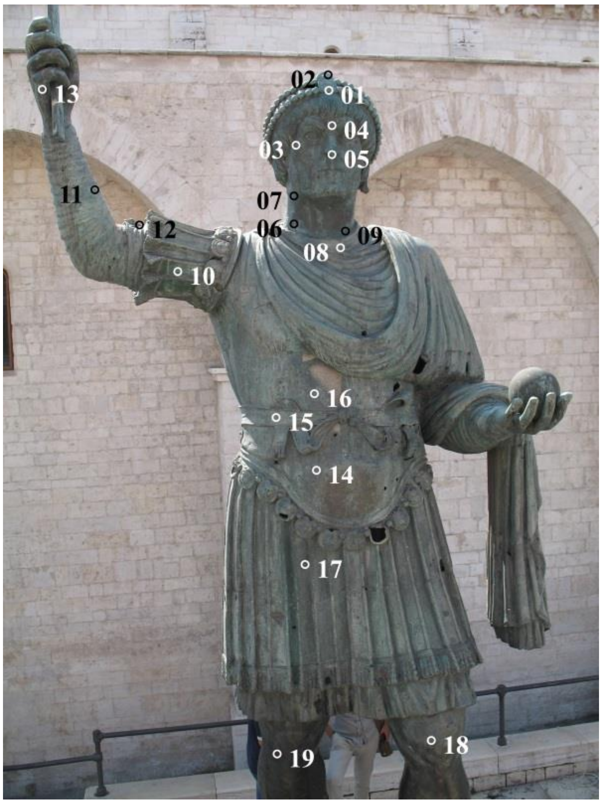

Table 1: Description of analyzed regions

Region	Description
01	Diadem, red area
02	Diadem, green area
03	Right cheekbone, smooth side
04	Nose, green area
05	Nose, black area
06	Neck, smooth
07	Neck, rough
08	Tunic
09	Junction neck-tunic
10	Sleeve right arm
11	Right forearm
12	Putty filler
13	Right hand, black area not exposed to runoff
14	Abdomen
15	Belt
16	Belt, top
17	kilt
18	Left knee
19	Right Knee

Table 2: Concentration (% wt) for each analyzed region

Region	Cu	Pb	Sn	Cl	Fe	Ca
01	39.2	17.7	19.7			
02	49.0	29.6	5.7			
03	59.2	17.1		0.3		
04	63.8	20.6	2.1			
05	59.5	11.4	5.0	0.5		
06	57.7	22.5		3.6		
07	58.8	18.1		3.8		
08	46.3	45.5		4.4		*
09	44.8	36.3		1.2	4.1	**
10	46.2	36.5	1.3			
11	43.3	37.7	3.4			
12	15.0	10.0				*
13	63.4	15.9		6.7		
14	47.0	36.7		1.6		**
15	30.6	50.8		0.6		*
16	47.6	42.1		1.0		*
17	50.5	40.0		1.6	1.0	*
18	57.8	24.3	1.7	5.1		*
19	53.5	31.4	4.2	0.9		***