

X-RAY FLUORESCENCE FOR THE STUDY OF THE PATINAS ON AN OUTDOOR BRONZE MONUMENT

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Abstract

The aim of this paper is the analysis of main elements of the patinas on an outdoor bronze monument, through the use of a portable Energy Dispersive X-Ray Fluorescence (EDXRF) equipment. In particular we investigated the concentration of copper, tin, lead, calcium, iron, sulphur and chlorine on the patinas of a bronze statue dedicated to Sigismondo Castromediano, which was created in 1905 and later placed in Lecce (Apulia, Southern Italy). Thanks to the versatility of the EDXRF portable apparatus we carried out a complete scan of the monument in a relatively short time. This has enabled us to obtain useful information on the patinas in a completely non-invasive way. EDXRF experimental data demonstrated that the two analysed parts of the monument are constituted by different bronzes, whereas the elements that characterize the depositions are equivalent in the two monitored parts. Moreover, multivariate statistical analysis was carried out in order to identify possible correlations and/or differences of elemental composition among the patinas of these two statues. Finally, a X-Ray Diffraction (XRD) analysis was carried out on a sample of deposit collected from an area of the statue not exposed to the washing away, in order to identify the phases of the deposit and to evaluate possible corrosion products. The main results of XRD analysis show that there are not corrosion products and the deposit is due to suspended particulate. The information obtained can be helpful for both archaeological and conservation studies for possible future monitoring and/or restoration work of the statue in object.

Keywords: Bronze patina; Non-destructive techniques; EDXRF portable; Statistical analysis; XRD

Introduction

Bronze is an alloy based on 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 integrity and the aesthetic appearance of an outdoor bronze monument can be altered by various environmental factors, natural and anthropogenic, such as changes of temperature and/or humidity, type and concentration of pollutants (acid rain, atmospheric particulate matter, sulphur oxides, nitrogen oxides), marine aerosol (which contains mainly chlorine and sulphates) and bird droppings. Moreover, it is well known that the presence of sulphur oxides can cause the deterioration of bronze [2, 3].

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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 [4-6]. 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 obvious result of this alteration is the appearance of a greenish thin layer of corrosion called *patina* [7-12]. The compounds frequently identified in the bronze corrosion are copper chlorides and cuprite, a copper(I) oxide, but of great significance are the four copper trihydroxychlorides, $\text{Cu}_2(\text{OH})_3\text{Cl}$, (atacamite, paratacamite, botallackite and clinoatacamite), which may occur as original corrosion products or as transformation products [13-21]. Moreover, the bronze *patina* achieves with time a steady state equilibrium producing on the surface of metallic monuments a protective effect against corrosion on the underlying metal. Protective characteristics of the different *patinas* depend on the quality of environment and environmental conditions [22-24]. Furthermore, since air pollutant concentrations and chemistry of rain-falls have markedly changed during the last decades, as a result of anthropogenic activity, one of the consequences of the high concentration of air pollution effects is the development of *patinas* and their stability.

In the field of cultural heritage, the Energy Dispersive X-Ray Fluorescence (EDXRF) is extensively used because of its several advantages [25-40]: it allows non-destructive, quick and *in situ* quantitative elemental analysis of solid, powder and liquid samples. Moreover, we underline the friendly user and good capability of the EDXRF procedure to perform a large number of measurements in a short time, in order to easily map the entire surface of statues. It has been shown on bronzes that, for corrosion layers of up to approximately $25\mu\text{m}$, a portable EDXRF can provide very accurate quantification results for major elements [41]. On the other hand, unfortunately, it does not enable the determination of light elements such as carbon and oxygen which are significant for the characterization of corrosive products. Thereby, EDXRF is a valid alternative to destructive analytical instruments performed in laboratory such as the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), the Graphite Furnace Atomic Absorption Spectroscopy (GF-AAS) and the Inductively Coupled Plasma Mass Spectrometry (ICP-MS). These techniques require micro sampling and long treatments resulting longer analysis time, higher costs and possible interference problems [42].

The object of this study is the bronze monument created in 1905 by Italian sculptor Antonio Bortone (1844-1938) and later located in Lecce, Southern Italy, in Sigismondo Castromediano square. The monument consists of three bronze statues: one representing Sigismondo Castromediano and other two located on the bottom of the latter, which are named “*Libertà*” and “*Aquila*”. The aim of this research is the EDXRF quantitative analysis of the main elements (such as copper, tin, lead, calcium, iron, sulphur and chlorine) of the *patina* on an outdoor bronze statue, since the chemical characterization of the superficial layer of a monument is an essential preliminary phase for every subsequent restoration treatments, cleaning methods and preservation works.

The experimental results obtained by EDXRF analysis were processed successively with multivariate statistical techniques, such as the Principal Component Analysis (PCA) and the Hierarchical Cluster Analysis (HCA), in order to better highlight the differences and/or possible correlations among the *patinas* object of study.

Moreover, X-Ray Diffraction analysis was carried out for a sample of deposit collected from an area of the statue not exposed to the washing away, in order to determine its chemical composition.

Materials and Methods

EDXRF

The EDXRF portable apparatus employed in this work is an instrument constituted by an X-ray tube constructed by MOXTEK (a beryllium window with thickness of 0.25mm and diameter of 2mm, an anode voltage of 4–40 kV, a current of 0–100 μ A, an anode of palladium and cooled air), a Si–Li detector provided by AMPTEK, model XR–100CR (with an energy resolution of 180eV for photon at 5.9keV, a window of beryllium of 25 μ m, Peltier cooled) and a pocket multi-channel analyser produced by AMPTEK, model MCA8000, interfaced with a portable computer [43-45].

Experimental conditions were: current of 5 μ A, acquisition real time of 200s and voltage of the anode of palladium of 17kV. These values were sufficient to excite by Bremsstrahlung radiation the line Cu-K $_{\alpha}$ (8.04 keV), Sn-L $_{\alpha}$ (3.44 keV), Pb-L $_{\alpha}$ (10.55 keV), Ca-K $_{\alpha}$ (3.69 keV), Fe-K $_{\alpha}$ (6.44 keV), S-K $_{\alpha}$ (2.31 keV) and Cl-K $_{\alpha}$ (2.62 keV).

The evaluation of the spectral interference between sulphur (K-line) and lead (M-line) is fundamental in their quantitative EDXRF analysis. The separation between K-line of sulphur and M-line of lead is equal to about 40eV, a value which is lower than the resolution of the detector (equal to about 180eV). To solve this problem, the separation of the two signals was obtained through the deconvolution of the peaks. This deconvolution is possible considering both the different concentration and the different fluorescent yields between the two elements [46]: K-line of sulphur (0.061) and M-line of lead (0.032). The EDXRF technique has been carried out on a thin superficial layer equal to or less than 10 μ m and the spot produced by the X-ray tube is an elliptical area with axes equal to 2.0mm and 1.5mm.

Four calibration standards were prepared for EDXRF analysis by mixing CuCl $_2$ ·2H $_2$ O, SnO $_2$, PbSO $_4$, CaSO $_4$ ·2H $_2$ O, FeCl $_3$ ·6H $_2$ O and CuSO $_4$ ·5H $_2$ O in different weight percentages, in order to reproduce chemical composition of bronze *patina*.

All chemical compounds were purchased from SIGMA-ALDRICH with analytical grade. Ultra-pure water, with resistivity equal to 18.2M \cdot cm, was obtained from a water deionized MILLIPORE model MILLI-Q. Chemicals compounds have been first weighed with an analytical balance KERN, model ABT 100-5M, subsequently mixed and homogenised in an agate mortar for ten minutes and finally compressed for ten minutes at 200 bar. The homogeneity of elements in the standard meets the requirements for the EDXRF quantitative analysis [47].

Moreover, the analysed samples are supposed to infinite thickness and therefore the quantitative results are expressed in terms of weight percentage (%wt). The experimental data were elaborate by the Microcal Origin Professional software.

Statistical analysis

Experimental results obtained by EDXRF analysis were elaborated with multivariate statistical analysis [48-51] in order to identify possible correlations and/or differences existing among the elemental composition of the two statue. The computer software package STATISTICA 10 (StatSoft Inc., Tulsa, OK, USA) was used for statistical analysis. In particular, the Principal Component Analysis (PCA) and the Hierarchical Cluster Analysis (HCA) were used as statistical techniques on a data set of twenty-one cases (ten samples from “*Aquila*” and eleven samples from “*Libertà*”) and seven variables (the values of concentration of copper, tin, lead, calcium, iron, sulphur and chlorine).

The PCA method calculates the orthogonal linear combinations of the autoscaled variables by using a correlation matrix based on the maximum variance criterion. Such linear combinations are called principal component scores and the coefficients of the linear combinations are called loadings. The numerical loading value, for each variable of a given principal component, shows how much the variable has in common with that component. PCA can give information about the similarities and groupings of the samples considered and if a trend exists, it enables us to evaluate the possibility of classifying the samples.

The HCA method is a statistical treatment designed to reveal groupings (or clusters) within a data set that could be not evident by the reading of data table. The purpose of this analysis is to join together objects into successively larger clusters, by using some measure of similarity or dissimilarities. Distance is the basic criterion for any clustering and probably the most straightforward way of computing the distances among objects in a multidimensional space is to compute Euclidean distances. Objects that are near each other should belong to the same cluster and objects that are far from each other should belong to different clusters.

The dendrogram is the graphical summary of the cluster analysis. The cases (or the variables) are listed along the horizontal axis, while the distance among the clusters is showed along the vertical axis.

XRD

A PHILIPS automatic diffractometer, model PW3020 X'Pert, has been used for X-Ray Diffraction (XRD) analysis of a sample of deposit collected from a part of the statue not exposed to the washing away. Experimental conditions were: Cu-K α radiation at 40kV and 45mA. The instrument was in a Bragg-Brentano configuration θ -2 θ with scan step of 0.02°, at 0.2mm receiving slit, 0.04 rad Soller slit, 1/2° divergence slit and 15mm beam mask.

Results and Discussions

First of all, a visual examination of the colour of the *patinas* was carried out on the two statues and it can be said that they have no substantial differences. The *patinas* are mainly green, blue and black, in addition to white deposits present on the surface.

Table 1 shows the chemical composition of four standards used in the EDXRF quantitative analysis. Table 2 summarizes the label, the description of each measuring point for two areas of the bronze statues indicated as “*Aquila*” (Aq) and “*Libertà*” (Lib) and the experimental results of EDXRF analysis. On an area Lib1 some cleaning tests were performed with water and paintbrush in order to evaluate the possible variations of elements concentration.

Table 1. Chemical composition (wt%) of the standards used in EDXRF calibration

Standard	Concentration (wt%)						
	Cu	Sn	Pb	Ca	Fe	S	Cl
1	22.1 ± 1.4	3.2 ± 0.9	2.6 ± 0.4	0.9 ± 0.2	1.4 ± 0.2	12.0 ± 1.4	1.4 ± 0.3
2	14.7 ± 0.9	22.8 ± 1.2	4.4 ± 0.9	1.3 ± 0.2	1.2 ± 0.2	8.9 ± 1.2	7.5 ± 0.9
3	7.4 ± 0.6	42.6 ± 2.2	5.3 ± 0.6	1.7 ± 0.3	0.9 ± 0.2	5.7 ± 0.9	13.1 ± 1.9
4	0.5 ± 0.2	62.2 ± 3.2	7.3 ± 0.9	2.3 ± 0.2	0.5 ± 0.2	2.7 ± 0.3	20.0 ± 1.3

Fig. 1 and Fig. 2 show the measurement points respectively for the statue called “*Aquila*” and the one called “*Libertà*”. In particular, ten points were chosen for “*Aquila*” (marked with Aq and progressive numbers) and eight points for “*Libertà*” (marked with Lib and progressive numbers).

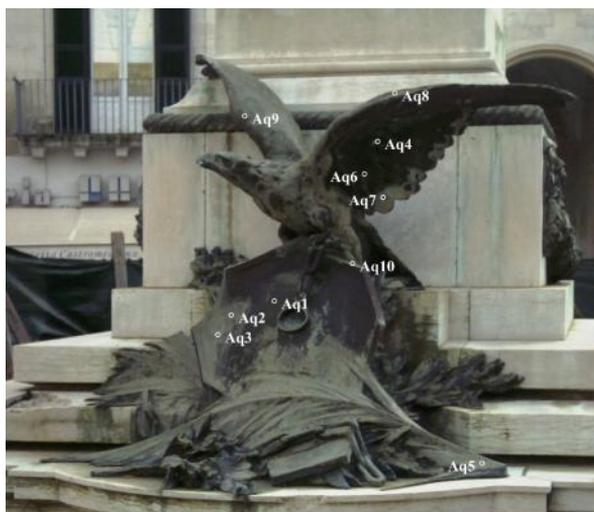


Fig. 1. Measurement points of the bronze statue called “*Aquila*”.



Fig. 2. Measurement points of the bronze statue called “*Libertà*”

Fig. 3 shows the comparison between the EDXRF spectrum of a monument area and of a calibration standard. The values of detection limit, all reported in wt%, for copper, tin, lead, calcium, iron, sulphur and chlorine are equal respectively to 0.3, 0.5, 1.4, 0.4, 0.3, 0.4 and 0.4.

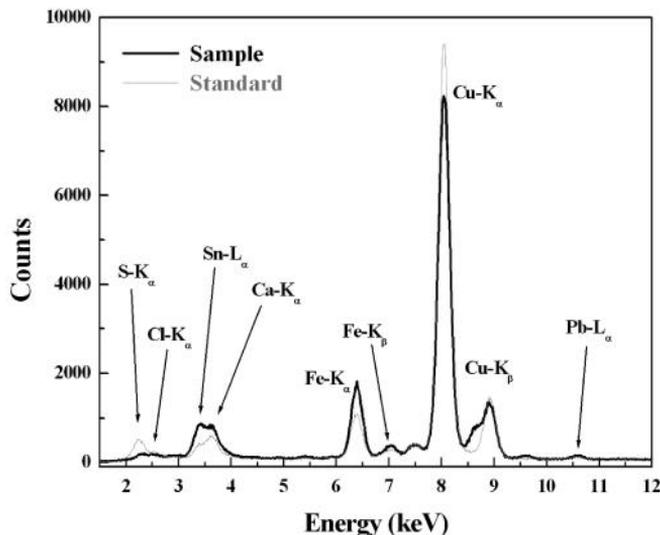


Fig. 3. Comparison between EDXRF spectra of the sample and the standard

Experimental data demonstrated that the two analysed parts of the monument are constituted by different bronzes and, in particular, “Aquila” shows lower concentration of copper and lead compared to “Libertà”. Also “Aquila” shows smaller iron concentration than the detection limit (0.3 wt%), while “Libertà” shows iron concentration between 0.8 wt% and 1.4 wt%. Tin concentration is comparable in both parts, in fact, the bronze called “Aquila” has values between the detection limit (0.5 wt%) and 7.6 wt% and the bronze called “Libertà” has values between the detection limit (0.5 wt%) and 8.7 wt%.

Moreover, the elements that characterize the depositions, such as calcium and sulphur are equivalent in the two monitored parts, demonstrating that they were exposed to similar microclimatic and environmental conditions for the same period of time. In particular, we specify that in Lecce air pollution is mainly due to vehicular traffic and that the natural component of the atmospheric particulate matter is mostly imputable to marine aerosol and to Saharan dust phenomena [52, 53].

The samples Aq1 and Aq2 are areas of the coat of arms upon which the statue “Aquila”. Aq1 is a black area, while Aq2 is blue-green. Copper concentration in the black *patina* is higher than in blue-green *patina*. Aq3 is a *patina* close to Aq2 and it has the same colour and a similar composition of the latter.

The sample Aq5 is related to a blue *patina* on the base of the statue, and it shows a high concentration of sulphur (1.4 wt%), probably due to sulphates. Aq6 is a black *patina* with higher concentration of both copper and chlorine. Aq7 and Aq8 have the same colour of Aq2 and Aq3, but they show higher concentration of copper and chlorine and lower concentration of tin.

The samples Aq4 and Aq9 are very distant from each other, but both have white colour. They show the absence of tin, lead and sulphur and low concentrations of copper. The experimental data obtained show that the only substantial difference between Aq4 and Aq9 is that Aq4 has a copper concentration greater than Aq9. The sample Aq10 is white too, but it is a deposit. This is confirmed by the lowest concentration of copper (one sample with 3.0 wt%), by high concentration of sulphur and calcium and by the absence of tin and lead. Moreover, this white deposit has iron content lower than the detection limit (0.3 wt%).

Besides, there is an interesting comparison between the areas Lib4 and Lib5 (Fig. 4), which are next to each other (about 0.5cm), but appear to be different: Lib4 is a blue-green

dripping over a darker area (Lib5). Probably, during rain washing processes some soluble salts slid along the bronze statue in different areas, giving rise to dripping depending on different exposures. The area Lib4, relative to a dripping, shows remarkable content of sulphur (2.9 wt%), most likely due to soluble (chalcantite) and insoluble (brochantite and antlerite) copper sulphates, content of copper (21.4 wt%) smaller than Lib5 (24.5 wt%) and content of tin (5.8 wt%) higher than Lib5 (lower than detection limit).

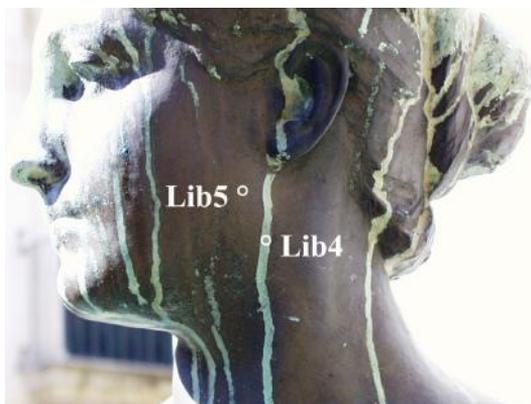


Fig. 4. Dripping processes on the bronze called “Libertà”.

Similarly interesting is the comparison between two other nearby areas, Lib7 and Lib8, different both in colour and in composition: Lib7, a black *patina*, shows tin and sulphur lower than the detection limit and chlorine equal to 2.3 wt%; Lib8, a blue-green *patina*, shows higher concentration of tin (8.2 wt%) and of sulphur (1.4 wt%) and lower concentration of chlorine (1.2 wt%).

Particular attention was devoted to the Lib1 area, which is characterized by a light green colour. On this area some cleaning tests were carried out by using a paintbrush and ultra-pure water: first strong brushing (Lib1*b*) and after by washing the area with ultra-pure water (Lib1*c*). Lib1*d* is an area, close to Lib1, that has been treated only with ultra-pure water. Experimental results show that a mechanical treatment which includes brushing plus ultra-pure water washing, substantially reduces the content of sulphur (from 2.2 wt% of Lib1 to 1.4 wt% of Lib1*b* till to values under the detection limit Lib1*c*, respectively after cleaning and washing), while a single treatment with ultra-pure water (Lib1*d*) does not modify, within the experimental uncertainties, the concentration of sulphur.

Moreover, after several treatments it is possible to show an increase of concentration of tin (from 5.1 wt% of Lib1 to 7.4 wt% of Lib1*c*) and copper (from 22.0 wt% of Lib1 to 23.2 wt% of Lib1*c*) as the outer layers are removed mechanically and by washing with ultra-pure water, while it is not possible to show significant variation of chlorine concentration after cleaning treatment. Then, in the *patina* growing mechanism, chlorine migrates within the same *patina* and forms, with copper, compounds in touch with the metallic alloy. The remaining differences of concentration are comparable within of the experimental error and, therefore, it no systematic evolution can be detected.

Then, it was fundamental the quantitative determination of main elements on outdoor monuments by using *in situ* non-destructive techniques. These analyses may be used in the field of the cultural heritage, for instance, in order to monitor the chemical composition of elements, both the majority and the in trace, during a restoration or cleaning treatments of the monument.

Experimental results obtained by EDXRF analysis were subsequently elaborated with the multivariate statistical treatment by using the method of the Principal Component Analysis (PCA) and the Hierarchical Cluster Analysis (HCA). The statistical analysis was applied on a

data set of twenty-one cases (ten samples from “*Aquila*” and eleven samples from “*Libertà*”) and seven variables (the concentration of copper, tin, lead, calcium, iron, sulphur and chlorine) (Table 2).

Table 2. Description of the measuring points for two areas of bronze statues indicated as “*Aquila*” (Aq) and “*Libertà*” (Lib) and results of EDXRF analysis

Sample	Description	Concentration (wt%)						
		Cu	Sn	Pb	Ca	Fe	S	Cl
Aq1	black <i>patina</i>	19.9 ± 1.6	< 0.5	1.6 ± 0.3	0.7 ± 0.1	< 0.3	< 0.4	1.5 ± 0.3
Aq2	blue-green <i>patina</i>	15.9 ± 1.4	6.1 ± 1.0	2.2 ± 0.4	0.8 ± 0.1	< 0.3	< 0.4	0.7 ± 0.1
Aq3	blue-green <i>patina</i>	17.2 ± 1.5	6.6 ± 1.1	1.6 ± 0.3	0.8 ± 0.1	< 0.3	< 0.4	0.8 ± 0.1
Aq4	white <i>patina</i>	13.8 ± 1.3	< 0.5	< 1.4	0.8 ± 0.1	< 0.3	< 0.4	0.7 ± 0.1
Aq5	blue <i>patina</i>	13.6 ± 1.2	7.6 ± 1.3	4.2 ± 0.6	0.8 ± 0.1	< 0.3	1.4 ± 0.7	0.7 ± 0.1
Aq6	black <i>patina</i>	20.0 ± 1.6	< 0.5	1.9 ± 0.3	0.7 ± 0.1	< 0.3	< 0.4	2.1 ± 0.2
Aq7	blue-green <i>patina</i>	18.5 ± 1.6	< 0.5	2.6 ± 0.4	0.7 ± 0.1	< 0.3	< 0.4	1.3 ± 0.1
Aq8	blue-green <i>patina</i>	18.5 ± 1.6	0.6 ± 0.2	2.2 ± 0.4	0.7 ± 0.1	< 0.3	< 0.4	1.1 ± 0.1
Aq9	white <i>patina</i>	8.6 ± 0.9	< 0.5	< 1.4	0.9 ± 0.1	< 0.3	< 0.4	0.6 ± 0.1
Aq10	white <i>deposit</i>	3.0 ± 0.3	< 0.5	< 1.4	1.9 ± 0.4	< 0.3	7.2 ± 1.3	0.7 ± 0.1
Lib1	green <i>patina</i>	22.0 ± 1.7	5.1 ± 0.9	6.9 ± 0.9	0.8 ± 0.1	1.3 ± 0.2	2.2 ± 0.8	1.1 ± 0.1
Lib1b	Lib1 after strong brushing	22.5 ± 1.8	6.4 ± 1.1	6.6 ± 0.9	0.8 ± 0.1	1.0 ± 0.3	1.4 ± 0.7	1.2 ± 0.1
Lib1c	Lib1b after washing with water	23.2 ± 1.8	7.4 ± 1.3	6.4 ± 0.9	0.8 ± 0.1	0.9 ± 0.3	< 0.4	1.2 ± 0.1
Lib1d	area near treated only with	20.8 ± 1.7	8.7 ± 1.6	7.0 ± 0.9	0.9 ± 0.1	1.4 ± 0.2	2.5 ± 0.8	1.0 ± 0.1
Lib2	black <i>patina</i>	24.2 ± 1.8	< 0.5	6.1 ± 0.8	0.7 ± 0.1	1.3 ± 0.2	< 0.4	2.4 ± 0.2
Lib3	dark green <i>patina</i>	22.7 ± 1.8	1.9 ± 0.4	5.8 ± 0.8	1.1 ± 0.1	1.0 ± 0.3	< 0.4	0.9 ± 0.1
Lib4	blue-green dripping	21.4 ± 1.7	5.8 ± 1.0	6.7 ± 0.9	0.8 ± 0.1	0.9 ± 0.3	2.9 ± 0.9	1.2 ± 0.1
Lib5	blue-green <i>patina</i> darker of	24.5 ± 1.9	< 0.5	6.3 ± 0.8	0.7 ± 0.1	0.8 ± 0.4	< 0.4	2.6 ± 0.3
Lib6	black <i>patina</i>	23.8 ± 1.8	0.5 ± 0.1	6.5 ± 0.9	0.7 ± 0.1	1.2 ± 0.2	< 0.4	1.8 ± 0.2
Lib7	black <i>patina</i>	24.3 ± 1.8	< 0.5	6.2 ± 0.8	0.7 ± 0.1	1.4 ± 0.2	< 0.4	2.3 ± 0.2
Lib8	blue-green <i>patina</i>	22.1 ± 1.7	8.2 ± 1.4	6.6 ± 0.9	0.8 ± 0.1	1.3 ± 0.2	1.4 ± 0.7	1.2 ± 0.1

As far as principal component analysis is concerned, three principal components were extracted covering 92.7% of the cumulative variance. The loading of the variables on the first two principal components (Fig. 5) shows that copper is the dominant variable for the positive values of the first principal component (Factor 1), chlorine is the dominant variable for the positive values of the second principal component (Factor 2) and tin is the dominant variable for the negative values of the second principal component. Moreover iron and lead are correlated and they have positive value for Factor 1 and negative value for Factor 2, whereas calcium and sulphur have simultaneously negative values of both components.

The scatter plot of the scores for the first two principal components PC1 and PC2 (Fig. 6) immediately shows the difference between the deposit (Aq10) and the remaining samples (all *patinas*). Moreover, the statistical treatment highlights that all the *patinas* from “*Libertà*” have a positive score on the PC1 and, on the contrary, all the *patinas* from “*Aquila*” have a negative score for the same component. Thus, it is possible to discriminate the *patinas* of the two bronze statues, whereas it is not possible to distinguish the *patinas* from different parts of the same statue. Also interesting is the difference obtained on component PC2 that allows to discriminate between darker and brighter *patinas*: the darker *patinas* have positive values (higher concentration of chlorine and minor concentration of tin), whereas the brighter ones have a negative value of the same component.

Last significant reflection is on the white *patinas* (Aq4 and Aq 9), which are easily distinguished from the remaining samples and as they are characterized by a lower concentration of copper.

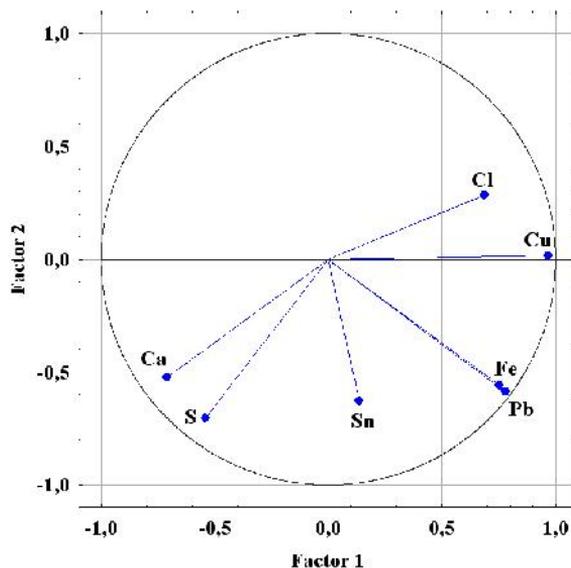


Fig. 5. Loading of the variables on the first two principal components.

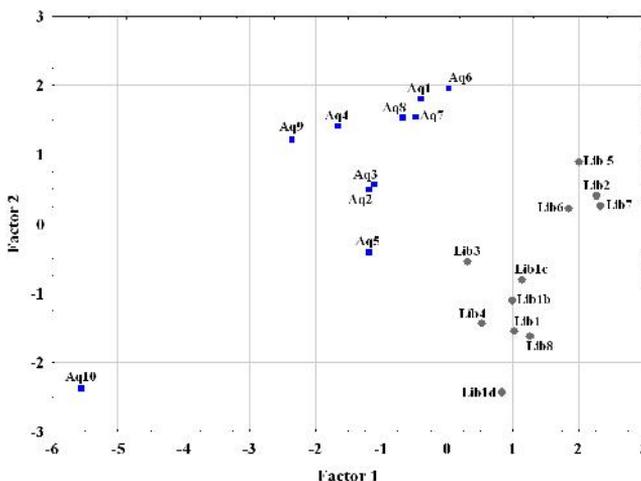


Fig. 6. Scatter plot of the scores for the first two principal components.

Hierarchical clustering analysis was carried out by using Complete Linkage procedure applied on the Euclidean distances and the dendrogram (Fig. 7) confirms the results obtained from the PCA. In fact, Fig. 7 shows the *patinas* divided into two main clusters: the first cluster contains the white deposit (Aq10) and the white *patinas* (Aq4 and Aq9), whereas the second cluster encloses the remaining samples with the same order determined previously by using the PCA. Therefore, the results obtained confirm that the *patinas* of the two statues have different elemental composition.

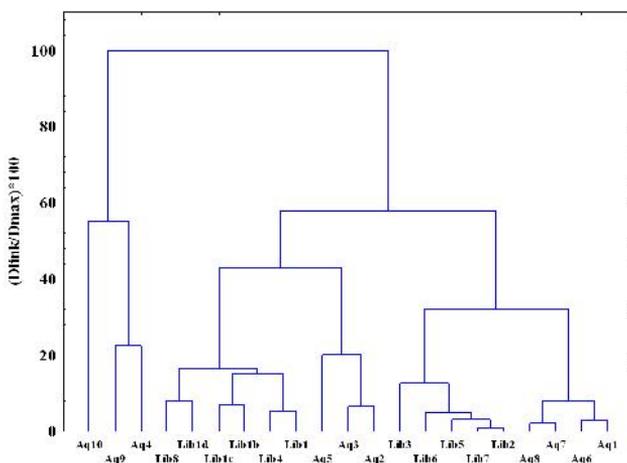


Fig. 7. Dendrogram of the *patinas*.

Finally, with the help of XRD analysis we determined the chemical composition of a sample of deposit collected from an area of the statue not exposed to the washing away. The XRD spectrum (Fig. 8) shows that the deposit sample was principally constituted by $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as well as by CaCO_3 , SiO_2 and $\text{Ca}(\text{Fe},\text{Mg})(\text{CO}_3)_2$. Therefore, the deposit is due to suspended particulate after innumerable cycles of water condensation and evaporation and there are not corrosion products.

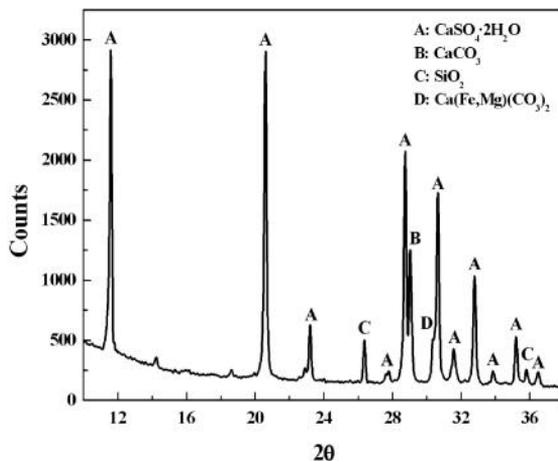


Fig. 8. XRD spectrum of an area not exposed to washing.

Conclusions

Analytical results highlight that the two studied bronze areas of the monument are constituted by different alloys, while the elements that characterize the depositions, such as calcium and sulphur, are comparable in the two areas, demonstrating that these statues were subjected to similar environmental conditions for the same exposure time.

The EDXRF portable instrument used for our research, successfully allowed the chemical characterization of the bronze *patinas* of these outdoor bronze monument, therefore it can be considered a powerful spectroscopic tool, which can be employed during cleaning treatments and/or preservation works of artefacts since it does not require any sample

preparation, it allows fast and non-destructive multielemental measurements *in situ*, it is relatively inexpensive and it provides quantitative mapping information.

Multivariate statistical analysis shows well the different chemical composition of the *patinas* from two bronze statues. This confirms, once again, that the statistic techniques can be combined with the analysis archaeometric in order to obtain more information and/or to show more clearly the experimental results.

In conclusion, the studied monument does not present, at the time, specific corrosion phenomena. In particular, it might be useful to remove particulate sediments and drippings through mechanical cleaning, not necessarily employing corrosion inhibitors such as benzotriazole (BTA).

In any case, it seems appropriate to set up a monitoring program for the surface of the bronze monument, to assess any possible changes of the *patinas* and/or the occurrence of corrosion products, in order to be able to intervene quickly and efficiently. This methodological approach should grant the protection of the bronze statue in object.

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