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XRF investigation of the Monument to the Fallen of the Great War by Francesco Jerace in San Ferdinando (Reggio Calabria, Italy)

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***Abstract* – The Monument to the Fallen of the Great War in San Ferdinando (Reggio Calabria, Italy) consists of a copper-based alloy sculpture, made in the 1920s by Francesco Jerace (1853-1937), dedicated in memory of the sub-lieutenant Vito Nunziante and the fallen soldiers from the Great War. It has an important heritage value for the city of San Ferdinando, of which it is considered an identity symbol, and for Southern Italy as well. Due to its proximity and exposure to the marine environment, the monument is a key – example for the characterization of the composition of the superficial layers of the alloy and the related corrosion products, gathering important in-formation on both the materials and the state of conservation of the sculpture. With this aim in mind, this research highlights the results of a study carried out in situ at elemental scale, by portable X-ray fluorescence (XRF) spectroscopy, on the occasion of the recent restoration of the monument promoted by the municipality of San Ferdinando.**

I. INTRODUCTION

Humans have extracted and processed copper for thousands of years, and its use can date to the Neolithic period [1-2]. Over the following centuries, the alloying of copper to make alloys and the employment of copper compounds have been central in the human use of this metallic material [3-4]. Despite of its use and importance, the copper-based alloy manufacts and sculptures are critically sensitive to the surrounding environment. Their corrosion products, usually found on outdoor copper-based alloys, are generated by the interaction between the alloy and the atmospheric pollutants [5, 6]. In this scenario, outdoor metal sculptures and their conservation have great significance in protecting cultural heritage.

As a matter of fact, properly characterizing the surface constituents of outdoor sculptures helps better understand the degradation processes and plan the correct conservation interventions [5, 7]. In this context, analytical methods aiming at identifying and evaluating corrosion products are fundamental and critical issues among metal conservators.

In particular, X-ray fluorescence (XRF) spectroscopy has extensive use, being a well-established analytical method for non-destructive elemental compositional analyses of materials and objects of interest for cultural heritage, offering practical and economic advantages [8].

This paper highlights the results of a study, conducted in situ by using X-ray fluorescence (XRF) spectroscopy, intended to characterize at elemental level the superficial layers of the alloy and the related corrosion products of the Monument to the Fallen of the Great War in San Ferdinando (Reggio Calabria, Italy), which is an imposing copper-based alloy sculpture, created between 1920 and 1926 by the famous Calabrian sculptor Francesco Jerace (1853-1937).

The research was carried out on the occasion of the recent monument restoration by Emanuele Ioppolo's company Art Novae, under the supervision of the Superintendence of Archaeology, Fine Arts and Landscape of the Reggio Calabria district (SABAP-RC). In particular, during the restoration an entirely dry cleaning of metal surfaces was carried out. The importance of studying the monument is mainly determined by the following factors: (a) the symbolic and heritage relevance of this artwork, and (b) the effects of weather and atmospheric pollution on the monument conservation, thus making urgent to acquire knowledge about the elemental composition of the sculpture and the main corrosion products present on its surface. The obtained data allowed both to select the most appropriate cleaning methods during restoration and to learn about little-known aspects of the execution techniques employed by Francesco Jerace, especially regarding the bronze casting processes.

II. MATERIALS AND METHODS

A. Site description and Materials

The Monument to the Fallen of the Great War in San Ferdinando is characterized by the presence of a copper-based alloy statue, installed in 1926 on a base of Trani stone, next to the matrix church of the Calabrian village [9]. The artwork was made to simultaneously celebrate the memory of the San Ferdinando fallen soldiers of the Great War and that of Second Lieutenant Vito Nunziante, who died in 1916 in the sinking of the Nave Regina Margherita [10]. The restoration brought to light both the signature of the famous sculptor Francesco Jerace (1853-1937) and the date when the bronze was made, 1920, engraved in the bollard that rises at the feet of the Second Lieutenant of the Vessel, depicted as he proudly advances, holding up the flag of the Royal Army with his right hand. In addition to being the identity symbol of San Ferdinando, Jerace's artwork is to be considered among the first monuments to the fallen of the Great War made in southern Italy.

In 1932 the monument was relocated to the center of the square, a few meters away from the original site, but without altering the arrangement devised by the sculptor, with the statue of the soldier facing the coast, in allusion to the death at sea of Second Lieutenant Vito Nunziante. From a conservation point of view, the sculpture has been constantly displayed in an open-air environment, in the center of San Ferdinando, a small coastal town in the Province of Reggio Calabria in the Italian region Calabria. The sculpture is located in proximity to San Ferdinando’s front sea (Figure 1(a)).

It is not known the origin of the raw materials used for the building of the monument, while a visual investigation established the use of two distinct casting techniques. If, in fact, the head of the statue was executed "by casting" in a single lost-wax casting, the rest of the work was obtained by assembling 16 bronze elements, cast in stirrups and welded together, employing in addition several "patches" in order to fill the voids created in the thin layer of the metal alloy.

A total of 15 areas (Figure 1(b-d), ID# = 1,…, 15), representative of different parts of the monument (patinas, structural elements, concretions, etc.) (Table 1) were investigated by a XRF spectrometer.

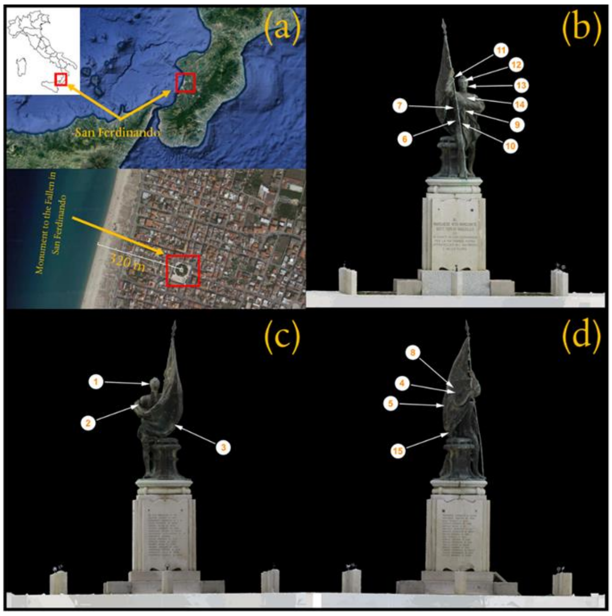

Figure 1. Geolocation map of the city of San Ferdinando, with the location of the Monument to the Fallen of the Great War (a). Frontal (b), back (c), and lateral (d) view of the monument and areas analyzed in situ by portable XRF spectroscopy.

Table 1. A list of the analyzed areas (ID#, # = 1,…,15), together with a structural description.

ID	Description
1	Ear (left side)
2	Flag
3	Structural elements (nails, pins, rivets)
4	Welding/brazing
5	Welding/brazing
6	Welding/brazing
7	Chest (patch)
8	Structural elements (nails, pins, rivets)
9	Structural elements (nails, pins, rivets)
10	Flagpole
11	Flag bow
12	Head
13	Head
14	Chest
15	Concretion

B. Methods

XRF analyses were carried out using a portable XRF Alpha 4000 analyzer (Innov-X systems, Inc., Woburn, MA, USA), which allows the detection of chemical elements with an atomic number (Z) between phosphorus (P) and lead (Pb). It is equipped with a Ta anode X-ray tube as source and a Si PIN diode (active area of 170 mm^2) as detector. For each point, two sequential tests were performed, the first with operating conditions of 40 kV and 7 µA and the second with 15 kV and 5 µA, for a total spectrum collection time of 120 s. The instrument was controlled by a Hewlett-Packard iPAQ Pocket PC (HP, Inc., Palo Alto, CA, USA), which was also used for the data storage. The calibration was performed using a soil light element analysis program (LEAP) II and was verified using alloy certified reference materials produced by Analytical Reference Materials International. When Cu is present, the Lα line of Ta is superimposed to the K_{α} line of Cu. The equipment was placed in direct contact with the sculpture surface, minimizing any atmospheric interference. The XRF analyses were performed without any previous removal of the corrosion layers covering the sculpture.

III. RESULTS AND DISCUSSION

Figure 2 and Table 2 respectively report the obtained X-ray spectra and the achieved elemental compositions for all the investigated areas.

The spectra are grouped according to the following criteria: measurements performed in correspondence of the head part of the monument (areas ID1, ID12 and ID13, Figure 2(a)), of several body parts of the monument (areas ID2, ID7 and ID14, Figure 2(b)), of welded or brazed areas of the monument (areas ID4, ID5 and ID6, Figure 2(c)), of the flagpole (separated and detachable from the monument) and the decorations related to the flagpole (flag bow) (areas ID10 and ID11, Figure 2(d)), of monument's structural elements (nails, pins, rivets) (areas ID3, ID8 and ID9, Figure 2(e)), and of concretion (area ID15, Figure 2(f)).

Figure 2(a) reports the XRF spectra concerning areas ID1, ID12, and ID13. The three spectra, collected in the head part of the monument, are overlapped, thus indicating a similar qualitative elemental composition. The alloy used to produce the monument corresponds to a ternary alloy (Cu+Sn+Zn), in which Cu was alloyed with Sn and Zn. In addition to major elements, Pb and Fe also occur as impurities. Analogously, the spectra reported in Figure 2(b), representing the areas ID2, ID7, and ID14 in the body part of the monument, show a broad similarity with the spectra reported in Figure 2(a). However, it should be noted that small variations in the intensity ratios of the characteristic elemental lines of the elements taken into consideration can be visible in the different areas.

In order to explain potential variations of the ternary composition of the alloy, it is useful to note that the measurements were directly performed on the superficial corrosion layers covering the sculpture. This implies that it is not possible to establish a bulk elemental composition of the alloy. The superficial layers (patinas) of outdoor copper-based alloys can have different chemical compositions depending on several parameters such as alloy composition, environmental conditions (for instance, urban, rural, marine, industrial), location of the monument (in exposed areas or sheltered areas) and exposure time [11].

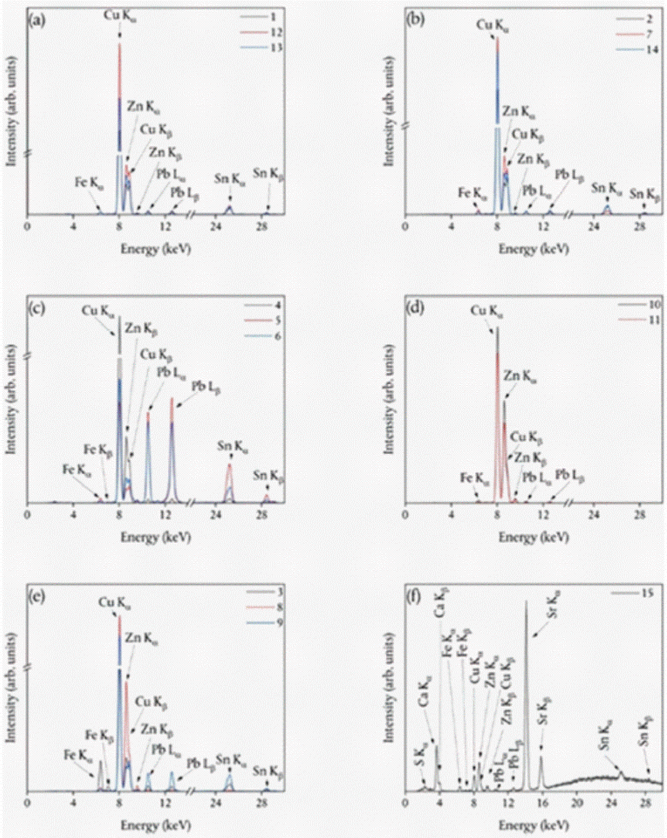

Figure 2. XRF spectra recorded on the investigated areas of the monument: ID1, ID12 and ID13 (a); ID2, ID7 and ID14 (b); ID4, ID5 and ID6 (c); ID10 and ID11 (d); ID3, ID8, and ID9 (e); and ID15 (f). See text for details on the grouping criteria.

Table 2. Qualitative elemental composition of the detected areas.

ID	Qualitative elemental composition
1	Cu, Zn, Sn (Fe, Pb)
2	Cu, Zn, Sn (Fe, Pb)
3	Cu, Zn, Sn (Fe, Pb)
4	Cu, Zn, (Fe, Sn, Pb)
5	Cu, Zn, Sn, Pb
6	Cu, Zn, Sn, Pb
7	Cu, Zn, Sn (Fe, Pb)
8	Cu and Zn (Sn, Fe, Pb)
9	Cu and Zn (Sn, Fe, Pb)
10	Cu and Zn (Fe, Pb)
11	Cu and Zn (Fe, Pb)
12	Cu, Zn, Sn (Fe, Pb)
13	Cu, Zn, Sn (Fe, Pb)
14	Cu, Zn, Sn (Fe, Pb)
15	Ca, Sr, S, Cu, Zn, Sn, Fe, Pb

Based on the visible results shown in Figures 2(a) and 2(b), it is not possible to determine with certainty if all the parts of the monument (for instance, the head and the rest of the monument) were produced in situ or in the laboratories by foundry plants. Yet, it is noteworthy that the variability of the elemental concentration in a copper-based alloy monument could be related to the technique employed to produce the monument itself [12-13]. The bracket fusion technique, in fact, has been commonly used for large monuments since it allows to produce the different sections of the sculpture separately, to be later attached. This means that the monument may have been made at different times or by two separate foundries, thus explaining the variability in terms of its composition. This variation in the composition of the bronze in diverse areas is not unusual in monumental bronze artworks [14]. The variability in the elemental composition of the alloy could be explained as an indicator of poor control over the production process by foundry workers, or due to the use of poor-quality raw materials. However, it should not be overlooked that selectively leached of alloy components can occur [3]. In this case, having analyzed the superficial patinas, enrichments or depletions of single elements of the alloy can be due to specific processes and reactions controlled by environmental factors [3].

Going on, Figure 2(c) shows the XRF spectra concerning welded or brazed areas, identified as ID4, ID5, and ID6, respectively. It is clear how the areas ID5 and ID6 are dominated by the presence of Pb, while, on the contrary, the area ID4 is mainly characterized by a binary alloy (Cu+Zn). A first inspection of Figure 2(d) reveals that the flagpole, separated from the monument and detachable, and the decorations related to the flagpole (flag bow), identified as ID10 and ID11, respectively, are characterized by a binary alloy (Cu+Zn). The interpretation of the XRF spectra in Figure 2(e) suggests different materials used in the monument's structural elements (nails, pins, rivets). In particular, the area ID3 is enriched in Fe compared with the areas ID8 and ID9. Also, the area ID9 appears to be characterized by a binary alloy (Cu+Zn), in which Sn, Pb, and Fe also occur as impurities. Not having the bulk composition of the alloy, it is possible to consider that the wide occurrence of Pb and Fe shown in the measurements performed in the monument can be linked both to the impurities of the raw materials or to the leaching of Pb and Fe from structural or welded elements of the monument. Finally, Figure 2(f) shows the XRF spectra concerning concretions deposited on the monument (ID15). The three spectra show the presence of Ca, S, and Sr, other than Cu, Zn, Sn, Pb, and Fe.

IV. CONCLUSIONS

In this paper the results of a study conducted in situ, by using XRF spectroscopy in order to characterize at elemental level the superficial layers of the alloy and the related corrosion products of the Monument to the Fallen of the Great War in San Ferdinando (Reggio Calabria, Italy), are reported.

The obtained results appear relevant in order to select the most appropriate cleaning method during restoration and to improve the knowledge about bronze casting techniques employed by the artist Francesco Jerace. Moreover, the approach reported in this paper can be employed, in principle, for the elemental characterization of the superficial layers and the related corrosion products of each copper-based alloy sculpture.

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