

X-ray fluorescence and μ -Raman analysis of bronze sculptures by Giuseppe Renda

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ABSTRACT

In this work, the elemental and molecular composition of three different bronze sculptures by Giuseppe Renda (one of the most famous interpreters of the Neapolitan Verism in the 19th and 20th centuries), respectively named "La Fortuna", "Scugnizzo" and "Non mi toccare", was performed. This was done for the first time and in a completely non-invasive way, through a combined approach involving portable X-ray fluorescence (XRF) and μ -Raman techniques.

The analysis of the investigated artefacts was aimed at improving the knowledge of the Southern Italy bronze art of the second half of the 20th century; this was done also in order to support the definition of optimized conservation strategies to be used by restorers in view of planning best restoration/cleaning interventions to minimize the conservation problems that could affect the durability of the precious artefacts.

Section: RESEARCH PAPER

Keywords: X-ray fluorescence; μ -Raman; bronze sculptures; Giuseppe Renda

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1. INTRODUCTION

Among the most important artworks by Giuseppe Renda (Polistena (RC) 1859 - Naples 1936), a Calabrian sculptor considered among the greatest interpreters of Neapolitan "verismo" in the 19th and 20th centuries, there are certainly three bronze sculptures named "La Fortuna", "Scugnizzo" and "Non mi toccare", respectively [1], [2]. These artworks, part of the collection of the Marchese srl company of Polistena (RC), are re-propositions of famous plaster casts made by the artist at the beginning of the 20th century and melted in metal in the second half of the same century.

In particular, "La Fortuna" was presented by the artist in Milan in 1906, during the exhibition organized for the opening of the Siplon Pass. The plaster "La Fortuna" was later given Banca Popolare di Polistena, which oversaw its bronze casting at the Chiurazzi Foundry in Naples, as would also be confirmed by the different stamps at the base of the monument now displayed in the atrium of Palazzo Avati in the Calabrian municipality, by the

heirs of the sculptor. Going on, from the plaster model of "Scugnizzo" (Cosenza, Renda heirs' collection), also made in the first decade of the 20th century, two bronze versions are instead known: the first one, kept at the Lanza Institute in Reggio Calabria, and the second one, preserved at the Marchese srl company in Polistena, of which, however, neither the year of casting nor the foundry executing the model are known.

Finally, in the Renda heirs' collection in Cosenza the plaster "Non mi toccare" is kept, from which the bronze artwork was made. As in the case of the "Scugnizzo", the bronze "Non mi toccare" also lacks information about the commissioner, place and period of execution.

As is well established, the combined use of XRF and Raman spectroscopies represents a successful multi-technique and multi-scale approach for a non-invasive study that allows for complementary compositional information, the first one at the elemental level, and the second one on a molecular scale. It has been already applied in a variety of findings of cultural heritage

interest such as potteries, frescoes, glasses, gemstones and paintings [3]-[7]. In fact, the elemental (qualitative and/or semi-quantitative) analysis performed by XRF results necessary for the unambiguous phase identification of both organic and inorganic materials by the Raman technique, and vice versa.

In this study, firstly the elemental compositional analysis of the three aforementioned bronze sculptures was performed, for the first time, on selected representative fragments, taken during restoration works. It is worth underlying that, due to the preciousness of the artefacts, only few fragments have been withdrawn from the sculptures. The investigation has been performed by means of portable non-destructive X-ray fluorescence (XRF) spectroscopy [8]-[13], with the aim: (i) of knowing the constituent elements of the bronze alloy of the three works now preserved in Polistena, in order to eventually support the hypothesis that the bronzes came from a single foundry, probably the same one that made “*La Fortuna*” in the second half of the 20th century, as supposed by the art historians; (ii) of identifying the main contaminants that in principle could affect differently the three artefacts, particularly in the case of the “*La Fortuna*” bronze sculpture, which is composed of several metal elements welded together [14]-[16] in order to eventually suggest most appropriate methodologies to carry out the cleaning during the restoration. Indeed, the chromatic and material differences in the bronze that constitutes the allegory of “*La Fortuna*”, represented as a naked woman, compared to the wheel that provides its base, executed by making use of an alloy with a definitely darker tone, are evident.

After that, we also applied non-invasive μ -Raman spectroscopy to unambiguously recognize specific mineralogical phases, as well as to assess the molecular composition of the surface corrosion products originating from several environmental and anthropogenic factors. Knowledge of such additional aspects furnishes crucial insights to stop or slow down the degradation processes occurring in bronze artefacts, by appropriate selection of the best cleaning methods, protective coatings or stabilization techniques according to the specific corrosion products present, thereby minimizing potential damage and maximizing the long-term preservation of the investigated statue.

2. MATERIALS AND METHODS

Photos of the investigated artworks, “*La Fortuna*” (front side (a) and back side (b)), “*Scugnizzo*” (c) and “*Non mi toccare*” (d) are reported in Figure 1.

The sampling procedure took into account the preciousness of the sculptures, hence even if the sampling occurred during the restoration works, only few representative fragments selected by the restorers, have been withdrawn. In particular, with reference to the artwork “*La Fortuna*”, four representative samples were analyzed: ID1, ID2 and ID4, all taken from the back side, and ID3, withdrawn from the front side. Furthermore, for “*Scugnizzo*” and “*Non mi toccare*” one sample for each of them withdrawn from the head, i.e. ID5 and ID6, respectively, was investigated. All the investigated fragments had a square-shaped surface of about 0.5 cm on each side.

For the analysis, 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 and lead was employed, in order to get a qualitative elemental composition of the samples [17]. It is equipped with a Ta anode X-ray tube as source and a Si PIN diode (active area of



Figure 1. Photos of the investigated artworks, “*La Fortuna*” (a, b), “*Scugnizzo*” (c) and “*Non mi toccare*” (d).

170 mm²) as detector. For each point, two sequential tests were performed, the first with operating conditions of 40 kV and 7 μ A, and the second with operating conditions of 15 kV and 5 μ A, for a total spectrum collection time of 120 s. The instrument was controlled by a Hewlett-Packard iPAQ Pocket PC, 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.

μ -Raman measurements were collected using a portable 'BTR 111 Mini-Ram™' spectrometer (B&W Tek, USA). The instrument utilized a diode laser with an excitation wavelength of 785 nm, delivering a maximum laser power of 280 mW at the excitation port, and a thermoelectric-cooled charge-coupled device (CCD) detector.

The possibility to continuously adjust the laser output power allowed to obtain the best signal-to-noise ratio in the minimum integration time. In particular, the 62-3153 cm⁻¹ spectral range was investigated, with a resolution of 10 cm⁻¹ and an acquisition time of 10 s x 32 scans. To guarantee the optimal instrument performance, a calibration procedure before each measurement, using the peak at 520.6 cm⁻¹ of a silicon chip, was carried out. The system was equipped with a BAC151B Raman microscope mounting a 40x objective with a working distance of 3.98 mm and laser beam spot size 50 μ m. To avoid unwanted thermal effect induced by laser, the maximum power at the samples was kept at \sim 15 mW. The identification of the peaks was attained by comparing the obtained spectra with those reported in various databases and in the literature [18]-[20].

It is worth underlying that XRF measurements permit a preliminary qualitative elemental composition study of the samples, useful for the identification of the Raman molecular bands.

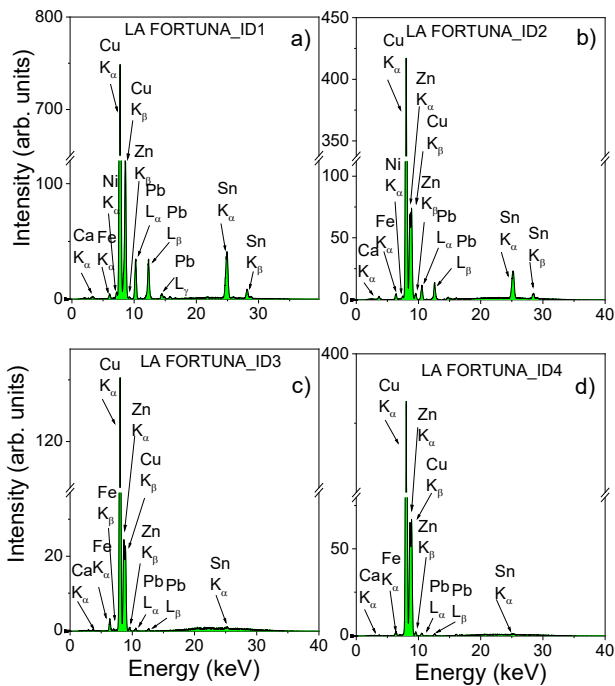


Figure 2. XRF spectra of “La Fortuna” analysed fragments, ID1-ID4.

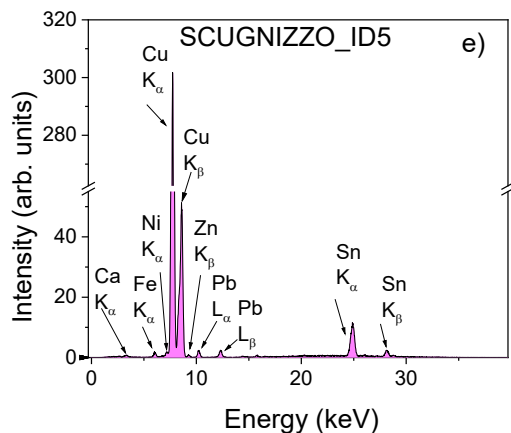


Figure 3. XRF spectra of “Lo Scugnizzo” analysed fragments, ID5.

3. RESULTS AND DISCUSSION

Figure 2 to Figure 4 show the XRF spectra of analysed samples, while Table 1 reports their elemental composition. As previously specified, XRF elemental composition is not quantitative but only an indication of the major or minor elements present in the samples. However, in the case of major elements the values were higher than 5×10^5 ppm while the content of minor elements was lower than contents 8×10^3 ppm. The different composition of the alloys used for the creation of the artwork “La Fortuna” indicates the artist’s will to obtain different material effects, related also to different chromatic nuances, in correspondence to the three main parts that constitute the artwork (base, wheel and female figure), cast by the Chiurazzi foundry in Naples in the last quarter of the last century.

In particular, the presence of Sn in the alloy of samples ID1 and ID2, taken from the back side of the hand of the female figure and the base respectively, can be attributed to the will to have a bronze as rigid as possible for stability reasons of the

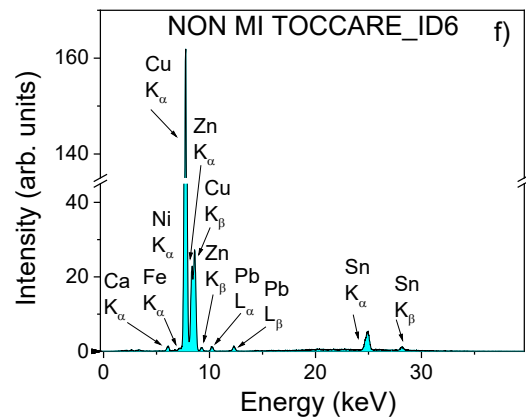


Figure 4. XRF spectra of “Non mi toccare” analysed fragment, ID6.

Table 1. X-ray fluorescence (XRF) elemental composition. Minor or trace elements reported in brackets.

Sample ID	Qualitative elemental composition
ID1 (“La Fortuna”) – back side, wheel	Cu, Sn, Pb (Fe, Zn, Ni, Ca)
ID2 (“La Fortuna”) – back side, base	Cu, Sn, Zn (Pb, Fe, Ni, Ca)
ID3 (“La Fortuna”) – front side, female figure	Cu, Zn (Pb, Fe, Sn, Ca)
ID4 (“La Fortuna”) – back side, wheel	Cu, Zn (Pb, Fe, Sn, Ca)
ID5 (“Scugnizzo”)	Cu, Sn, Zn (Pb, Fe, Ni, Ca)
ID6 (“Non mi Toccare”)	Cu, Sn, Zn (Pb, Fe, Ni, Ca)

artwork. In addition, the detection of Pb on the female figure (ID3) is determined by the need to obtain a surface as homogeneous as possible. On the other hand, the traces of Ca, present in all the investigated fragments, can be attributed to the casting earth [21]-[24].

Finally, the results of the analysis of the samples taken from the sculptures “Scugnizzo” (ID5) and “Non mi toccare” (ID6), showed that the two artworks were probably cast by the same foundry. In any case, the alloys used are entirely compatible to the materials used in Neapolitan foundries in the 20th century, so it cannot be ruled out that these two artworks were also made in the second half of the 20th century by the Chiurazzi Foundry in Naples.

As far as μ -Raman measurements are concerned, Figure 5 reports the experimental μ -Raman spectra collected on the two back side fragments taken from the sculptures “La Fortuna” (ID1 and ID2, Figure 5a), and on the sampled fragment taken from the sculptures “Scugnizzo” (ID5, Figure 5b) and “Non mi toccare” (ID6, Figure 5c). No background has been subtracted from the data for avoiding any unwanted alteration of the spectral features.

Concerning samples ID1 and ID2 (Figure 5a), the detected μ -Raman profiles revealed two main contributions centered at ~ 147 cm^{-1} and ~ 622 cm^{-1} , ascribable to the A_{1g} mode of lead (α -PbO, litharge) [25] and tin-oxide (SnO_2 , cassiterite), respectively [26]. Furthermore, we can observe also another weak band centred at ~ 740 cm^{-1} , less intense in ID2 sample that could be again assigned to cassiterite [26]. All these observations agree with the obtained concentrations of Pb and Sn achieved through XRF spectroscopy. No copper containing species were identified. Concerning the presence of α -PbO, this secondary mineral should be considered as an intermediate-products of the typical lead corrosion route readily activated in O_2 , CO_2 and H_2O -rich environment ($2\text{Pb} + \text{O}_2 \rightarrow 2\text{PbO}$ (litharge) $\rightarrow \text{PbCO}_3$ (cerussite) $\rightarrow \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ (hydrocerussite)).

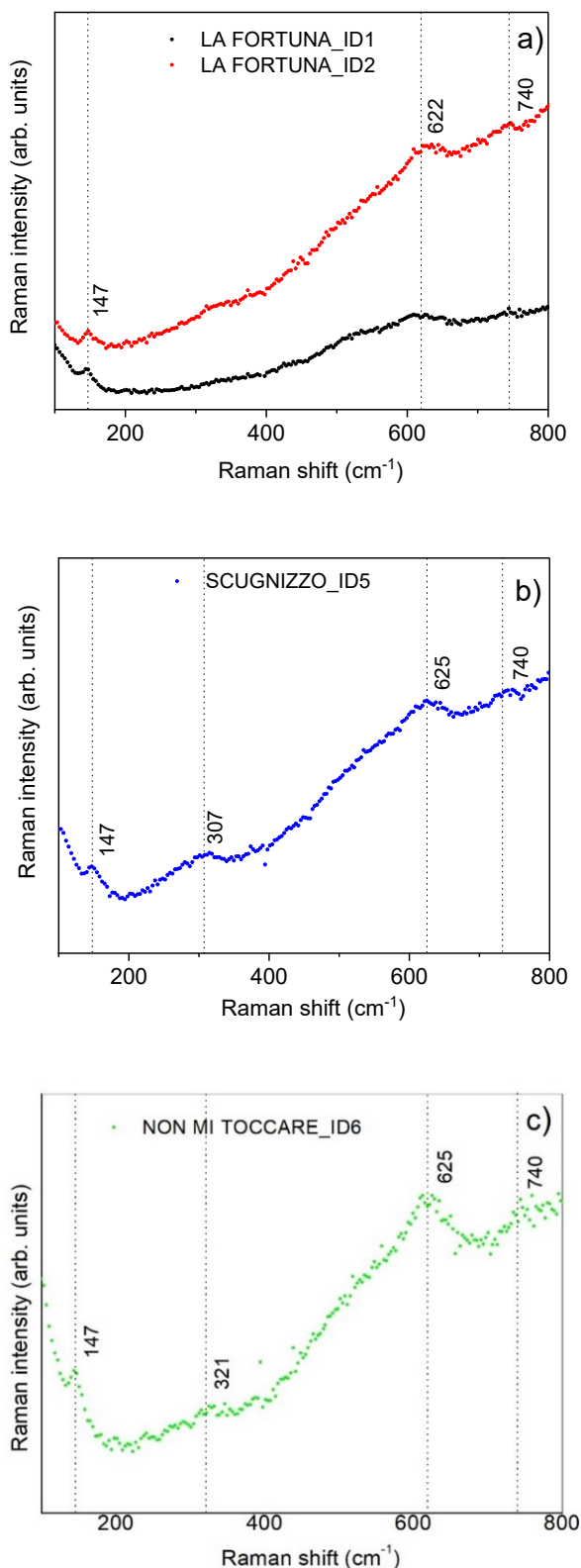


Figure 5. Raman spectra recorded on (a) the two back-side fragments taken from the sculpture “La Fortuna” (ID1 and ID2); (b) the sampled fragment from the sculpture “Scugnizzo” (ID5) and (c) “Non mi toccare” (ID6).

When tin is alloyed to copper, the structure of the oxide undergoes modifications that are visible in the Raman spectrum. Interestingly, for what concerns the observed center-frequencies of SnO_2 it is worth of note that the A_{1g} mode of “pure” SnO_2 microcrystals of the cassiterite type typically falls at $\sim 638 \text{ cm}^{-1}$

and 782 cm^{-1} . Hence, in our case, the observed down-shift of such peaks implies the existence of a Cu-based atom-doped phase of the SnO_2 cassiterite structure, whose extent strongly depends on the Cu-content within the alloy [26]. Notably, other alloying elements such as Fe or Pb, previously detected through XRF, can also be involved in such substitution processes, forming new phases of the $\text{Sn}_{1-x}(\text{CuFePbSi})_x\text{O}_2$ -type that foster the frequency down-shift of the A_{1g} mode of SnO_2 .

μ -Raman spectra collected on sampled fragments taken from the sculptures “Scugnizzo” (ID5) and “Non mi toccare” (ID6) revealed the presence of bands at $\sim 147 \text{ cm}^{-1}$, $\sim 310 \text{ cm}^{-1}$ and $\sim 625 \text{ cm}^{-1}$, ascribable to the A_{1g} mode of lead-oxide (α - PbO , litharge) and to the symmetric stretching ($\sim 310 \text{ cm}^{-1}$) and bending modes ($\sim 625 \text{ cm}^{-1}$) of copper(II)-oxide (Cu(II)O, tenorite) Cu-O bonds, respectively [27]. Considering the high concentration of Sn observed in samples ID5 and ID6, it is reasonable to assume that this last feature ($\sim 625 \text{ cm}^{-1}$) is superimposed to the A_{1g} mode arising from an atom-doped phase of SnO_2 -cassiterite. Again, we observed for both the sculptures the presence of the weak band centred at about 740 cm^{-1} ascribable to cassiterite.

The detection of Cu(II)O in ID5 and ID6 suggests that both “Scugnizzo” and “Non mi toccare” sculptures were patinated at high-temperature (slow heat in air environment) or thanks to a prolonged exposure to strong alkaline solutions (pH 12-13) [28], [29].

4. CONCLUSIONS

Three bronze sculptures, respectively named “La Fortuna”, “Scugnizzo” and “Non mi toccare”, made by Giuseppe Renda, a Calabrian artist considered among the greatest interpreters of Neapolitan “verismo” in the 19th and 20th centuries, were investigated.

In particular, the compositional analysis, both at the elemental and molecular scales, of the three aforementioned artworks was performed, for the first time, on representative fragments taken during restoration operations, by means of portable X-ray fluorescence (XRF) and μ -Raman spectroscopy. From obtained results, we can conclude that the different composition of the alloys used for the achievement of the artwork “La Fortuna” indicates the artist's desire to obtain different material effects in correspondence to the three main elements that constitute this artwork (base, wheel, and female figure). Moreover, the traces of calcium, present in all the investigated fragments, can be attributed to the casting earth. Going on, the alloys composition of the samples taken from the sculptures “Scugnizzo” and “Non mi toccare” put into evidence that these two artworks were probably cast by the same foundry, probably the Chiurazzi Foundry in Naples, being fully compatible with the materials used in Neapolitan foundries in the 20th century. Finally, as far as the restoration operations of these bronze sculptures are concerned, the presence of calcium in the XRF spectra could suggest the use of bisodium EDTA (Ethylene-Diamino-Tetra-Acetic Acid), while the presence of different alloys leads to the hypothesis of the use of this tetracarboxylic acid at different concentrations, mixed with ammonium carbonate and bicarbonate. On the other side, μ -Raman spectroscopy allowed for a non-destructive identification of specific mineralogical phases deriving from surface corrosion products originating from several environmental and anthropogenic factors, furnishing useful notions in the view of preserving and maintaining bronze sculptures.

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