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Controlling the effectiveness of the cleaning treatments of bronze using X-ray diffraction: The equestrian sculpture of "El Cid Campeador" (Seville)

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ABSTRACT: Copper and its alloys (bronze and brass) are materials which are widely used in sculptures and ornamental pieces of cultural heritage due to their ability to develop stable protective patina in oxidant atmosphere conditions. However, depending on the environmental conditions, they can suffer the effect of corrosion due to urban pollution. One of the most common alterations is the so-called "bronze disease", a cyclic corrosion caused by the presence of chlorides on their surface. The equestrian sculpture of "El Cid Campeador" was donated by the Hispanic Society to the city of Seville (Spain). In fact, the Society's founder, Archer Milton Huntington, and his wife, Ana Hyatt (author), donated the sculpture for the Ibero-American Exhibition of 1929. It is located between Prado de San Sebastián Gardens ("Jardines del Prado de San Sebastian") and the Royal Tobacco Factory ("Real Fabrica de Tabacos") in Seville, which is an urban area where atmospheric pollution is very high (SO_2, NOx, VOCs, particles in suspension, etc.). Due to the severe degradation of the sculpture, in 2012 it was included in a campaign for the conservation and restoration of public monuments promoted by Seville's Town Planning Department ("Gerencia de Urbanismo de Sevilla". The methodology followed in studies prior to any intervention on the sculpture involved the chemical characterisation of the bronze alloy by means of XRF. Then, once the most abundant patinas had been identified according to their colour tone (brown, green, yellow, white), the compounds were identified by means of XRD. During the process, it was possible to differentiate between stable and unstable compounds. After reviewing the available literature, four cleaning treatments were selected and applied to the different patinas. Their efficiency was evaluated based on the decrease in the concentration of unstable compounds using XRD semi-quantification. Finally, the stabilization of bronze was completed and a protective layer of varnish (based on an acrylic resin with antioxidant additives) was applied.

1 INTRODUCTION

The equestrian sculpture of "El Cid Campeador" was donated by the Hispanic Society to the city of Seville (Spain). In fact, the Society's founder, Archer Milton Huntington, and his wife, Ana Hyatt (author), donated the sculpture for the Ibero-American Exhibition of 1929 (Melendreras, 1985). The prototype of the monument was produced in around 1927. During that year, the colossal sculpture was modelled and cast. From the very beginning the Monument dedicated to El Cid attracted the attention of Seville's residents and visitors to the Ibero-American Exposition, drawing great praise (Trillo, 1980). The El Cid monument was immediately acknowledged and its author gained popularity, prompting her to create other copies. The first copy is at the Hispanic Society in New York. (Martínez Martín, 2000). The renovation process follows the general criteria established in Heading II, Article 20 of Law 14/2007 on the Historical Heritage of Andalusia. The first step in the establishment of the general criteria for the renovation of the sculpture was to examine the monument, analysing its conservation status and defining its pathologies and their causes. The aim was to develop a methodology for treating the damage, guaranteeing its repair, as well as the future conservation of the statue. In this sense, it is obvious that the main problems affecting the El Cid Monument derive from its constituent materials and their evolution in the local climatic and meteorological conditions, characterised most notably by the severe pollution in the area.

The statue presented a high level of deterioration due to the presence of micro-pores and the exposure of the sculpture to weathering in an urban environment where contamination caused by the presence of SO_2, NOx, VOCs, particles in suspension, etc. is very severe. This has caused alloy corrosion resulting in the dusty appearance of the surface, different shades of green and blue (Figure 1).

Figure 1. Formation of unstable patinas due to pollution.

2 OBJECTIVE

The main objective was to evaluate the effectiveness of the cleaning treatments of bronze using X-ray diffraction (XRD). This effectiveness was based on the decrease in the concentration of unstable compounds using XRD semi-quantification.

3 MATERIALS AND METHODS

The chemical characterization of the bronze alloy was determined by XRF (AXIOS model). Then, once the most abundant patinas had been identified according to their colour tone (brown, green, yellow), the compounds were identified by means of XRD (Bruker-AXS D8 Advance model). Once the available literature had been reviewed (Diaz, 2011), four cleaning treatments were selected and applied to the different patinas, and their efficiency was evaluated by means of XRD semi-quantification: treatment 1 (Treat.1): 5% ammonium citrate solution at pH=9 (3 applications); treatment 2 (Treat.2): 3% benzotriazole in isopropyl alcohol (3 applications); treatment 3 (Treat.3): 25% sodium potassium tartrate solution (3 applications); treatment 4 (Treat.4): 5% ammonium citrate solution at $pH = 9 + 3\%$ benzotriazole in isopropyl alcohol (2 applications + 1 application). The concentration was evaluated by quantifying the net area of the peaks located between 15.4° and 16.6° using the XRD software EVA. The aforementioned peaks corresponded to the high intensity of atacamite and pararacamite and to the third in terms of intensity for brochantite.

4 ANALYSIS OF RESULTS

4.1 *Chemical analysis*

Taking into account the composition in terms of the majority and minority elements Cu (88.22%), Sn (6.44%), Zn (2.60%) and Pb (1.54%), we were able to conclude that this was a Pb-bronze alloy. Given its American origin, it corresponds to a bronze that meets the chemical composition requirements for C92200 alloy as defined by the CDA (Copper Development Association Inc.). It is a bronze with multiple industrial applications and is used in architecture for ornamental foundry work.

Table 1. Mineralogical composition of the patinas.

Samples	Minerals identified
Green patina	Cpr, Cst, Bro, Antl, Atc, Pat, Ang, Qtz
Brown patina	Cpr, Bro, Atc, Pat, Nan, Qtz, Cal
Yellow patina	Cpr, Bro, Atc, Pat, Nan, Qtz, Cal

Abbreviations of mineral names: Cpr: cuprite; Qtz: quartz; Cst: cassiterite; Bro: brochantite; Antl: antlerite; Atc: atacamite Pat: paratacamite; Ang: anglesite; Nan: nantokite

Figure 2. Sampling in yellow patina after treatments.

4.2 *Mineralogical analysis*

Table 1 shows the minerals identified in the different patinas.

The minerals quartz, calcite and dolomite do not form part of the chemical composition of the statue. Their presence may have been due to dust suspended in the environment being deposited on the surface of the statue due to gravity.

Cassiterite SnO_2 and cuprite CuO_2 are oxides resulting from the interaction of oxygen and metals of the bronze alloy. The most abundant and important is cuprite. In most cases, it is a direct alteration of the metallic surface of bronze and it is generally the first one to appear. It is considered a stable patina. As regards the copper sulphates, brochantite or brochantite $Cu_4SO_4(OH)_6$ and antlerite $Cu_3SO_4(OH)_4$ have been identified (Díaz, 2011). These compounds form on the exterior in urban and contaminated atmospheres, bronchantite being the most stable and frequent compound. The following copper chlorides were identified: atacamite $Cu_2(OH)_3Cl$, paratacamite $(Cu^{2+})_3(Cu,Zn)(OH)_6Cl_2$ and nantokite (CuCl). These compounds are responsible for the so-called "bronze disease", these being the unstable patinas (Cantalapiedra, 1994).

Cuprous oxide and cupric chlorides produce hydrochloric acid when combined with oxygen and water present in air. That combination results in pale green to greenish blue spots (first stage). These spots are soft and dusty and corrode the surface and produce more copper chlorides (second stage). The process

Table 2. Quantification of the net areas between 15.4° and 16.6° (2θ) of the patina samples after the different treatments.

Samples	Original patina (Cpsxdeg)	Treat.1	Treat.2	Treat.3	Treat.4
Green patina	9.41	5.86	14.69	6.05	6.06
Brown patina	4.69	5.75	5.60	4.52	2.71
Yellow patina	5.57	1.50	3.62	2.27	2.34
Sulfates only	14.98	$7.36^{(1*)}$	$18.31^{(4*)}$	$8.32^{(2*)}$	$8.4^{(3*)}$
Chlorides only	13.35	$11.61^{(3*)}$	$20.29^{(4*)}$	$10.57^{(2*)}$	$8.7^{(1*)}$
Σ 3 patinas	19.67	$13.11^{(3*)}$	$23.91^{(4*)}$	$12.84^{(2*)}$	$11.1^{(1*)}$

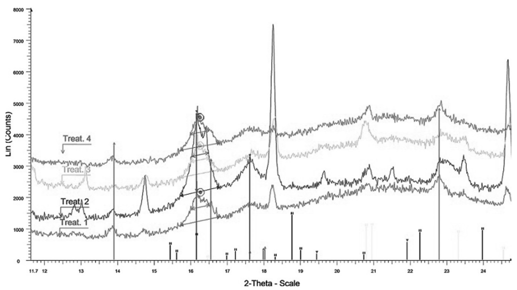

Figure 3. Semi-quantification of the reduction in the net area of the copper chlorides (green patina) after different treatments.

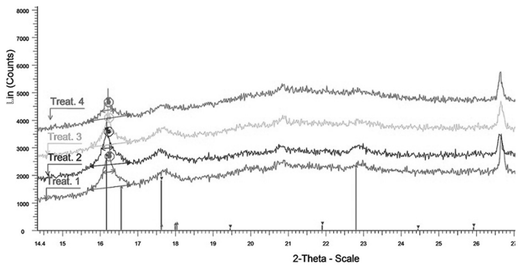

Figure 4. Semi-quantification of the net area reduction of copper chlorides (brown patina) after different treatments.

continues until the object finally disappears, according to the following reactions (Stambolov, 1987):

$$4CuCl_{(s)} + O_{2(g)} + 4H_2O = 2Cu_2(OH)_3Cl_{(s)} + 2HCl_{(aq)}$$
(first stage)

$$2Cu_{(s)} + 2HCl_{(aq)} \dashrightarrow 2CuCl_{(s)} + H_{2(g)}$$
(second stage)

In terms of the semi-quantitative analysis of the mineralogical composition of the patinas, on whitish-greenish and yellow patinas copper sulphate is more abundant than copper chlorides, but on brown patinas copper chlorides are more abundant than copper sulphate.

4.3 *Application of treatments and control of effectiveness by means of XRD*

Once the mineralogical and applied compounds had been identified, the treatments were re-sampled as shown in Figure 2.

The quantified net area is directly proportional to the concentration of these compounds; the results obtained after the application of the different treatments are shown in Table 2.

As can be observed in Figures 3 and 4 and Table 2, none of the treatments succeeded in completely removing the green or yellow patina.

5 CONCLUSIONS

From the study carried out on this important monument in the city of Seville, it follows that the type of material used to make the sculpture is a lead-bronze alloy.

The mineralogical analysis performed to identify the compounds present in the alterations of the bronze confirmed the presence of copper sulphate (brochantite) and copper chlorides (atacamite and paratacamite), and quartz, calcite and dolomite belonging to deposits of dirt and cuprite as stable patina.

Finally, this study confirmed that XRD could be used as an instrumental analytical technique, based on the quantification of net areas, to select the most effective chemical treatment for cleaning the bronze, treatment no. 4 (5% ammonium citrate solution at $pH = 9 + 3\%$ benzotriazole in isopropyl alcohol (2 applications + 1 application)) offering the best results for the removal of the unstable patina. It is also important to note that the application of benzotriazole, without the application of prior treatments to remove chlorides or sulphates, causes these compounds to bind and form complexes with this product without being eliminated, a situation which may be negative in the long term.

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