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Laser cleaning of a bronze bell

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ABSTRACT

In this paper we report the experimental results of the study of evaluation of an UV laser cleaning treatment on a bronze bell outdoor, dating from the second half of the 600.

Energy dispersive X-ray fluorescence (EDXRF) non-destructive analysis was performed on the bell before, during and after the cleaning treatment in order to assess the laser ablation threshold, to define the efficiency of laser cleaning process, to avoid possible damage of laser on the bell, to determine the concentration of the constituents of both the *patina* and the alloy. In particular, an EDXRF portable apparatus was used in order to evaluate the variation of concentration of sulfur, chlorine, calcium, copper, lead and tin during the laser cleaning.

1. Introduction

Bronze and copper manufacts produce thin layers of corrosion products, so called *patina*, as a result of a large number of chemical, electrochemical and physical processes which occur spontaneously during interaction of metal surface with the environment, especially with outdoor bronze. Moreover, both morphology and chemical composition of the patina can vary significantly depending on what has been the location of the sample over the years.

In particular, outdoor bronze artefacts, exposed to urban atmosphere (presence, for example, of sulfur oxides, nitrogen oxides, atmospheric particulate matter and acid rains) for various decades, exhibit a greenish *patina* containing several constituents.

The deterioration of a bronze exposed to sulfur dioxide and nitrogen dioxide produces sulfuric acid and nitrous acid according to the following chemical reaction:

$$SO_2 + 2NO_2 + 2H_2O \leftrightarrows 2H_2SO_4 + 2HNO_2 \quad (1)$$

Accordingly the corrosion rate of a bronze tends to increase by dissolving any passivating film and by forming a solution of hygroscopic metal sulfates. The metal ions in this solution will be chiefly copper and zinc [1,2].

Lasers are used from some years in the field of cultural heritage for the cleaning treatments of metallic materials [3–8].

In this paper, experimental results about the laser cleaning of an outdoor bronze bell by UV laser are reported. Throughout the work, the laser cleaning operations were accompanied by non-destructive energy dispersive X-ray fluorescence (EDXRF) analysis in order to monitor the effects of interaction laser-sample, to avoid possible damage to substrate and/or *patina* and to assess the level of cleaning. EDXRF has allowed qualitative and quantitative analysis of the elements constituting the *patina* (S, Cl, Ca, Cu, Pb and Sn) and, therefore, it has allowed us to establish the validity and accuracy of laser cleaning treatment. These elements were chosen since constituting the elements normally present on patina of alteration of ancient bronzes.

In particular, the treatment of laser cleaning has been carried out on a bronze bell, which was held outdoor (Fig. 1). The bell, dating from the second half of the 600, it is high 25 cm and it is located in San Michele delle Grotte, in Gravina di Puglia (Bari, Italy). It has been kindly granted by the Soprintendenza P.S.A.E. per le Province di Bari e Foggia, where it is currently for restoration

2. Material and methods

2.1. Instrument

A portable apparatus for energy dispersive X-ray fluorescence analysis was used in order to evaluate the variation of S, Cl, Ca, Cu, Pb and Sn concentration before, during and after the treatment of laser cleaning.

The instrument consists of an X-Ray tube manufactured by Oxford Instruments, with Be window of 0.25 mm, diameter of 2 mm, voltage of 1–30 kV, current of 0–100 μA, with tungsten anode and air-cooled [9,10]. The detector used is a Si(PIN), produced by AMPTEK, model XR_100CR, resolution of 190 eV at 5.9–keV, with Be window of 25 μm, thermoelectric cooling. The

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Fig. 1. Photo of the bronze bell used for this study of laser cleaning.

instrument is completed also with a card produced by AMPTEK, model MCA8000A, interfaced with a portable computer.

In the treatment of laser cleaning has been used an UV laser at KrF excimer, with wavelength of 248 nm and a pulse duration ranging from 20 to 30 ns. In particular, it is a multi-gas laser, manufactured by Lambda Physik, model COMPEX 250.

The use of a converging lens, with a focal length of 50 cm, allowed to choose the appropriate laser spot area. The spot size of rectangular cross section was performed with a gauge measuring the size of a mask used to define the beam during the diagnostic phase.

The energy associated with the laser impulse was measured with a Joulemeter, assessing the mean and standard deviation of several measurements.

Both the size of the spot and the laser energy were evaluated from time to time in different operating conditions in order to determine the density of energy deposited on the target by a single laser pulse (fluence).

Consequently, the uncertainty associated with the laser fluence was evaluated by propagating the errors committed in assessing causal energy and the laser spot.

2.2. Quantitative EDXRF analysis

Calibration standards used in this work represent the chemical composition and chemical-physical properties of the *patina*, which consists of Cu_2O, $CaCO_3$, Cu, CuSn, CuCl, $CuCl_2{\cdot}2H_2O$, SnO_2, $CaSO_4{\cdot}2H_2O$, $CuSO_4{\cdot}5H_2O$ and Pb_3O_4. Each standard was made by mixing these compounds in different proportions by mass, weighed with an analytical balance (sensitivity 0.1 mg), homogenized in an agate mortar for about 10 min and subjected to compression press (200 bar) for 20 min.

EDXRF measurements were performed at different operating conditions: voltage of 5 kV and current of 80 μA for the analysis of light elements such as S, Cl, Sn (L-lines) and Ca; voltage of 30 kV and current of 5 μA for the analysis of heavy elements such as Cu, Sn (K-lines) and Pb.

In both cases, the different analytical lines were excited with the braking radiation of the tube and the spectra were acquired for 120 s.

In the analysis of the spectra of both standards and sample, analytical determination of the signal intensity was performed by using a specific program (Microcal-Origin).

Table 1
Half-value layer for different values of laser energy.

Energy (keV)	HVL_{Cu} (μm)	$HVL_{alloy\ Cu80\%Sn20\%}$ (μm)
3	1	1
8	15	9
25	35	33

Quantitative analysis are relative to a surface layer of the sample: the energy levels allow it to analyze layers of a few microns. The Table 1 shows the half-value layer (HVL), for copper and bronze (Cu80Sn20) in the case of photons of 3, 8 and 25 keV of energy, corresponding to the measures considered in this paper. These values provide the magnitude of the thickness analyzed.

2.3. Laser ablation threshold

Laser ablation threshold is defined as the minimum fluence value at which there is a detectable removal of matter from the surface of a solid matrix subjected to laser irradiation.

In the operations of laser cleaning of metal artefacts, knowledge of the ablation threshold associated with the metal matrix is essential in order to perform a laser cleaning confined to the superficial layer of alteration, so as to avoid possible mechanical damage and/or chemical and physical changes the bulk, as well as any noble *patina* present.

For values above to ablation threshold, the laser pulse interaction with a solid medium can form craters. The characterization of a crater, as a function of its depth, is a practical and effective method to determine the ablation threshold.

In this study we assessed the ablation threshold for a sample with similar chemical composition to the bell. The sample was subjected to laser ablation in different areas, each with a precise value of fluence.

The ablation rate as a function of the used laser fluence forms a linear trend: the ablation threshold was determined graphically by evaluating the value for which the ablation rate is void. Fig. 2 shows the patterns obtained experimentally for a bronze sample. The value of ablation threshold is equal to $1.8 \pm 0.3\ \mathrm{J\,cm^{-2}}$.

3. Results

The surface of the bell it appeared very homogeneous, smooth and free of fouling. EDXRF analysis at low energy showed that the

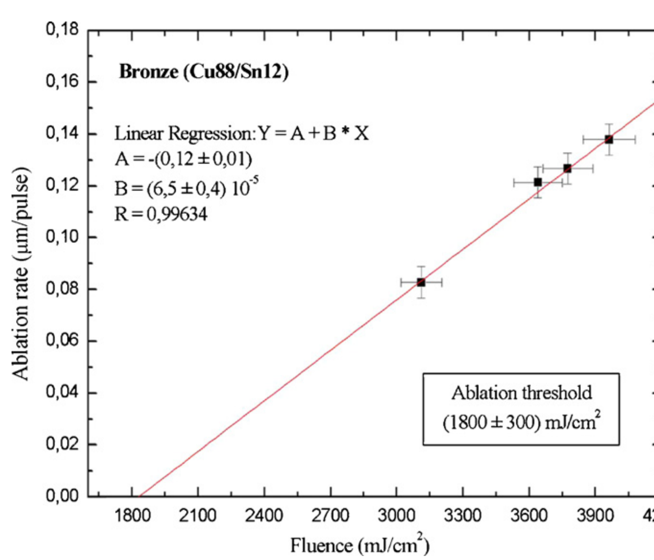

Fig. 2. Laser ablation rate on a bronze target as a function of laser fluence.