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EVALUATION OF THE CONSERVATION STATUS OF THE FOUNTAIN ENSEMBLE FROM BRĂILA'S TRAJAN SQUARE, USING LASER INDUCED BREAKDOWN SPECTROSCOPY

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In situ LIBS analyses of the metal surfaces of the Braila Fountain Ensemble were necessary in order to determine the conservation status and the proper restoration approach. The LIBS spectra provided an evaluation of the rust and paint layers present, as well as of the active corrosion products. Stratigraphy LIBS was also used in order to acquire a primarily assessment of the cleaning depth (in number of pulses) that may be applied further on.

Keywords: LIBS, stratigraphy, corrosion, cast iron

1. Introduction

The Braila Fountain ensemble is located in square Traian from Brăila, in the old Little Garden of the city - as it was called in that time. The 1890's town plan included the positioning of fountains, with decorated metal bodies and stone basins, in the different Squares of Brăila city, such as: Royal Square, Public Garden Square and even a polygonal structure (hexagon) for the Poligona Square.

Fig. 1. Overview of s*quare Traian*, end of the XIX^{-th} century [1]

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The ensemble is not dated, and its author is unknown. The central piece of the Fountain is represented by the metal statuary structure - 300 cm height and 185 cm wide, made from cast iron. The surrounding water basin – with a diameter of 600 cm, is made from cement.

Fig.2. The Fountain ensamble

Fig.3. Detailed view of the metal base

From the visual investigation of the statue ensemble, it was clear that numerous layers of primer and paint brush were applied over time, a more thorough investigation being necessary in order to identify exactly the elemental composition of the layers applied on the original surface, without sampling.

The visual metallographic characterization was made under microscopic investigation in order to identify the structure of the metal.

LIBS (Laser Induced Breakdown Spectroscopy [2]) method was selected for the in situ investigation of the metal surfaces of the Fountain, which besides the characterization of the piece also provided an evaluation of the rust and paint layers present.[3] Stratigraphy LIBS will also give us a primarily assessment of the cleaning depth (in number of pulses) that may be applied further on in the restoration project of the fountain ensemble.[4]

2. Metallographic characterization

The metallographic characterization was made on a detached metal micro-fragment from the interior part of the metal ensemble. The sample was processed in the restoration laboratory of Brăila Museum and the microscopy investigations were performed using a classic microscope.

In order to highlight the metal microstructure, NITAL 2% (nitric acid in alcohol) was used on the sample previously polished with diamond dust. The pictures were taken on ORWO 4 DIN, black and white film.

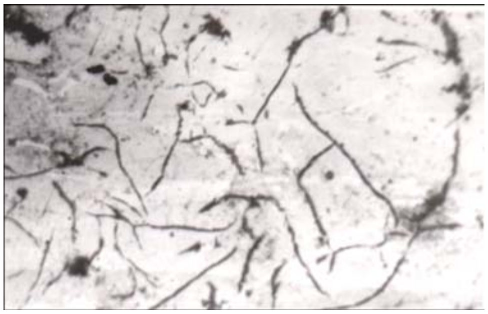

Fig. 4. Original sample, 150x magnification,

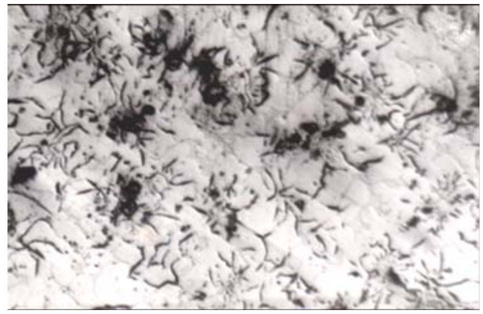

Fig. 5. After Nital 2%, 150x magnification

Based on the investigations made on the original sample, the structure of the metal was identified as soft cast iron with vermicular graphite at the limit of ferrite grain and interstitial graphite nests (*see Figure 5*). This alloy presents a high structural content of phosphorous eutectic (P between 0.9% - 1.2%) characteristic to the casting of thin pieces and decorations due to its high fluidity.

3. LIBS investigations

The LIBS technique consist in the application of a ns laser pulse (from a Q-switched Nd: YAG Laser) incident on the target surface that will vaporize a very small volume of material (microgram order) creating a high-temperature plasma plume. An optical fibre is used to collect the information from the plasma, directing it through an Echelle grating spectrometer.

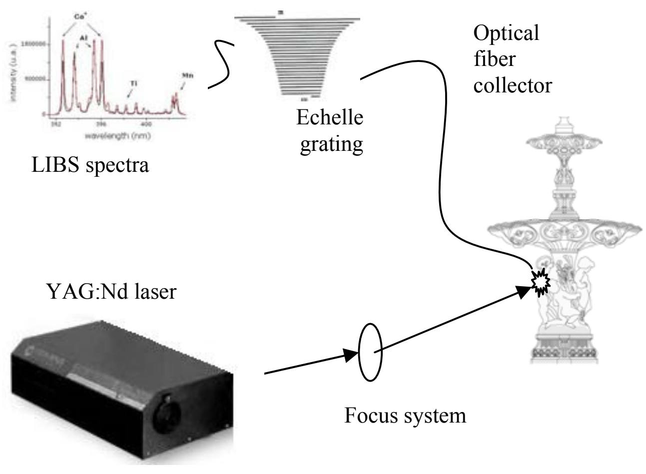

Fig.6. LIBS experimental setup

The atomic/ionic emission peaks are analyzed using dedicated software, in order to determine the elemental components of the investigated material, even in underwater conditions [5,6].

The method is applicable in situ, without any sampling or previous preparation of the investigated area. [7] Firstly, dp LIBS analyses were made on several areas of the Fountain's metal ensemble, in order to determine the chemical elements present in the investigated piece of art. Two selected spectra are presented below.

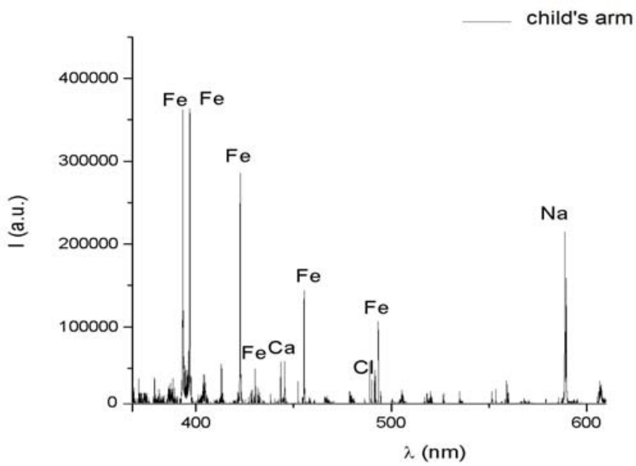

Fig.7. *double pulse* LIBS spectra acquired on the arm of one of the child statues

The major chemical elemental lines present in the spectra are: Fe - as expected, but also Ca, Mn, Na and Cl lines.

From the visual and microscopically examination there were noticed layers of rust, but he Cl lines are the ones that may indicate problems.

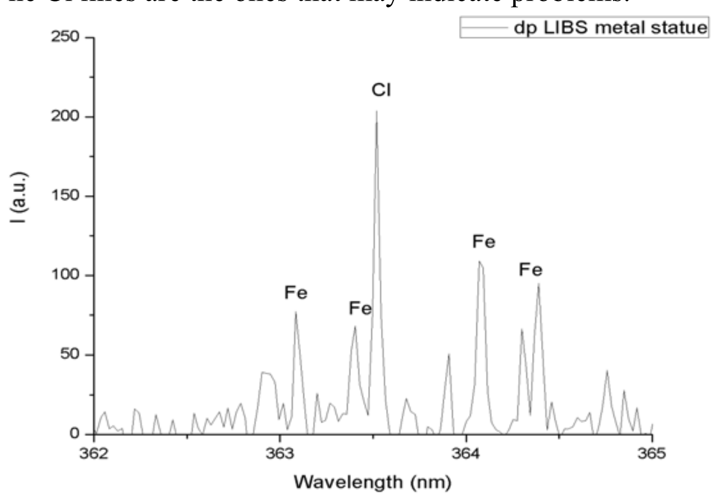

Fig.8. *double pulse* LIBS spectra selection for Fe and Cl lines visualization

Recent studies made on rust indicated that in some cases corrosion-protective rust films ($Fe(OH)_2$) may occur, a stabile pH: *9.31*, being inflicted by the formation of impenetrable self-regenerated rust films (the rate of oxidation being high) that protect the original layer.[8] So rust can sometimes help preserve the artifact original layer in a good condition.

But in the case of the fountain metal surfaces the situation is critical, as proved by the following LIBS spectrum.

The protective rust layer is clearly deteriorated and most probably presents fissures that allow water to infiltrate between it and the original layer, where $FeCl_2$ is formed, that is shortly followed by the incidence of acidic corrosion. Taking into consideration the permanent flux of water, this process will go on and on, further affecting the original layer.

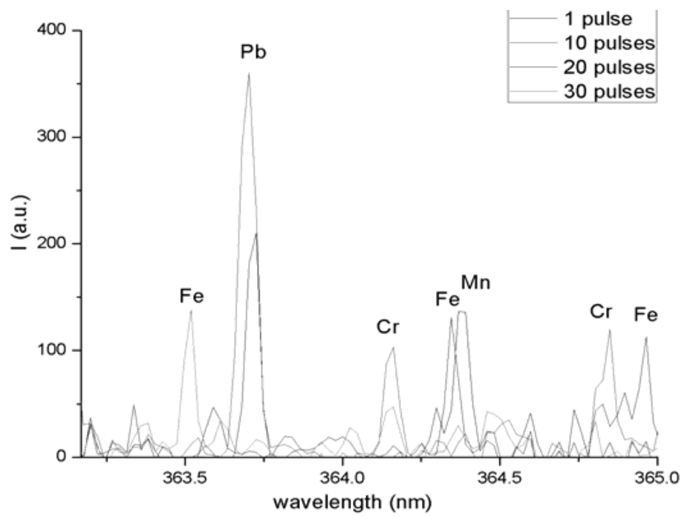

Fig. 9. Stratigraphy investigations: 1 to 30 pulses

In Fig. 9.there is presented a selection of the LIBS stratigraphy spectra acquired using a delay of 2 μs, gatewidth = 6 μs, gain = 220. From the spectrum, Pb lines were identified by the middle pulse, proving that lead based paint was once applied on the metal surface. Some Cr lines appear in the stratigraphy layers above the lead, fact which implies that the casted iron statue underwent chromium based treatment, also. We can observe that as we go deeper in the stratigraphy with the number of pulses, Fe lines come into sight.

As was described before, LIBS stratigraphy investigations are very useful for laser cleaning monitoring. The evaluation of the cleaning depth can easily be made using this technique that generates pulse with pulse a chart of the elements present in the investigated micro-layer. Therefore, in the case of laser cleaning of thick layers of adherent deposits interposed between different levels of paints, we can have an accurate map that can guide us through the right steps.

4. Conclusions

From the visual and microscopic investigations there was noticed that corrosion layers are present, but the corrosion products seemed inactive. A further detailed investigation using *in situ* LIBS micro-destructive technique identified the existence of Cl between the corrosion layer and the original surface, thus the presence $FeCl_2$, which indicates an acid corrosion taking place.

From the stratigraphy investigations undertaken with the help of LIBS technique, the presence of several distinct paint layers were noticed (based on lead or manganese). Also, the pulse by pulse investigation had as a result an elemental map that will be used for the restoration procedure that will follow soon.

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