Roman glasses from Augusta Emerita. Study of degradation pathologies using LIBS

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Introduction

Most of historical glasses have been conserved in burial conditions and experienced degradation processes strongly dependent on their chemical composition and the environment. The techniques used for their characterization are usually destructive. Therefore, they cannot be applied for non-destructible samples from museum collections or from items that must be reintegrated into works of art.

Objectives

- To study the glass surface degradation pathologies and the chemical corrosion mechanisms.
- To characterise glass chromophores and opacifiers, specially in non-destructible samples.

Samples

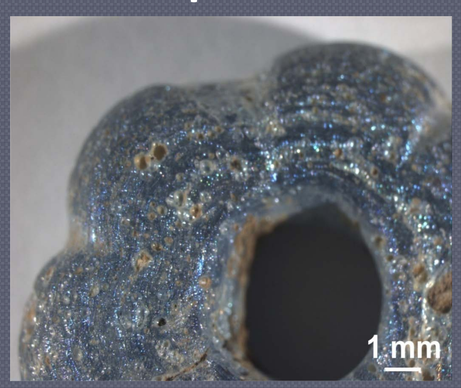
13 samples (seven entire beads and six glass fragments) from the ancient Roman town of Augusta Emerita (SW Spain) have been studied. The samples have different typology, colours and degradation pathologies.

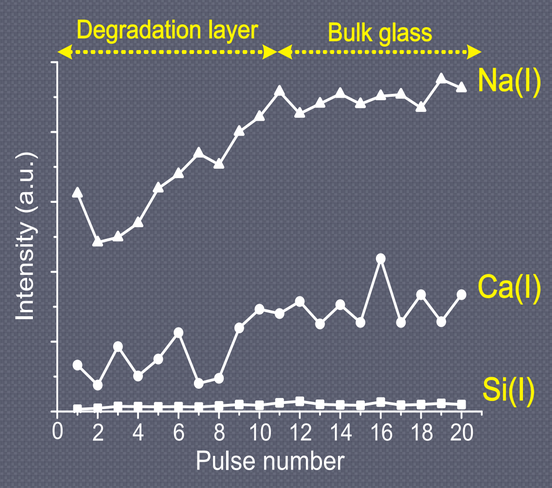
Seven non-destructible beads

LIBS system employed

Pulsed Nd:YAG laser (Q-switched), 266 nm, 5 ns, 10 Hz; with fluences up to 6.6 J cm^{-2}. LIB spectra were acquired in the range 275-600 nm by using 0.30 m spectrograph coupled to a time gated ICCD camera (2151 Andor Technologies).

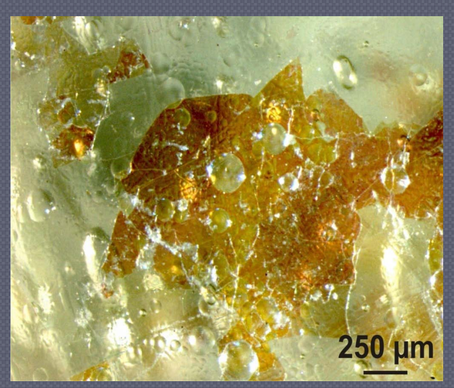
Composition

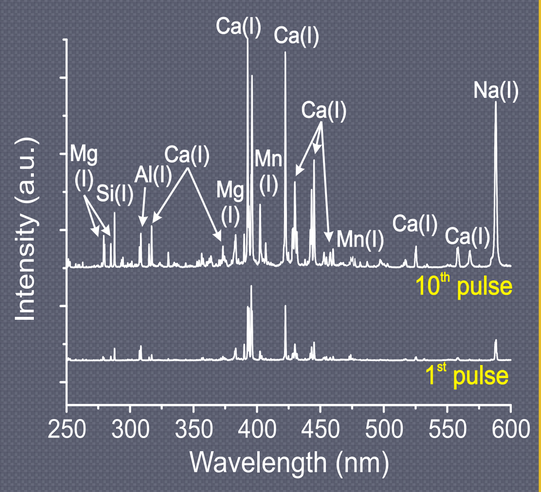




- The analyses from the 1st to the 10th pulses showed an increase of the intensity of the sodium and calcium signals. This is related with the *degradation layer*.
- The intensity of lines from the 10th to 20th pulses was constant as correspond to signals from bulk glass.
- The glass has experienced a PROGRESSIVE DE-ALKALINIZATION from the most external surface to the unaltered bulk glass.

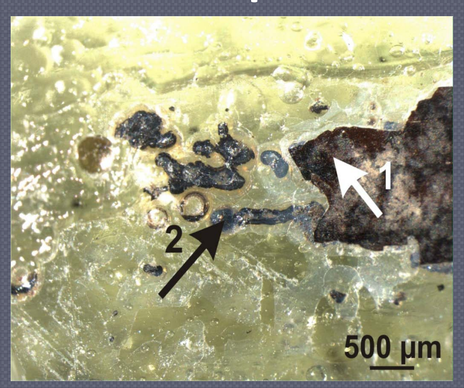
Dealkalinization

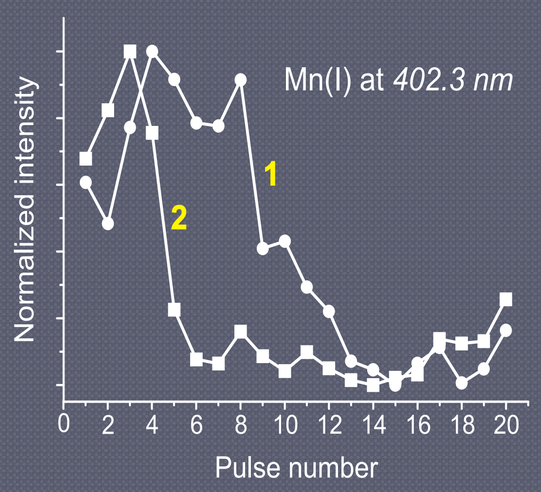




- The intensity of the spectrum assigned to the bulk glass (10th pulse) is *three times more intense* than that attributed to the de-alkalinization layer (1st pulse).
- This fact is related with the RELATIVE DENSITY of the two zones analyzed.
- The bulk glass is characterized by a compact network, whereas the de-alkalinization layer has an open network enriched with silanols ≡Si–OH and water molecules adsorbed by hydrogen bonds.

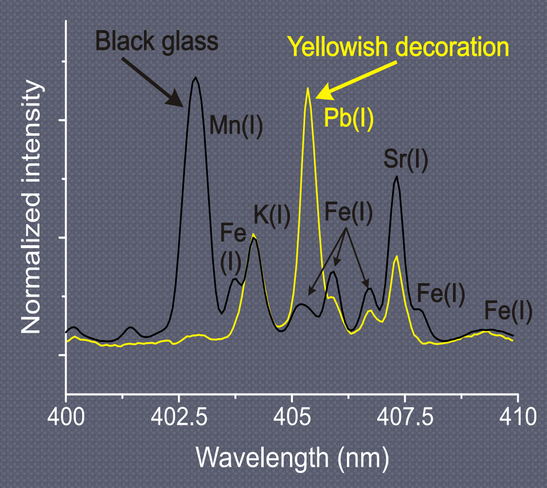
Dark deposits





- Manganese dark deposits appeared as a superficial continuous *dark layer* (circles, 1) or as deeper *isolated deposits* in between the de-alkalinization layers (squares, 2).
- The LIBS stratigraphic analyses focused on the manganese band showed, after eight pulses (circles, 1) or three pulses (squares, 2), an abrupt decay up to 88 % of the original intensity.
- The analyses demonstrated a HIGH MANGANESE CONTENT in these zones.

Decoration



- The optimal technique for detecting chromophores is visible spectrophotometry, but it is a destructive method.
- The CHROMOPHORES detected by LIBS were iron, manganese, copper and cobalt, among others.
- The white decorations exhibited high content of *antimony* as an OPACIFIER ($CaSb_2O_6$, $Ca_2Sb_2O_7$). *Antimony* and *lead* were detected in the yellowish decoration ($Pb_2Sb_2O_7$).

Conclusions

- LIBS, in combination with other conventional analytical tools (e.g. EDS, XRF, visible spectrophotometry), provides valuable information on the chemical composition of historical glasses, as well as on their degradation processes, especially for non-destructible glass samples.
- The LIBS stratigraphic analysis is a very useful tool to determine the depth of corrosion products (de-alkalinization layer and dark deposits).
- LIBS allows detection of major, minor and trace elements in glasses. Consequently, it is an optimal technique to determine chromophores in non-destructible samples with historical value.
- LIBS can be considered as an alternative to other spectroscopic techniques as far as the glasses study is concerned, because it does not require cutting and preparing cross sections, there is no limit in sample size and it only affects to a small sample area (< 200 µm).

Bibliography:

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