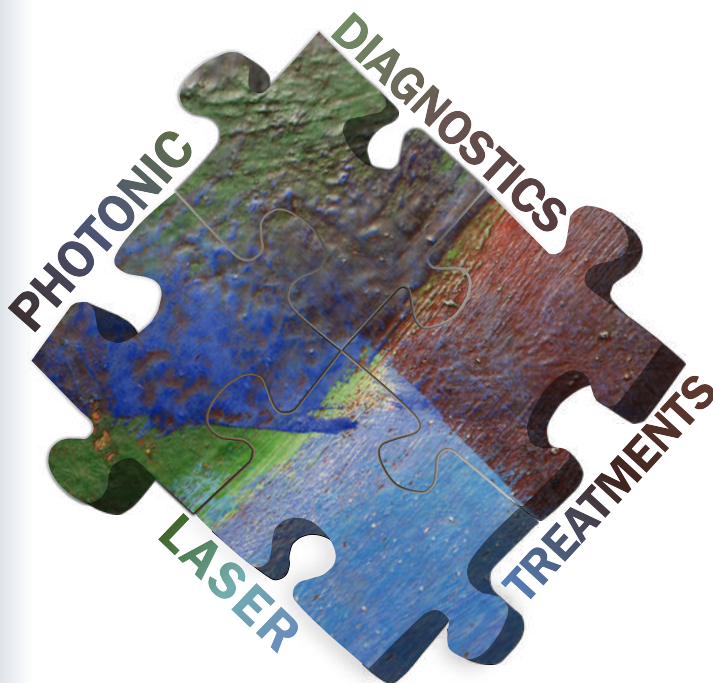


Lasers in the Conservation of Artworks

LAGONA XIII

Florence - September 12-16, 2022



Abstract Book



Consiglio Nazionale delle Ricerche

LIBS vs XRF APPLICATION ON UNDERWATER HERITAGE: THE CASE STUDY OF THE SILVER COINS OF THE FRIGATE “NUESTRA SEÑORA DE LAS MERCEDES”

I. Donate Carretero^{1*}, *M. Oujja*², *M. Martínez-Weinbaum*², *S. Díaz*¹,
*E. García*¹, *M. Bueso*¹, *M. Castillejo*², *M. Martín*¹

¹ Instituto del Patrimonio Cultural de España, Ministerio de Cultura y Deporte, C/ Pintor el Greco 4, Madrid, Spain

² Instituto de Química Física Rocasolano, CSIC; C/ Serrano 119, Madrid, Spain

KEYWORDS: Laser induced breakdown spectroscopy, X-ray fluorescence, Frigate Mercedes, Underwater metallic heritage, Silver alloy.

Underwater cultural heritage entails complex conservation problems. Particularly, metallic artefacts under aerobic marine conditions suffer from severe corrosion that produces thick patinas, in addition to the deposition of concretions of the seabed. The nature of these degradation layers depends on several factors: the original composition of the metallic alloys, along with the minor elements and traces, the metallurgical processes for obtaining metals and manufacturing and the environmental conditions on the seabed [1]. As a consequence, the conservation and study of these metal objects are challenging.

This work presents a comparative investigation using two non-invasive elemental analytical techniques, laser-induced breakdown spectroscopy (LIBS) [2] and X-ray fluorescence (XRF) [3], for chemical characterization of underwater corroded metals.

In this case study, the considered pieces were selected from the treasure of the Spanish frigate “Nuestra Señora de las Mercedes”, a ship loaded with funds and products from the Viceroyalty of Peru and sank by the British Army in 1804 off the coast of Algarve in Portugal. In 2007 the treasure was plundered by the commercial company *Odyssey Marine Exploration*, but after a legal battle in a US court it was recovered by the Spanish State [4]. The pieces are six coins (“reales de a ocho”) made of 925 sterling silver, belonging to two different Spanish-American mints, Potosí and Lima, and produced between the years 1797 and 1804.

LIBS analyses were carried out in air under nanosecond laser

*Correspondence: inmaculada.donate@cultura.gob.es

excitation at 266 nm and XRF studies were performed in the same areas explored by LIBS, using an X-ray tube with rhodium anode and peak voltage of 50 kV.

The comparison of the obtained results indicates that, while XRF is effective in characterizing the main corrosion products of the surface of the coins, such as silver chloride and bromide, copper chlorides and carbonates, LIBS analysis allows to identify the original composition of the metallic core, including minor elements as Ni, Hg and Co, regardless of the patina components. Therefore, the complementarity of both techniques is demonstrated: XRF helps to answer inquiries associated to the conservation and restoration of the metallic pieces and LIBS can solve questions about their core composition and metallurgical techniques.

ACKNOWLEDGEMENTS

This research has been funded by the Spanish State Research Agency (AEI) through project PID2019-104124RB-I00/AEI/1013039/501100011033, by the H2020 European project IPERION HS (Integrated Platform for the European Research Infrastructure ON Heritage Science, GA 871034). Support by CSIC Interdisciplinary Platform "Open Heritage: Research and Society" (PTI-PAIS) is acknowledged.

REFERENCES

- [1] E. Angelini, S. Grassini, S. Tusa. Corrosion and conservation of cultural heritage metallic artefacts: 12. Underwater corrosion of metallic heritage artefacts. European Federation of Corrosion (EFC) Series. Elsevier Inc. Chapters. 2013.
- [2] J. P. Sing, S. Thakur (Eds.). Laser-Induced Breakdown Spectroscopy. 2nd Edition. Elsevier, 2020.
- [3] C. Strelí, P. Wobrauschek, P. Kregsamer, X-ray Fluorescence Spectroscopy, Applications, Encyclopedia of Spectroscopy and Spectrometry, 1999, pp: 2478-2487.
- [4] S.G. Ramirez, C. M. Alonso. El último viaje de la fragata Mercedes. La razón frente al expolio. Un tesoro cultural recuperado. RdM. Revista de Museología: Publicación científica al servicio de la comunidad museológica, 2014, no 61, pp. 89-99.