LIBS in cultural heritage: recognition and identification of objects in an underwater archaeological shipwreck

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Nowadays, one of the most important areas of interest in archeology is the characterization of the submersed cultural heritage. Mediterranean Sea is rich in archaeological findings due to storms, accidents and naval battles since prehistoric times. Chemical analysis of submerged materials is an extremely valuable source of information on the origin and precedence of the wrecks, and also the raw materials employed during the manufacturing of the objects found in these sites. Nevertheless, sometimes it is not possible to extract the archaeological material from the marine environment due to size of the sample, the legislation or preservation purposes. In these cases, the in-situ analysis turns into the only alternative for obtaining information. In spite of this demand, no analytical techniques are available for the in-situ chemical characterization of underwater materials.

The versatility of laser-induced breakdown spectroscopy (LIBS) has been successfully tested in oceanography [1]. Advantages such as rapid and in situ analysis with no sample preparation make LIBS a suitable alternative for field measurements. To further exploit the inherent advantages of the technology, a mobile fiber-based LIBS platform capable of performing remote measurements up to 50 meters range has been designed for the recognition and identification of artworks in underwater archaeological shipwrecks. The LIBS prototype featured both single-pulse (SP-LIBS) and multi-pulse excitation (MP-LIBS) [2]. The use of multi-pulse excitation allowed an increased laser beam energy (up to 95 mJ) transmitted through the optical fiber. This excitation mode results in an improved performance of the equipment in terms of extended range of analysis (to a depth of 50 m) and a broader variety of samples to be analyzed (i.e., rocks, marble, ceramics and concrete). In the present work, the design and construction considerations of the instrument are reported and its performance is discussed on the basis of the spectral response, the remote irradiance achieved upon the range of analysis and its influence on plasma properties, as well as the effect of the laser pulse duration and purge gas to the LIBS signal. Also, to check the reliability and reproducibility of the instrument for field analysis several robustness tests were performed outside the lab. Finally, the capability of this instrument was successfully demonstrated in an underwater archaeological shipwreck (San Pedro de Alcántara, Malaga).

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References:
[1] S. Guirado, F.J. Fortes, V. Lazic and J.J. Laserna, *Spectrochim. Acta Part B,* **137**, 74-75 (2012).
[2] S. Guirado, F.J. Fortes and J.J. Laserna, *Talanta,* **137**, 182–188 (2015).