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CHEMICAL FINGERPRINTS IN AN UNDERWATER ARCHAEOLOGICAL SHIPWRECK USING A REMOTE LASER-INDUCED BREAKDOWN SPECTROSCOPY SYSTEM**M. López-Claros, F.J. Fortes, S. Guirado, J.J. Laserna**

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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. Sometimes extracting the archeological material from the marine environment is not practical due to the size of the sample, or is not permitted by the legislation or preservation practices. In these cases, the in-situ analysis turns into the only alternative.

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. A fiber-optics-based remote instrument 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). 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 this work, parametric studies in the laboratory such as gas flow pressure, beam focal conditions and angle of incidence, among others, were performed to optimize the best conditions for field analysis. Finally, results obtained in these field trials confirmed the capability of remote LIBS for in-situ analysis of underwater archeological samples.

[1] S. Guirado, F.J. Fortes, V. Lazic and J.J. Laserna, *Spectrochim. Acta Part B* 74-75 (2012) 137.