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LIBS ANALYSIS OF ARCHAEOLOGICAL MATERIALS UNDERWATER

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Laser-ablation based methods are widely used as an advanced tool in the conservation of cultural heritage (laser cleaning of artworks), as well as for the chemical analysis of sample of interest. In this sense, analytical response provided by LIBS offers additional information concerning the environmental processes involves during the oxidation of artworks. One of the LIBS applications receiving more attention is the chemical analysis of submersed materials. Preliminary researches have demonstrated the capability of LIBS for the chemical analysis of archaeological materials underwater. Objects present in a sub-aquatic archaeological site must be catalogued and possibly restored underwater, especially when highly oxidized surfaces are encountered. LIBS inspection underwater offers the possibility for material recognition and ensure the chemical composition without needed of extract the artwork from the submersed archaeological site. The possibility to perform in-situ measurements, and its high spatial discrimination and speed of analysis is the main advantages of LIBS over other analytical techniques normally used in routine analysis.

LIBS TECHNOLOGY

LIBS technology could be considered as an alternative method in cultural heritage analysis. LIBS is based on the laser-matter interaction when a laser pulse of high power impacts the sample surface to generate a microplasma of high temperature and electron density.

Figure 1. Schematic diagram of a portable LIBS instrument used for underwater cultural heritage analysis.

Pulses from a laser source are focused on the sample using an optical assembly. Then, the plasma light (containing the analytical information concerning the sample) is collected and transported to the detector. The characteristic atomic emission peaks in the LIB spectrum enable identification of the elements contained in the material and establish the abundance of elements in the sample. In the case of the instrument employed in AQUALAS project, the laser beam is directed to the sample surface through a optical fiber cable of 50 meters. Figure 1 shows a schematic diagram of a portable LIBS instrument used for underwater cultural heritage analysis.

LIBS ADVANTAGES

Advantages of laser-induced breakdown spectroscopy (LIBS) in cultural heritage analysis are:

- Analysis at atmospheric pressure and room temperature
- No sample restriction in size and shape
- In-situ analysis in real environments
- Good lateral and in-depth resolution
- Fast analytical response
- Qualitative and quantitative analysis
- Spot size in the order of a few micrometers in diameter
- No destructive analysis
- Capability for remote and stand-off analysis

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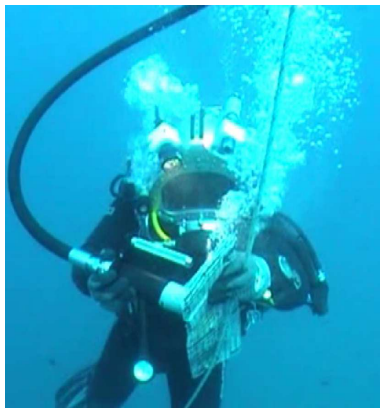

Figure 2. Photo of the LIBS probe taken during a LIBS analysis underwater (30 m).

UNDERWATER LIBS APPLICATIONS

In the last few years, the Laser Laboratory of the University of Malaga has designed and constructed different portable systems for stand-off and in-situ applications. A photo of the LIBS probe taken during a LIBS analysis underwater at 30 meters deep in the coast of Malaga is shown in Figure 2. A typical LIBS spectrum of an archaeological bronze underwater is presented in Figure 3. The emission lines of Cu, Pb, Zn and Sn were identified in the spectra.

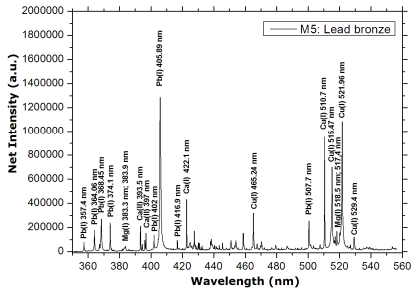

Figure 3. Chemical characterization of an archaeological bronze underwater.

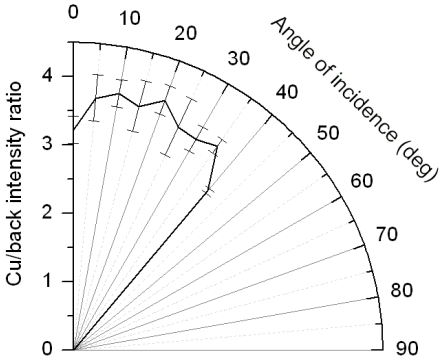

Figure 4. Evolution of the LIBS signal as function of the angle of incidence.

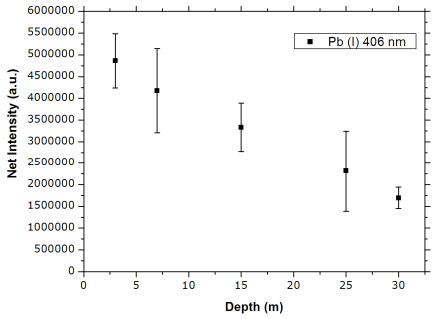

Figure 5. Evolution of the LIBS signal as function of the depth during the underwater analysis.

LIBS analysis underwater is not a trivial task. In a first step, parametric studies in laboratory such as the gas flow pressure, the laser-to-sample distance and the angle of incidence (Figure 4) were achieved to optimize the better conditions for field analysis. A gas flux was applied to create sample-air interface prior to the laser ablation and avoid the water incoming inside the instrument. For this reason, the gas flux pressure needs to be higher than the external pressure. The evolution of the LIBS signal as function of the depth during the underwater analysis is shown in Figure 5.

CONCLUSIONS

Minimal sample destruction and the portability of laser methods make LIBS an ideal technique for cultural heritage analysis underwater. Optimization of experimental parameters allows the LIBS analysis at 50 meters depth.

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