

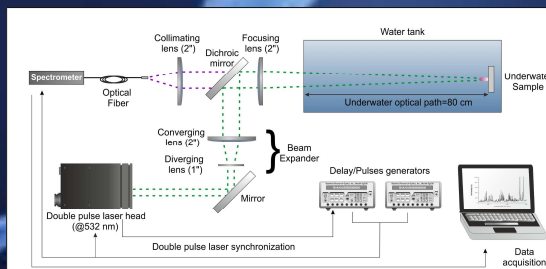
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INTRODUCTION

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. Advantages such as rapid and in situ analysis with no sample preparation make LIBS a suitable alternative for field measurements. Laser Laboratory of the University of Malaga is evaluating the capability of stand-off LIBS (ST-LIBS) for seafloor exploration (2000-3000 meters deep). Several experiments including the transmission of laser radiation through water or the influence of the range of analysis over LIBS signal, has been performed in laboratory inside a water tank. Preliminary results are quite satisfactory and suggests the possibility of integrating LIBS technology in a remotely operated vehicle (ROV) for geological/mineralogical exploration, cultural heritage investigation and/or the inspection of oil and gas pipelines in the seafloor, among others.

EXPERIMENTAL SETUP

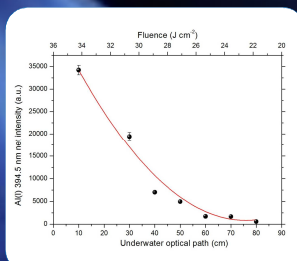
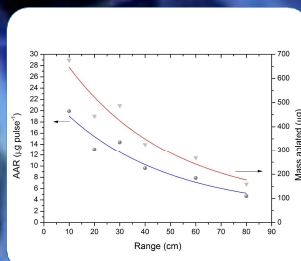


✓ Laser: A pulsed Q-switch 532 nm Nd:YAG twins laser (250 mJ pulse⁻¹; 10 Hz; 5 ns pulse width) was used as excitation source. The beam was 4x expanded by an optical system and then focused on the sample submersed in the water tank.

✓ Spectrometer: Crossed Czerny-Turner scheme with a holographic diffraction grating of 1200 lines mm⁻¹ (Avantes, AvaSpec-2048-USB2 model). This configuration provides a spectral resolution of 0.1–0.2 nm/pixel in the spectral range of 300–550 nm.

ST- LIBS ANALYSIS OF ARCHAEOLOGICAL MATERIAL UNDERWATER

Influence of range of analysis over LIBS signal



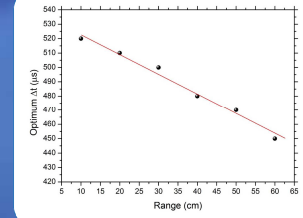
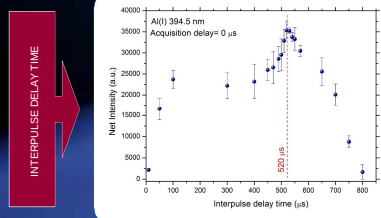
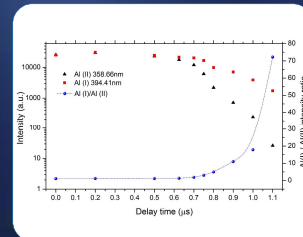
With the objective to evaluate the capability of ST-LIBS for seafloor exploration, the range of analysis has been increased up to 80 cm. LIBS spectra were acquired on a submersed Al target. As observed, the standoff LIBS signal emission at 394.5 nm drops markedly with increasing operational range. This fact is attributed to two main contribution:

- The delivery of tightly focused laser pulses towards the underwater optical path.
 - The transmission of the light emitted by the laser-induced plasma will be also affected by the absorption spectrum of water in the optical path back to the spectrometer.
- The laser transmission progressively decreases within the underwater optical path, reducing the laser fluence from 34 J cm⁻² at 10 cm to approximately 22 J cm⁻² at 80 cm. Furthermore, both average ablation rate (AAR) and mass ablated follow a similar trend that Al (I) 394.5 nm, which could explain the LIBS signal behavior. Moreover, for long distance analysis (i.e. ST-LIBS), plasma light collection should decay with the inverse square range for identical plasma conditions. However, for an underwater optical path up to 80 cm, this factor is negligible. Nonetheless, the presence of particulate matter may alter the collecting light as a result of different phenomena such as scattering and absorption.

As a detail, the focal distance in water becomes longer than its value in air, due to the different refraction index of air and water.

Optimization of temporal conditions

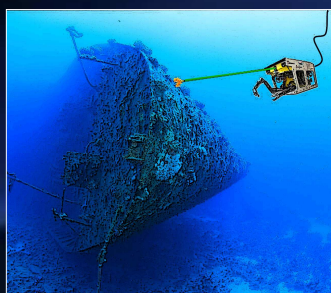
The use of DP-LIBS appears to be the best way to perform underwater LIBS analysis. In this case, chemical characterization is obtained by focusing two suitably delayed laser pulses in the same volume, directly onto a submersed Al target. Due to this circumstance, optimization of temporal conditions turns critical for improving the analytical response. Figure shows temporal evolution of the spectral lines of Al (I) 358.66 nm and Al (II) 394.41 nm on a logarithmic scale. The different trend in the time evolution of atomic and ionic species, due to the recombination of ions with electrons during the plasma cooling, is well evident. This behavior is also observed in the Al (I) / Al (II) ratio. From here, a delay time of 0.7 µs was fixed.



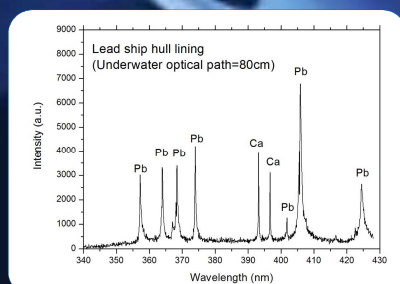
In fact, the plasma features of DP- LIBS are strongly dependent on the first pulse induced bubble evolution. The life-time of the bubble is in the order of a few hundreds microseconds, while the duration of LIP in the bubble is of few microseconds. The time delay yielding the maximum expansion is more suitable for enhancing the emission spectrum sensitivity. ST-LIBS analysis has been performed in a range up to 80 cm. The bubble expansion remarkably depend within the range of analysis. The higher the range, the lower laser fluence, affecting to the expansion of the laser-induced bubble and consequently on the optimum Δt.

Application for underwater archaeology

The concept of stand-off LIBS underwater

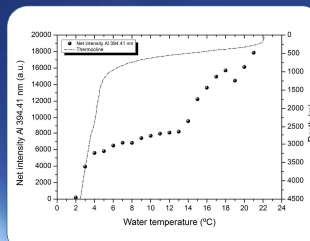


Archaeological material



Finally, after optimization of the experimental conditions, a real archaeological sample was analyzed at 80 cm underwater optical path. The piece was a lead lining from the wreck of *Delta II* (a boat from Italy) and provided by the Subaquatic Archaeological Centre, located in Cadiz (South of Spain). As shown, LIBS spectra is mainly composed by Pb. The main emission lines are labelled in the spectra. This results demonstrated the potential of ST-LIBS for the chemical characterization of archaeological materials at distance and suggest the possibility of integrating LIBS technology within a remotely operated vehicle (ROV). The idea and concept of underwater ST-LIBS is illustrated in the picture. This application could be considered as a new LIBS frontier and open the door for geological/mineralogical exploration, cultural heritage investigation and/or the inspection of oil and gas pipelines in the seafloor (3000-4000 meters deep).

Effect of water temperature over LIBS signal



In ST-LIBS underwater, the ambient conditions (water temperature, depth...) considerably affect to the LIBS signal. In the case of water temperature, the thermocline is a layer within a water body where the temperature fastly changes with depth. As shown, LIBS intensity falls almost linearly with temperature until 3°C. No signal was detected below this temperature. For comparative purposes, the thermocline (water temperature as function of depth) is also plotted in the graph. In this sense, LIBS analysis could be feasible until a depth of approximately to 4500 meters. On the other hand, it is worth mentioning that the effect of pressure has not been evaluated here.

CONCLUSIONS

- ✓ The potential of ST-LIBS for the underwater chemical characterization of archaeological materials at distances up to 80 cm has been demonstrated.
- ✓ The underwater analysis of a wide range of materials (including metals, ceramic, rocks and marbles, among others) can be performed in a marine environment.
- ✓ The DP-LIBS configuration turns into the best alternative for underwater LIBS analysis. The optimization of temporal conditions is a key factor for enhancing the emission spectrum sensitivity.
- ✓ The effect of water temperature and the influence of the range of analysis over LIBS signal has been also evaluated in this work. No signal was detected below 3°C.
- ✓ The results obtained suggest the possibility of integrating LIBS technology within a remotely operated vehicle (ROV) for geological and mineralogical application in the seafloor (3000-4000 meters deep).