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Remote method and set-up for the characterization of the submerged archaeological remains

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Laser Induced Breakdown Spectroscopy is a technique that is proven its numerous advantages for different types of applications, and now its use range have been increased, giving us the possibility of making underwater investigation on cultural heritage objects, right in the environment where they are placed, without requiring any sampling or removal of the object from its original conditions. In the present paper we present results – part of a complex study - concerning LIBS underwater investigations with the purpose of identification of the chemical composition of archaeological artifacts that are found in saline mediums.

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1. Introduction

Along the times, unpredictable irreversible and fast phenomena have damaged precious archaeological remains right in the moment when they were apparently saved for long time. Today, the transfer of objects into free atmosphere from underwater environment is strongly limited before a complete characterization of the constituent material and of the conservation status of the remains.

The available instrumentation for safe non-contact archaeological material characterization is still limited and not enough tested up to now. The optoelectronic methods for investigation and diagnosis in art restoration and terrestrial archaeology are very promising. Particularly laser spectroscopy method LIBS – Laser Induced Breakdown Spectroscopy - is one of the very effective methods [1]. It is a non-contact, remote method and micro-invasive (very little amount of material is consumed), easily focused on details of the surface and easily controlled for the multilayer of the characterization structures [2,3].

There is no doubt that ancient objects that have been preserved underground or underwater for years have to be cared for appropriate conservation methods once they are exposed to the air. Conservation is usually done in a laboratory but sometimes objects are so fragile that some work to save or stabilize them must be attempted in the field. The type of materials is crucial regarding the conservation intervention procedure, and, particularly, organic materials decay more quickly [4].

The detection of different materials immersed in seawater has been successfully studied by means of Laser Induced Breakdown Spectroscopy after 2000.

Different sort of materials that are usually found in the underwater archaeological parks, such as iron, copper-based alloys, precious alloys, marble and wood have been examined by induced plasma using a Q-Switched Nd:YAG laser operated at 1064 nm in a dual pulse mode [5,6].

The present work is focused on comparative study of several investigations on same sample, but through different media – water with different salt concentration.

Qualitative chemical analysis was performed on submerged copper samples, after generating calibration curves with standards of similar matrix composition. A series of LIBS investigation has been carried out on the same sample in free environment (before the immersion).

The investigation relevance related to induced disturbance from the fluid was studied and compared with the known sample's composition. Because slight spectral modifications were expected due to possible sedimentary layers deposited on the underwater remains, the prepared concentrations of NaCl were under known maximum concentration (35.7 gr/100ml@100°C).

Further developments will address the signal detection improvement and signal transportation from deeper tanks or from on-site conditions. Experimental results are also sustaining the combination of optoelectronic applications with laser scanning of objects interior.

2. Experimental set-up

In all the experiments the double pulse LIBS method was applied. It consists in focusing on the target two pulses, with a 1-100 μs delay. The double pulse technique was selected due to the fact that in the cases of submerged objects the first laser pulse will form a weak plasma in an air bubble created in the aqueous medium and the second laser pulse creates a secondary plasma in the rarefied medium formed, exciting further more the ionized chemical compounds. The main condition for the best applicability is that the second laser pulse should hit the air bubble in the moment of its maximum expansion.

A typical LIBS setup is described in Fig. 1, underlining in the grey triangle the optoelectronic part that is added for double pulse investigations: a second laser and its focus system, and a pulse generator that allows us to set the delay between the two laser pulses.

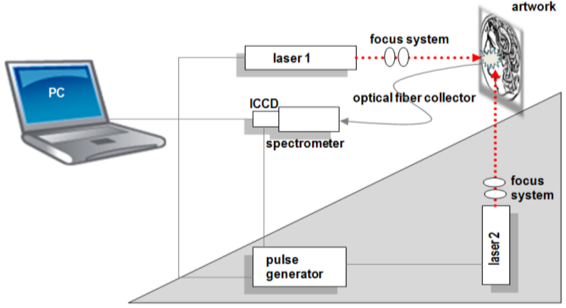

Fig. 1. Single and double pulse LIBS set-up.

The investigated object consisted in a plain copper foil sample with the length of 4 cm and the width of 5 cm, as the underwater archaeology is very rich in copper artifacts starting from copper and bronze nails, coins, sculptures, ingots etc. and ending with considerable remains from sunken ships - in all these cases a major factor in their preservation and conservation implies in-situ underwater investigations that would not affect or change their current environmental conditions.

The quantity of NaCl necessary for obtaining the desired concentrations for the LIBS underwater measurements in saline media was measured using an analytical balance. After accurate measurements the NaCl was dissolved in distilled water by completing one hundred mixture rotations for each probe. *Table 1* describes the density, mass and optical transmission values corresponding to the 3 salt concentrations.

Table 1. The density, mass and transmission values corresponding to the selected concentrations

Concentration (%)	Density (kg/m^3)	NaCl mass (g/l)	T@355nm (%)
6	1041.3	62.478	96.3655
12	1085,7	130,24	95.3826
24	1180,4	283,296	94.8584

The optical transmission through the three saline solutions was measured using a common spectrophotometer. The graphs obtained are presented in Figure 2.

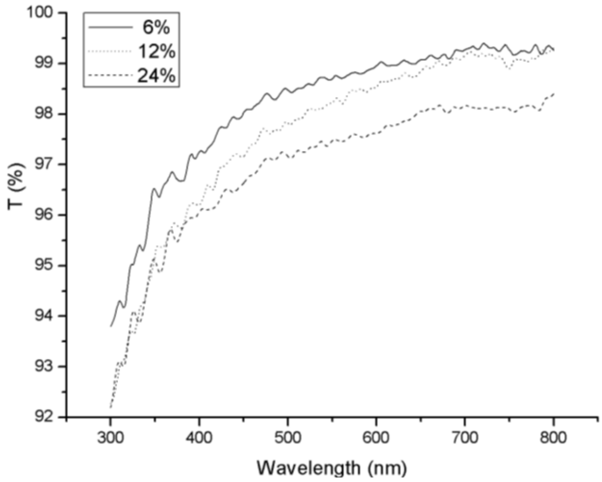

Fig. 2. Optical transmission graphs for the 3 concentrations of NaCl in distilled water.

The LIBS double pulse laboratory setup consists in two Nd:YAG pulse lasers – one emitting at 1064 nm and the other one at 355 nm – with 8 ns pulse duration and 1Hz frequency. The lasers are triggered by an external controller that also allows us to set the delay between the two pulses. The emitted light from the plasma plume is collected by a fiber optic collector - accurate for underwater investigations, and transmitted through an optical fiber to an Echelle spectrometer. The spectrometer is coupled to a gateable intensified CCD camera for detection of the dispersed light. The overall linear dispersion ranges from 0.05 nm/pixel (at 170 nm) to 0.25 nm/pixel (at 1100 nm). The laboratory setup is shown in Fig. 3.

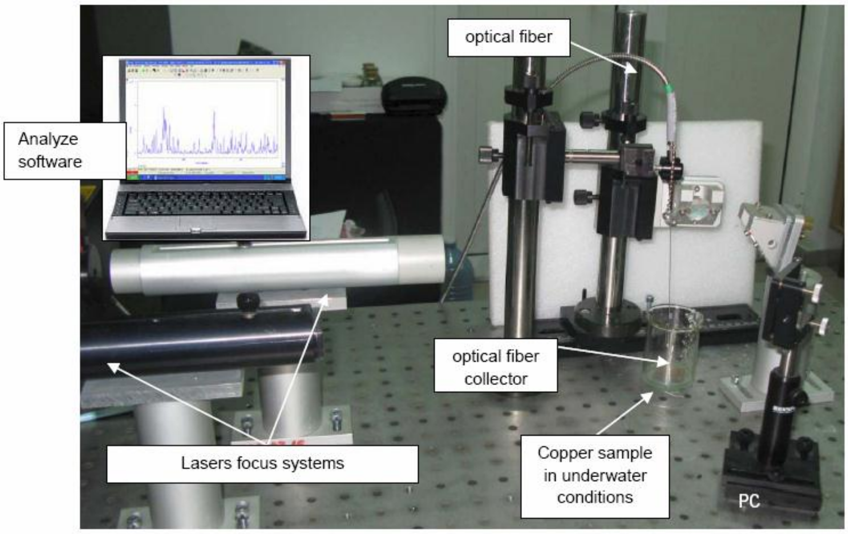

Fig. 3. The laboratory setup for underwater LIBS investigations.

3. Experimental results

The LIBS investigations have provided a lot of information, here is presented a selection of the spectra for 324 nm - 328 nm interval, for all three NaCl concentrations: 6%, 12% and 24% (Fig. 4,5 and 6).

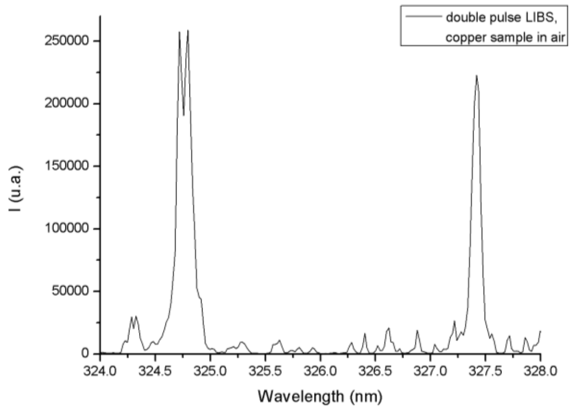

Fig. 4. Double pulse LIBS for copper sample in air.

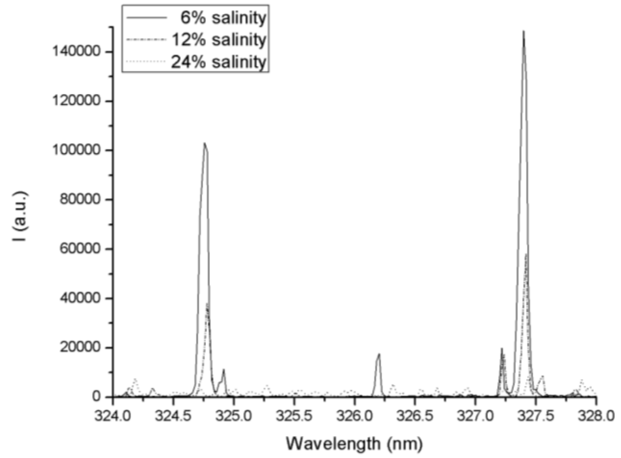

Fig. 5. Underwater double pulse LIBS for Copper sample submerged in different saline concentration.

The graphs above present a selected part of the recorded spectra analyzed using a specialized LabVIEW application. The significant copper lines that were found in this spectrum selection are 324.7 nm and 327.3 nm. The underwater LIBS spectra were recorded for three cases, using collinear double pulse regime: 1064 nm wavelength and 355 nm wavelength, the delay between the two pulses was set at 3 µs. In all the cases the acquisition was made with a delay of 2µs from the last laser pulse, and with a gate width of 8 µs.

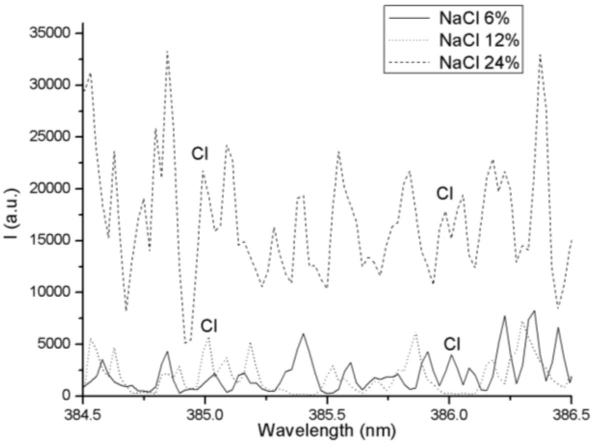

Fig. 6: Underwater double pulse LIBS for the saline compound identification

Besides the copper lines, in the LIBS spectra there were found lines belonging to the salt composites. In Fig. 6 there is presented a selection of the obtained spectra for the 384.5 – 386.5 nm interval where is shown the Cl II lines existence at 385 nm and 386 nm.

4. Conclusions

The current research generates interesting preliminary conclusions, but - very important - a clear direction for further experiments. The identification of the main specific lines in all spectra and the quality of the collected signal supports the observation that in the case of the three saline concentrations (6%, 12% and 24%) there is a poor relation between the liquid transparency indicated by the optical transmission measurements and the signal collected, an evidence that the determination was done into a laser generated air bubble. The collected signal in the case of 24% salt concentration solution is weaker – but still present – due to a loss of intensity during the transmission of the bubble forming IR radiation (1064 nm) throughout the solution's salt ionized particles (Cl, Na). As a forthcoming conclusion, the correlation between the plasma signal intensity, laser beam intensity and the liquid's transparency implies a new series of experiments with expected results to some extent. Strong variations of signal are noticed in the cases of low transparency, but have not been systematically studied yet. Thus, clarification of these aspects is necessary for further LIBS analysis which involves variable transmission coefficients that will be generated by the expulsion of sediment ablated material, with the intention of investigating in-depth archaeological artefacts' layers, as well as the sediments above them. The improvement of the optical instrumentation is as important as the ablation conditions, and it is taken into consideration for further development.

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