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UNDERWATER LIBS INVESTIGATIONS SETUP FOR METALS' IDENTIFICATION

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LIBS este o tehnică analitică promițătoare ce este folosită în detectarea compoziției chimice a materialelor. În lucrarea de față sunt prezentate rezultate preliminarii obtinute pe probe de metal în condiții subacvatice, în vederea investigarii in situ a obiectelor arheologice, fără a le sustrage din microclimatul lor. Investigatiile au fost făcute în principal pe probe de cupru, dar este prezentat şi un studiu de caz pe o broşă ce face parte dintr-o colecție particulară. Rezultatele obținute sunt mai mult decat satisfăcătoare, iar setup-ul LIBs a fost ajustat pentru aceste cazuri speciale ce implică măsurători în mediu acvatic.

LIBS is a promising analytical technique that can be used to detect the chemical composition of various materials. In this paper we have focused on preliminary investigations made on metal samples in underwater conditions in order to investigate archaeological objects without pulling them out of their microclimate. The investigations were made on copper samples (in air and in water environments) and they envisage also a study case in a broche from a private collection. The results obtained were more than satisfactory and the experimental air LIBS setup was adjusted for specific underwater in-situ investigations.

Keywords: LIBS, underwater, metal

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is developing more and more as the time passes, proving to be a reliable technique with many advantages, including on-line, real time, standoff and multi-element detection etc. Till now most of the LIBS applications, developed in the past 2 decades, were focused on investigations with a wide range of applications, involving many areas - one of the most sensitive consisting in the Cultural Heritage field.

The newest approach that enhances the advantages that this powerful photonic technique brings consists in its applicability in underwater conditions. This is a major plus to the conservation/restoration area because of the given possibility to investigate an object without pulling it out of its microclimate. It is a

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well known fact that most of the underwater archaeological objects are suffering an accelerated degradation process from the minute they are removed from water. Not to mention the current atmospheric pollution degree that also may contribute more to their ruin [1].

The present paper presents the first Romanian preliminary investigations made on underwater samples, experiments made with current air LIBS setups in order to see the limitations and the characteristic features necessary, as well as to adjust and develop a specific underwater in-situ setup. A very important fact is that the LIBS underwater setup is part of a mobile laboratory - a complex instrument with special applications in cultural heritage conservation and restoration, bringing in the possibility to perform analysis using non-invasive photonic techniques, non-contact in situ, without being necessary sampling and then their preparation. The included techniques and methods are aimed to a large range of materials and are extremely versatile [2].

2. Underwater LIBS basics

Spectrally resolved plasma emission generated by laser ablation of solid targets or by breakdown in different mediums (air or liquid) allows a qualitative investigation of the elemental composition of the samples. It is also possible to do quantitative determinations (concentration of the elements) by applying a calibration on reference materials.

In the case of the underwater LIBS investigations, focusing a short laser pulse (8ns) with sufficient energy into a liquid, a dielectric breakdown takes place generating plasma. The rapid heating of the liquid is followed by an explosive expansion and formation of a gas bubble [2]. The intensity of the plasma emission produced in bulk liquids (water in this case) is generally lower than at water–air interface due to several factors that include: water absorption of the laser and plasma emission and their scattering on suspended particles and micro-bubbles, radiation shielding by the high density plasma [3] and fast quenching in the dense medium and the emission lines are strongly broadened by the high electron plasma density [4, 5]; all effects mentioned in the previous paragraph had been proven to lead to a fairly poor signal for the single pulse LIBS measurements. This is why a double laser pulse LIBS is preferable to be used, not only in air environments, but also for the underwater experiments. It the case of the underwater investigations, the first laser pulse produces a cavitation bubble in water and the second laser pulse (send with an ns delay) excites the plasma inside the bubble, a relatively intense and narrow spectral emission being observed. A major factor that must be taken into consideration where the double-pulse LIBS are applied consists in delay time between the 2 pulses. Form the reported studies we know that the maximum LIBS signal is obtained if the second pulse hits the sample when the gas bubble produced by the first pulse reaches its maximum expansion. The time evolution and maximum radius of the laser-induced air bubble in a certain liquid are strongly dependent on the experimental conditions, such as laser wavelength, pulse duration and numerical aperture after the focusing lens. Different experimental aspects, important for the improvement of the LIBS signal intensity are up to further discussions.

3. Experimental setup

The experimental setup we have used for this preliminary investigations is mostly the basic LIBS setup: both laser pulses are generated by a Nd:YAG Q-switched laser, 1Hz frequency, pulse duration: 8 ns. The first one is emitted at 1064 nm and the second one at 355 nm wavelength, and they are externally triggered by a control unit, that also allows us to set the appropriate delay between the two laser pulses. A quartz optical fibre collects the plume's emission, carrying it to a spectrograph coupled to a time gated ICCD that enhances and transmits the signal to an acquisition board mounted on the computer. The acquisition parameters are set up using special software, provided by the spectrograph manufacturer.

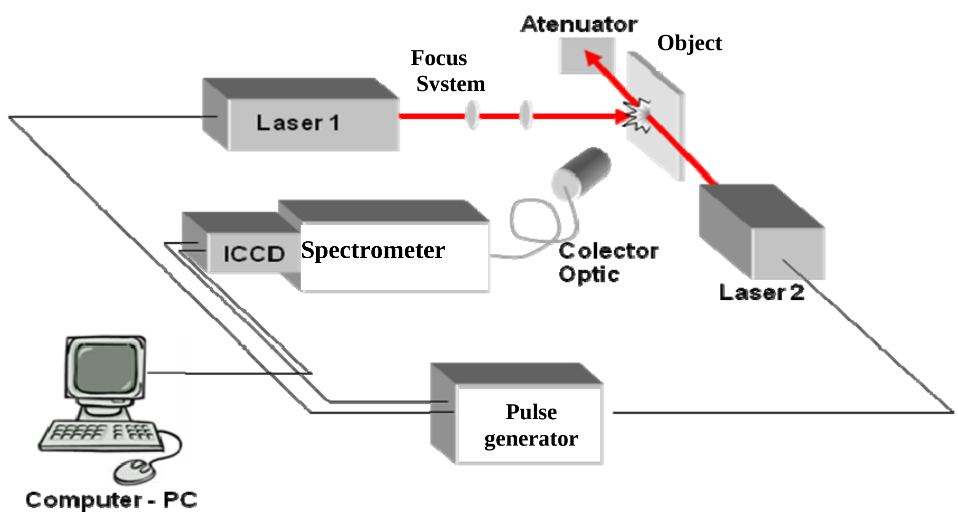


Fig. 1: The experimental setup for LIBS

4. Results and discussions

The underwater LIBS investigations were made on several metals, from which we present below the copper and silver data. All the samples were subjected to LIBS investigations in air and underwater, the data being recorded using 1 pulse method, as well as the 2 pulses method in order to calibrate and adjust our LIBS setup for greater underwater performances. The results obtained are accurate and precise, and give us precious information about the elemental composition of the analyzed samples.

LIBS on Copper samples:

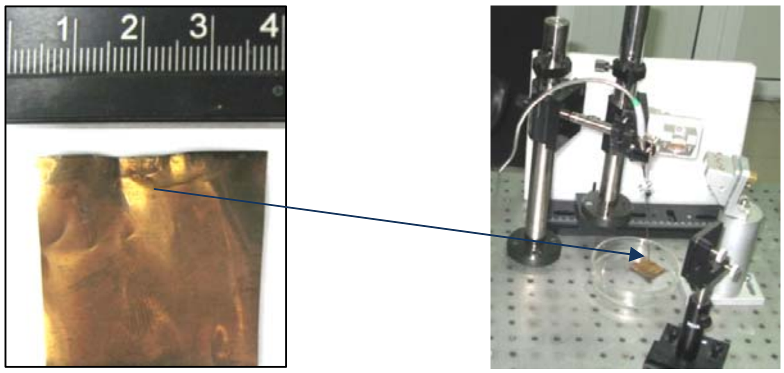
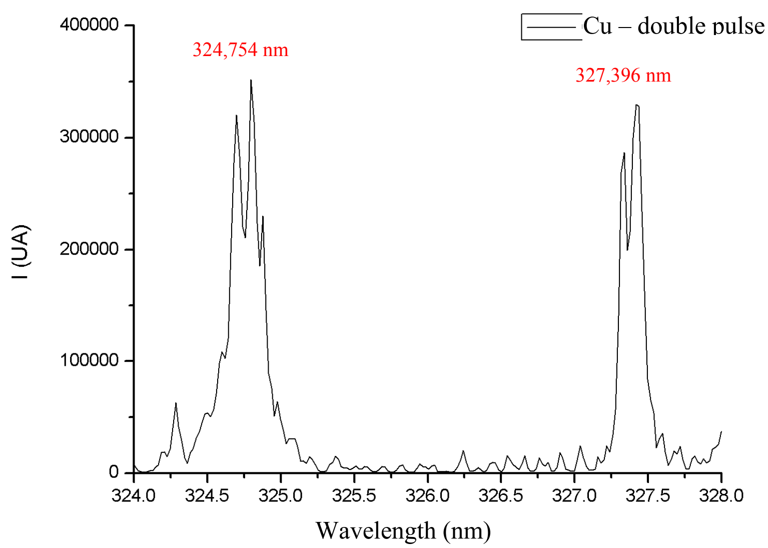
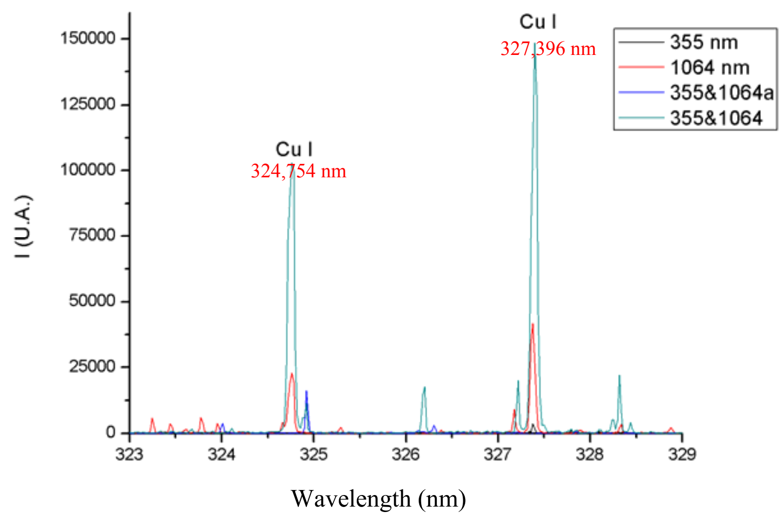


Fig. 2: The copper sample used in the investigations

Further on, we present you a part of the graphs comprised in the study.



Graph 1: double pulse in air

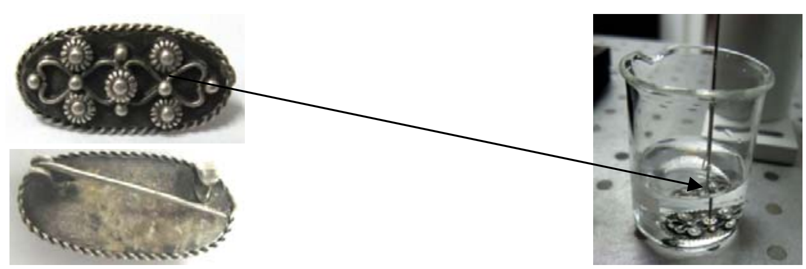


Graph 2: underwater LIBS single pulse: 355, 1064 nm, and double pulse

The graphs above present a selected part of the recorded spectra, for LIBS in air (graph 1) and LIBS underwater (graph 2), analyzed using a specialized LabView application. The significant copper lines that were found in this spectrum selection are the ones at 3247.54 nm and 3273.96 nm, marked on the graphs. The underwater LIBS spectra were recorded for three cases, using radiation from the 1064 nm wavelength, 355 nm wavelength and with both 1064 and 355 nm – double pulse technique - the delay between the two pulses was set at 3 μs. The LIBS spectrum in air was recorded using the double pulse setup. 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.

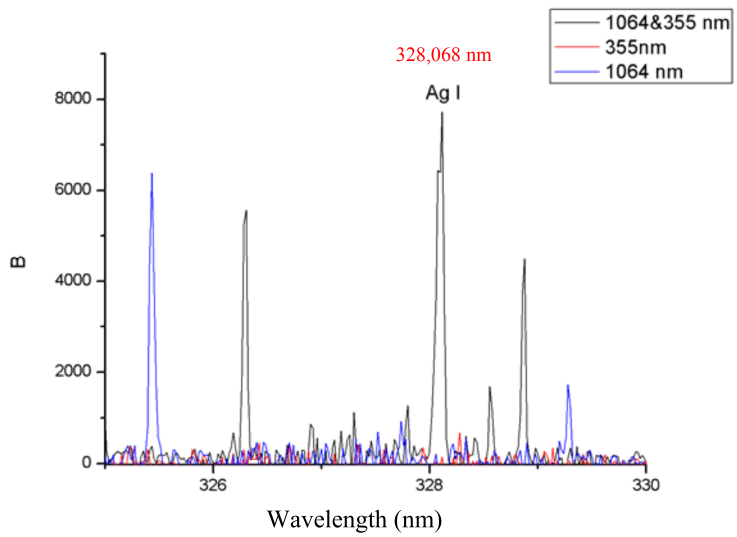
Case study – Silver Broche:

The object under investigation is a contemporary broche, part of a private collection, that was given to us by its owner in order to analyse the elemental composition and to determine whether it's made from silver, or just silver plated.

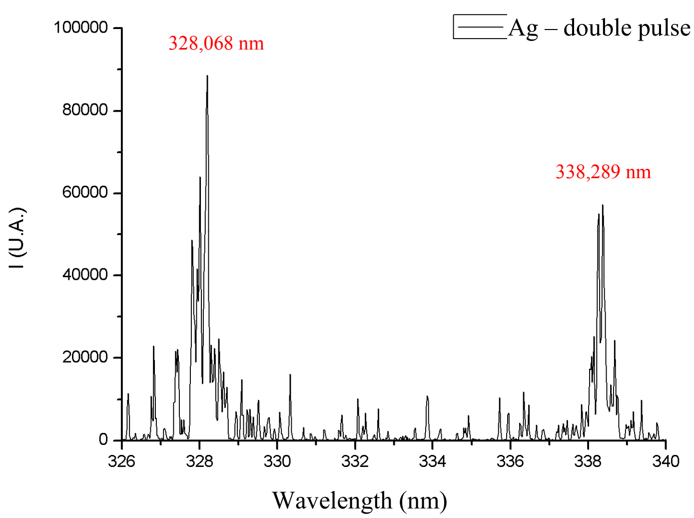


a. b.

Fig. 3 – Photos of the broche under investigation: a. front and verso, b. in underwater setup



Graph 3: underwater LIBS: single pulse: 355, 1064 nm, and double pulse



Graph 4: double pulse in air

A selected part of the spectra is presented above, for LIBS in air (graph 3) and LIBS underwater (graph 4) conditions. The silver lines that were found are the ones at 328,068 nm and 338,289 nm, marked on the graphs. The underwater LIBS spectra were recorded for three cases, using radiation from the 1064 nm wavelength, 355 nm wavelength and with both 1064 and 355 nm – double pulse technique - the delay between the two pulses was set at 3 μs. The LIBS spectrum in air was recorded using the double pulse setup. 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. After analyzing the elemental compounds of the broche, using LIBS underwater technique, we can say for sure that the broche is made from silver, and not plated

5. Conclusions

From all the recorded data, we have presented below some distinctive parts of the spectra obtained (the information provided by the other parts is in concordance with these ones). The results of the underwater LIBS analysis of the spectral lines prove that this photonic technique is more than suitable for underwater investigations, providing reliable and accurate information, without requiring the removing the object from its aqueous environment. Yes, there is a difference in the intensity of the analyzed lines between the 2 mediums, but the information provided by the underwater spectra is more than enough for the interpretation and discrimination of the elemental compound. In any case, we are still continuing these experiments in order to get better intensities, by adjusting the parameters and the experimental setup. It is very clear, as stated before, that the double pulse LIBS technique is the one that give us the most interesting and clear results after the analyzes of the spectra.

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