An educational setup for a Laser Induced Breakdown Spectroscopy (LIBS) system and its usage for the characterization of cultural heritage objects

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Abstract

An experimental setup for laser induced breakdown spectroscopy (LIBS) has been developed for educational purposes, to be used in the physics curriculum of science students and of students who are specializing in the field of cultural heritage. The setup comprises basically a Q-switched Nd:YAG laser and a fiber optic spectrometer. All components were already existing equipment at the physics laboratories at the TEI of Athens, so that they could be assembled in-house to a considerably economic LIBS setup. The proposed laboratory exercises are focused on one hand on imparting the knowledge about physical principles and phenomena associated with the creation of plasma and the radiation processes, while on the other hand, the students will be trained in the operation and handling the actual analytical process, in terms of specific applications. Various parameters are examined, concerning the laser-matter interaction and the process issues, such as calibration, interpretation of spectra and evaluation of results. Exemplary measurements as an autonomous learning and teaching module were implemented, demonstrating the qualitative and quantitative analysis of various materials typically associated with cultural heritage objects, such as metal standards and original objects and replicas of mural paintings.

1. Experimental setup

The experimental setup was implemented by assembling existing components. It is based on a Q-switched Nd:YAG laser, an optical system for focusing the beam and collecting the signal from the sample and a spectrometer. Accompanying the spectrometer and detector is a delay generator which accurately gates the detector's response time, allowing temporal resolution of the spectrum. Figure 1 presents three photographs of the setup, while Figure 2 shows schematically the arrangement of the individual components.

The laser (Quantel, Brilliant B) exhibits a beam energy of 850 mJ and a pulse duration and frequency of 5μs and 10 Hz respectively. The 9 mm diameter beam is focused through a high power, planar convex lens with focal length f = 50 mm on the sample surface. In order to degrade the high energy density, a neutral filter with 10% transmission is inserted between laser and lens. The plasma light produced by the laser pulse is measured with a compact CCD spectrometer (HR2000, Ocean Optics), which is coupled with the optical fiber cable transmitting the plasma light from the target position. The sample was placed in a manual X-Y translation stage, which made possible sample manipulation as required. Because the Nd:YAG laser radiation is not visible, a 632 nm He:Ne laser is used for system alignment and for illumination the area of interest

The delay generator, commonly used as trigger in most LIBS systems, was replaced by a delay module (Figure 3) that has been developed in house as a cheap and affordable solution for triggering. The trigger delay module is based on a Propeller microcontroller board (Parallax®) clocked at 80MHz. The purpose is to detect the Q-switch laser trigger pulse and to generate a delayed trigger pulse for the spectrometer. In order to minimize the response time, the controller is programmed in low level language (Propeller Assembly). In this way the delay time can be software controlled in steps of 0.012 μs with a minimum delay of 330 ns.

For acquiring and preliminarily processing the spectra the software Spectra Suite from Ocean Optics was used. For the peak characterization and the graphic presentation a demo versions of Plasus - SpecLine and the software Origin, respectively, have been used.

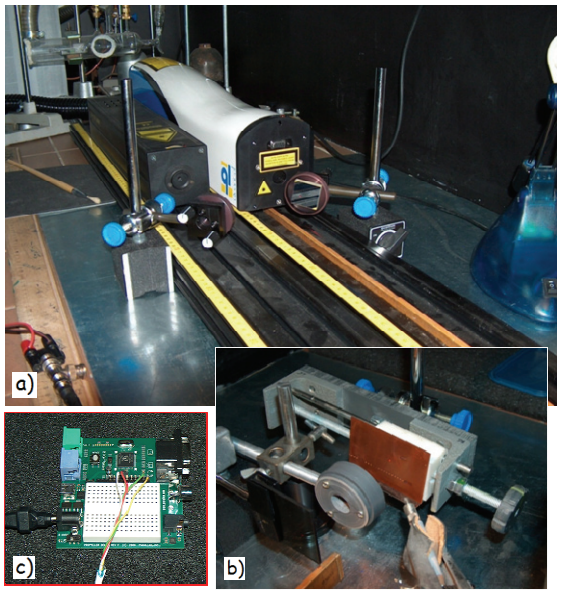

Fig 1.: Photos of the experimental setup: a) the Laser systems, Nd:YAG and HeNe, on the optic table, b) the sample on the manual X-Y translation stage with the focusing lens and the neutral density filter, c) the time delay module.

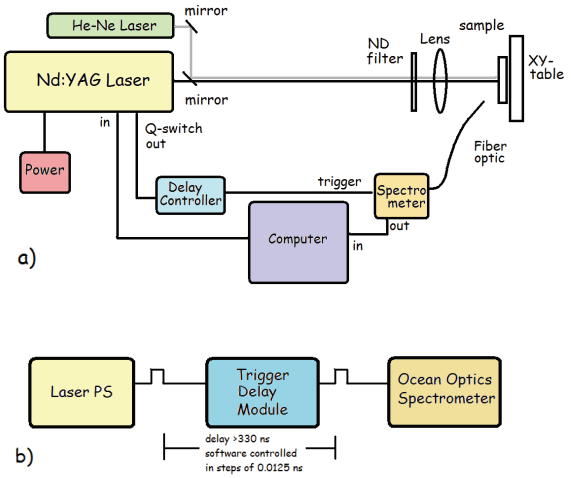

Fig.2.: a) A schematic draw of the experimental setup with the individual components and their connections. b) A schematic draw of the Trigger Delay Module

2. LIBS fundamentals

In LIBS, a high power laser pulse is focused onto the surface of the sample. Enough energy is delivered to a small volume to not only vaporize the material but to break all chemical bonds and ionize the elements present creating a small plasma plume. As the species in the plasma relax they emit at a characteristic wavelength. The spectrum evolves over time, becoming more distinct after several micro seconds. From this emission spectrum the constituent elements of the sample can be determined. For the first few hundred ns after ablation the spectrum is dominated by continuum emission. Electron ion collisions in the plasma plume produce bremsstrahlung radiation across the bandwidth. Only the strongest elemental spectral lines can be observed over this background. As the plasma cools, the electron density of the plasma decreases and the continuum emission fades. After approximately 10 µs the spectral lines are clear enough to detect elements. The spectrometer needs to be able to gate the emission spectrum so that the early measurements can be disregarded. As the plasma plume expands, constituent atoms in the ionized gas become excited. Over just a few µs, the excited atoms began to relax, resulting in characteristic spectral emissions.

A Sequence of events following the striking of a focused short laser pulse (ca. 5 ns) on the surface of a solid sample is showed schematically in figure 3, adopted from [1], while in figure 4a and 4b is showed the temporal history of the laser-induced plasma and the different species of his composition in the time evolution, immediately after the pulse excitation {2}.

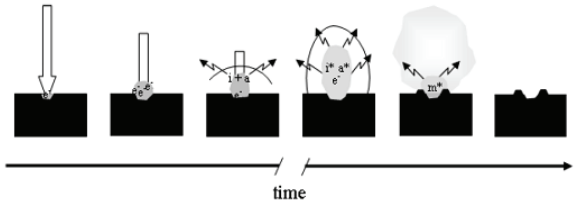

Fig.3: Schematic representation of the different phases during the LIBS process since the reaching of the laser pulse to the sample surface. The thick arrow represents the laser pulse and its length the pulse duration. e-, free electrons; i, ionic species; a, atomic species; m, molecular species; *, excited species.

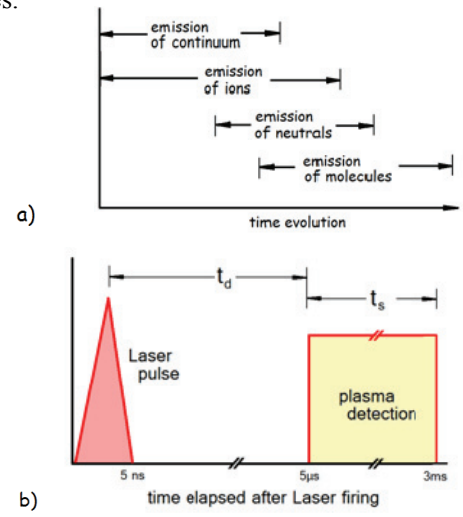

Fig.4: a) The important time periods after plasma formation, during which emission from different species predominate. b) The yellow box represents the time during which the plasma light is monitored using a gatable detector. Here t_d is the delay time and t_s the gate pulse width.

3. Measurements and Results

The first part of the educational experiments is focused on demonstrating the principles of the method and testing the setup in terms of LIBS measurement parameters:

a) Calibration: The spectra are evaluated qualitatively, i.e. through calibration of the energy/wavelength axis. Therefore, the peaks are identified, according to the matching spectral lines of the elements, provided by the NIST Atomic Spectra Database. For this reason the demo software Plasus is applied (Fig. 5).

b) Effect of time delay: The effect of the delay time of the trigger as an important parameter on the spectrum evaluation process is demonstrated in terms of recording evaluable spectra and in terms of controlling the spectrum quality. In Figure 6 a series of spectra is presented, obtained by changing gradually the delay time. While the intensity of the spectral lines is reduced, the spectral resolution is improved, as a consequence of the cooling of the plasma and the emission radiation originating from atoms and molecules. As optimum value a delay time of 4-5 μs was found.

c) Influence of laser beam energy: In order to examine the effect of laser beam energy on the spectrum quality, a series of spectra are recorded using different laser energies. For this reason various neutral filters with different transmission are applied. Figure 7 demonstrates the dependence of the line intensities on the laser pulse energy.

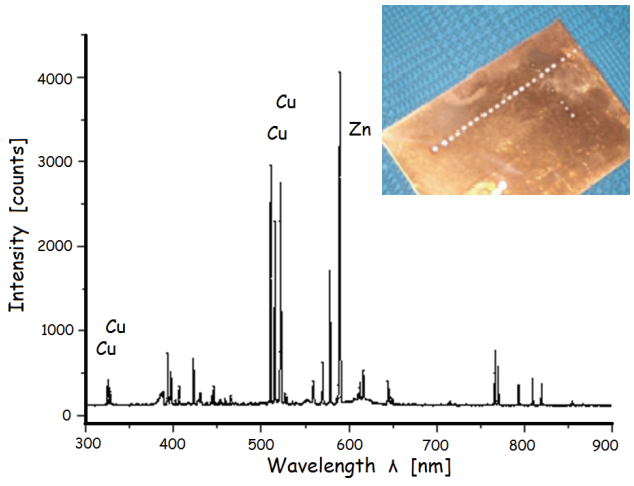

Fig. 5.: An indicative LIBS spectrum from a Bronze metal standard alloy (EB375), obtained with a single pulse excitation.

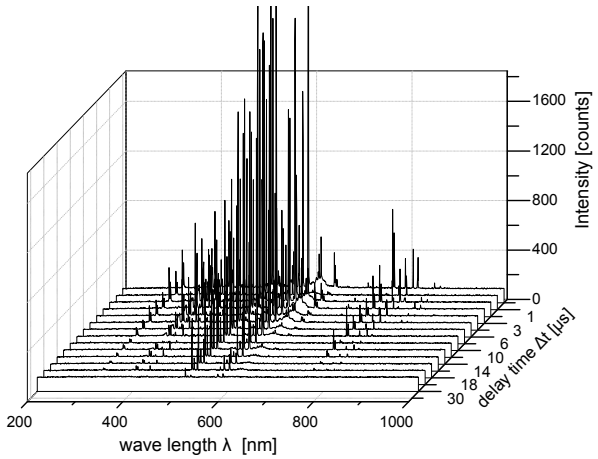

Fig. 6.: Spectra from a copper alloys sample obtained by a single pulse excitation, applied a different delay time (0 - 30 μs) between the pulse of Laser triggered and the spectrometer

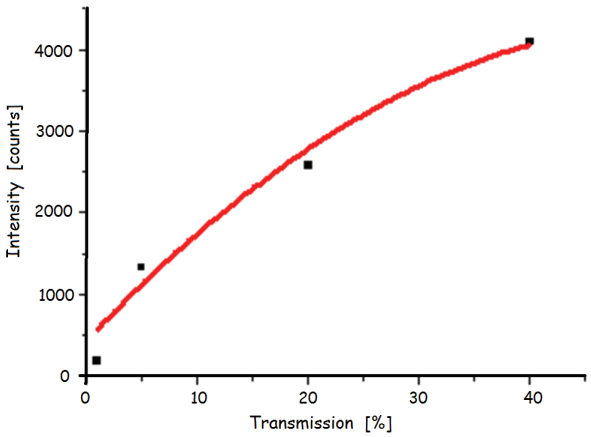

Fig. 7.: The graph shows the dependence of a Cu-line intensity from the beam energy of the Laser, expressed in transmission % of the used filter, as measured in spectra from a copper alloys sample obtained by a single pulse excitation,

4. LIBS applications on cultural heritage objects

Analytical examination has become an integral part of the study and conservation of cultural heritage objects in terms of material characterization and in terms of monitoring deterioration processes. For this reason, students who are educated in this field, such as in archaeological science, or in conservation science, have to pass commonly theoretical and practical training concerning the possibilities and limits of various analytical methods. During the recent years, LIBS, as a micro-invasive elemental analytical technique, has gained in importance as tool for material characterization of cultural heritage objects. Even though LIBS is not absolutely non-destructive the actual damage to the object remains considerably small and is compensated by advantages, such as the immediate spectrum generation, the portability and

the absence of absorption effects for light elements in contrast to methods like XRF [3]. Therefore LIBS is applied both as complementary technique and as stand alone technique, particularly in the analysis of ancient metal objects and of pigments [4].

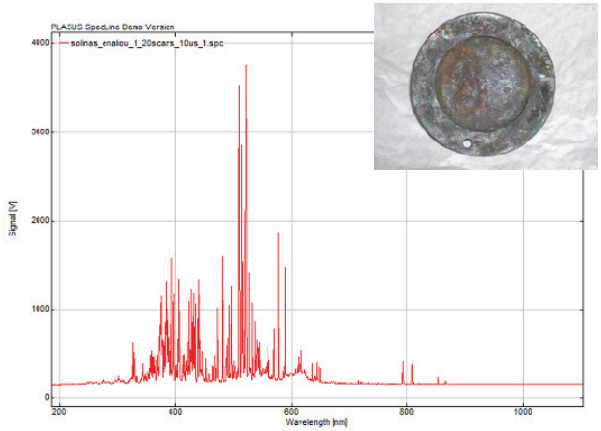

Fig. 8: A LIBS spectrum of a fragment of a pipe recovered from the 'Patris' shipwreck. In the inserts are shown the XRF spectrum and a photo of the pipe fragment respectively.

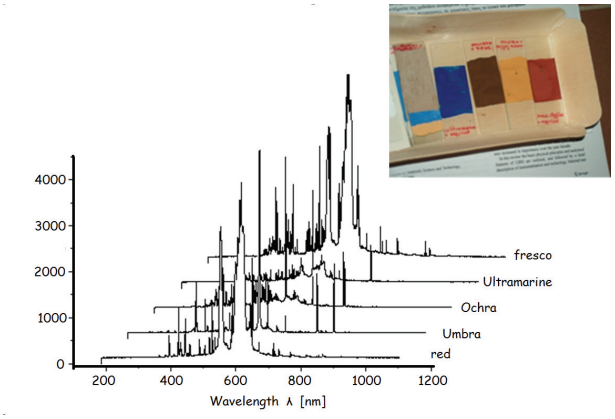

Fig 9.: A series of LIBS spectra of Spectra of the wall painting pigments red, Umbra, Ochre, Ultramarine and the substrate fresco, as showed in the insert photo.

In collaboration with the Department of Conservation at the TEI of Athens a series of educational sample applications were developed demonstrating the practical operation of LIBS. Figure 8 illustrates the analysis of a metal object, which was recovered from the 'Patris' shipwreck and which was examined in view of the suitable corrosion treatment. The same object has been already analyzed with X-ray fluorescence (XRF) [5], indicating the elemental composition of the alloy. On the basis of the XRF spectrum the lines in the LIBS spectrum could be identified, revealing additionally the presence of light elements, which could not be detected with XRF, due to the absorption low energy X-rays in the air environment. Figure 9 presents a series of spectra acquired in measurements of replicas of mural paintings, representing the substrate and pigments from a typical palette from the Byzantine Period. Finally the feasibility of quantitative analysis is demonstrated with measurements of modern coins the elemental composition of which is known (Figure 10). The sample applications will be integrated in the laboratory curriculum of the students at the Department of Conservation.

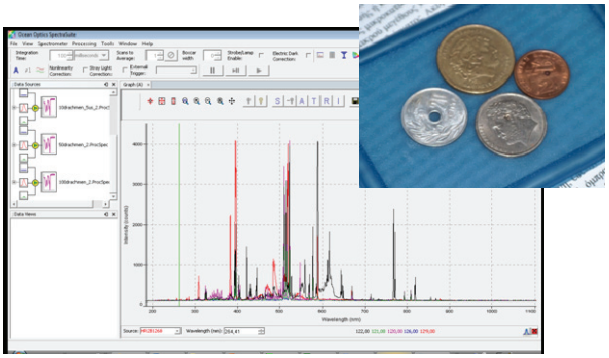

Fig 10.: A print screen of the program SpectraSuite, where shows indicative spectra taken from measurements at a number of new Greek coins, Drachmas, as shown in inserted photo.

5. Conclusions

A setup of a Laser Induced Breakdown Spectroscopy (LIBS) system has been developed, in order to be used for educational purposes. The LIBS setup was composed of a laser and low cost spectroscopy devices, which were available in the physics laboratory at the TEI of Athens. In essence, the experiment was designed to adequately manage cognitive resources of a number of familiar and conventional laboratory exercises, such as obtaining atomic emission spectra or qualitative evaluation of the spectra. Furthermore the influence of several operational parameters on the spectrum quality was studied, such as the energy density of the laser beam, the time delay for triggering the spectrometer or the focal length of the lens used. The assembled LIBS setup was successfully tested, in terms of the proposed experiments and it is expected to constitute a helpful educational package for laboratory exercises of students in physical sciences.

Apart from teaching the scientific and technical aspects of LIBS, the system can be used as well for the education of students, who are trained in the field of Cultural Heritage, such as in archaeological science or in conservation science. These applications were demonstrated with a series of measurements focusing on the material characterization of metal objects and pigment layers.

6. Acknowledgments

We would like to thank Dr. Aris Tzavaras from the Department of Medical Instruments Technology at the TEI of Athens for the technical support in developing of the delay controller.

7. References

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