DOUBLE PULSE LASER ABLATION AND PLASMA: TIME RESOLVED SPECTRAL MEASUREMENTS

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Introduction

Due to the relative experimental simplicity and immediate analyte response, laser-induced breakdown spectroscopy (LIBS) has gained popularity among researchers interested in real-time or in situ material detection and analysis for a wide range of sample forms. The elemental concentrations in the material are determined by spectrally analyzing the optical emission from the laser-produced plasma[1]. Although well suited for rapid in situ analysis, the LIBS technique possesses a lower sensitivity and precision than other methods of elemental analysis[2]. For several applications of LIBS, it is important to enhance the detection of atomic spectral lines by increasing the analyte signal while minimizing the background continuous emission (i.e. by improving the sensitivity and detection limits).

It was recently demonstrated that double pulse LIBS represents a very effective approach for improvement of analytical capabilities of the LIBS technique[3–8]. The use of double pulse LIBS can provide enhanced emission intensities, lower detection limits and longer sustained emission[9,10]. Two main beam geometries were suggested for realization of double pulse LIBS: orthogonal and collinear. For the orthogonal re-heating mode, the first pulse irradiates the sample and the second re-heating pulse propagates parallel to the target surface. In the collinear mode the second laser pulse is incident both on the surface and the plasma formed by the first pulse. A review of recent results of the studies of double pulse plasma and ablation for laser induced breakdown spectroscopy applications was reported by Babushok *et al* in 2006 (ref.[11]).

In the recent years, there has been increasing interest in the characterization of plasmas formed in laser ablation, a necessity for understanding the physical processes involved and improving the results of the diverse applications[12–16].

Most of the studies on double-pulse LIBS have been performed using an intensified CCD (ICCD) detection. Using ICCD, spectral information over wide range can be recorded on each laser pulse[17–19]. Besides ICCD, also photomultipliers (PMT) can be used to monitor single emission lines[20–22]. The output of the PMT is a current proportional to the intensity of the incident light. PMT´s are not integrating devices as they provide a signal simultaneous in time with the incident light intensity. The combination of ICCD and PMT can be useful to determine both, the spectral and time resolved plasma emission.

In this study, we present orthogonal re-heating double pulse experimental system equipped with both ICCD and PMT detection and preliminary measurements of temperatures of plasmas generated on an iron sample.

Experimental setup

The experimental double pulse system was designed to reach high sensitivity maintaining high spatial resolution and possibilities of line or raster scanning. This paper presents for the first time double pulse LIBS system utilizing modified commercially available laser ablation system (New Wave, UP 266 MACRO). This UV Nd-YAG laser ablation system was specifically designed for ICP-OES and ICP-MS solid sampling analysis. For these purposes, the laser ablation device incorporates a 30 µm to 750 µm expandable, aperture imaged beam delivery system. The control software offers a wide variety of ablation methods such as spot ablation for depth profiling, line scanning for lateral analysis and raster scanning for bulk or surface analysis. The laser ablation software program controls all laser parameters, sample viewing and stage positioning. It also offers the possibility of external triggering.

For double pulse LIBS experiments the ablation chamber used for connection UP 266 MACRO to ICP spectrometry, was replaced with a sample holder, which was equipped with inclination alignment (Fig. 1).

Fig. 1. **UP 266 MACRO Laser Ablation System modified for double-pulse LIBS measurements.** The ablation chamber was replaced with sample holder; the second laser pulse was focused by side glass lens and the laser induced plasma emission was collected by fiber placed in the front part

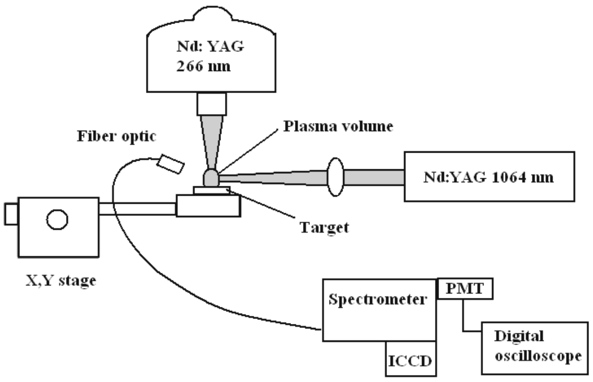

Fig. 2. **Schematic drawing of the experimental set-up**

The radiation of the second Nd:YAG laser (Quantel, Brilliant) with fundamental wavelength 1064 nm was focused parallel to the sample surface by 80 mm focal length glass lens. The two lasers were aligned such that their intersecting beam path resulted in a coincident spark just 0.5 mm above the sample surface. A schematic of the optical configuration is shown in Fig. 2.

Both lasers were externally triggered using a digital delay generator (Stanford Research Systems, DG 535) which was initialized by starting pulses from UP 266 MACRO laser module. Hence the starting of measurement, sample position and parameters of first laser pulse was controlled by UP 266 MACRO software. The ablation repetition rate had to be reduced to 1 Hz in order to transfer all data from the ICCD camera for each investigated spot. This was achieved by fixing the repetition rate of both laser's flashlamp to 10 Hz, and triggering the Q-switch for every tenths pulse by laboratory made pulse counter/divider. The laser-induced plasma radiation was transported by a fiber optic system onto the entrance slit of a monochromator (Jobin Yvon TRIAX 320). ICCD detector (Jobin Yvon Horiba) or a photomultiplier (R928 Hamamatsu) gated by a laboratory-built control unit were employed as detectors. For the gate-time delay monitoring and time-resolved signal recording, a digital storage oscilloscope Tektronix TDS 1012 was used. The double pulse LIBS system control block scheme with ICCD and PMT detection is shown in Fig. 3.

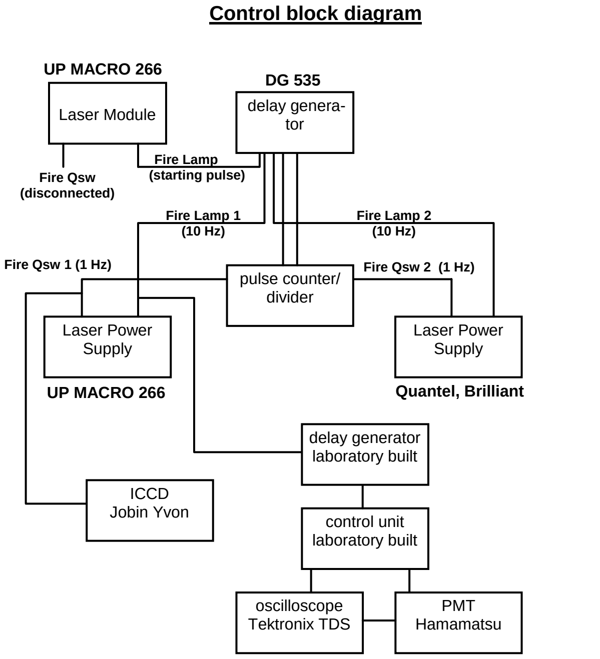

Fig. 3. **The double pulse LIBS system control block scheme with ICCD and PMT detection**

Results and discusion

The oldest and simplest method to determine the plasma temperature by emission spectroscopy is based on the measurement of the relative intensities of two lines from the same element and ionization stage. If E is the energy of the upper level and defining for each line $y \equiv \varepsilon\lambda/(gA)$, where ε is the line emissivity ($Wm^{-3}\ sr^{-1}$) integrated over the line profile, λ is the transition wavelength, g is the statistical weight of the upper level and A is the transition probability, the temperature results from the Bolzman equation: $\ln(y_1/y_2) = -1/kT(E_2-E_1)$.

This temperature has sometimes been called excitation temperature although, in conditions of local thermodynamic equilibrium (LTE) assumed for LIBS analysis, it should be equal to the electron kinetic temperature. The main disadvantage of the Boltzmann two-line method is that it may lead to considerable uncertainties of the determined temperatures. The accuracy of temperature determination may be improved by measuring a number of different lines. Moreover, to increase the accuracy, the range of upper level energies of the so-called Boltzmann plot should be as large as possible[16].

In this study the temperatures have been obtained from the intensity of eight iron atomic lines which are shown in Tab. I.

Table I
Series of iron atomic emission lines selected for temperature determination

Wavelength [nm]	Upper level energy [J]
371.993	$5.34 \cdot 10^{-19}$
373.486	$6.69 \cdot 10^{-19}$
373.713	$5.40 \cdot 10^{-19}$
374.826	$5.47 \cdot 10^{-19}$
374.948	$6.76 \cdot 10^{-19}$
375.823	$6.82 \cdot 10^{-19}$
376.379	$6.86 \cdot 10^{-19}$
376.719	$6.89 \cdot 10^{-19}$

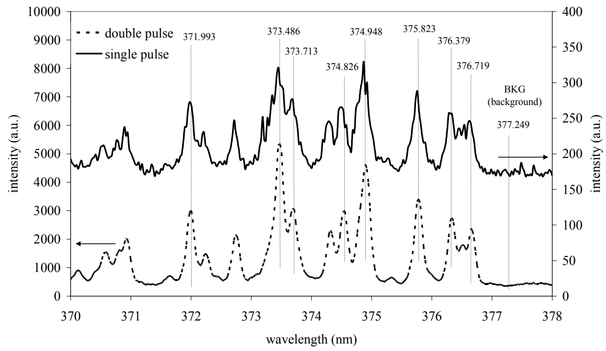

Fig. 4. **Comparison of the single and double-pulse signals in spectral region of selected iron lines and neighboring background**

The selected spectral lines fulfill several criteria, important to obtain reasonable results. They do not have any spectral interferences and their atomic parameters are known. Moreover, the selected spectral lines are grouped in close wavelengths in order to allow using single ICCD spectral detection window. All the measurements in single or double pulse mode were performed using high purity Fe target (high purity iron S11 – 2theta Czech Republic). The energy of first laser pulse was set to 10 mJ corresponding to irradiance on the target of 25 GW cm^{-1} with a spot size of 100 μm in diameter. The second laser pulse had energy of 100 mJ, with interpulse delay of 500 ns. The ICCD delay time between the first laser pulse and detection was of 1.5 μs and the acquisition time was 5 μs. These values were found in preliminary measurements as optimal for the investigated sample. The spectral data acquired for single and double-pulse are compared in Fig. 4.

From Fig. 4 is evident that the double pulse signal is more than 10 times enhanced in comparison to the signal obtained in single pulse mode. The wavelengths of iron emission lines (Tab. I) and the background position that were subsequently used for time resolved measurement by PMT are marked.

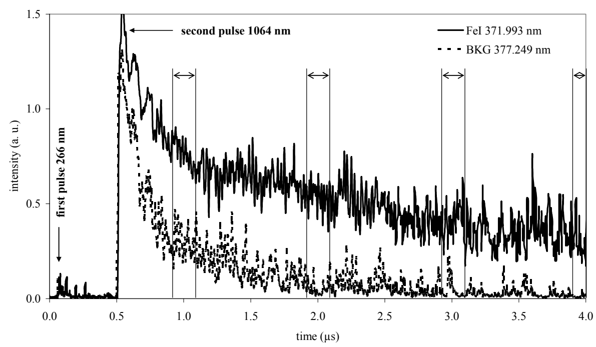

Fig. 5. **Comparison of temporal emission signal of double pulse laser induced microplasma on iron atomic emission line at 371.993 nm and background at 377.249 nm.** The marked time intervals (200 ns width) were averaged and used for calculation of plasma temperature

Table II
Temperatures of plasmas calculated from time dependent emission signal of eight iron atomic lines measured by gated PMT

Delay time [μs]	Temperature [K]
0.9–1.1	8920
1.9–2.1	8690
2.9–3.1	7580
3.9–4.1	7310

Fig. 5 show the time resolved intensity signal of the FeI 371.993 nm line and corresponding time dependent signal of background (at 377.249 nm) measured by gated PMT. The noisy signal is caused by the fact, that only single double-shot signal was recorded.

For the rest of above indicated iron atomic lines (Tab. I) the time dependent emission signal was measured in the same way as it is presented on Fig. 5. The Boltzmann plots were constructed after the background subtraction form the averaged intensity signals in marked regions (Fig. 5). The plasma temperatures derived from these plots for delay time intervals (1.0 ± 0.1, 2 ± 0.1, 3 ± 0.1 and 4 ± 0.1 μs) after the first laser pulse are summarized in Tab 2. These values are comparable with values formerly obtained at similar experimental conditions (see for example ref [16] and reference therein).

Conclusion

In this work, we present a double pulse LIBS system utilizing modified commercially available Laser Ablation System (New Wave, UP 266 MACRO), second Nd:YAG laser (Quantel, Brilliant) and a unique combination of ICCD and PMT detection. It was shown that combination of these two detectors in one experimental setup can be useful to determine both, the spectral and time resolved plasma emission. Preliminary measurements with this setup were focused on determination of the plasma temperature in different time intervals after the first laser pulse reaches the target. The plasma temperatures calculated from time dependent signals of iron atomic emission lines series demonstrate the advantages of this system for such type of measurements. The temporal emission signal measured by gated PMT can be useful not only for direct plasma diagnostic, but also for selecting the best ablation conditions including the optimum delay time between the two laser pulses and the delay and duration of ICCD acquisition. Moreover, in case of complicated samples the gated PMT can help to discover the matrix effect or spectral interferences. The aim of this reliability study was to proof the potentialities of the developed instrumentation. On the frame of the ongoing work more detailed study of the influence of double pulse conditions on the laser induced plasma properties and application of this technique for different samples are planned.

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