Diagnostics of laser-induced plasma by optical emission spectroscopy

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Abstract. The procedure for diagnostics of laser induced plasma (LIP) by optical emission spectroscopy technique is described. LIP was generated by focusing Nd:YAG laser radiation (1.064 nm, 50 mJ, 15 ns pulse duration) on the surface of pellet containing among other elements lithium. Details of the experimental setup and experimental data processing are presented. High speed plasma photography was used to study plasma evolution and decay. From those images optimum time for plasma diagnostics is located. The electron number density, \( N_e \), is determined by fitting profiles of Li I lines while electron temperature, \( T_e \), was determined from relative intensities of Li I lines using Boltzmann plot (BP) technique. All spectral line recordings were tested for the presence of self-absorption and then if optically thin, Abel inverted and used for plasma diagnostic purposes.

1. Introduction
Laser-induced breakdown spectroscopy (LIBS) is an emerging analytical technique for elemental analysis of various materials in all aggregate states. Driven by rapid technological development of pulsed lasers, compact and high-performance spectrometers and detectors, LIBS has found promising applications in many areas, such as elemental analysis in hazardous environments, material recycling, quality control in the industry, biomedical applications, environmental survey, interplanetary exploration and art conservation [1-4].

Recently, wider use of Laser Induced Plasma (LIP) as a plasma source for line shape studies has been noticed. There are several reasons for this interest. The main advantage over other plasma sources is simplicity and reproducibility of spectral line shapes for variety of elements very difficult to introduce or excite in traditionally used plasma sources. Some of these new spectroscopic data are of importance not only for theory testing but for diagnostics and development of LIBS analytical techniques, which require plasma diagnostics for further improvements and applications, see e.g. [3, 4, 5]. The determination of plasma parameters, in the first place electron temperature, \( T_e \), and electron density, \( N_e \), are of importance for the application of LIBS. The main difficulty in characterization of laser-induced plasma arises from its spatial and temporal inhomogeneity, which has to be carefully inspected before analyzing line shape and application of relevant plasma diagnostics. This can’t be achieved without high speed photography, line self-absorption test and taking into account plasma inhomogeneity along the observation direction.
In this work, the procedure for LIP diagnostics by optical emission spectroscopy is presented. LIP is generated by focusing Nd:YAG laser to the solid target. Spatially resolved plasma optical emission is recorded at different delay times from the laser pulse. The back mirror technique for self-absorption test is described and applied. The experimental setup and processing of spectral recordings are described in detail. As a result, spatially and temporally resolved electron density and electron temperature distributions are obtained.

2. Experimental setup and data processing

The details of the experimental setup and procedure were described in detail recently [5] and therefore only a short description will be given for completeness. The schematic diagram of used experimental setup is given in figure 1. The plasma was induced by Nd:YAG laser radiation at 1064 nm having 15 ns pulse width and 50 mJ pulse energy. The laser beam was perpendicularly directed toward target surface and focused by means of a 100 mm focal length lens. Laser induced plasma is generated in front of a solid state surface. The sample target was laboratory made from the homogenous powder mixture of Al$_2$O$_3$ 900 mg : Li$_2$CO$_3$ 400 mg : MgCO$_3$ 100 mg. The target was formed by compressing powder mixture into a cylindrical pellet (8 mm diameter and 2 mm thick). The ratio of target constituents was determined empirically by aiming to avoid strong self-absorption of studied lines. Spectroscopic measurements were performed in air at atmospheric pressure. The image of plasma plume was projected with 1:1 magnification, using lens with 170 mm focal length, onto the entrance slit of the spectrometer (Shamrock sr-303i, Czerny–Turner type, focal length 303 mm) supplied with three gratings 300, 1200, and 2400 grooves/mm. Quartz lens, 50 mm diameter with a focal length of 100 mm, flat mirror and mechanical shutter were mounted behind LIP at the opposite side from spectrometer to verify whether line self-absorption is present. The plasma radiation was recorded with the ICCD detector (Andor Technology, model DH720-18F-63, with 1024 × 256 pixels, 26 × 26 μm$^2$ pixel size, 18 mm intensifier diameter), mounted at the exit slit plane of spectrometer. The ICCD was operated by a pulse generator (DG-535, Stanford Research Systems). Spectral lines were recorded with 2400 grooves/mm grating. The instrumental profile is close to Gaussian with FWHM of 0.093 nm. Instrumental profiles are measured using low pressure Hg and Ne spectral calibration lamps. The wavelength sensitivity of spectrometer, ICCD system and all optical elements is calibrated against standard tungsten coiled-coil filament quartz halogen lamp (EG&G, model 597-1). The focal plane of laser radiation was set 1 mm below the target surface. The diameter of impact spot at the sample surface was 200 μm. The target was rotated or translated after 16 laser shots. Each recording is an average of 10 accumulations, each one obtained with 16 laser shots. The plasma plume was observed perpendicularly to the laser beam and parallel to the target surface at the distance of 0.5, 1 and 1.5 mm from the target surface.

The recorded spectral image represents spectral radiance emitted by the observed LIP layer as a function of the lateral position and wavelength. The radiation detected by each pixel of the ICCD matrix corresponds to an integrated intensity of the plasma emission along the line-of-sight across the radius of the plasma plume. An example of spectrum is given in figure 2a.

Spectral lines were recorded in “imaging” mode. First column in the matrix of image recording with ICCD camera represents wavelengths while in the first row are lateral positions. In this way other columns represent spectra at different lateral positions and other rows lateral intensity distribution at different wavelength. The program procedure used for experimental data processing is described in the next paragraphs.
Figure 1. a) Experimental setup for the study of laser induced plasma; b) schematic setup for self-absorption testing; 1 – Nd:YAG laser, 2 – spectrometer, 3 – target holder; L1, L2, L3 – lenses; M1, M2 – laser beam deflecting mirrors at 45°, M3 – flat mirror, S – mechanical shutter. c) Typical overall spectra.

In the first step matrices of experimental data are imported along with correction factor (apparatus function). After intensity and wavelength correction, the image is cropped by specifying cropping limits along wavelength and along lateral axis, see figure 2a. Next step is symmetrisation, which is done by reflecting the upper part of the plasma image about its symmetry axis and averaging with the lower part. This step is important because of the Abel inversion, which can only be applied to plasma with cylindrical symmetry. The image matrix after symmetrisation is shown in figure 2b.

Next step is data smoothing, which is a valuable tool for noise removal and represents an important step for preparation of image matrices for self-absorption test. By specifying number of points and polynomial order of Savitzky – Golay filter, the noise can be removed while preserving spectral line shape and lateral intensity distribution. By testing various combinations of filter parameters the optimal smoothing can be selected. After the selection of filter parameters, the matrices
recorded with and without back mirror, see figure 1 and figure 2c and 2d are smoothed along lateral and then, optionally, along wavelength axis.

The most important is the third section, see figure 2e, dealing with self-absorption correction (SAC). The theoretical background is given in [5,6]. The input parameters for SAC procedure are ratios of continuum at different lateral positions \( d \), \( R_c(d) \), recorded with and without back mirror and ratios of recorded line profiles, \( R_\lambda(d) \), with and without back mirror. The advantage of this procedure: the ratios for each lateral position are calculated and then the correction factor, \( K_\lambda(d) \), for each lateral position determined. The ratios of continuum are calculated in the following way. For every data column of matrix recorded without or with mirror far wing intensity values are averaged and set to be continuum intensity. Here “far wing” is the wavelength region 3-5 half widths away from line centre. Next step is the calculation of line intensity ratios along lateral position \( R_\lambda(d) \). Using these values with the following formula (1), the correction factor is evaluated.

\[
K_\lambda(d) = \frac{\ln \frac{R_c(d) - 1}{R_c(d)} - 1}{\frac{R_\lambda(d) - 1}{R_\lambda(d)} - 1}
\]

The optical depth \( k_\lambda l(d) \) is calculated also for different lateral positions. Here \( k_\lambda \) is the absorption coefficient and \( l \) is the length of a homogenous plasma layer. If \( k_\lambda l(d) \) is smaller than unity, spectral profiles were reconstructed to the optically thin case, see e.g. [6]. The spectral lines with \( k_\lambda l(d) \) approaching unity were not used in further procedure. The example of SAC for the line profile originating from the plasma axis (centre of matrix) is given in figure 2g and examples of SAC for the lateral profiles at line maximum (460.28 nm) are shown in figure 2h.

The final step of experimental data processing is Abel inversion, see figure 2f. The measured lateral intensity after the correction for self-absorption or optically thin lateral intensity distribution is converted into radial intensity with the help of the Abel inversion performed in two steps [7]. In the first step, the experimental lateral intensity distribution is fitted with Jacobi orthogonal polynomials and in this way, the experimental data distribution is represented by an analytical curve. The advantage of this technique is the possibility of testing and selecting best type and order of Jacobi polynomials. The choice of polynomial and selection of the polynomial degree depends on the overall shape of experimental data and noise contribution. Once the optimal analytical curve is determined, the Abel integral is easily solved in the next step. The described two step procedure of Abel inversion works also well when the experimental lateral profiles have a dip in the middle.

3. Plasma evolution and decay

Serious difficulties for spectroscopic diagnostics of LIP may arise from spatial inhomogeneity and time variation of plasma shape, which is simultaneously followed by the change of plasma parameters. Consequently, the emission of ablated material in plasma plume changes intensity as well. These difficulties are even more pronounced if one intends to perform spatially and temporally resolved measurements. In that case, it is of greatest importance to choose optimum observation time for plasma diagnostics, such as: delay time after laser irradiation of target, gate width and time with good radial plasma symmetry. To achieve this goal plasma images at different delay times after the laser
Figure 2. The steps of experimental data processing on the example of Li I 460.28 nm line with forbidden component: a) data matrix recorded without back mirror (WOM) after corrections for apparatus function, wavelength correction and crop; b) WOM after symmetrisation; c) WOM after smoothing; d) data matrix recorded with back mirror (WM) after steps a), b), c); e) data matrix after self-absorption (SA) correction; f) data matrix after Abel inversion. Examples of self-absorption correction and Abel inversion: g) line profiles from plasma axis h) lateral distributions at line maximum.
pulse are recorded, see figure 3, with an objective (focal length 75 mm) mounted with macro bellows on the ICCD camera (1024×1024 pixels). Each pixel covers the area of 0.011 × 0.011 mm. From recorded images it is evident that until 1 µs, plasma dimensions and shape were rapidly expanding. After 1 µs, plasma shape was changing much slower and thus, plasma is more appropriate for diagnostics. To avoid time integration and inhomogeneity, which may affect spectral line profiles, special care was taken to select delay time and gate width. Finally the optimum gate width of 200 ns and delay times for plasma observation of 1, 2, 3, 4, 5, 7 µs after laser pulse were selected. For these delay times and with 200 ns gate width, plasma is assumed to be quasi-stationary. The selected gate width and delay times were appropriate also to avoid strong plasma continuum emission and to enhance signal-to-background ratio.

To obtain spatial distribution of plasma parameters, three different cross sections of plasma plume at $z = 0.5; 1; 1.5$ mm (starting from target surface) were observed. Because of unity magnification of optical system, the thickness of observed cross sections is equal to the slit width (10 µm).

There are certain constrains for the application of experimental self-absorption test with back mirror, see Fig. 1. Those constrains are related to plasma expansion speed and finite speed of light. At early phase of plasma expansion (up to 700 ns after laser pulse) estimated average plasma speed is $4.3 \times 10^3$ m/s so during round trip of plasma light towards and from back mirror (2.66 ns), the observed plasma layer moved along plasma axis for 11 µm, what is more than slit width, 10 µm. One microsecond after laser irradiation of target, the plasma expansion speed is significantly lower (less than 500 m/s) so for the same round trip of light the observed plasma layer moved less than 1 µm, so the mismatch between emitting and reflecting volume is only 10%. Thus, by selecting later times for plasma observation and by using reasonably narrow gate width the self-absorption test with back mirror is considered valid.

![Figure 3](image_url)

**Figure 3.** Temporal and spatial evolution of plasma plume. For the first row of images the exposure time (gate width) was 10 ns while for the second row the exposure time was 100 ns. Each image represents an average of 5 laser shots. The emission intensity within images is scaled according to the colour map shown below images.
4. Results and discussion

For the electron temperature \( T_e \) determination Boltzmann plot (BP) technique was employed, using relative intensities of Li I lines given in Table 1. Prior to calculation of \( T_e \), the issue of BP technique applicability under LIP conditions was addressed. The discussion about BP technique and partial local thermal equilibrium (pLTE) existence in LIP plasma is given in recent publications [5,8]. The upper levels of transitions used for \( T_e \) determination have to be in pLTE in order to have valid \( T_e \) diagnostic by the Boltzmann plot technique. Applying the same procedure as in [5,8] determined critical quantum number at pLTE limit is 2, calculated using eq. (7.77) from [9] for lowest \( N_e \) and \( T_e \). This means that all Li I lines with the upper level principal quantum number 3 (ground state + next level) or higher can be used for the \( T_e \) determination using the BP technique. From Table 1 one can see that all three Li I lines fulfil pLTE condition. On the other hand, the so called McWhirter criterion, commonly used for estimation of LTE presence in LIP, gives value of \( N_e = 6.38 \cdot 10^{15} \text{cm}^{-3} \) (eq. (12) in [10], see also [11]) for critical electron density above which LTE is established. According to this criterion, all levels of Li I could be used under given experimental conditions. These two considerably different results indicate that, generally speaking, criteria for LTE assessment are not well defined in literature, see also [10].

A typical Boltzmann plot with Li I lines is shown in Fig. 4a, while radial distributions of \( T_e \) are given in Fig 4b,c,d. The estimated uncertainty of \( T_e \) measurements is in the range 8% to 12% depending upon delay time i.e. intensities of Li I lines.

Table 1. Transition array, multiplet, wavelengths, lower and upper energy levels, upper level statistical weight for Li I lines used for the Boltzman plot [12]

| Transition | Multiplet | Wavelength (nm) | \( E_i \) (cm\(^{-1}\)) | \( E_k \) (cm\(^{-1}\)) | \( g_k \) | \( A \) (\(10^8 \text{s}^{-1}\)) | \( S \) |
|------------|-----------|-----------------|----------------|----------------|--------|----------------|-----|
| 1. \( 1s^22p^{-}1s^24s \) | \( ^2P^o–^2S \) | 497.166 | 14 903.66 | 35 012.06 | 2 | 3.460 \(10^{-2} \) | 0.42 |
| 2. \( 1s^22p^{-}1s^25s \) | \( ^2P^o–^2S \) | 427.307 | 14 903.66 | 38 299.50 | 2 | 1.59 \(10^{-2} \) | 0.122 |
| 3. \( 1s^22p^{-}1s^25d \) | \( ^2P^o–^2D \) | 413.262 | 14 904.00 | 39 094.93 | 4 | 1.81 \(10^{-2} \) | 0.252 |

After all necessary line tests and, if necessary corrections, like for the case of self-absorption, interference with neighbouring lines, the experimental line profile of Li I 497.17 nm line was fitted with an asymmetric profile and from the best fit \( N_e \) is determined. The procedure for \( N_e \) determination from an experimental line profile is described in [3]. For the fitting of experimental profiles electron impact width \( w_e \) and ion broadening parameter \( A \) from [13] were used. Typical fitting results are presented in figure 5. Radial distributions of \( N_e \) obtained in this way are shown in figure 6. From figure 6 it can be seen that \( N_e \) has highest value at early delay time and it is decreasing at later delay time. Also \( N_e \) is higher at plasma centre and it is slowly decreasing towards plasma periphery.
Figure 4. a) Typical Boltzmann plot of Li I lines. Radial distributions of electron temperature at different delay times (D) at the observation distances b) $z = 0.5$ mm, c) $z = 1$ mm, d) $z = 1.5$ mm from the target surface.

Figure 5. Best fit examples of the Li I 497.17 nm line, for the delay times of a) 2 $\mu$s, b) 3 $\mu$s. Both experimental profiles originate from the plasma axis at $z = 1.5$ mm from the target surface.
Figure 6. Radial distributions of $N_e$ at different delay times at a) $z = 1.5$ mm, b) $z = 1$ mm, c) $z = 0.5$ mm from the target surface.
5. Summary and conclusions
Spectroscopic diagnostics of LIP is not an easy task. Inherent drawbacks of the source, in the first place inhomogeneity and plasma transient nature are pointed out, followed by the proposed methods to overcome those constraints. The results of spectroscopic diagnostic study of LIP are presented. LIP was generated by focusing Nd:YAG laser radiation (1064 nm, 15 ns pulse duration) on the surface of the pellet containing among other elements lithium. High speed plasma photography was used to determine optimum time for plasma diagnostics. The high speed photography is followed by the tests for the presence of line self-absorption. If spectral lines were optically thin or could be corrected to an optically thin case, the Abel inversion procedure was applied.

All necessary steps towards time and space resolved acquisition and diagnostics are given on the example of Li neutral lines. Some of the results are shown on graphs 4,6. Abel inverted profiles were used to determine radial line intensity distribution for \( N_e \) measurement. The line profiles of Li I lines were fitted with asymmetric profile convoluted with Gaussian. The radial distributions of \( N_e \) values are shown in Fig. 6. The electron number density, \( N_e \) is measured by fitting profiles of Li I 497.17 nm line while radial distribution of electron temperature, \( T_e \), was determined from relative intensities of Li I lines using Boltzmann plot (BP) technique.

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