Enhanced Laser Induced Break-down Spectroscopy

M. Anguš, J. Krištof, J. Rakovský, M. Kocianová, and P. Veis
Department of experimental physics, Faculty of mathematics physics and informatics, Comenius University in Bratislava, Mlynská dolina, 842 48, Bratislava, Slovakia.

Abstract. Laser induced break-down with/without a supplementary RF discharge excitation was investigated by means of optical emission spectroscopy. Calibration free method in LIBS for determination of concentrations in sample has problems with self-absorption of emission lines. This could lead to incorrect determination of concentration of electrons. Electron temperature is used to determine concentration of examined elements in sample. Atoms and radicals ablated from the Cu target and excited by laser beam are further re-excitated by RF discharge in order to prolong their life-time. Laser induces break-down spectra of copper sample under argon atmosphere at pressure of 380 Pa were measured and electron temperatures from Boltzmann plot using argon and/or copper neutral lines were deduced. The results for two different experimental conditions (delay of spectra recording 1 $\mu$s and 200 $\mu$s after laser shot) were compared. After 200 $\mu$s delay no influence of laser induced breakdown presence on RF discharge spectra was observed. The results from laser induced break-down and additional RF discharge excitation were compared.

Introduction

Laser induces break-down spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a highly energetic pulsed lasers as the excitation source. The laser beam is focused on the target in order to form plasma containing particles from ablated target, mainly neutral and single ionized excited states. Because all elements emit light of characteristic frequencies when excited to sufficiently high temperatures, LIBS can perform the detection of practically all elements. This detection is limited only by the power of the laser as well as by the sensitivity and wavelength range of the spectrograph and detector.

The focused laser beam can ablate a very small amount of target material, which generates a plasma plume. Electrons are created by multi-photon ionization. After sufficient amount of electrons break-down occurs. During this time, the plasma emits a continuum of radiation which does not contain any useful information about the present species, but within a very small timeframe the plasma expands at high velocities and cools. At this point the characteristic atomic emission lines of the elements can be observed. The delay between the emission of continuum radiation and characteristic radiation is in the order of 100 ns, this is why it is necessary to temporally gate the detector.

The first use of laser-induced breakdown for elemental analysis was only a few years after the invention of the gas laser in 1961. [1] Since then The LIBS technique evolves.

New laser-induced air plasma source assisted by locally intensified microwave radiation was recently developed. Microwaves generated by a magnetron were radiated from the antenna, which was put inside the chamber. To generate a source of plasma, pulsed Nd-YAG laser beam was passed through the pipe and focused on the target just in the vicinity of intensified microwave field. The microwave pulse was set to be coincident with laser injection. [2]

The LAMPS technology (Laser Assisted Microwave Plasma Spectroscopy) is employing a special microwave cavity. The plasma is injected into this cavity where it reacts with free electrons, greatly increasing sensitivity and producing better line stability and reproducibility. A lower power 50 mJ laser is used in the LAMPS, resulting in less ablation imprint to the sample and greater sensitivity. [3]

For quantitative analysis of samples, LIBS needs calibrated samples or to use calibration-free method [4]. Laser inducted plasma is very short and it is not optically thin. That means that self-absorption can occur. This is the problem with calibration-free method. From self-absorbing lines is not possible to determine the temperature of electrons and then concentration of examined element right. There was developed method for correction of this phenomenon [5]. Another solution can be using discharge as excitation source where self-absorption does not occur, where we inject ablated
particles. Our goal was to enhance the LIBS by adding another source of electrons – RF discharge and to observe changes in Boltzmann plot and emission spectra for combination with and without RF discharge in two time distances from laser shot (1 μs and 200 μs).

**Experimental**

The experimental setup is shown schematically in Figure 1. We used Nd-YAG laser (second harmonic at 532 nm, 165 mJ, 4 ns) for creation laser induced plasma. The laser pulse is focused through prism and lens into the chamber, where the copper sample is placed on movable holder. Chamber is pumped by scroll pump XDS 10. Pressure in system was measured by digital pressure gauge Super Bee and held at 380 Pa. The gas flow 20 sccm was controlled by MKS mass flow controller.

RF discharge was generated by RF 27 MHz discharge maintained in quartz tube of inner diameter of 18 mm in pure argon flowing regime. The electrodes consisted of copper rings (width 10 mm, separation 20 mm) situated outside of the tube. Delivered power to RF discharge was 30 W determined by output meter. Discharge was placed at the very edge of chamber, so the plasma was above the sample.

Emitted light was collected through optical fiber into spectrometer Mechelle 5000, detected by Andor CCD camera and then processed in PC. We have worked in two regimes. In first regime, we collected signal 1 μs and 200 μs after laser shot. In second regime, we collected signal with the same condition but plus with second source of excitation – RF discharge above the sample.

**Electron temperature**

Spontaneous emission occurs after transition of atom from \( m \) energy state to \( n \) energy state. The transition is associated with emission of quantum of energy:

\[
E_m - E_n = h\nu_{nm}. \tag{1}
\]

Radiated intensity can be expressed

\[
I_{nm} = A_{nm} N_m h\nu_{nm}, \tag{2}
\]

where \( A_{nm} \) is Einstein’s coefficient of spontaneous emission and \( N_m \) is amount of atoms in quantum state \( m \).

![Figure 1. Schematic view of experimental apparatus.](image)
Relation of atoms in individual quantum states $\frac{N_m}{N_n}$ at thermodynamic equilibrium is defined by Boltzmann distribution:

$$\frac{N_m}{N_n} = \frac{g_m}{g_n} \exp\left(\frac{E_m - E_n}{kT}\right) = \frac{g_m}{g_n} \exp\left(-\frac{\hbar\nu_{nm}}{kT}\right),$$  

(3)

where $g_m$ and $g_n$ are degrees of degeneracy of states $m$ respectively $n$. At calculation of intensity of spectral line we have started from equation (2) where we replaced number of excited states by their concentration and then we replaced the concentration by concentration of any excited atoms by Boltzmann distribution.

$$\frac{[X_m]}{[X]} = \frac{g_m}{Z} \exp\left(-\frac{E_m}{kT}\right) = \frac{g_m}{Z} \exp\left(-\frac{E_n}{kT}\right) \exp\left(-\frac{\hbar\nu_{nm}}{kT}\right),$$  

(3)

where $Z = \sum_n g_n \exp\left(-\frac{E_n}{kT}\right)$ is partition function (state sum of ground state). After setting into (2) we obtain an equation for intensity of spectral line

$$I_{nm} = A_{nm} \hbar \nu_m \frac{g_m}{Z} [X] \exp\left(-\frac{E_m}{kT}\right),$$  

(4)

or for concentration of energy states $m$

$$[X_m] = \frac{I_{nm}}{A_{nm} \hbar \nu_m} = \left[\frac{X}{Z}\right] \exp\left(-\frac{E_m}{kT}\right).$$  

(5)

We use natural logarithm for both sides of equation (5).

$$\ln\left(\frac{I_{nm}}{A_{nm} \hbar \nu_m}\right) = \ln\left[\frac{X}{Z}\right] - \frac{E_m}{kT}.$$  

(6)

If we plot $\ln\left(\frac{I_{nm}}{A_{nm} \hbar \nu_m}\right)$ for individual lines as a function of $E_m$ we can fit these points by linear function

$$y = y_0 + \tan \alpha x,$$  

(7)

where $y_0 = \ln\left[\frac{X}{Z}\right] = \text{const}$. From $\tan \alpha$ we can calculate the temperature

$$kT = -\frac{1}{\tan \alpha}.$$  

(7)

**Results and discussion**

Laser induced plasma is in thermodynamic equilibrium. However, electron temperature and concentration of electrons is quickly decreasing in laser spark. As our exposure time was 1 s we cannot assure that the determined temperature is real, but an average value between 0 eV and maximal temperature of electrons. But our goal is not the determination of electron temperature, but to illustrate the influence of self-absorption on Boltzmann plot. RF discharge is continuous without strong change of electron temperature and we suppose local thermodynamic equilibrium. We recorded spectra during the exposition time of 1 s and determined temperature of electrons. For comparison we calculated electron temperature for two elements – argon and copper which should be equal. Used atomic lines and constants are in Table 1.

Average electron temperatures for conditions in Table 2 for used Ar lines are shown in Figure 2.
Table 1. Used atomic lines of Ar and Cu and used constants. [6, 7, 8, 9].

<table>
<thead>
<tr>
<th>Wavelength of Ar lines [nm]</th>
<th>$A_{nm} \times 10^{-6}$ s</th>
<th>$g_{nm}$</th>
<th>$E_m$ [eV]</th>
<th>Wavelength of Cu lines [nm]</th>
<th>$A_{nm} \times 10^{-6}$ s</th>
<th>$g_{nm}$</th>
<th>$E_m$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>675.2835</td>
<td>1.93</td>
<td>5</td>
<td>14.74</td>
<td>296.116</td>
<td>3.76</td>
<td>8</td>
<td>5.57</td>
</tr>
<tr>
<td>687.1289</td>
<td>2.78</td>
<td>3</td>
<td>14.71</td>
<td>324.754</td>
<td>139</td>
<td>4</td>
<td>3.82</td>
</tr>
<tr>
<td>696.5430</td>
<td>6.39</td>
<td>3</td>
<td>13.33</td>
<td>327.396</td>
<td>137</td>
<td>2</td>
<td>3.79</td>
</tr>
<tr>
<td>703.0251</td>
<td>2.67</td>
<td>5</td>
<td>14.84</td>
<td>333.784</td>
<td>0.38</td>
<td>8</td>
<td>5.10</td>
</tr>
<tr>
<td>727.2935</td>
<td>1.83</td>
<td>3</td>
<td>13.33</td>
<td>406.264</td>
<td>21</td>
<td>6</td>
<td>6.87</td>
</tr>
<tr>
<td>750.3868</td>
<td>44.5</td>
<td>1</td>
<td>13.48</td>
<td>465.112</td>
<td>38</td>
<td>8</td>
<td>7.74</td>
</tr>
<tr>
<td>751.4651</td>
<td>40.2</td>
<td>1</td>
<td>13.27</td>
<td>510.554</td>
<td>2</td>
<td>4</td>
<td>3.82</td>
</tr>
<tr>
<td>772.4207</td>
<td>117</td>
<td>3</td>
<td>13.33</td>
<td>515.324</td>
<td>60</td>
<td>4</td>
<td>6.19</td>
</tr>
<tr>
<td>794.8176</td>
<td>18.6</td>
<td>3</td>
<td>13.28</td>
<td>521.820</td>
<td>75</td>
<td>6</td>
<td>6.19</td>
</tr>
<tr>
<td>800.6156</td>
<td>4.9</td>
<td>5</td>
<td>13.17</td>
<td>529.252</td>
<td>10.9</td>
<td>8</td>
<td>7.74</td>
</tr>
<tr>
<td>801.4785</td>
<td>9.28</td>
<td>3</td>
<td>13.09</td>
<td>570.024</td>
<td>0.24</td>
<td>4</td>
<td>3.82</td>
</tr>
<tr>
<td>810.3692</td>
<td>25</td>
<td>3</td>
<td>13.15</td>
<td>578.213</td>
<td>1.65</td>
<td>2</td>
<td>3.79</td>
</tr>
<tr>
<td>811.5311</td>
<td>33.1</td>
<td>7</td>
<td>13.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>826.4521</td>
<td>15.3</td>
<td>3</td>
<td>13.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>840.8209</td>
<td>22.3</td>
<td>5</td>
<td>13.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Experimental conditions.

<table>
<thead>
<tr>
<th>Case</th>
<th>Case</th>
<th>Case</th>
<th>Case</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
<td>c</td>
<td>d</td>
</tr>
<tr>
<td>1 µs after laser shot</td>
<td>1 µs after laser shot</td>
<td>200 µs after laser shot</td>
<td>200 µs after laser shot</td>
</tr>
<tr>
<td>discharge on</td>
<td>discharge off</td>
<td>discharge on</td>
<td>discharge off</td>
</tr>
</tbody>
</table>

Figure 2. Boltzmann plot obtained from Ar lines and calculated temperature of electrons.
Figure 3. Boltzmann plot obtained from Cu lines and calculated temperature of electrons.

Figure 4. Two spectrum parts were normalized to Cu line 521.82 nm. The spectrum taken 1 μs after laser shot (case b) was multiplied by 30. On left side are shown Cu lines 324.754 nm and 327.396 nm and on the right are lines 510.554 nm, 515.324 nm and 521.820 nm.

We noticed no signal after 200 μs when discharge was off (case d). There are calculated electron temperatures in Figure 3 for Cu lines. Self-absorption strongly occurs for resonant transitions (transitions to ground state) – marked on Figure 3 in circles. There were not used any argon emission lines with transitions to ground state in Boltzmann plot and points fulfill linear dependence, so we assume that there is no or weak self-absorption of argon lines. Therefore temperatures of electrons calculated from argon lines we consider as reference. The temperature of electrons calculated from copper lines should be close to them. Temperatures in Figure 3 do not include transitions to ground state except case “c” where including or not including these transitions has minimal influence (difference is 0.05 eV). In case “a” the increase of temperature of electrons after including resonant transitions is 0.13 eV and in case “b” 0.3 eV. The least change after including copper resonant transitions is in case “c.” We assume that in this case the self-absorption is the least of all. The
differences between electron temperatures calculated from argon and copper lines will be objects for our next study.

Resonant transitions 324.754 nm and 327.396 nm are seen in Figure 4 where the lines are normalized to one at 521.82 nm.

Conclusion

LIBS is versatile technique, fast, easy and cheap, but has its disadvantages. We have compared spectra and electron temperatures for 2 elements and 4 condition named above. We found out that it is observed most likely self-absorption for some Cu lines in cases “a” and “b” what can cause problems at calculation of concentrations. But for case “c” (200 μs after laser shot + discharge on), electron temperature was influenced at least by self-absorption. Another advantage is that it is still possible to observe Cu lines in discharge in stable condition (constant $n_e$, $T_e$) for longer time. This is not possible for signal only from laser spark.

Acknowledgments. This research has been financially supported by the Scientific Grant Agency of Slovak Republic VEGA, numbers of projects 1/0851/09, 1/0512/10, 1/1157/11, by Slovak research and development agency under the number APVV-0544-07 and by the grants of Comenius University, numbers of projects UK/300/2011 and UK/449/2011.

References