Determination of plasma temperature and electron density of iron in iron slag samples using laser induced breakdown spectroscopy

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Abstract. Plasma temperature and electron density of iron in iron slag samples taken from a local plant is studied. Optimal experimental conditions were evaluated using Nd: YAG laser at 1064 nm. Some toxic elements were identified and quantitative measurements were also made. Plasma temperature and electron density were estimated using standard equations and well resolved iron spectral lines in the 229.06 - 358.11 nm region at 10, 20, 30 and 40 mJ laser pulse energy with 4.5 µs delay time. These parameters were found to increase with increase in laser pulse energy. The Boltzmann distribution and experimentally measured line intensities support the assumption that the laser-induced plasma was in local thermal equilibrium. It is worth mentioning that iron and steel sector generates tons of solid waste and residues annually containing variety of contaminants which can be harmful to the environment and therefore knowledge, proper analysis and investigation of such iron slag is important.

1. Introduction
Knowledge of the plasma temperature is vital to understand the dissociation, atomization, ionization and excitation processes occurring in the plasma and helpful in utilizing the plasma to maximize analytical potential of LIBS. The method most frequently used for determination of excitation temperature of the plasma is the Boltzmann plot method. In this method, the relative intensity of the thermometric species is measured and used for the calculation of the excitation temperature of the plasma by assuming the local thermal equilibrium (LTE) condition. The LTE assumption is justified by the fulfilment of the Mc Whirter criterion [1, 2]. For LTE to exist in the plasma, the electron density has to be high enough so that the collision rates exceed the radiative rates. Plasma temperature can be determined from the ratio of the intensities of:

I. Neutral to neutral lines and
II. Ion to neutral lines, usually for the same element

Laser-induced plasmas have been used with increasing frequency as spectroscopic sources for the measurement of Stark widths [3]. The plasma temperature of iron slag sample was estimated using Boltzmann plot of LIBS intensity for neutral iron lines and Stark broadening.

This study is made due to the reason that classification, identification and knowledge about electron density and plasma temperature of iron in iron slag has been the burning issue in various research laboratories of the world and a variety of techniques are being used for this purpose[4].
interaction of high power laser beam with material has been investigated by various researchers [5]. Due to huge demands of iron and steel to fulfil the needs of the construction industry, automobile industry and various other industrial sectors, environmental issues related to iron slag are gaining importance. The LIBS system was designed and developed at KPUPM. Prior to application of LIBS for quantitative analysis of slag samples, the plasma parameters such as temperature and electron density were measured as these parameters play vital role in the sensitivity of LIBS system. When high power laser pulse falls on a solid target, the irradiation in the focal spot can lead to rapid local heating and intense evaporation. The ablated material compresses the surrounding gas and leads to the formation of shock wave. In this process a number of phenomenons including heating, melting, evaporation, atomization, excitation and ionization are involved. The emission spectrum produced from the plasma plume can be collected, spectrally resolved and used for the identification and quantification of the emitting species present in the ablated material [6]. Pulsed laser induced plasma has a very short temporal existence and is transient in nature with a fast evolution of the characteristic parameters that are dependent on irradiation conditions such as incident laser intensity and irradiation spot size. The characteristics of the plasma plume are dependent on laser irradiance, target composition and atmospheric condition [7].

The hot vapor plasma can interact with the surrounding atmosphere in two ways:

I. The expansion of the high-pressure vapor drives a shock wave into atmosphere, and
II. Energy is transferred to the atmosphere by a combination of thermal conduction, radiative transfer and heating by the shock wave.

The subsequent plasma evolution depends on irradiance, size of vapor plasma bubbles, target vapor composition, ambient gas composition, pressure and laser wavelength. The important quantities such as radiative transfer, surface pressure, plasma velocities and plasma temperature are strongly influenced by the nature of the plasma. It is therefore, the emission lines of the plasma can be used to determine the temperature and the density of electrons [8]. The plasma is initiated and sustained by inverse bremsstrahlung absorption during collisions among atoms and ions, electrons and the gas species. This is the reverse of the well-known bremsstrahlung process in which high-energy electrons, upon traversing a gas or solid, emit radiation as they slow down. The theoretical considerations on plasma production and heating by means of laser beams have been proposed by several workers [9].

2. Experimental setup
2.1 LIBS system
Nd: YAG Laser (Spectra Physics, Model GCR100) in Q-switched mode with ability to deliver maximum pulse energy of one joule with a pulse width of 8 ns and operating at a 10 Hz was employed for production of plasma spark at the sample surface. A convex lens having focal length 30 mm was used to focus Nd-YAG laser pulse onto the surface of sample at fundamental wavelength 1064 nm. The range of pulse energy was 20-120 mJ. The laser energy was measured with a calibrated energy meter (Ophir Model 300) for the study of dependence of LIBS signal on incident laser energy. The spectrometer used was Ocean Optics LIBS 2000+ system. The light from the plasma spark is collected by a collimating lens using UV graded silica 1 meter, multimode sampling fiber with SMA connector and is transferred to LIB2000 + Spectrometer (Ocean Optics). Our LIBS 2000+ has four spectrometers modules to provide high resolution (FWHM 0.1 nm) in the 200 nm to 620 nm wavelength region. The detector has a gated CCD camera having 14,336 pixels. This makes it possible to measure a LIBS spectrum over broad spectral range (200–620 nm) simultaneously with high spectral resolution (0.1 nm). The emission is observed at a 45° angle to the laser pulse.
2.2 Sample preparation
Iron slag samples were collected from a major steel manufacturing plant situated in Jubail, Saudi Arabia. These samples were ground in spectro mill ball pestle impact grinder (Model 1100-11, Chemplex Industries, Inc. 10707, USA) to suitable mesh size for preparation of pellets. Generally, the Stark widths are measured using a single sample with a small content of the element of interest, in order to reduce self-absorption [10-12]. Two slag samples under investigation were pressed to pellets shape by applying a load of 8.6×10^7 Nm^-2 for half an hour by placing the homogenous mixture in a die. These pellets have diameter of 20 mm and thickness of 10 mm. While for testing on ICP, the samples were digested with aqua regia, ashed, dissolved in nitric acid and analyzed using inductively coupled plasma emissions spectroscopy. As Mg is present in abundance in iron slag samples, its pellets were also prepared by mixing it in KBr.

3. Results and discussion
3.1 Optimization of various parameters of LIBS
Prior to the application of LIBS system to iron slag samples, the LIBS spectrometer was carefully optimized for the improvement of LIBS efficiency. The major parameters which were optimized are as under:
I. Laser pulse energy
II. Dependence of LIBS signal on pressure for pellets formation
III. Sample rotation speed
IV. Influence of laser energy on binding materials

3.2. Dependence of LIBS on laser energy.
The dependence of LIBS signal intensity on incident laser energy was carried out by recording the spectra of standard samples at different laser energies. For this purpose sample of Mg in known concentration were prepared. Laser produced plasma emission spectra from pellet samples prepared in KBr matrix, was recorded in the 400-620 nm region at 15, 20, 25, 30, 35 and 40 mJ energy per laser pulse. A time delay of 4.5 µs was applied at which maximum signal was recorded. The laser pulse energy dependence of LIBS signal intensity for Mg is depicted in Figure 1. It is clear from Figure 1 that LIBS signal increases with increase in laser energy. LIBS signal shows strong linear dependence on the laser energy which is clear from the least square fit of 0.999.

![Figure 1. Plot of dependence of the intensity of Mg 518.36 nm emission line on laser energy](image)

The higher laser energy generates optically thick plasma and strong background continuum, so, saturation region can be expected at higher laser pulse energies. It was noted during the
experimentation that a pulse of 25 mJ was enough in case of these elements under investigation to obtain sufficient intensity and good precision.

3.3. Dependence of LIBS signal intensity on pressure for pellet formation

The trend of increase in intensity of emission lines with the pressure applied for the formation of pellets is depicted in Figure 2. The emission line intensity increases linearly with applied pressure. This is due to the fact that with increase in pressure pellets become more dense and rigid which help in reduction of the dust produced by ablation from the powder samples. The dust generated by powder samples hinders the incident laser energy to the target sample. It also generates more complexity in the excitation process and increases the value of Relative Standard Deviation (RSD) in the acquired data. In addition to above mentioned facts, the density of trace elements in pellet also increased due to high pressure for pressing the pellets, which could be attributed to high density of compressed material inside pellet.

![Figure 2. Dependence of the emission line intensity of Mg 518.36 nm line on the pressure applied to form the pellets](image)

3.4. Effect of sample rotation speed on LIBS signal intensity

A typical plot of LIBS signal intensity versus the sample rotation speed is presented in Figure 3. It can be seen that the LIBS signal intensity increases linearly with sample rotation speed. For the stationary sample, the emission intensity decreases with time and is almost zero after approximately 100 seconds (1000 laser shots for repetition rate 10 Hz) from the start of the acquisition cycle. The decrease in the LIBS intensity is due to the crater produced by the laser pulses in a stationary sample. The size of the crater increases with time. The crater not only affects the sample ablation rate but also the plasma images produced onto the optical fiber. The sample rotation speed of 12 rotations per minute (rpm) was applied to acquire data for most of the test samples where maximum LIBS signal intensity was recorded.
3.5. Influence of Laser Energy on binding materials

The dependence of Mg signal intensity on the incident laser energy and the used binding material was also studied in this experimental work. Among different binding materials like potassium bromide, poly vinyl alcohol, starch, silver and aluminium, KBr found to be better [13]. The dependence of Mg signal on laser pulse in the matrix of KBr is presented in Figure 1. The LIBS signal for Mg 518.36 nm line intensity is plotted as a function of incident laser energy. It is clear from Figure 1 that LIBS signal is linearly dependent on the incident laser energy which is indicated by the least square fit with R²= 0.999. With higher irradiation laser energy, more material is ablated from the pellet and thus the LIBS signal intensity increases.

3.6. Plasma temperature of iron slag (sample)

The plasma temperature of iron slag sample was calculated using equation 1 and 2 along with Fe lines in the 249.06 to 358.11 nm spectral region, instead of two lines method. The intensity of a spectral line is given by equation 1 [14].

\[ I = \frac{hcAN}{4\pi\lambda U} e^{-\frac{E}{KT}} \]  

(1)

Where in this equation, h is Planck’s constant, c is the velocity of light, λ is the wavelength of the optical transition between two levels, g is the statistical weight of upper state, E is the energy of the upper state, U is the partition function, K is the Boltzmann constant and T is the electrons’ temperature. By taking the natural logarithm of both sides above equation can be written as:

\[ \ln \left( \frac{I}{Ag} \right) = -\frac{E}{KT} + \ln \left( \frac{hcN}{4\pi\lambda U} \right) \]  

(2)

In the above equation, for a given species, the last term is constant, therefore, plotting \( \ln (I/Ag) \) against \( E \) for number of spectral emission lines, will give a straight line of slope \( -\frac{1}{KT} \) and intercept \( \ln \left( \frac{hcN}{4\pi\lambda U} \right) \). Thus by measuring slope, plasma temperature can be determined. In order to be more accurate in temperature determination using LIBS technique, those lines were chosen which were well resolved and also the transition probabilities were known. The spectra were recorded with a 4.5 µs delay time and 20 mJ laser pulse energy. Table 1 gives the values obtained from the measurements to calculate the plasma temperature. The plasma temperature was calculated at 10, 20, 30 and 40 mJ laser pulse energy and was found to be 3626 K, 3876 K, 4149 K and 5554 K.
respectively. The NIST database was used for the calculations of plasma temperature. The Boltzmann distribution and experimentally measured line intensities support the assumption that the laser-induced plasma was in local thermal equilibrium.

| Wavelength (Å) | A×10^{8} s^{-1} | g_i | g_k | E_i (eV) | E_K (eV) |
|----------------|------------------|-----|-----|---------|---------|
| 249.06         | 3.8              | 5   | 7   | 0.087   | 5.06    |
| 252.28         | 2.9              | 9   | 9   | 0       | 4.9     |
| 271.90         | 1.4              | 9   | 7   | 0       | 4.5     |
| 344.09         | 0.084            | 7   | 5   | 0.05    | 3.65    |
| 358.119        | 1.02             | 11  | 3   | 0.85    | 4.3     |

Table 1. Spectroscopic constants of iron lines used in temperature determination for slag sample-1

The variation of temperature of Fe laser produced plasma in slag sample no.1 at delay time of 4.5 µs and laser pulse energy 10, 20, 30 and 40 mJ is shown in Figure 4 below. This figure clearly indicates that with the increase in the laser pulse energy the plasma temperature is also increased.

![Figure 4](image1.png)

**Figure 4.** Variation of temperature of Fe laser produced plasma in slag sample no.1 versus laser pulse energy recorded at delay time of 4.5µs

Boltzmann plot for temperature determination of Fe laser produced plasma slag sample no.1 is shown in Figure 5.

![Figure 5](image2.png)

**Figure 5.** Boltzmann plot for temperature determination of Fe laser produced plasma slag sample no.1 at delay time of 4.5 µs and laser pulse energy 10, 20, 30 and 40 mJ, respectively

3.7. Electron density

In this experimental work the electron densities for Fe lines for iron slag sample were calculated using equation no. 3:

\[ N_e \geq 1.6 \times 10^{16} \Delta E^3 T_e^{-1/2} \]  \hspace{1cm} (3)

Where in the equation no. 3, \( \Delta E \) is the largest observed transition energy for which the local thermal condition holds and \( T_e \) is the excitation temperature (K). The electron density and plasma temperature at laser pulse energy of 10, 20, 30 and 40 mJ are given in Table 2 at 4.0 µs delay time.
Table 2. Plasma temperature and electron densities at different laser pulse energies of sample no.1

| Laser pulse energy (mJ) | Temperature(K) | Electron density (cm⁻³) |
|------------------------|----------------|------------------------|
| 10                     | 3623           | 1.18x10¹⁶               |
| 20                     | 3875.9         | 1.22x10¹⁶               |
| 30                     | 4149.3         | 1.27x10¹⁶               |
| 40                     | 5554           | 1.46x10¹⁶               |

From Table 2 it is clear that with increase in laser pulse energy the plasma temperature and electron densities both increase.

3.8. Analysis of iron plant slag

Slag outputs in iron and steel production depend on the feed material chemistry and the type of furnace. Typically for an ore feed of 60 - 66% iron blast furnace, slag production ranges from about 220 to 370 kilograms per metric ton of pig iron produced. Lower grade ores produce much higher slag fraction. Iron scraps material collected from various locations, contain variety of contaminants. The contaminants present in scrap material can be harmful to the environment and therefore proper analysis of such iron slag is important. The primary hazardous components of iron slag are zinc, lead, cadmium, nickel and chromium [15]. As demand of iron is increasing day by day rapid elemental identification is required for waste management of slag. There are numerous health risk involved to the steel/iron factory workers at workplace and surrounding environment due to solid waste generated from the iron and steel mill industry. The major problem is due to a large volume of the waste generated and of hazardous metals present therein. Quantitative elemental analysis of slag samples was also conducted besides plasma temperature and electron density measurements. The elements like magnesium, lead, copper, calcium, chromium, manganese, sulphur, zinc, titanium, strontium, vanadium, and zirconium in slag samples were identified and quantitative measurements were made. Results obtained on iron slag samples are briefly presented here.

3.9. LIBS spectra of different slag samples

Figures 6 and 7 depict the emission spectra of iron slag samples recorded at 4.5 µs delay time in 200-620 nm regions. Here the laser pulse energy was 20 mJ. The distance between the optical fiber and the plasma was 40 mm. The selected lines of iron were used to study the effect of different experimental parameters and to compare the signal intensities with the calibration curves of the elements under investigation. Elements detected in slag samples and comparison of concentration detected with LIBS and ICP is presented in Table 3.
From Table 3 it is clear that Ba, Cr, and S are present in very high concentrations. For example in sample no. 1, the concentration of Ba = 564 ppm, Cr = 1866 ppm and S = 1397.4 ppm while the maximum permissible limits set by EPA and other regulatory authorities for these elements are: Ba = 2, Cr = 1 and S = 800 ppm respectively. Barium is harmful for skin if it is inhaled during breathing or water containing it is taken. Similarly chromium concentrations is detected to be higher than the maximum permissible limit and breathing a high level of chromium can cause irritation to the nose. However, a limited amount of chromium is an essential nutrient that helps the body to use sugar, protein and fat. During several industrial processes (such as iron slag formation) sulphur compounds are added to the environment that is hazardous to animals as well as humans. These sulphur compounds are toxic and have unpleasant smell: may have other affects on human health [16-18]. For slag samples the precision of LIBS measurements depend on the complexity of the sample, homogeneity, and the reproducibility of the laser shots. Typical RSD values for LIBS are in the range 1–10% and for slag samples, the precision was 2%. The relative accuracy (RA) is calculated using equation no. 4

\[
RA = \frac{|d| + SD \times t_{0.975}}{M} \sqrt{n}
\]

In above equation, d is the difference between the LIBS measurement and the ICP (standard method). SD is the standard deviation of LIBS measurement, M is the measurement from standard method, n is the number of measurements and \( t_{0.975} \) is the value at 2.5% error confidence. It can be seen from Table 4, the relative accuracy is in the range of 0.001 – 0.049, which is quite acceptable for any good instrument.

| Element | Wavelength (nm) (Striganov and Sventitski, 1968) | Sample1 LIBS (ppm) | Sample1 ICP (ppm) | Sample2 LIBS (ppm) | Sample2 ICP (ppm) |
|---------|-----------------------------------------------|----------------------|--------------------|----------------------|--------------------|
| Ba      | 553.5                                         | 564.06               | 553                | 542.28               | 514                |
| Ca      | 393.3                                         | 188700               | 185000             | 188720               | 185000             |
| Cd      | 361.2                                         | 54.4                 | 52                 | 59.97                | 58.8               |
| Cr      | 427.3                                         | 1866.6               | 1830               | 1438.2               | 1410               |
| Fe      | 526.9                                         | 281520               | 276000             | 314100               | 308000             |
| Mg      | 518.2                                         | 80194                | 79400              | 63529                | 62900              |
| Mn      | 403.4                                         | 16564                | 16400              | 16463                | 16300              |
| Na      | 588.9                                         | 1131.2               | 1120               | 751.44               | 744                |
| P       | 438.5                                         | 2747.2               | 2720               | 2272.5               | 2250               |
| S       | 373.8                                         | 1397.4               | 1370               | 1458.6               | 1430               |
| Si      | 288.1                                         | 79285                | 78500              | 64741                | 64100              |
| Ti      | 498.2                                         | 5635.8               | 5580               | 4231.9               | 4190               |
Table 4. Comparison of LIBS with ICP, relative accuracy, limit of detection and delay times for different elements detected in slag sample.

| Element | Wavelength (nm) (Striganov and Sventitski, 1968) | Sample 1 | Relative accuracy (RA) | Standard deviation (S.D) LIBS | LOD LIBS (ppm) | Delay time (µs) |
|---------|-----------------------------------------------|----------|------------------------|------------------------------|----------------|----------------|
|         | LIBS (ppm)                                  | ICP (ppm) |                        |                              |                |                |
| Ba      | 553.5                                       | 564.06   | 553.0                  | 0.020                        | 0.098          | 14.0           | 5.5            |
| Ca      | 393.3                                       | 188700   | 188500                 | 0.001                        | 0.122          | 11.0           | 5.0            |
| Cd      | 361.2                                       | 54.4     | 52.0                   | 0.049                        | 0.129          | 10.0           | 4.0            |
| Cr      | 427.3                                       | 1866.6   | 1830                   | 0.020                        | 0.091          | 7.0            | 5.5            |
| Fe      | 526.9                                       | 281520   | 276000                 | 0.028                        | 0.132          | 6.0            | 4.5            |
| Mg      | 518.2                                       | 80194    | 79400                  | 0.010                        | 0.115          | 9.0            | 5.0            |
| Mn      | 403.4                                       | 16564    | 16400                  | 0.012                        | 0.095          | 6.0            | 4.5            |
| Na      | 588.9                                       | 1131.2   | 1120                   | 0.015                        | 0.119          | 5.0            | 4.0            |
| P       | 438.5                                       | 2747.2   | 2720                   | 0.018                        | 0.125          | 13.0           | 4.5            |
| S       | 373.8                                       | 1397.4   | 1370                   | 0.020                        | 0.128          | 16.0           | 4.5            |
| Si      | 288.1                                       | 79285    | 78500                  | 0.017                        | 0.130          | 10.0           | 4.0            |
| Ti      | 498.17                                      | 5635.8   | 5580                   | 0.013                        | 0.135          | 9.0            | 5.0            |

3.10. Calibration curves for elements under investigation

In order to test the validity of LIBS spectrometer for quantitative analysis on actual iron slag samples, the spectrometer was calibrated for each trace metal of our interest. For the construction of the calibrations curves, two stoichiometric samples of iron slag were prepared. Pure metals in powder form were mixed with the matrix material KBr. Then, pellets were pressed in a 10 bar pellet press. In order to test the homogeneity of our samples, several LIBS measurements were performed at different locations at the surface of the pellets. Four samples of known concentration such as 100,000, 10,000, 1000, and 100 ppm of elements under investigation were prepared in the matrix of KBr and LIBS spectra were recorded for these four concentrations of each element. All these spectra were recorded with an average of 20 laser shots at three different locations on the sample surface. The calibration curves for Cd and Cr are depicted in Figures 8-9.

Thus in this study, two slag samples collected from the local iron plant were characterized qualitatively as well as quantitatively for elemental detection. Ba, Ca, Cd, Cr, Fe, Mg, Mn, Na, P, S, and Si were detected in reasonable abundance in these samples. The results showed excellent correlation with the results obtained from a standard method such as inductively coupled plasma analysis. The calibration curves were effective in quantifying the trace metal concentration in slag samples and for estimation of spectrometer limits. The detected concentration of some of the elements such as Ba, Cr and S was higher than the permissible safe limits.
Conclusion

Laser Induced Breakdown Spectroscopy (LIBS) is applied for the determination of plasma temperature and electron density of iron in iron slag samples. The LIBS spectrometer was carefully optimized for the improvement of LIBS efficiency. The plasma temperature was calculated at 10, 20, 30 and 40 mJ laser pulse energy using standard equations and well resolved spectral lines in the 229.06-358.11 nm region and was found to be 3626 K, 3826 K, 4149 K and 5554 K respectively. The NIST database was used for the calculations of plasma temperature. The Boltzmann distribution and experimentally measured line intensities support the assumption that the laser-induced plasma was in local thermal equilibrium. It was observed that with the increase in the laser pulse energy the plasma temperature is also increased. Electron densities for Fe lines for iron slag sample were calculated which is also increased with increase in pulse energy. Quantitative elemental analysis of slag samples from a local plant was conducted besides plasma temperature and electron density measurements. Concentration of detected elements by LIBS was compared with ICP. The results showed excellent correlation with the results obtained from inductively coupled plasma analysis.

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