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Determination of Different Metals in Steel Waste Samples Using Laser Induced Breakdown Spectroscopy

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Abstract

Elemental analysis of waste samples collected from steel products manufacturing plant (SPS) located at industrial city of Jeddah, Saudi-Arabia has been carried out using Laser Induced Breakdown Spectroscopy (LIBS). The 1064 nm laser radiations from a Nd:YAG laser at an irradiance of 7.6×10^{10} W cm $^{-2}$ were used. Atomic emission spectra of the elements present in the waste samples were recorded in the 200 – 620 nm region. Elements such as Fe, W, Ti, Al, Mg, Ca, S, Mn, and Na were detected in these samples. Quantitative determination of the elemental concentration was obtained for these metals against certified standard samples. Parametric dependences of LIBS signal intensity on incident laser energy and time delay between the laser pulse and data acquisition system were also carried out.

Keywords: *Multi-elemental analysis, steel waste, Laser Induced Breakdown Spectroscopy (LIBS), Hazardous waste, Waste management, trace metals, Emerging analytical technique.*

Introduction

Due to industrial growth and other man made activities, solid waste generated by iron and steel manufacturing plants has been increasing on an alarming rate over the last few decades. There is a need to recognize the impact of solid waste on the environment and its management especially in developing countries for steel manufacturing plants [1]. This waste is contaminating the precious resources such as surface and ground water in addition to the contamination of the fertile soil [2]. There is a growing demand to develop a sensor for rapid determination of the concentration of contaminants present in the solid industrial waste, in particular for those of toxic heavy metals like Pb, Cr, Hg and others [3, 4]. Most available methods such as Atomic Absorption (AA) or Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) require expensive equipment, special sample preparation protocols and are time consuming. To overcome these problems, research community is continuously working on development of new methods which are fast, cost effective and applicable for in situ analysis [5].

Laser-induced breakdown spectroscopy (LIBS), initially introduced by Loree and Radziemski [6], is a powerful analytical method which has undergone a rapid development during the past years. The LIBS technique utilizes a pulsed laser focused on a small spot to create a micro-plasma on the sample surface. The resulting light emission is collected optically and then resolved spectrally to produce intensity versus wavelength spectrum containing emission lines from the atomic, ionic, and molecular species present in the plasma. The power of LIBS lies in its non-intrusive character, permitting on-line analysis in harsh or inaccessible environments [7-10]. The range of applications that utilizes LIBS is also growing rapidly, driven by the material processing industries [11-15]. The technique can be used in a variety of complex analysis such as determination of alloy composition, origin of manufacturer (by monitoring trace components) etc., in vivo medical investigations [16], analysis of biological and pharmaceutical samples [17], archaeological investigations [18], art restoration and paint pigment analysis [19] etc.

In this paper, we present the results of our studies on detection of various metals by LIBS technique in solid waste samples collected from an industrial plant manufacturing steel products, near the Industrial city of Jeddah, Saudi Arabia. The objective is to gauge its

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impact on contamination of soil and ground water, near the plant and the waste dumping sites. We also present the effect on sensitivity of LIBS signal of experimental parameters like incident laser energy and delay time between laser pulse and detector gate opening.

Experimental Setup Details

The experimental set up used for the analysis of steel waste is depicted schematically in Figure 1 and is similar to published in earlier publications [21-26]. The LIBS system consists of Ocean Optics LIBS 2000$^+$ spectrometer, a sample chamber, Nd:YAG Laser (Spectra Physics, Model GCR100) and OOILIBS software. The 1064 nm radiations emitted at fundamental frequency from Nd:YAG laser were applied for production of plasma spark at target surface. Laser beam was focused by a convex lens of focal length 30 mm onto the sample. The pulse energy utilized in these experiments was in the range of 10 - 40 mJ, measured with a calibrated energy meter (Ophir Model 300). The light from the plasma spark is collected by a collimating lens and coupled to LIBS2000$^+$ Spectrometer using a 1 meter UV grade fused silica, multimode sampling optical fiber with SMA connector. The LIBS 2000$^+$ has four spectrometer modules to provide high resolution (FWHM 0.1 nm) with a gated CCD detector having 14,336 pixels for simultaneous recording of the spectrum in the 200 nm to 620 nm wavelength region. The emission is collected at a 45º angle to the incident laser radiation. The spectrometer software reads the data from the detector and reconstructs the spectrum. The sample was mounted on a rotary table. The table was rotated using a step motor having 12 revolutions per minutes. The table was positioned such that the focal volume of the laser pulse was centered on the sample. Twenty laser pulses were directed into the cup to complete one measurement.

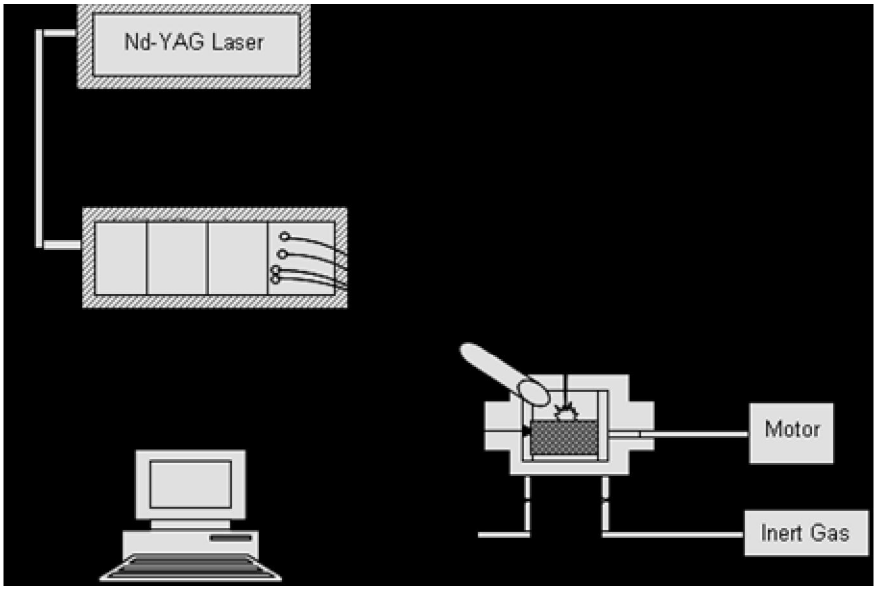

Figure 1. Schematic diagram of the experimental set up applied for recording the LIBS Spectra for steel waste samples.

Sample Preparation

The steel waste samples were colleted from the marked locations at the manufacturing plant using the standard procedure in plastic bags and was stored carefully to avoid any type of external mixing or moisture. This is due to the fact that the mixing of the samples can affect the results. Around 50 waste samples under investigation were dried and ground in Spectro-Mill Ball Pestle Impact Grinder Model 1100-11 from Chemplex industries Inc, USA to a suitable mesh size for Pellets preparation. The sample was mixed thoroughly with KBr matrix, and homogeneity was ensured. In a similar way, standards were prepared by taking pure metals and mixing them with the matrix in known concentrations in the range 0.01 to 10% by weight for each element. The circular disc pellets having diameter 20 mm and thickness 8 mm were made on hydraulic press of Carver laboratory Press model C Sterling W/s 53051 USA. A load of 12500 Pounds per square inch was applied for fifteen minutes.

Results and Discussion
Factors influencing LIBS analysis

A large number of complex processes occur due to the interaction of intense laser radiation with solid sample surface, which are still not completely understood. The focused laser beam produces intense heat at the focal spot, ablates a small part of the solid sample into vapour, excites and ionizes and generates micro plasma. The plasma initially emits continuum radiation due to a variety of processes like recombination, brehmstrahllung etc. and later as it cools down, emits characteristic spectral lines from the neutral and ionic species present in the plasma. The plasma spectrum maybe used to identify the constituents and their concentrations, by a suitable wavelength and intensity calibration methodology.

The intensity of an emission line in the plasma is given by [6, 27, 28].

$$I = h\nu_{ji} A_{ji} N g_j Q^{-1} \exp(-E_j/kT) \quad (1)$$

where ν_{ji} = frequency of the transition from state j → i

A_{ji} = Einstein coefficient for spontaneous emission

N = population density of the atom exited by plasma

h = Planks constant

E_j = energy of the upper excited state of atom

Q = partition function

According to Equation 1, one can determine the population density of the relevant species (atoms or ions) for an element in plasma from a measurement of the absolute intensity of corresponding transition and knowledge of the excitation temperature and atomic constants. However it is not possible to derive a theoretical expression relating N and concentration of that element in solid sample under investigation. Hence, in practice, an empirical relationship is sought between the observed line intensity (I_j) and corresponding concentration (C) i.e.

$$I_j = F(C) \quad (2)$$

Here F (C) is called analyte calibration function and the graph between the LIBS intensity of a line of specific element and the concentration is called the calibration curve. Such curve can be drawn by measurements of reference samples of known concentrations termed as standard samples and can be used to determine the elemental concentration in unknown samples.

The important experimental parameters [20-33] which can influence the sensitivity of LIBS system include the laser pulse (pulse width, energy), the sample homogeneity and the optical sampling geometry (distance from the focusing lens to the sample, focal length of the collecting lens, fiber optics etc). All these parameters were optimized to achieve the optimum conditions (best limit of detection) using the system prior to its applications for the analysis of actual samples. Some of these studies are discussed below.

Effect of Time Delay on LIBS Signal Intensity

Measurements were carried out to find the optimum time delay between the laser pulse and the beginning of the LIBS spectrum acquisition. The delay times were chosen according to the detection of maximum LIBS signal intensity for each element present in steel waste samples.

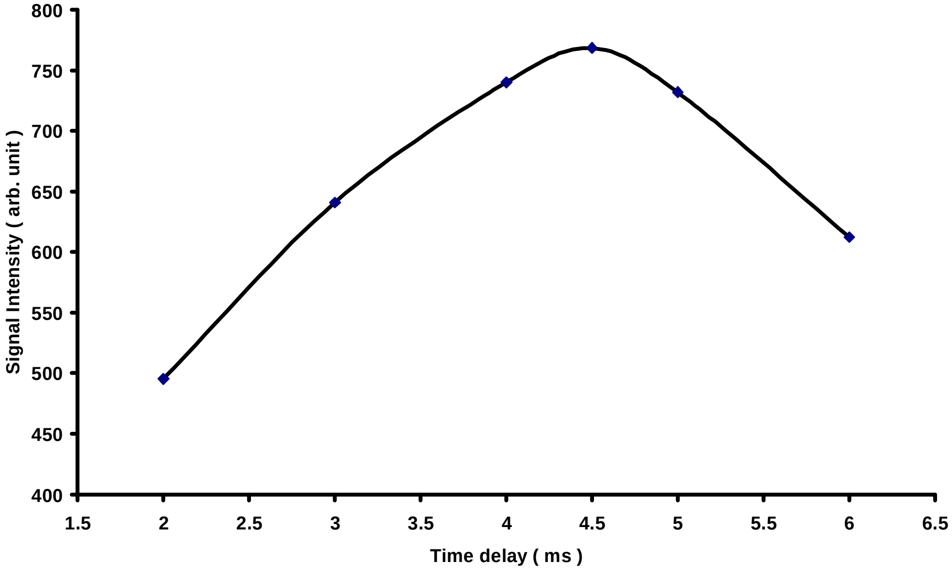

Figure 2. Dependence of LIBS signal intensity on the delay time for (Fe) present in the steel waste sample.

These delay times were controlled by a Q switch trigger pulse to the laser and the trigger pulse to gate of the CCD. A typical plot of dependence of LIBS signal peak intensity (at a wavelength of 526.95 nm) on delay time for Fe I is depicted in Figure 2. It is clear form the figure that the maximum LIBS signal is recorded at around 4.5 µs of delay for Fe I. Other Elements under investigation show the maximum spectral line intensity between 3.0 and 5.0 µs delay time. Clean shots were applied to clean the sample surface before the actual measurements for time delay were carried out.

Effect of Laser Energy on LIBS Signal Intensity

To study the effect of the laser energy on the line emission intensity, we recorded the spectra at different laser energies. All other parameters such as time delay, target rotation speed, laser beam diameter were kept constant. Laser produced plasma spectra from a iron standard sample were recorded in the 200 to 620 nm region at laser energies of 5, 10, 15, 20, and 25 mJ per pulse and the emission intensity of Fe I (526.95nm) line was monitored. A time delay of 4.5 µs was fixed, where maximum signal was recorded. Figure 3 shows a typical trend of energy dependence of laser produced plasma emission spectra for Fe 526.95 nm line intensity. The LIBS signal showed linear dependence on the laser energy with least square fit having R^2 = 0.9999. It can be seen that the intensity increases with increasing laser energy from 5 to 25 mJ per pulse. At higher laser energies (>50 mJ), the rate of increase becomes slower and saturation sets in. It was noticed that a laser pulse energy = 20 mJ per pulse was enough to obtain reasonable line intensity and precision for detection of elements present in steel waste samples under investigation.

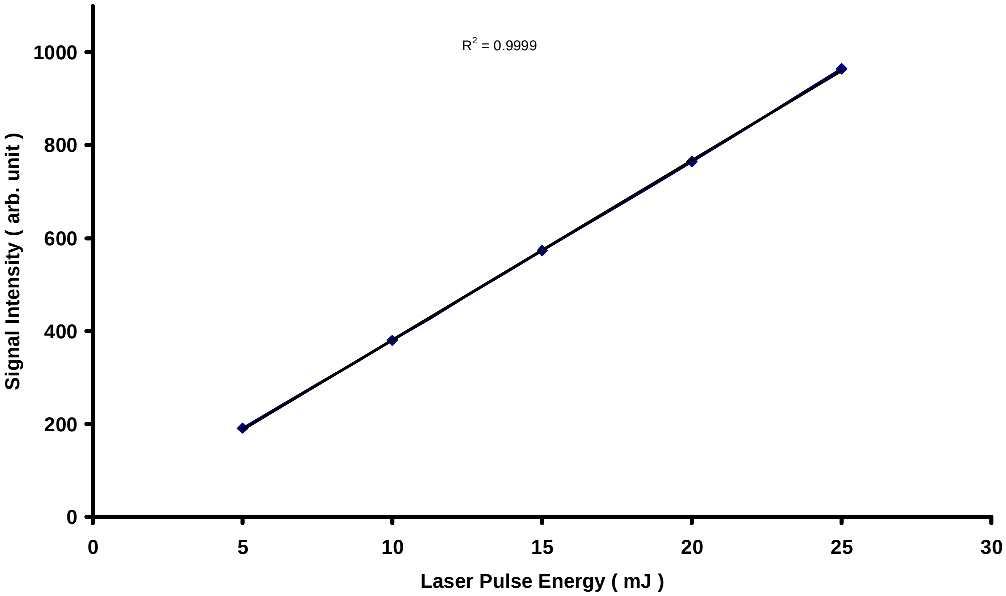

Figure 3. The dependence of the intensity of the Fe 526.95 nm emission line on laser energy recorded with our LIBS system for steel waste sample collected from the steel manufacturing plant.

Calibration Curves for Elements under Investigation

Calibration curves for the standard samples of each element were obtained for several so called signature transition lines of every element. It is worth mentioning that the chosen emission lines have minimal interference from emission lines of other elements and do not involve the ground state so that self-absorption is negligible, and are intense enough. Due to these reasons, these lines are useful for quantitative analysis. A small portion of the spectrum of an iron standard sample is shown in figure 4, in order to depict the resolution and performance of the spectrometer. The transitions are identified and are also marked in the figure. A typical calibration curve for one transition of Fe I is shown in figure 5. The standard samples were also analyzed by ICP-AES method and a relative standard deviation of 2-3% was observed between the two techniques.

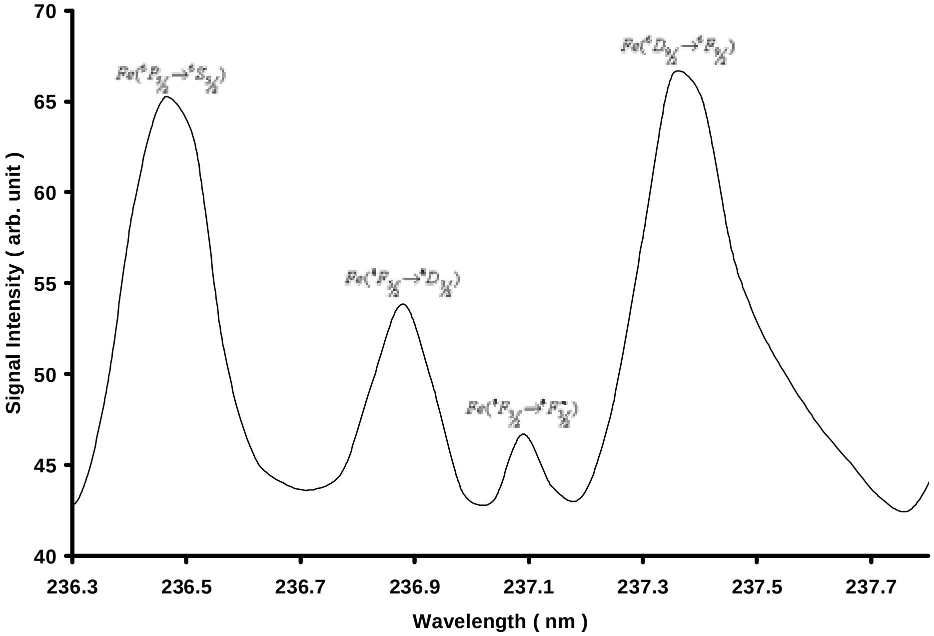

Figure 4: Fine structure components of Fe II present in steel standard sample. This spectrum was recorded in the 236 - 238 nm region at delay time of 4.5 µs and laser pulse energy of 20 mJ.

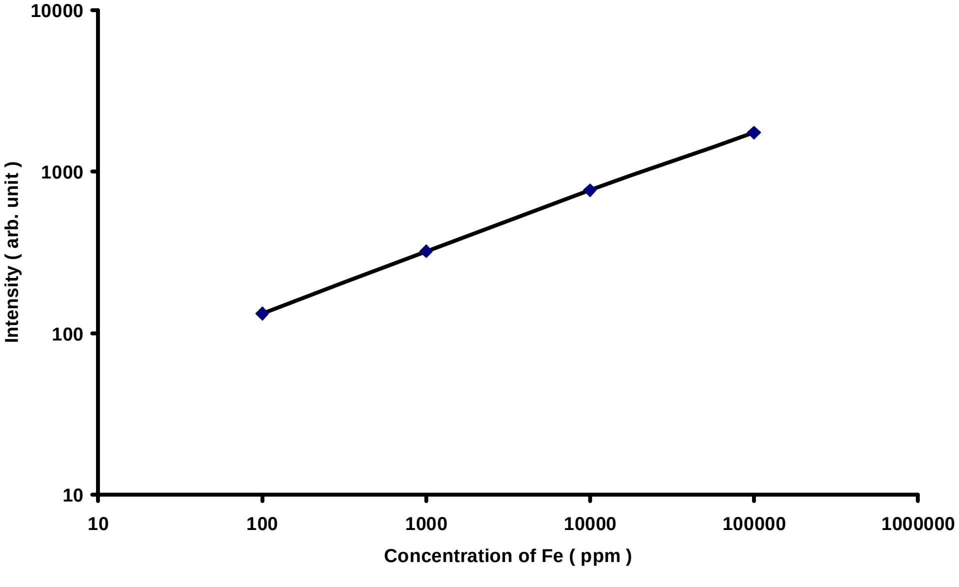

Figure 5: Calibration Curve for Fe I (526.95 nm) line.

Analysis of the steel waste sample

A typical LIBS spectrum of the steel waste sample recorded in the 200 – 620 nm spectral region with our setup is depicted in figures 6. The spectrum was recorded under identical experimental conditions as was done for the standard samples. The laser pulse energy was fixed at 20 mJ. The delay time between laser trigger and the opening of shutter of CCD detector was set at 4.5 µs. Average spectra due to 20 laser shots were recorded for each data point. The averaging of the 20 laser shots reduces the back ground noise to a great extant when compared to the single shot spectrum of the sample.

The LIBS spectrum of steel waste was recorded to identify each element present by finger print wavelength in waste sample. The most sensitive lines were identified in the 200 to 650 nm region. The identification of spectral lines was done by OOILIBS software of the spectrometer. The software compares the observed transitions with its database for several atomic and ionic lines of each element. The assignment of the transitions to a particular element is done on the basis of a confidence factor which is decided by the number of observed transitions as compared to the database values. This assignment was further manually confirmed in the following manner. The upper level of a transition of element is noted and transitions to other levels originating from the same upper level were checked. All the spectral lines for above mentioned elements recorded with our LIBS setup were identified using the NIST atomic spectral data base [34] and using the reference data book [35].

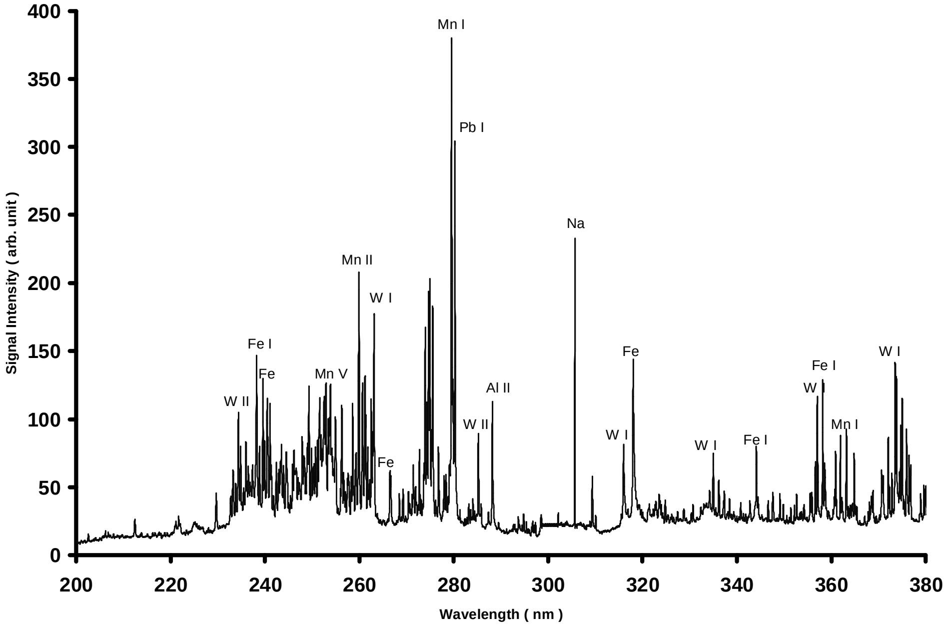

Figure 6. Typical LIBS spectrum for the steel waste sample. The metals detected in steel waste samples are identified using the NIST data base [34] and reference [35].

The metals present in the steel waste sample were thus identified and are marked in figure 6. The major elements detected in the sample are Iron, Tungsten, Titanium, Aluminum, Magnesium, Zinc, Calcium, Phosphorus, Sulfur, Manganese and Sodium. Following signature lines of various elements are observed and selected for quantitative analysis for the reasons discussed above; Fe I (526.95 nm), W I (508.07 nm), Ti (544.66 nm), Al (422.79 nm), Mg (518.35 nm), Ca (585.74 nm), S (616.18 nm), Mn (360.91 nm) and Na (588.9 nm).

Table I summarizes the transitions used for quantitative estimation of concentration of various elements obtained by the intensity calibration procedure. The measurements were carried out for 50 samples collected from the plant and for at least 20 different spots on each sample pellet averaged over 20 laser pulses at each spot. The table shows the maximum, minimum and mean values obtained by this procedure. There are so many health risk involved to the steel factory workers at work place and surrounding environment due to solid waste generated from the iron and steel mill industry. The major problem is due to lot of volume of the waste produced and of hazardous metals present in it. The iron and steel sector generates tons of solid waste and residues annually containing heavy metals due to different sources including iron slag. From Table.1 it is clear that Ti, S, Mn are present in very high concentration. Sulphur is important for humans because it is part of the amino acid methionine, which is an absolute dietary requirement for us. The amino acid cysteine also contains sulphur. The intake of average person per day is around 900 mg of sulphur, mainly in the form of proteins. Elemental sulphur is not toxic, but many sulphur derivates such as sulphur dioxide (SO_2) and hydrogen sulfide are very toxic. Sulfur can be found commonly in nature as sulphides. During several industrial processes (such as iron slag formation) sulfur compounds are added to the environment that are hazardous to animals, as well as humans. These sulphur compounds are unwanted because of their unpleasant smells and are highly toxic.

Sulphur can have different effects on human health. Neurological and behavioral changes, disturbance of blood circulation, heart damage, effects on eyes and eyesight, reproductive failure, damage to immune system and Stomach upset are most common effects on human health due to overexposure to Sulphur containing compounds like iron waste.

Element	**Measured Wavelength (nm)**	**Spectral Assignment of Observed Transitions** **Lower State → Upper State**	**LIBS Signal Intensity (arb. units)**	**Concentration of various elements detected with LIBS(ppm)**		
				Minimum	***Mean***	***Maximum***
Fe I	238.18	$4s\ ^5D_1 \rightarrow 4p\ ^5P_2$	146	21728	22400	23072
	396.92	$3d^7 4s\ ^3F_4 \rightarrow 3d^7 4p\ ^3F_3$	809			
	526.95	$4s\ ^5F_5 \rightarrow 4s4p\ ^5D_4$	768			
	532.80	$4s\ ^5F_4 \rightarrow 4s4p\ ^5D_3$	418			
	537.14	$4s\ ^5F_3 \rightarrow 4s4p\ ^5D_2$	292			
Fe II	558.81	$3d^7\ ^4P_{5/2} \rightarrow 4s\ ^4D_{3/2}$	938			
W I	263.07	$5d^4 6s^2\ ^3H_6 \rightarrow$	178	4947	5100	5253
	357.06	$5d^4 6s^2\ ^5D_3 \rightarrow 6p\ ^5D_4$	116			
Al II	288.145	$3s3d\ ^1D_2 \rightarrow 3s8f\ ^1F_3$	112	6208	6400	6592
	422.79	$3s4d\ ^3D_1 \rightarrow 3s8f\ ^3F_2$	451			
Mn I	360.91	$3d^6\ 4s\ ^6D_{3/2} \rightarrow 3d^6 4p\ ^6P_{3/2}$	70	21340	22000	22660
Ti I	393.42	$4s^2\ ^3F_4 \rightarrow 4s4p\ ^5D_3$	991	4973	5100	5227.5
	455.54	$3d^3 4s\ ^5F_5 \rightarrow 3d^3 4p\ ^5F_4$	142			
	544.66	$4s^2\ ^3F_3 \rightarrow 4s4p\ ^5D_2$	260			
S II	445.63	$4p\ ^4D_{1/2} \rightarrow 5s\ ^4P_{1/2}$	237	1552	1600	1648
	616.18	$3d\ ^2F_{5/2} \rightarrow 4p\ ^4S_{3/2}$	689			
Mg I	518.36	$3s3p\ ^3P_2 \rightarrow 3s4s\ ^3S_1$	419	75855	77800	79745
Ca I	585.74	$4s4p\ ^1P_1 \rightarrow 4p^2\ ^1D_2$	327	20467	21100	21633
	612.22	$4s4p\ ^3P_1 \rightarrow 4s5s\ ^3S_1$	490			
Na I	588.99	$3s\ ^2S_{1/2} \rightarrow 3p\ ^2P_{3/2}$	1600	927	954	981
	589.59	$3s\ ^2S_{1/2} \rightarrow 3p\ ^2P_{1/2}$	1730			

Conclusions

The elements present in steel waste samples were determined using Laser Induced Breakdown Spectroscopy. The elements present in the sample collected from steel manufacturing plant (SMP) located in Jeddah Saudi-Arabia such as Fe, W, Ti, Al, Mg, Calcium, P, S, Mn, and Na were identified accurately. The concentration and the spectral assignment of the transitions of elements detected with our setup are listed in Table-1. Here, the sensitive lines for above mentioned elements were identified for the elemental analysis. Standard deviation of 2 - 3% in concentration values was obtained by rigorous intensity calibration procedure.

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