Laser induced breakdown spectroscopy (LIBS) as a rapid tool for material analysis

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Abstract. Laser induced breakdown spectroscopy (LIBS) is a novel technique for elemental analysis based on laser-generated plasma. In this technique, laser pulses are applied for ablation of the sample, resulting in the vaporization and ionization of sample in hot plasma which is finally analyzed by the spectrometer. The elements are identified by their unique spectral signatures. LIBS system was developed for elemental analysis of solid and liquid samples. The developed system was applied for qualitative as well as quantitative measurement of elemental concentration present in iron slag and open pit ore samples. The plasma was generated by focusing a pulsed Nd:YAG laser at 1064 nm on test samples to study the capabilities of LIBS as a rapid tool for material analysis. The concentrations of various elements of environmental significance such as cadmium, calcium, magnesium, chromium, manganese, titanium, barium, phosphorus, copper, iron, zinc etc., in these samples were determined. Optimal experimental conditions were evaluated for improving the sensitivity of developed LIBS system through parametric dependence study. The laser-induced breakdown spectroscopy (LIBS) results were compared with the results obtained using standard analytical technique such as inductively couple plasma emission spectroscopy (ICP). Limit of detection (LOD) of our LIBS system were also estimated for the above mentioned elements. This study demonstrates that LIBS could be highly appropriate for rapid online analysis of iron slag and open pit waste.

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a useful technique that requires optical access to the sample surface and can be used as a fast method for the detection and quantification of the contaminants in various categories of samples. It is an emerging technique for elemental determination in a wide range of environmental samples, metallurgical, metallic and non-metallic, sewage sludge, liquid, aerosol, gases and biological samples etc [1-7]. Several elements can be measured with this technique simultaneously even at parts per million concentration level. In this technique, laser pulses are applied for ablation of the samples, resulting in the vaporization and ionization of sample in hot plasma which is finally analyzed by the spectrometer. The elements are identified by their unique spectral signatures [8-10].

Recent developments towards improving analytical capabilities of this technique have led to more applications of LIBS. However, still more efforts are required to improve the precision and the sensitivity of this technique. Some improvement in methodology is needed for its wide applications in terms of its efficiency and limit of detection [11-13].
The quantification and characterization of large variety of samples of various natures require special technique like LIBS. Some capabilities of LIBS as a rapid tool for analysis of sample are pollution monitoring in air, soil, sewage sludge, ground and wastewater, determination of ore composition during mining, chemical analysis of explosive materials, forensics and biochemical applications, detection of radioactive contamination and hazardous materials. This technique can also be used for rapid identification of metals and alloys during recycling of scrap materials, on-line compositional analysis of the molten metals, on-line compositional analysis of liquid glass for process control (iron, lead etc), depth-profiling and compositional analysis of surface coatings (galvanized steel, plastic coating and heavy-metals in paint), on-line monitoring of particulates in air (stack emission monitoring etc.) [14].

Some of the potential benefits of this technique include, that sample analysis cost by LIBS is low as compared to other conventional analytical techniques and can analyze large number of samples in short span of time. It is capable of doing multi elemental analysis simultaneously. All state of matter (solid, liquid and gases) can be analyzed. LIBS can be used for analysis of extremely hard materials that are difficult to digest or dissolve, e.g. ceramics and superconductors. In LIBS minimal sample preparation is required which reduces worker exposure to hazardous radioactive or toxic substances. LIBS requires small amount (µgm) of sample, and element detection limit can be achieved in the range of ppm/ppb. In addition to its potential benefits there are some inherent disadvantages of this technique: It is difficult to obtain suitable standards for LIBS analysis because of matrix effect. For quantitative analysis, the sample matrix must closely match the matrix of the standards. The detection limits for solids are generally not as good as established by others techniques [15-16].

The detection and quantification of heavy metals within liquid samples are pertinent to industrial processing, environmental monitoring and waste treatment. In the last decade laser-induced breakdown spectroscopy has become a prime area of scientific and technological interest for researchers in the various fields of science. To-date, laser-induced breakdown spectroscopy (LIBS) has been tested with limited success for liquid samples. Dissolved gases, particulate material and bubbles produced by prior laser pulses can lead to misfocusing of the laser beam and can also serve as breakdown sites prior to the laser beam focus and additionally, the high local density within the liquid leads to rapid quenching which prohibits temporally selective detection, high collision rates which broaden spectral transitions and confines the plasma emission spatially rendering spatially selective detection. Due to these inherent problems, in LIBS analysis of liquids has not been widely successful [17].

In this study the LIBS was applied for characterization of iron & steel plant slag and open pit ore samples. By considering various needs for optimum LIBS measurement a sample chamber and sample rotating system was developed and fabricated. In this system the solid sample is placed in the aluminum cup and sample is rotated by a step motor. The important parameters such as laser energy, distance between fibre optics and target material, sample rotation speed and delay time were optimized. The optimized parameters were tested for the preparation of the calibration curves for Mg, Pb, Cu, Ca, Cr, Cd, S, Mn, P, K and other element of interest. Limits of detection (LOD) of our system were also estimated for these elements. The application of LIBS for the analysis of iron and steel plant slag waste residue is very innovative and environmentally significant. Similarly the use of LIBS for the analysis of waste generated from open pit mine are of diverse in nature. Wastes produced by open pit mine are in large quantity and most of their constituents are hazardous. Similarly iron slag is produced annually as a by-product of iron in the steel production industry. Steel plants normally use electric arc furnaces to produce steel from steel scrap. During melting of scarp steel, a slag forms on the top surface of the molten metal and is removed. Steel plant slag is a hard, dense material. Slag output in iron and steel production depend on the feed material chemistry and the type of furnace. Typically for an ore feed of 60% to 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. Steel slag output is typically 20% by mass of the steel output as per U.S. geological survey report. Indeed, the steel industry slag has been classified as hazardous waste and has been of great concern to the U.S Environmental Protection Agency [18].

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 slag is important. The primary hazardous components of iron slag are zinc, lead, cadmium, nickel and chromium [18]. Classification and identification of slag has been the subject of most government environmental agencies in the world and different research laboratories are using different techniques for elemental identification of slag waste. 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 now becoming important and gaining high priority. There are numerous health risk involved to the steel factory workers at workplace and surrounding environment due to solid waste generated from the iron and steel mill industry.

The second sample under investigation was open pit ore sample. The reason to select this kind of sample is that, from an environmental prospect, the acidity and metal concentrations originating from the open pits are extremely toxic. Changes in surface water and groundwater due to waste-dumps at open pits and mining sites could cause significant environmental effect. For example, under certain conditions, surplus water discharged from mine dump into the nearby streams disrupts riparian ecosystems, can effect local and regional groundwater qualities. Due to these environmental concerns, the characterization and analysis of ore samples from open pit mining are very important and needs rapid detection. We tested our LIBS spectrometer for the analysis of these ore samples.

2. Materials and Methods
Two different types of samples iron slag and open pit ore sample were analyzed using LIBS technique to study its capabilities as a rapid tool for material analysis. The details about each sample collection and its preparation are as follow: - Iron slag samples were collected from a major steel manufacturing plant situated in Jubail, Saudi Arabia. These samples were grinded in spectro mill ball pestle impact grinder (Model 1100-11, Chemplex Industries, Inc. 10707, USA) to suitable mesh size for preparation of pellets. The slag samples under investigation were pressed to pellets shape by applying a load of 8.6×107 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. The second sample under investigation was the ore sample. The ore samples tested in this study were collected from an open pit of the Al-Khnaiguiyah Zn-Cu mine, located at GPS: N, 24°16'10.2"; E, 45°05'24.5". For calibration purposes, the elements used were Pb, Cu, Cr, Ca, S, Mg, Zn, Ti, Sr, Ni, Si, Fe, Al, Ba, Na and Zr. All these elements were obtained in powder form with high purity 99.99%. For the construction of calibration curves, stoichiometrically different samples comprising these metals were prepared. Metals in powder form were mixed with the matrix material KBr in a ball milling apparatus in order to ensure good mixing and homogeneity.

For the analysis of ore samples using the ICP technique, the ore samples were ground to powder form, digested by concentrated HNO3 (99.99%, Fisher Scientific, USA) and were left over night. The resulting residue was then dried at 500°C. The dried samples were further treated with HNO3 and the resulting solution was analyzed for poisonous metals using the inductively coupled plasma spectrometer. For LIBS, ore samples under investigation were prepared in the dimensions 4 cm x 6 cm and a thickness of 2 cm. These samples were filed, polished and were placed in to LIBS ablation chamber for analysis.

The experimental setup applied for the analysis of slag and ore sample is presented in Figure 2. Nd:YAG Laser (Spectra Physics, Model GCR100) was employed for production of plasma spark at the sample surface. This laser can deliver maximum pulse energy of one joule with a pulse width of 8 ns and operate at a 10 Hz pulse repetition rate in Q-switched mode. A pulse from this Nd-YAG laser at fundamental wavelength 1064 nm was focused by a convex lens having focal length 30 mm onto the surface of samples to create a plasma spark in the sample. The pulse energy utilized in these experiments was in the range of 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 and a locally-designed sample chamber as shown in Figure 1, along with the OOLIBS software.
Figure 1. Locally designed sample chamber

The light from the plasma spark is collected by a collimating lens using UV graded fused 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. Prior to the application of our LIBS technique on samples under investigation the spectrometer was calibrated for each trace element present in the sample. The detection limit for various elements under investigation was also measured. Detection limit here means the lowest concentration that can be detected with LIBS. The limit of detection (LOD) was estimated using the equation [19].

\[
\text{Limit of detection (LOD)} = \frac{2\sigma_b}{S}
\]

Where \(\sigma_b\) is the standard deviation of the background (noise level) and \(S\) is calibration sensitivity (\(S = \text{slope of the calibration curve}\)) which is the ratio of the line intensity to the concentration. The standard deviation of the mean value was calculated from these measurements. All kinds of electronic noise (e.g., CCD dark current) were measured separately and were subtracted from the measured spectra prior to the analysis of samples.
2.1. Optimization of various parameters of LIBS
Before going to perform experiments on actual samples the LIBS system developed at our laboratory was optimized for various parameters involved. The optimization of signal intensity Vs laser pulse energy for Mg 518.36 nm line, signal intensity Vs time delay for Mg 518.36 nm line, variation of the intensity of the Mg 518.36 nm emission line with the change in the position of collecting lens from the sample, effect of lens distance on focusing signal intensity and sample rotation speed are shown in the following diagrams.

Figure 2. Schematic diagram of the LIBS experimental setup applied for the analysis of samples
Figure 3.
(a) Signal Intensity Vs Laser pulse energy for Mg 518.36 nm line.
(b) Signal Intensity Vs Time delay for Mg 518.36 nm line.
(c) Variation of the intensity of the Mg 518.36 nm emission line with the change in the position of collecting lens from the sample.
(d) Effect of lens distance on focusing signal intensity.
(e) Sample Rotation Speed.
3. Results and Discussion

3.1. Analysis of Iron and Steel plant slag

Figure- 4 depicts the emission spectra of iron slag samples recorded at 4.5 µs delay time in 200-620 nm region. Here the laser pulse energy was 20 mJ. 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 1. From Table 1, it is clear that Ba, Cr, and S are present in very high concentrations. For example in sample under investigation, the concentration of Ba = 564 ppm, Cr = 1866 ppm and S = 1397 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. The health risk associated with barium to workers in iron and steel mill are breathing dust, eating soil or drinking water that is polluted with barium and harm to skin due to contact with soil or scrap. Similarly we detected chromium concentrations also higher than the maximum permissible limit although a limited amount of chromium is an essential nutrient that helps the body to use sugar, protein and fat. However, breathing a high level of chromium can cause irritation to the nose. During several industrial processes (such as iron slag formation) sulfur compounds are added to the environment that is hazardous to animals, as well as humans. These sulphur compounds are unwanted because of their unpleasant smells and are highly toxic, and they can have different effects on human health [20–23]. For slag samples the precision of LIBS measurements depend on the complexity of the sample, homogeneity, and the reproducibility of the laser shots.

![Typical spectrum of slag sample in 200 to 620 nm region recorded at delay time of 4.5 µs and laser pulse energy of 20 mJ](image)

**Figure 4.** Typical spectrum of slag sample in 200 to 620 nm region recorded at delay time of 4.5 µs and laser pulse energy of 20 mJ

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 1

\[
RA = \frac{|d| + SD \times t_{0.975} n^{-1/2}}{M}
\]

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 t value at 2.5% error confidence. As it
can be seen from Table 1 the relative accuracy is in the range of 0.001 – 0.049, which is quite acceptable for any good instrument.

Table 1. 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) | Slag Sample | Relative accuracy (RA) | Standard deviation (S.D) LIBS | LOD LIBS (ppm) | Delay time (µs) |
|---------|-------------------------------------------------|-------------|------------------------|-------------------------------|----------------|----------------|
| 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           |

3.1.1. Calibration Curves for Elements under Investigation

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 5 and 6.

Thus in this study, slag samples collected from the local iron and steel 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 detected concentration of some of the elements such as Ba, Cr and S was higher than the permissible safe limits.

Figure 5. Signal intensity versus Cd concentration at 4.5 µs time delay and laser pulse energy 20 mJ. Error bars denote 95% confidence limits and are based on triplicate measurements.
Figure 6. Signal intensity versus Cr concentration at 4.5 µs time delay and laser pulse energy 20 mJ. Error bars denote 95% confidence limits and are based on triplicate measurements.

Calibration curves for elements under investigation were also estimated by the total intensity of a spectral line 'I' from an excited atom or ion in homogenous and optically thin plasma for a transition from state \( j \rightarrow i \). It is given by [24].

\[
I = h \nu_{ji} A_{ji} N_j
\]  

(2)

Where \( \nu_{ji} \) is the frequency of the transition from state \( j \rightarrow i \), \( A_{ji} \) the Einstein coefficient for spontaneous emission, \( N_j \) the population of the upper level \( j \) and \( h \) is the Planks constant.

If the energy levels concerned are in local thermodynamic equilibrium (LTE), then population density of upper level \( N_j \) is related to ground level number density (\( N \)) by Boltzmann’s equation [29].

\[
N_j = N g_j Q^{-1} \exp \left( \frac{-E_j}{kT} \right)
\]

(3)

In above equation \( g_j \) and \( E_j \) are the statistical weight and energy of upper level \( j \), respectively and \( Q \) is the partition function of relevant species, \( K \) is the Boltzmann’s constant and \( T \) is the electron temperature of the plasma. So from above two equations, we get:

\[
I = h \nu_{ji} A_{ji} N g_j Q^{-1} \exp \left( \frac{-E_j}{kT} \right)
\]

(4)

According to equation 4, 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.:

\[
I_j = F(C)
\]

(5)

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 sample like our solid samples. A plot of intensity \( I_j \) as a function of elemental concentration \( n_j \) yields the calibration curve. If the dependence of LIBS signal intensity on the elemental concentration is linear then we can determine the unknown concentration of particular element at any LIBS signal intensity \( I_j \) provided that the same experimental parameters (time delay, incident laser energy, collecting fiber optics and incident focusing optics distance, target rotation speed, atmospheric pressure) are selected.
3.2. Analysis of ore samples

Figure 7 shows the emission spectrum of the ore sample at time delay of 4 µs recorded in 200 nm to 620 nm spectral region. In this case the laser pulse energy was 25 mJ. The LIBS spectra of Fe, Cr, Mn, Si, and Al were recorded in 200 to 620 nm spectral region to detect the lines of each element. The Cu lines were detected at wavelength of 515.3 and 521.8 nm. The Mg line was detected at 516.7 nm while other lines detected for Ca, Si and Fe are listed in Table 2.

![Emission spectrum of ore sample in 200-620 nm spectral region](image)

**Figure 7.** Emission spectrum of ore sample in 200-620 nm spectral region

| Element | Wavelength (nm) | LOD (ppm) | Concentration LIBS (ppm) | Concentration ICP (ppm) | Delay time (µs) |
|---------|----------------|-----------|--------------------------|-------------------------|-----------------|
| Cu      | 521.82         | 14.0      | 805                      | 716                     | 5.0             |
| Zn      | 330.6          | 12.0      | 145                      | 125                     | 4.5             |
| Ca      | 442.5          | 6.0       | 1215                     | 1110                    | 5.0             |
| Ti      | 498.17         | 3.5       | 73                       | 69.6                    | 4.5             |
| Fe      | 537.14         | 5.0       | 597,000                  | 591,000                 | 5.0             |
| Si      | 594.85         | 10.0      | 81,150                   | 80,600                  | 4.0             |
| Mg      | 516.73         | 11.0      | 3478                     | 3380                    | 4.5             |
| Mn      | 404.13         | 2.0       | 1150                     | 1060                    | 5.5             |
| Cr      | 427.48         | 4.0       | 72.1                     | 60                      | 5.5             |
| Al      | 237.31         | 10.0      | 10,205                   | 10,100                  | 4.5             |

The major elements detected in the sample are copper, chromium, calcium, magnesium, zinc, titanium, silicone, iron, aluminum and manganese are shown in Figure 7. All the spectral lines for the above-mentioned elements recorded with our LIBS setup were identified using the NIST atomic spectral data base and also using the reference [24]. It is clear from the Table 2 that concentration of iron, aluminum and calcium is relatively high which is due to natural geological composition of area. Reasonable amounts of Cu, Zn and Mg are also present in the sample. The concentration of aluminum and chromium in the ore sample are 10,205 ppm and 72.1 ppm which are quite high as compared to permissible safe limits of 30 ppm and 1 ppm set by Environmental Regulation Standards by Royal Commission Jubail, Saudi Arabia. These high concentrations can effect the nearby surface water resources and soil through run off during rain.
Plasma plume images of laser induced plasma recorded at ore sample at laser pulse energies of 25, 30, 35 and 40 mJ are shown in Figure 8.

Figure 8. Images of laser-induced plasma plume produced on the ore sample at different laser energies.

The concentrations of trace metals estimated with our LIBS setup are in close agreement with the results achieved with the inductively coupled plasma spectrometry (ICP). The experience gained through this work can be useful for the development of a portable system for rapid online analysis of solid waste from open pits, mineral processing units and geological rock analysis.

4. Conclusions
In this study, the ability of LIBS as a rapid tool for material analysis was discussed briefly. Two samples slag from iron and steel plant and open pit ore sample was tested. Slag samples collected from the local iron and steel 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 detected concentration of some of the elements such as Ba, Cr and S was higher than the permissible safe limits. Similarly the second sample under investigation was the open pit ore sample. The concentration of various trace elements (Cu, Cr, Ca, Mg, Zn, Ti, Si, Fe and Al) present in the ore sample collected from the Al-Khnaiguiyah open pit mine, west of Riyadh in Saudi Arabia, was measured to study the capabilities of LIBS. The sensitive lines for above mentioned elements in both sample iron slag and ore were identified using standard data published by NIST for the elemental analysis and the calibration curves were effective in quantifying the trace metal concentration in samples. The concentrations of trace metals estimated with our LIBS setup agree with another well-established standard method such as the inductively coupled plasma spectrometry (ICP). The experience gained through this work can be useful for the development of a portable system for rapid online analysis of solid waste from open pits, mineral processing units, geological rock and iron slag analysis.
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References

[1] Ying M, Xia Y, Sun Y, Lu Q, Zhao M and Liu X 2003 Study of the plasma produced from laser ablation of a KTP crystal Appl. Surf. Science 207 227-235
[2] Russell S H, Frank C D, Andrzej W M, Kevin L M, Roy A W and Patrick D F 2005 Laser-induced breakdown spectroscopy (LIBS) – an emerging field-portable sensor technology for real-time, in-situ geochemical and environmental analysis Environment Analysis 5 21-28
[3] Lazic V,Colao F, Fantoni R, and Spizzichino V 2005 Laser-induced breakdown spectroscopy in water: Improvement of the detection threshold by signal processing Spectrochimica Acta Part B 60 1002-1013
[4] Gondal M A, Hussain T, Yamani Z H and Bakry A H 2007 Study of hazardous metals in iron slag waste using laser-induced breakdown spectroscopy J. Environment Science and Health Part A 42 (6) 767-775
[5] Gondal M A, Hussain T, Yamani Z H and Baig M A 2007 The role of various binding materials for trace elemental analysis of powder samples using laser-induced breakdown spectroscopy Talanta 72(2) 642-649
[6] Gondal M A, Hussain T, Ahmad Z and Bakry A 2007 Detection of contaminants in ore samples using laser-induced breakdown spectroscopy Journal of Environmental Sciences and Health Part A 42 879-887
[7] Hussain T and Gondal M A 2008 Detection of toxic metals in waste water from dairy products plant using laser-induced breakdown spectroscopy Bulletin of Environmental Contamination & Toxicology 80(6) 561-565
[8] Gondal M A, Hussain T, Yamani Z H and Ahmad Z 2007 Determination of toxic metals in petroleum, cultivated land and ore samples using laser-induced breakdown spectroscopy Bull. Environ. Contam. Toxicol 78 270-274
[9] Hussain T, Gondal M A, Yamani Z H and Baig M A 2007 Measurement of nutrients in green house soil with laser-induced breakdown spectroscopy Environmental Monitoring and Assessment 124 131-139
[10] Gondal M A, Hussain T, Yamani Z H and Baig M A 2006 Detection of heavy metals in Arabian crude oil residue using laser-induced breakdown spectroscopy Talanta 69 1072 -1078
[11] Gondal M A, Hussain T and Yamani Z H 2008 Optimization of the LIBS parameters for detection of trace metals in petroleum products Energy Sources Part A-Recovery, Utilization and Environmental Effects 30 441-451
[12] Radziemski L J and Cremers D A 1989 Laser-induced plasma and applications (New York: Marcel Dekker) pp 295-325
[13] Natrellla M G 1963 Experimental Statistics NBS Handbook vol 91 (National Institute of Standards and Technology, Gaithessburg, MD)
[14] Cho H H, Kim Y J, Soo JoY, Arai N and Lee Y 2001 Application of laser-induced breakdown spectrometry for direct determination of trace elements in starch-based flours J. Anal. At. Spectrum 16 622-627
[15] Radziemski L J 2002 From LASER to LIBS, the path of technology development Spectrochimica Acta part B Atom Spectrosc 57 1109-1113
[16] Rusak D A, Castle B C, Smith B W and Winefordner J D 1998 Recent trends and the future of laser-induced breakdown spectroscopy. Trends in Anal. Chem. 17 453-461
[17] Cremers D A, Radziemski L J and. Loree T R 1984 Spectrochemical analysis of liquids using the laser spark Appl. Spectrosc. 38 (5) 721-729
[18] 1998 World Bank Handbook Pollution Prevention and Abatement, Iron and Steel manufacturing: Draft technical background document (Washington, DC: environment...
[19] Telle H H, Beddows D C S, Morris G W and Samek O 2001 Sensitive and selective spectrochemical analysis of metallic samples: the combination of laser-induced breakdown spectroscopy and laser-induced fluorescence spectroscopy Spectrochim Acta Part B 56 947–960

[20] Lee P N and Corning D M 1993 Experimental toxicology: The basic issues (Cambridge: The Royal Society of Chemistry) pp 405-440

[21] 1999 (Royal Commission: Jubail Industrial City-Saudi-Arabian Environmental Regulation Standards) and Greenberg A E 1992 Standard Methods for the examination of water and wastewater 18th ed., ed. Clescerl L and Eatom A D. (American Public Health Association: Washington, D.C).

[22] Abdellatif G and Imam H 2002 A study of laser plasma parameters at different laser wavelength Spectrochimica Acta Part B 57 1155-1165

[23] Song K, Lee Y I and Sneddon J 1997 Application of laser–induced breakdown spectroscopy Applied Spectroscopy Reviews 32 183-235

[24] Striganov A and Sventitski N 1968 Handbook Table of Spectral Lines of Neutral and Ionized Atoms (New York: Plenum)