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Detection of heavy metals in Arabian crude oil residue using laser induced breakdown spectroscopy

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Abstract

Laser induced breakdown spectroscopy (LIBS) was applied for the elemental analysis of Arabian crude oil residue samples. The spectra due to trace elements such as Ca, Fe, Mg, Cu, Zn, Na, Ni, K and Mo were recorded using this technique. The dependence of time delay and laser beam energy on the elemental spectra was also investigated. Prior to quantitative analysis, the LIBS system was calibrated using standard samples containing these trace elements. The results achieved through this method were compared with conventional technique like inductively coupled plasma.

Keywords: Laser induced break down spectroscopy (LIBS); Analysis of solid crude oil waste; Continuous emissions monitoring; Environmental impacts of trace metals; Trace metals detection; LIBS applications

1. Introduction

The growth of petroleum industry worldwide and marketing of petroleum products has resulted in the pollution of the environment with heavy metal due to oil spills and leakage from oil tanks or tanker trucks and waste oil dumps. The effects of such pollution on the environment, humans, live stocks, wild life, aquatic life, crops and soil have been enormous [1]. Petroleum exploration and development also generates large amounts of gaseous, liquid and solid wastes containing hazardous species which have strong impact on our environment [2,3]. The hazardous waste generated from the petroleum industry poses great dangers to human and animal health since some of the waste is non-degradable; i.e. it could stay in the soil for many years and pollute precious water resources. An example of water contamination is in the supply of drinking water in Bangladesh and west Bengal in India where arsenic levels are much above the permissible level due to the contamination of various heavy metals.

In addition, long and even short term exposure to small quantities of metals such as Copper (Cu), Nickel (Ni), Arsenic (As), Beryllium (Be), Molybdenum (Mo), Zinc (Zn), Chromium (Cr) and Antimony (Sb) can lead to long-term health consequences. These elements have exhibited a propensity to accumulate in the human body, causing irreversible damage [3,4].

The other adverse effect of trace metals in crude oil is represented in the form of marine pollution through oil spillage, effluent discharge from industrial units, and waste disposal of crude oil into the ocean. Phytoplankton serves as food for fishes and higher organisms. Phytoplankton was found to absorb significant amounts of dissolved matter from the seawater, and phytoplankton has been found to be highly susceptible to various contaminations including hydrocarbon, crude oil and heavy metals [4].

The other motivation of trace elements detection in oil residue is for oil exploration. Information on trace element concentrations in crude oil is getting increasingly important for the geochemical characterization of source rocks and basins and for corrective actions during oil production and refining (e.g. prevention of scale formation and catalyst poisoning, corrosion and pollution control). Trace metals occur in crude oil partly as organo-metallic compounds, from which the geoporphyrins of V, Ni, Cu and Zn have been identified. The contamination of oil with Fe, As and Ba, and Vanadium has been reported [5,6]. The ability to separate each phase contribution (oil–water-

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particulate) together with the low concentration of trace elements in crude oil, and the instrumental limitations of the most common methods employed until now is not possible.

Solid wastes generated from oil are of diverse nature in its characteristics, large in number and most of the constituents are hazardous. Thus, quantifying and characterizing the generated amounts in association with their types, classes and sources require special techniques. Recently, inductively coupled plasma mass spectrometry (ICP-MS) has been applied for trace element determination in oil and its derivatives due to the known advantages of this technique, such as lower limits of detection (LOD), multi-element and isotopic-ratio measurement capability, and steadily decreasing investment costs. Nevertheless, ICP-MS has been applied not only for the inorganic characterization of crude oil and its derivatives, but also as a valuable tool for studying the physico-chemical fundamentals of plasma–solvent interactions. However, detection of heavy metals in crude oil using ICP-MS is neither straightforward nor problem free. In ICP-MS, the presence of solvent vapor in the plasma causes carbon deposition on the cooler surfaces of the sampler/skimmer and on the ion lenses, affecting the transport efficiencies of ions. In addition, polyatomic interferences caused by carbon–argon species seriously limit the quantification of Mg, Cr and some other elements. Moreover, common analytical techniques for environmental monitoring of heavy toxic metals in oil sample are usually time consuming. Thus, new and alternative techniques for rapid identification of elements in waste crude oil samples need to be investigated and developed.

In order to overcome the above-mentioned problems, laser induced breakdown spectrometry (LIBS) has been assembled at our laboratory for the detection of trace metals in crude oil. The development of the LIBS system for environmental and other analytical applications is a continuity of our group activities for development of laser based pollution monitoring systems like Photoacoustic and LIDAR system [7–11]. The unique features of LIBS are: it is a simple, rapid, remote, real-time analysis without sampling requirements.

LIBS is based on the analysis of the spectral emission from laser induced sparks or plasma from the sample. LIBS permits real-time qualitative identification of trace elements in solids, gases and liquids via optical detection of elemental emission spectra. Using this technique, little sample preparation is required and calibration-free quantitative analysis has been reported [12–17]. In recent years, LIBS technique has been successfully applied for fast multi-elemental pollutant analysis in atmosphere and in solid matrix. LIBS can be useful for analysis of liquid and solid samples for a variety of applications such as industrial materials analysis, prospecting and mining, environmental monitoring, homeland security measures, military chemical and biological agents, forensics analysis, pharmaceutical research and development, engine oil analysis, in addition to gemology and counterfeit detection [18–32].

The primary objective of this study is to estimate the concentrations of trace metals (Ca, Fe, Mg, Cu, Zn, Na, Ni, K and Mo) inside oil residue. This study is also important for oil waste treatment of hydrocarbons in gross sediments that are known to have been exposed to: (a) long-term natural oil seepage; (b) anthropogenic activities with refined petroleum products input; and/or (c) pristine conditions. This study could be also useful to develop a portable system for detection of trace metals and hydrocarbon accumulations in sea water resulting from the accidental crude oil spills into the sea during the transportation of crude oil by ships which pollutes the marine environment.

This can also be useful for soil analysis contaminated with crude oil due to petroleum industry installations, at oil dumps, crude oil production terminals and for finger printing of oil slicks.

For the detection and analysis of crude oil samples obtained from a local major oil producing company, a LIBS spectrometer was used. A Q-Switch Nd-YAG laser was employed to vaporize material from solid crude oil samples and to generate the plasma for trace elemental analysis. The spectrally resolved emissions due to different trace metals present inside the oil residue sample were recorded and used for detection of trace metals.

2. Experimental setup details

The schematic diagram of our LIBS experimental setup for detection of trace metals and other contaminants in crude oil samples is depicted in Fig. 1. It consists of a Q-switched Nd-YAG laser (Spectra physics Model GCR 100) operating at 1064 nm wavelength. It can deliver maximum pulse energy of 1 J with a pulse width of 8 ns and operates at a 10 Hz pulse repetition rate. The collimated beam at 1064 nm is tightly focused on solid crude oil sample using a convex lens of focal length = 50 mm to create a spark or breakdown in the sample. 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 light from the plasma spark is collected by a collimating lens using UV graded multimode fused silica fiber with length of 1 m and is transferred to LIB2000 + Spectrometer (Ocean Optics). Our LIBS 2000 + has four spectrometer modules to provide high resolution (FWHM 0. 1 nm) in the 200 to 620 nm wavelength region. The detector has a CCD camera having 14,336 pixels. The emission is observed at a 90° angle to the laser pulse. Software built in the spectrometer read the data from the chip and reconstruct the spectrum. This makes it possible to measure a large wavelength range (200–620 nm) simultaneously with high spectral resolution (0.1 nm).

The software provides element identification through a spectral database for qualitative measurements. Samples can be quickly measured and saved to log-file. Options allow customization of spectral search algorithms. Custom compound element libraries can be created or searched using LIBS 2000 + spectrometer.

We performed a series of measurements on various solid crud oil samples, with the purpose of determining the optimum time delay between the laser pulse and the beginning of the LIBS spectra acquisition system. It is worth mentioning that the early stages of plasma discharge are characterized by the brehmsstrahlung continuum emission, and only subsequent stages show the characteristics of atomic and ionic patterns, which allow for the quantitative analysis of the sample composition through LIBS technique.

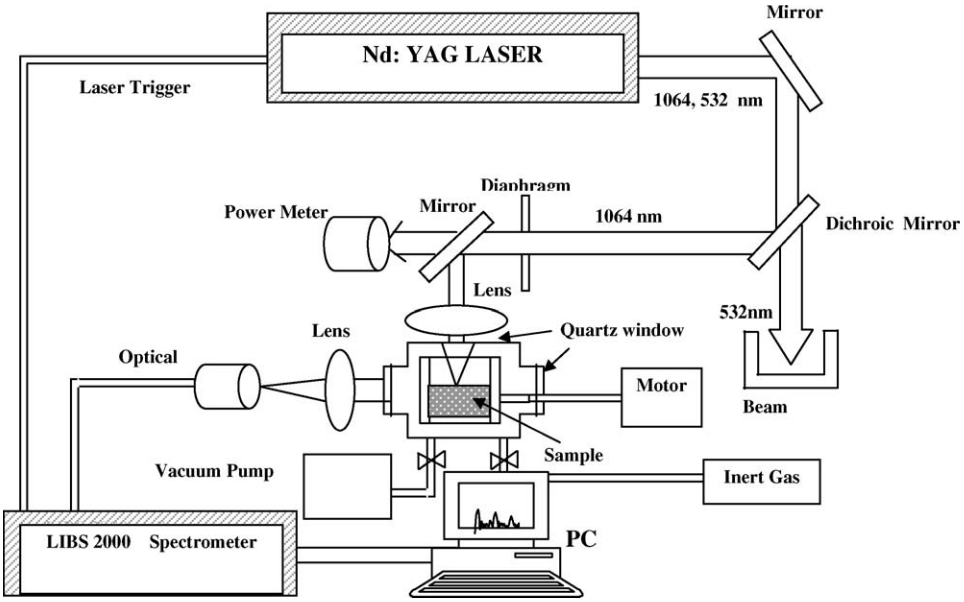

Fig. 1. Schematic diagram showing experimental setup details of the laser induced breakdown spectrometer applied for the analysis of oil residue samples.

2.1. Sample preparation

Many LIBS measurements such as analysis of rocks or metallic samples do not require any sample preparation or pretreatment. This is considered to be one of the unique features of LIBS. As our samples were initially in liquid phase, we adopted the following procedure. The crude oil in liquid phase was obtained from Saudi Aramco, one of the major oil producing company in the Middle East. The initial phase of the residue was obtained by true boiling point (TBP) distillation process at 350 °C under atmospheric pressure. In order to get a solid paste of the residue, the sample obtained by TBP process, was further distilled under vacuum at 550 °C over a longer period of time. In order to prepare the pellets for the LIBS analysis, the solid sample was first heated in an electric furnace up to 150 °C. Then the molten material was poured into a special stainless steel mold designed to obtain a specific round shape. The samples were in the form of cylindrical discs approximately 20 mm diameter and 10 mm thick. The samples thus prepared were then mounted on a circular target holder driven by a computer controlled motor to avoid any crust formation on the target sample and to continuously irradiate a fresh spot of the sample.

3. Results and discussion

Before, we discus the results obtained through this study, it is worthwhile to discuss the main parameters which affect the laser induced breakdown emission and ultimately the sensitivity of the LIBS spectrometer. These parameters are laser energy, laser pulse width, laser pulse shape, laser power fluctuations and time delay between the laser pulse and detection of the plasma emission. The physical and chemical characteristics of target material and surrounding environment composition and pressure can also effect the laser induced breakdown emission and the sensitivity.

The parametric dependence for optimization of our laser induced breakdown spectrometer and the elemental composition of the oil residue sample are described in the followings sections. A typical LIBS spectrum of oil residue sample is presented in Fig. 2. The trace elements present in the oil residue sample is clearly identified on the spectra and is listed in Table 1. These elements were identified using the NIST Atomic Data Base for neutral and ionized elements and reference data book [33]. The list includes Ca, Fe, Mg, Cu, Zn, Na, Ni, K and Mo. It is worth mentioning that the strongest lines due to trace elements were detected in the visible region where our CCD camera has the highest spectral response. Due to this reason, most of our work is concentrated in the visible region.

3.1. Effect of time delay

When a pulsed laser radiation is focused on to a small spot on a sample material, a high-temperature, high electron density laser

Table 1
List of elements detected in oil residue sample

Sr. no.	Element	Wave length (nm)[a]	LOD (ppm)	Concentration LIBS (ppm)	Concentration ICP (ppm)
1	Ca	422.6	14	74.9	67.5
2	Fe	567.9	9	177	170
3	Mg	518.3	6	20	14
4	Cu	521.8	3.5	5	2.1
5	Zn	492.4	5	6	4.28
6	Na	589.5	10	21	16
7	Ni	480.6	11	51.6	46.5
8	Mo	553.5	2	3.18	2.5

The comparison of concentration of detected elements with conventional technique (ICP) is also presented.

[a] The peak wavelength were identified from reference [33] and also confirmed from NIST atomic spectra data base.

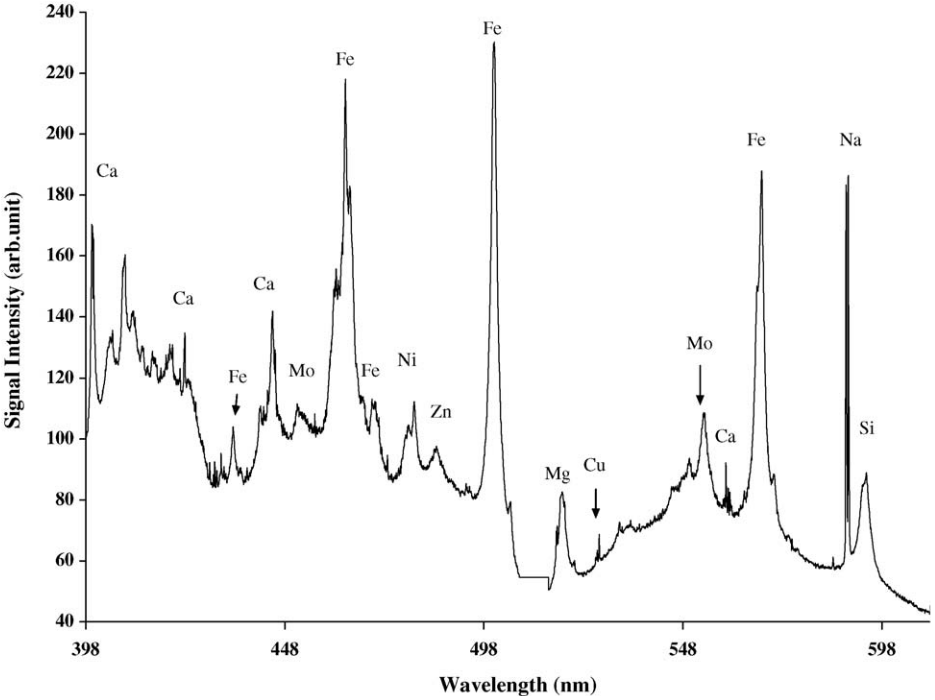

Fig. 2. Typical LIBS spectra of oil residue sample recorded in the 398–620 nm region. The emission peaks due to different trace metals present in oil residue sample are indicated on the spectra.

spark or micro plasma is formed. The temperature of this plasma is so high that the sample material is vaporized and ionized. In the early stages of plasma thermalization, as electrons interact and recombine with ions, energy will be released over a broad spectral range, from UV through the visible to the near IR. These early stages of plasma glow results in an intense continuum emission that can be gated off by the detection system. After a suitable time delay, the plasma cools down to the point when atomic and ionic emissions could be observed. Hence, the study on time delay between laser pulse and the start of acquisition system is essential.

We performed a series of measurements on various waste crude oil samples, with the purpose of determining the optimum time delay between the laser pulse and the beginning of the LIBS spectra acquisition. The importance of careful setting of the time delay has been stressed in several papers [26–28]. As a matter of fact, the LIBS spectra show a dramatic dependence on time delay. Delay times were chosen according to the experimental needs, and they were controlled by a Q-switch trigger pulse to the laser and the trigger pulse to gate the CCD camera. This option is provided in our LIBS 2000 + spectrometer.

The effect of time delay between laser trigger pulse and intense plasma continuum emission for detection of trace elements in the crude oil sample was recorded for different delays starting from 0 to 7 μs. A typical plot of dependence of LIBS signal peak intensity (at a wavelength of 492.4 nm) on delay time for Zn (one of the trace metal present in crude oil residue) is depicted in Fig. 3. It is clear form the figure that the maximum LIBS signal is recorded at around 5 μs of delay for Zn.

3.2. *Effect of the laser energy*

The other important factors that influence the light emitted by the plasma are its temperature, the number density of the emitting species and the electronic density. The number density of the emitting species (e.g. atoms, ions, etc.) depends on the total mass ablated by the laser, the plasma temperature and the degree of the excitation and/or ionization of the plasma. The vaporized amount from the surface, in turn, depends on the absorption of the incident laser radiation by the surface which is dependent on the incident laser fluence (energy).

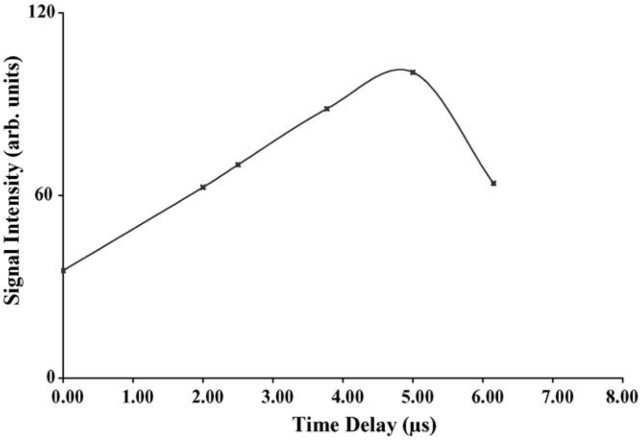

Fig. 3. Dependence of LIBS signal intensity on the delay time for trace metal (Zn) present in the oil residue sample.

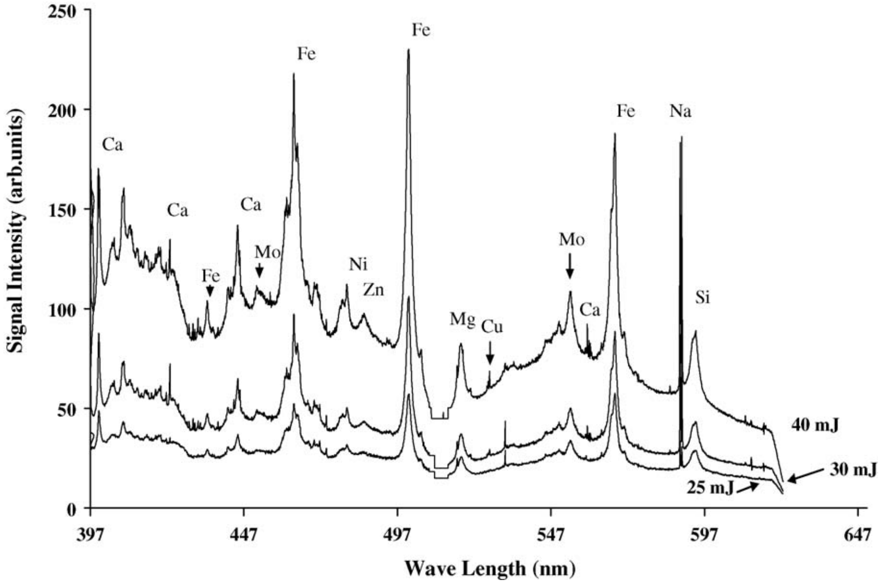

Fig. 4. The evolution of laser induced breakdown spectra of oil residue sample at different incident laser energies. The emission peaks due to different trace metals present in oil residue sample are indicated on the spectra.

To study the effect of laser energy on the line emission variation, laser produced plasma emission spectra from oil residue sample were recorded in the 390–620 nm region at laser energies of 25, 35 and 40 mJ per pulse. A time delay of 5 μs was used where maximum LIBS signal was achieved for a given Zn line. The evolution of spectra at different energies is presented in Fig. 4. The trend of dependence on laser energy of laser produced plasma emission spectra for Mg element present in oil residue sample is presented in Fig. 5. It can be seen from Fig. 5 that the intensity increases with increasing laser energy from 20 to 40 mJ per pulse. The energy dependence shows some linear dependence on the laser which is indicated by the least square fit of 0.99.

3.3. Calibration of the LIBS system

Prior to quantitative analysis with our LIBS spectrometer on actual oil residue samples, the spectrometer was calibrated for each trace metal of our interest. For the construction of the calibrations curves, different stoichiometric samples of each metal were prepared. Pure metals in powder form purchased from Alfa Aesar were mixed with the matrix material KBr in a ball milling apparatus in order to ensure good mixing and homogeneity. Then, they 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. The concentration of the prepared samples was also verified by a calibrated inductively coupled plasma (ICP) spectrometer. The detection limit (lowest detectable concentration) is the concentration that produces a net line intensity equivalent to two times the standard deviation of the background signal of the our system. This was estimated by using the expression for the limit of detection (LOD) [34,35].

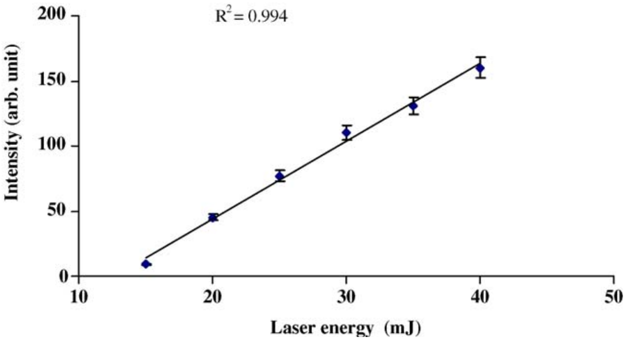

Fig. 5. Plot of dependence of the intensity of the Mg 518.36 nm emission line on laser energy.

$$\text{Limit of detection} = \frac{2\delta_b}{S}$$

where δ_b is the standard deviation of the background (noise level) and S is calibration sensitivity (= slope of the calibration curve) which is the ratio of the line intensity to the concentration. The LOD estimated using the calibration curves is listed in Table 1. It is worth mentioning that LOD of our system is quite below the concentrations detected in oil residue sample.

LIBS signal quantification was done using the area of an atomic peak for a particular atomic emission line, divided by a representative baseline area [34]. The peak area is roughly proportional to the ablated amount of sample. The baseline, which is the continuum fluorescence, is proportional to the laser power. The peak area to baseline area ratio is proportional to the elemental concentration alone which is referred to as the peak/base ratio. 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.

A typical calibration curve for magnesium using standard samples is presented in Fig. 6 for our system. Here, four samples of known concentrations (100 to 100,000 ppm) of Mg were

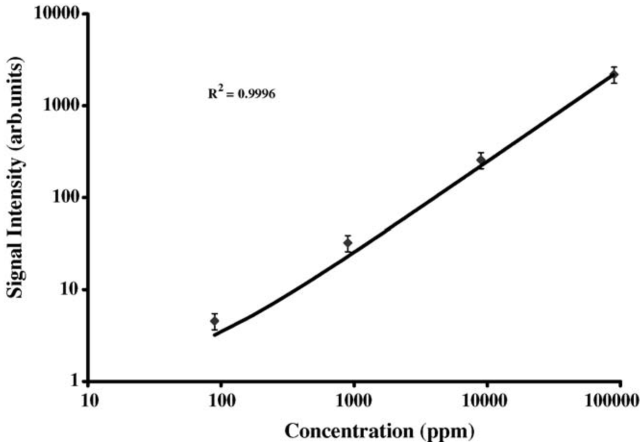

Fig. 6. Calibration curve for LIBS measurements of magnesium. The curve was plotted by recording the LIBS signal intensity at various known concentration in standard samples of magnesium.

prepared in base material of KBr and LIBS spectra of Mg line at 518.36 nm was recorded with our setup. All LIBS spectra detected at 518 nm are the average of 20 laser pulses, at three different places on the sample's surface. The 518.36 nm line of magnesium was selected where there is no interference from the base material.

As clear from the Fig. 6, the LIBS signal shows linear dependence on the concentration of Mg over a broad dynamic range (100–100,000 ppm). This strong linear dependence of LIBS signal on concentration is indicated by the least square fit of $R^2 = 0.9996$.

3.4. *Elemental composition of oil residue sample*

A typical laser induced emission spectra from oil residue samples recorded in the 390–640 nm region is depicted in Fig. 2. The spectra were recorded after 20 laser pulses, at laser energies of 40 mJ per pulse and a time delay of 5 μs. The trace metals present in residue crude oil waste sample were identified and are marked in Fig. 2. The major elements detected in the sample are listed in Table 1. This list includes Ca, Fe, Mg, Cu, Zn, Na, Ni, K and Mo.

In order to get the quantitative estimate of the concentration of trace elements present in light Arabian Crude oil waste sample, the peak area of the intensity recorded from laser produced plasma emission for each trace metal was measured and correlated with the intensity measured for the specific element in a standard sample as reported under calibration section of the system. In order to test the validity of our LIBS calibration, the analysis of the oil residue sample was also carried out by conventional analytical technique such as inductively coupled plasma (ICP).

The concentration estimated with our technique as listed in Table 1 agrees reasonably well with the concentration measured using ICP. This is a worthy indicator that our LIBS spectrometer is a useful tool for the rapid analysis of oil samples as well as other solid waste samples. The unique features of our laser induced breakdown spectrometer are: rapid analysis, little or no sample preparation and possibility of multi-elemental analysis.

4. Conclusion

Multi-elemental analysis for trace metals present in Arabian light crude oil residue sample was carried out using laser induced breakdown spectroscopy for the first time. The parametric dependence of LIBS signal and the elemental composition of oil residue sample were investigated. The trace metals concentration present in oil samples were estimated and results achieved are in agreement with the conventional techniques such as inductively coupled plasma spectrometry. This work demonstrates that LIBS technique for waste crude oil is equally applicable and does not need as much sample preparation as other analytical methods such as ICP and atomic absorption spectrometry. LIBS could be useful and applicable for on-line analysis of trace metals at oil terminals, oil storage and oil waste dumps and for finger printing of oil slicks.

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