

Application of Laser Induced Breakdown Spectroscopy to Identify the Elements in Sudanese Crude Oil Extracted from Balila Oil Field

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Abstract

Laser Induced Breakdown Spectroscopy (LIBS) has been used to identify the constituents and the differences between crude oil samples. The radiation emitted from the plasma of the samples, due to the breakdown, was used to identify the samples contents. An exhaustive analysis of two crude oil samples collected from Balela Oilfield, south of Republic of the Sudan (Balela 1, Balela 2) was performed. Characteristics elements in petroleum such as C, H, N, and O, were detected. The spectra due to heavy elements in crude oil samples such as Ca (II), Ca(I), N(I) were recorded using this technique. The use of intensity ratios of line and band emissions in the crude oil samples allowed a better characterization. Although significant differences were observed, no structural identification of the hydrocarbons components has been obtained. Using laser technology in the oil industry can make a real addition because of its benefits, (e.g. real time, precision, sensitive, selective and fast technology).

Keywords

Laser Spectroscopy, LIBS, Balila Crude Oil, Sudanese Oil, Laser in Oil Industry

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is an elemental analytical tool that has been extended to a wide range of applications. The technique is based on the generation of emitting plasma on solid, liquid or gaseous samples and the collection of the radiation emitted from the plasma which is used to determine the composition of the sample qualitatively or quantitatively (Celis, *et al.* 2008).

The technique as based on the laser interaction with the material under study and provides numerous advantages such as rapidity, multi-elemental analysis, and minimal or no sample preparation suitable for onsite analyses (Miziolek *et al.* 2006). LIBS can be considered as an analytical technique useful in oil industry for, as example, crude oil investigation.

Crude oil is formed from inclusion of biomass of mostly aquatic plants and animals in the sediments.

The organic material is altered and decomposed in several steps, and this process results in a complex mixture containing a large variety of compounds and molecular species. The composition of petroleum can vary depending on many factors, like the location and the age of the field. Crude oil mainly consists of carbon and hydrogen (from organic materials). In addition, small amounts of nitrogen, oxygen, sulfur and metals can be found (Speight 2008).

In fact, its chemical and physical composition can vary not only with the location and age of the oil field but also with the depth of the individual well. Indeed, two adjacent wells may produce petroleum with markedly different characteristics. In addition, when the many localized or regional variations in maturation conditions are assessed, it is perhaps surprising that the ultimate compositions are so similar. Perhaps this observation, more than any other observation, is indicative of the similarity in nature of the

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precursors from one site to another (Borgund 2007).

LIBS has been also evaluated for the analysis of oil spill by many authors (Gondal *et al.* 2006, Hussain and Gondal 2008). They demonstrated the capability of this technique in the chemical detection of toxic metals in oil spill contaminated soils (OSCS). Alternatively, laser ablation has been also reported as an advanced tool for the laser cleaning of the Prestige tanker oil spill from coastal rocks (Fortes 2010).

The aim of this work was to identify the elements in Sudanese crude oil extracted from Balila oil field south of republic of Sudan using laser induced breakdown spectroscopy, and to evaluate this technique in Sudanese oil industry.

2. Materials and Methods

2.1. Experimental Set-Up

The LIBS set-up was consisted of a Quantel Brilliant Ultra Q-Switched Nd:YAG laser (20 Hz, 1064 nm, 8 ns pulse width) as a excitation source and a spectrograph beside optical fiber and set of optics. The laser beam was conducted up to the target through an optical system integrated by a 1064 nm plane mirror and a plane-convex quartz lens of a focal length of 15 cm. The generation of plasma in the targets was achieved by focusing laser pulses, with energy of 41 mJ each, on a spot size of 470 μm in diameter, thus reaching 3 GW/cm^2 of irradiance working for ablation.

Light emitted from the plasma was collected using a collimating lens model 74-UV (200-2000 nm) from Ocean Optics Inc., coupled to the tip of a 600 μm optical fiber (model FC4-UV600-2, four-furcated cable, 4x600 μm fibers, all legs SMA terminated, total 2 m long, splitting point in the middle) which guided the light to the entrance of a miniature Czerny–Turner spectrograph (model AvaSpec-2048-USB2 from Avantes, with four channels) (75 mm focal length). An effective spectral window spanning from 230 nm to 950 nm was achieved. The spectrometer was fitted with CCD detectors. A delay time of 1.28 μs and an integration time of 1.1 ms, were used as timing parameters for spectral data acquisition. The Sketch diagram the LIBS set-up is shown in Figure (1).

2.2. The Materials

In this work, two sites were used for the collection of crude oil samples, namely: Balela Oilfield (1 and 2) situated on the borders between south Darfur and south Kordofan, where crude oil had been released. Two samples were collected in glass bottles, then labelled and carefully stored to avoid any type of contamination, and taken to a laboratory for analysis.

2.3. Preparation of Samples for Analysis

For each Laser Induced Breakdown Spectroscopy analysis, a sample of crude oil was prepared and placed in a stainless steel holder for direct irradiation.

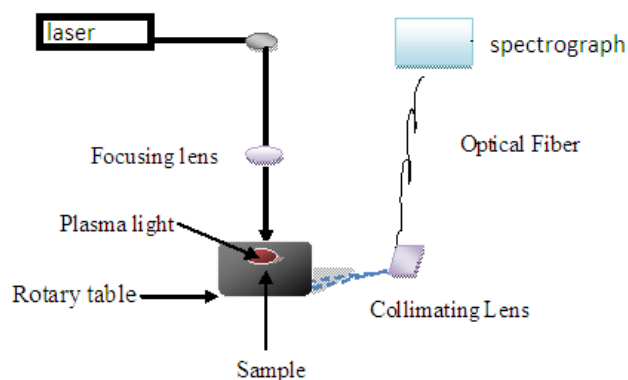


Fig. 1. Sketch of the LIBS set-up.

The sample was positioned such that the focal volume of laser pulse was centered in the sample holder holding sample. Fifty laser pulses were directed into the sample for each measurement to ensure higher accuracy.

2.4. Experimental Procedure

The collimated beam at 1064 nm was focused on the target sample using a focusing lens to create breakdown in the sample. The detector has a gated Charged Coupled Device camera that made it possible to measure LIBS spectrum over broad spectral range (240–950 nm), simultaneously, with spectral resolution of (0.7 nm). The plasma emission was recorded at a 90° angle to the laser direction. The light from the plasma spark was collected by a collimating lens using optical fiber. There is a software built in the spectrometer to read the data and reconstructed the spectrum. This made it possible to measure a large wavelength range with high spectral resolution. To reduce the effect of the air environment within the analytical plasma, all the LIBS spectra were recorded in an argon atmosphere.

3. Results and Discussion

Laser Induced Breakdown Spectroscopy spectra of the samples were acquired in the range: 230–950 nm, in order to identify the spectral lines for elements in each sample.

To achieve an acceptable degree of accuracy in the results and ensure the reproducibility of the data, the spectrum was acquired by averaging fifty laser shots on adjacent positions for each sample. Emission lines of samples have minimal interference, so that self-absorption was almost absent. To make sure of lines identification, NIST and Avasoftware 7.5.0

databases were used.

The representative LIBS spectra of oil samples are presented in figures (2) and (3).

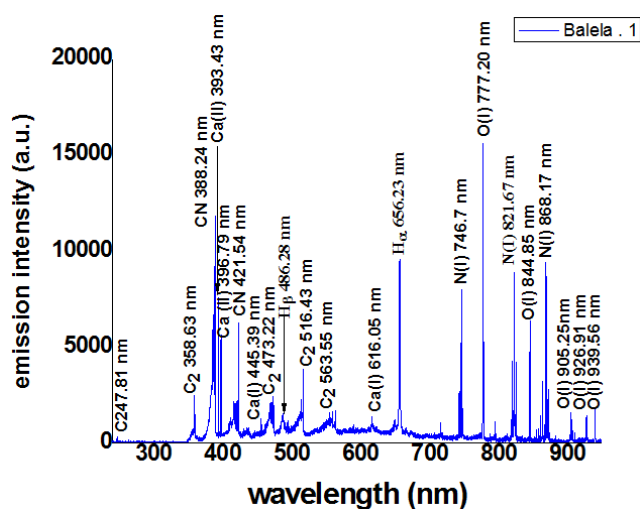


Fig. 2. LIBS spectrum of Balila 1.

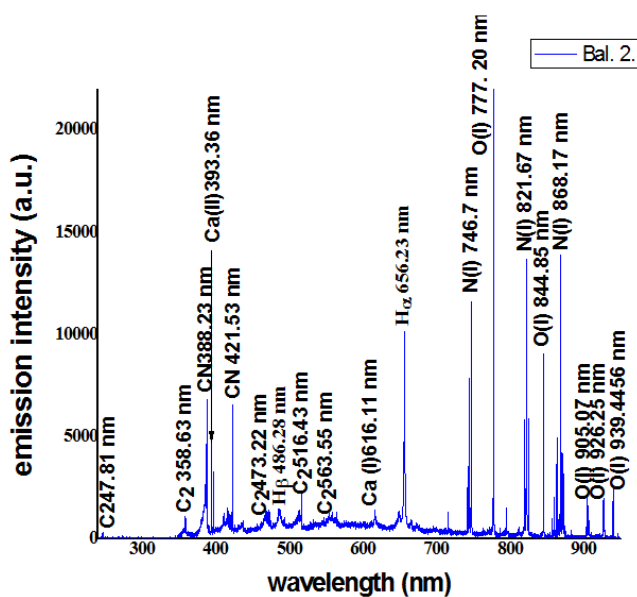


Fig. 3. LIBS spectrum of Balila 2.

The wavelengths of the most relevant emissions that detected from the analysis of the two crude oil samples are listed in table (1).

Based on the atomic spectroscopy, the emitted plasma contained spectral lines of atoms and ions of C, H, N, and O, as expected for organic samples, and CN, C₂ molecular bands. It is also possible to observe the presence of atomic lines of sodium (589.81 nm), calcium (445.79 nm) and two ionic lines of calcium (393.43 nm, 396.99 nm).

Several other lines in the recorded spectra can be observed; including the strong line at 777.20 nm belong to oxygen, which is related to three overlapping transitions, at 777.19,

777.42, and 777.54 nm. We can see also the spectral window of 840–950 nm, which permits observation of nitrogen (868.34 nm) and oxygen (844.97 nm) lines, simultaneously.

Table 1. The detected emission lines in the libs spectra of balila samples.

Peak No.	wavelength	species
1	247.81	C
2	358.63, 473.22, 516.43, 563.55	C ₂
3	393.43, 396, 445.39, 616.44	Ca
4	385.13, 385.52, 386.22, 387.18, 388.24, 415.21, 415.87, 416.77, 418.12, 419.68, 421.54	CN
5	486.28	H _β
6	656.23	H _γ
7	742.36, 744.23, 746.7, 821.67, 868.17	N
8	589.81	Na
9	777.20, 844.85, 905.25, 926.91, 939.56	O

When the oxygen content is phenomenally high it means that the oil has suffered prolonged exposure to the atmosphere either during or after production because the percentage of oxygen in fresh crude oil is usually very low (Fahim *et al.* 2010). In fact, the non-volatile residue may have oxygen contents up to 8% w/w. There is an approximate correlation between the nitrogen content and the carbon residue, the distribution and characteristics of these species (saturates, aromatics, and heteroatoms) can be account for the rich variety of crude oils (Speight 2007). If LIBS spectra are recorded in air then there is a possibility of interference between atmospheric O₂ and N₂ and oxygen and nitrogen in samples. Such interaction of ambient air with signals gives false information about sample composition (Rai *et al.* 2011).

This has been a challenging technical problem for standoff detection of organic material in air. To overcome this issue, some authors suggested including emission bands of CN violet system and C₂ Swan system to the atomic ratio criterion for discrimination of samples spectra under atmospheric conditions (Yang 2012).

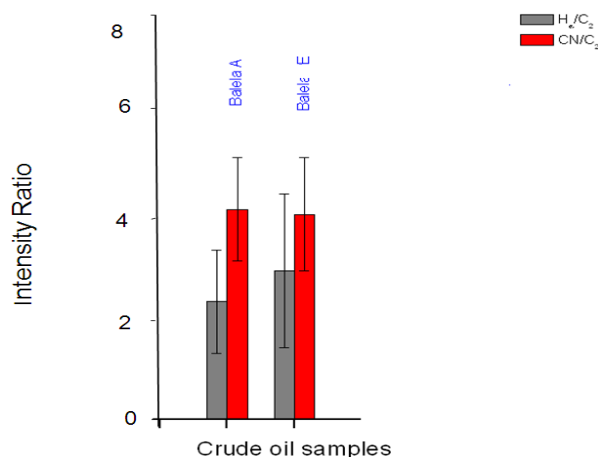


Fig. 4. Intensity ratios of CN/C₂ and H_γ/C₂ for the two crude oil samples.

In the case of organic compounds there is a relationship between the presence of unsaturation (containing carbon-

carbon double bonds) and the C_2 emission intensity. The presence of CN bands emission in the spectral range 388.24 - 421.54 nm and C_2 emission bands around 473.22, 516.43 and 563.55 nm confirmed the organic molecular nature of the samples. The detection of these molecular bands offered additional information about the aromatic contents of the petroleum. In order to emphasize the differences observed in our samples, a correlation between the intensity of the major elements ($H\infty$ 656.28 nm, CN 388.22 nm and C_2 516.50 nm) was conducted.

Figure (4) shows the intensity ratios of CN/ C_2 and $H\infty$ /C calculated for the two crude oil samples.

Considerable differences can be seen in these ratios. Changes occurring in the organic compounds during the aging of the petroleum could be explained by the variations observed in CN/ C_2 . The H/C atomic ratio indicates that Balila 1 (A) crude oil sample has a lower H/C atomic ratio and being more aromatic in character, and it would require more hydrogen for upgrading to liquid fuels.

4. Conclusions

The plasma emitted from Balila crude oils showed specific spectral features including sequences of the CN violet system and the C_2 Swan system, besides H, C, N, and O atomic and ionic lines. CN, O, and N originate not only from the crude oil samples, implying that they are partially due to the interaction of the plasma with the ambient air. The principle for identification of organic compounds was based on their spectral features and on the integrated intensity ratios of the molecular (CN, C_2) and atomic ($H\infty$, C_2). Laser Induced Breakdown Spectroscopy showed good potential in identification of different elements in Balila crude oil.

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