



Laser Induced Breakdown Spectroscopy Applied to Elemental Analysis Using Samples of Crude Oil from Adaril Oilfield

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Authors' contributions

This work was carried out in collaboration between all authors. Author NAA designed the study, wrote the protocol, and wrote the first draft of the manuscript. Author SYM managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aim: In this work Laser Induced Breakdown Spectroscopy (LIBS) has been used to identify the constituents of certain type of Sudanese crude oil.

Study Design: This study was designed to use LIBS technique to analyze the emission spectral lines and to evaluate this technique in identifying the constituents of certain type of Sudanese crude oil.

Place and Duration of Study: Department of laser system, institute of laser in Sudan university of Science and Technology – Republic of the Sudan and department of analytical chemistry, Malaga University – Spain, between June 2011 and July 2012.

Methodology: Q-switched Nd: YAG laser was used to irradiate the samples and produce its plasma. The emission spectra of the plasma were collected via optical fiber and analyzed by a miniature Czerny–Turner spectrograph attached to CCD camera.

Samples: Three crude oil samples collected from, Adaril Oilfield in south of Sudan were included in this work.

Results: Characteristics elements in this crude oil, such as C, H, N, O, Ca, and Na were detected. The use of intensity ratios of the emission lines and bands in the samples allowed better characterization of the samples than the simple use of peak intensities.

Conclusions: The analysis of crude oil samples led to efficient detection of different

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constituents in these samples. Using LIBS technique in the oil industry can make a real addition because of its countless benefits, (e.g. real time, precision, sensitivity, selectivity and high speed).

Keywords: LIBS; emission spectroscopy; laser in oil industry; Adaril crude oil.

1. INTRODUCTION

Petroleum or rock oil has become the world's most important source of energy since 1950 due to its high energy density, easy transportability and relative abundance [1]. Rock oil is a flammable liquid found in rock formations consisting of a complex mixture of hydrocarbons of various molecular weights, mostly alkenes, cycloalkanes and various aromatic hydrocarbons, and other organic compounds containing N, O and S, and trace amounts of metals such as Fe, Ni, Cu and V. The chemical composition and physical properties of petroleum widely vary as a function of its origin, the nature of the oil (which is constantly changing), the temperature and the nutrient availability but typically, the content is 83–87% C, 10–14% H, 0.1–2% N, 0.1–1.5% O, 0.5–6% S and < 1000ppm metals [2]. The determination, identification and characterization of element species in crude oil, and derivatives, and fuel residues are actual tasks in the environmental field [3]. Analytical techniques such as high performance liquid chromatography (HPLC), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectroscopy (ICP-OES), flame and graphite furnace atomic absorption spectrometry, near infrared spectroscopy (NIR), and X-ray fluorescence spectrometry (XRF), have been extensively used in lab analysis of petroleum derivatives, obtaining high accuracy and precision in the results. Most of these methods have been employed together with statistical tools in order to study the mechanisms involved in the biodegradation of the crude oil. The photochemical processes regarding the degradation of petroleum and its products are reasonably well known [4]. In addition, biodegradation of the crude depends on its composition, which also varies along the time during the ageing processes. Petroleum is not a uniform material. In fact; the precise chemical composition of petroleum can vary with the location and age of the field in addition to any variations that occur with the depth of the individual well. Two adjacent wells may even produce petroleum with very different characteristics [5]. In this sense, Andrade *et al.* demonstrated that the total aromaticity index can be used to characterize the weathering process [6]. They used a chemometric protocol of three ways in order to extract the maximum information from the IR spectra of six different oil spills made under controlled conditions.

Recently, a statistical procedure based on similarity indices (correlation coefficient) was proposed by Li and co-workers [7]. This methodology used the peak-to-peak comparison when applying the linear correlation procedure to the IR spectra of petroleum.

However, the main problem associated with the analytical techniques described above is related to the availability of real matrix standard and the impossibility to perform in situ analysis. Nowadays, laser induced breakdown spectroscopy (LIBS) has been recognized as an appropriate analytical method for the direct spectro-chemical analysis of environmental, archaeological and geological materials, even in extreme environment. Although LIBS is essentially an elemental technique, it has been successfully tested as a powerful method for the chemical detection and identification of organic and biological materials. In the case of organic materials, the analysis is based on the detection of four universal elements, C, N, O and H, and molecular bands of CN and C₂. At present, the method of atomic and molecular

LIBS emission intensity ratio prior to the chemometric analysis is widely recognized in this task. Different statistical tools (flow chart analysis, linear correlation, principal component analysis (PCA), the soft independent method of class analogy, and partial least squares discriminate analysis (PLSDA) have been used to differentiate plastic [8], organic wastes, biological [9], forensic [10], toxic substances and explosives. LIBS has been also evaluated for the analysis of oil spill. Gondal et al. [11,12] 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 [13]. The most important parameter in LIBS is the laser irradiance. In general, the radiant flux incident on the unit detector area is called irradiance, while in the spectroscopic literature it is often termed intensity. The unit of irradiance is W/cm^2 or $photons/cm^2$.

With an increase in irradiance, both electron temperature and density increase and saturate at higher irradiance levels. In order to determine the irradiance produced by a laser, it is necessary to know the spot size to which the beam can be focused. Maximum irradiance is obtained with minimum focal area of the laser spot. The primary mechanisms operative during ablation depend on the laser irradiance. In general, for low intensity nanosecond laser pulses, the dominant mechanism is thermal vaporization. For picosecond laser pulses and high intensity nanosecond laser pulses, both thermal and non-thermal mechanisms exist [14].

For high intensity femtosecond laser pulses, Coulomb explosion is the primary ablation mechanism. Therefore, the laser pulse duration and irradiance are the most important factor for defining experimental conditions.

The average irradiance of a typical collimated pulsed laser beam at the focusing area (beam waist) is given by:

$$I_f = \frac{\pi E_L D^2}{4\tau_L f^2 \lambda^2 (M_2)^2}$$

where: I_f = irradiance (usually expressed in $W m^{-2}$), E_L = energy of the laser pulse, D = the laser beam diameter, τ_L = pulse duration, f = lens focal length, λ = the laser wavelength, M_2 = beam propagation ratio. For a beam ideally Gaussian, M_2 is equal to 1. Typical values for beams produced by Nd: YAG lasers are between 2 to 10. Fluence is the time integrated value in $J m^{-2}$.

In this work LIBS was used to identify and characterize one of the Sudanese crude oils extracted from Adaril oil well south of the republic of Sudan.

2. EXPERIMENTAL DETAILS

2.1 The Equipments

The set-up used in this work was consisted of a Q-Switched Nd:YAG laser (1064 nm, 20 Hz, 8 ns pulse width) supplied from Quantel Brilliant Ultra. Laser beam was conducted up to the target through an optical system integrated by a plane mirror and a plane-convex quartz lens with a focal length of 15 cm. The generation of plasma in the targets was achieved by

focusing the laser pulses, with energy of 41 mJ each, on a spot size of 470 μm in diameter, thus reaching irradiance of 3 GW/cm^2 .

The plasma emission was collected using a collimating lens model 74-UV (200-2000 nm) coupled to a tip of 600 μm optical fiber which guided the light to the entrance of a miniature Czerny–Turner spectrograph (model AvaSpec-2048-USB2 from Avantes, with four channels) attached to CCD camera. This spectrograph has a grating with 2400 line/mm with a spectral resolution of 0.7 nm. A delay time of 1.28 μs and an integration time of 1.1 ms were used as timing parameters for spectral data acquisition. A sketch diagram of the LIBS setup is shown in Fig. 1.

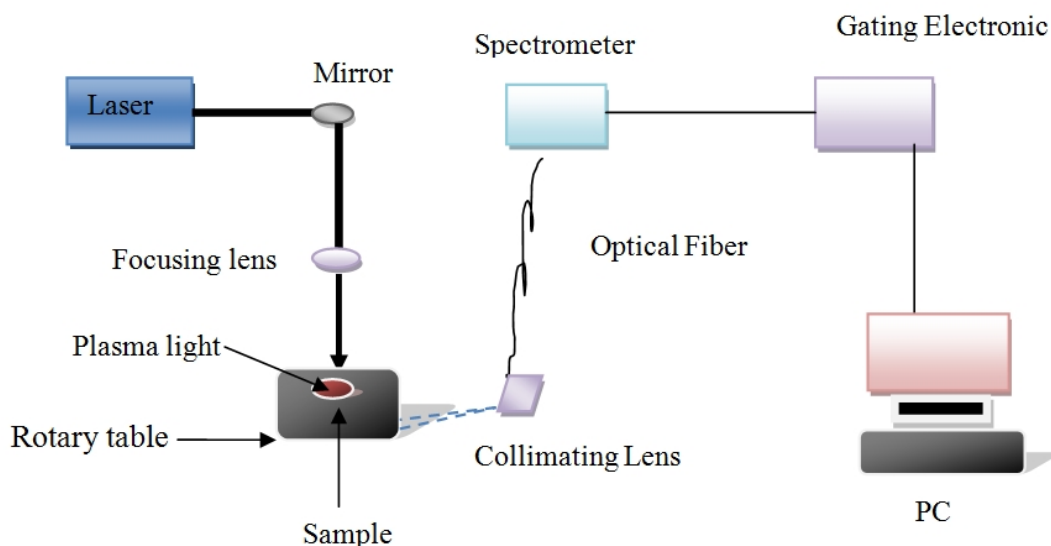


Fig. 1. Sketch diagram of LIBS setup

2.2 The Materials

In this work, three crude oil samples were collected from different locations of Adaril oil well which is situated in the Melut Basin in south Sudan close to the border of Ethiopia, located at GPS: N, 10°00 E, 32°95.

2.3 Experimental Procedure

For each Laser Induced Breakdown Spectroscopy analysis, a sample of crude oil was placed in a flat aluminium foil on a rotary table for direct irradiation. It was positioned such that the laser pulse was focused on the sample. More than twenty laser pulses were used for each measurement.

Plasma emission spectra were collected, using the optical fiber, and recorded by the spectrograph over broad spectral range (230–950 nm). To reduce the effect of the air environment within the analytical plasma, all the LIBS spectra were recorded in an argon atmosphere. To achieve an acceptable degree of accuracy in the results and to ensure the

reproducibility of the data, each LIBS spectrum was acquired by averaging fifty laser shots on adjacent positions for each sample to obtain a typical spectrum.

3. RESULTS AND DISCUSSION

Emission lines of samples have minimal interference, so that self-absorption was almost absent. Due to these factors, the recorded lines were useful for quantitative analysis. The LIBS spectra of the crude oil samples are presented in Figs. from (2) to (4). The wavelengths in these emission spectra are listed in Table (1). One can see that the spectra contain atomic lines of atoms and ions of C, H, N, and O, as expected for organic samples, and CN, C₂ molecular bands. Also one can observe the presence of atomic lines of sodium and two ionic lines of calcium. To make sure of lines identification, NIST and Avasoft 7.5.0 databases were used.

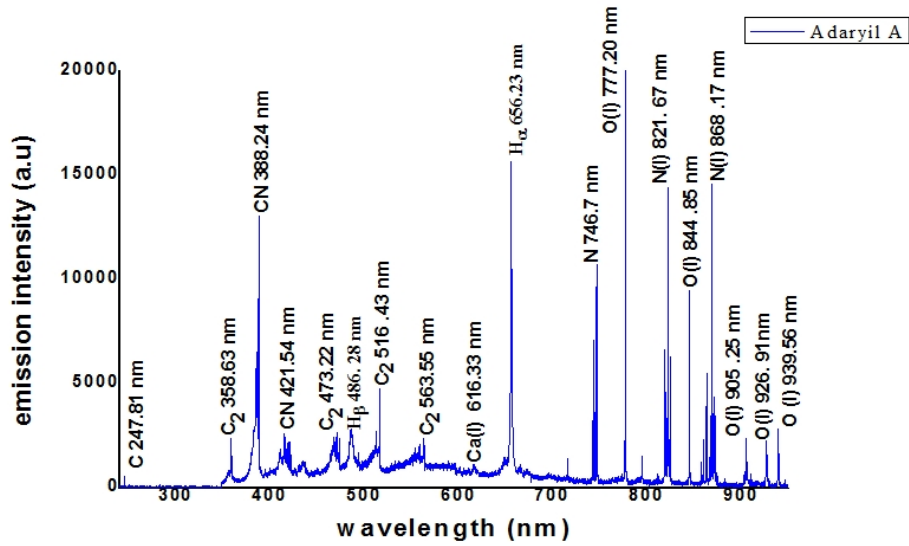


Fig. 2. Typical LIBS emission spectrum of the crude oil (Adaryl A) sample

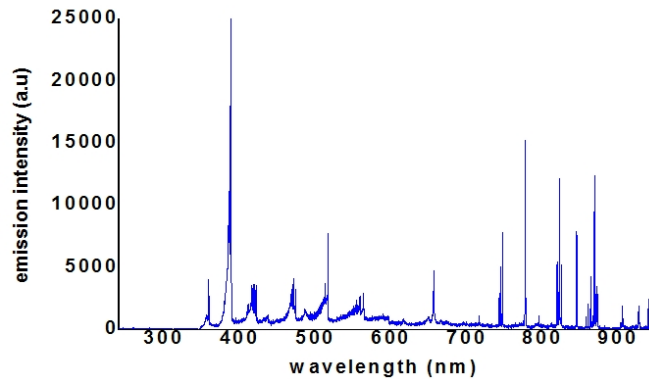


Fig. 3. Typical LIBS emission spectrum of the crude oil (Adaryl B) sample

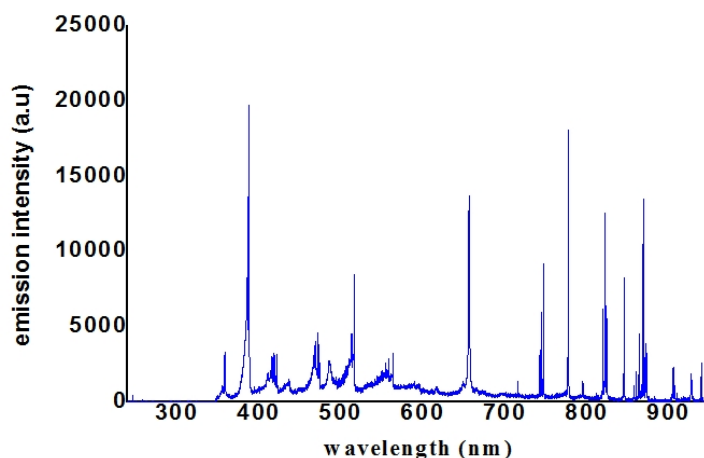


Fig. 4. Typical LIBS emission spectrum of the crude oil (Adaril C)

Table 1. Main emission lines in LIBS spectra of the three samples

Sr. no.	Species	Wavelength (nm) ^a
1	C	247.81 (I)
2	C ₂	358.63 ,473.22 ,516.43 , 563.55
3	Ca	393. 43 (II) , 396 (II) ,445.39 (I) ,616.44 (I)
4	CN	385.13, 385.52, 386.22, 387.18, 388.24, 415.21, 415.87, 416.77, 418.12, 419.68, 421.54
5	H _β	486.28
6	H _α	656.23
87	N	742.36 (I) ,744.23(I) 746.7 (I),821.67 (I), 868.17 (I)
8	Na	589.81 (I)
9	O	777.20 (I),844.85 (I),905.25 (I),926.91(I), 939.56 (I)

^aWavelengths are followed by (I) or (II) refer to emission from neutral atoms or emission from singly charged ions, respectively.

When the oxygen content is 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 [15]. 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 species like: saturates, aromatics, and heteroatoms can be account for variable crude oils [16].

Atomic ratios of neutral lines of nitrogen, oxygen and carbon have been used for differentiation of samples. When the spectra are recorded in air, there is a possibility of interference with atmospheric O₂ and N₂ with the lines of oxygen and nitrogen in samples which may gives false information about sample composition. This is a challenging technical problem for standoff detection of organic materials in air. To overcome these issues, 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 [17].

The presence of CN band emission in the spectral range 388.24, 421.54nm and C₂ emission band around 473.22, 516.43, 563.55 nm region, confirmed the organic molecular nature of the samples. The detection of these molecular bands offered additional information about the aromatic content of the crude oil.

Fig. 5: shows the mean intensity of the most significant spectral lines in which the compositional differences between crude oil samples are more noticeable.

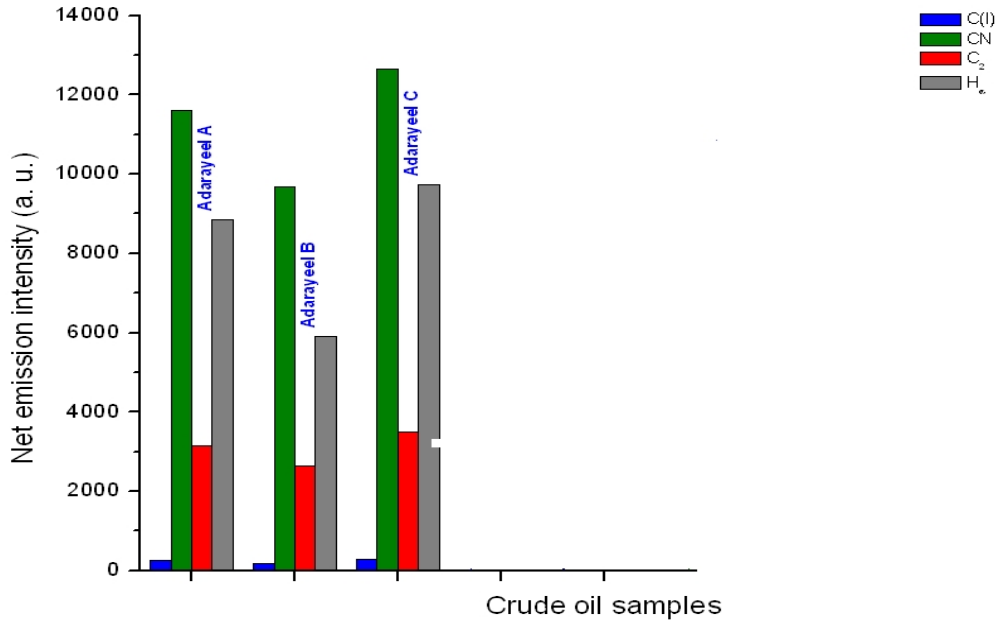


Fig. 5. Mean intensity (n=50) of the most significant emission signals exhibited by LIBS spectra from crude oil samples

Fig. 6 shows the intensity ratios of (CN, C₂) and atomic (H_α, C₂) calculated for the crude oil samples. As shown, the differences in the ratios are appreciable. Changes occurring in the organic compounds during the aging of the petroleum could be explained by the variations observed in CN/C₂. The H/C atomic ratio indicates that some crude oil samples (having a lower H/C atomic ratio and being more aromatic in character) would require more hydrogen for upgrading to liquid fuels.

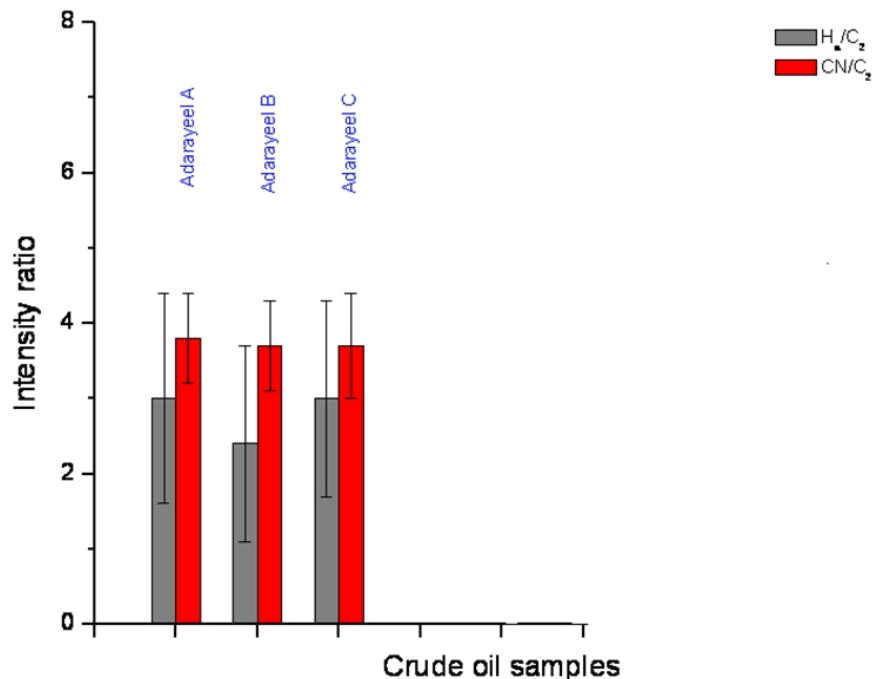


Fig. 6. Intensity ratio of the most significant emission signals exhibited by LIBS spectra from crude oil samples

4. CONCLUSIONS

The emission lines of different elements in Adaril crude oil were identified in the region from 230 to 950 nm. Organic compounds showed specific spectral features including sequences of the CN violet system and the C₂ Swan system, and H, C, N, and O atomic and ionic lines. The principle for identification of organic compounds was based on their spectral features and on the integrated intensity ratios of the molecular (CN, C₂) and atomic (H ∞ , C₂).

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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