Optimal Behavior of Spectral Line Analysis Through Fine Identification of Heavy Metal Lines in Crude Oil Using LIPS-Technique

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Abstract. Assessment of the quality of minerals, especially heavy ones, in crude oil by identifying spectral lines is very important to determine the quality and specifications of crude oil and the following treatments in production of the lines. In this study heavy metals lines (HMs) found in crude oil extracted from Iraq south field were identified that are unique spectral lines by using the laser-induced plasma spectroscopy (LIPS – mechanism), which were analyzed later by spectrometer based on the principle of finger print. The optimum spectrum (analytical lines) of metals emitted from the crude oil plasma in air were selected and determined. By determining the optimization behavior for evaluation procedure, the important condition was laser spot number (scan area). Comparison was performed between the fundamental wavelength and harmonic generation (HG) used in the laser beam to determine the optimum spectrum and optical insulator to cover the selected sample at atmospheric air pressure and room temperature. The results obtained from the actual raw spectrum were determined to represent the emission lines without the influence of foreign light (no noise) using the optical isolator, and unique new analytical lines were identified when increasing the number of lasers points up to 5 points, and a balanced spectrum was determined with good absorption when using a basic wavelength of 1064 nm. Difficulties were presented due to the characteristics of the crude oil as organic liquid case. The optimum results obtained indicated that the LIPS technique is effective and a control technique to well identify the spectrum lines of the heavy metals (HMs) presented in the crude oil.

Keywords: Crude Oil, heavy metals, laser-induced plasma, fine- identification unique lines

1. Introduction

The Crude oil (petroleum) is an important and complex material and its composition depends on its geographical and geological origin. It consists of saturated and aromatic hydrocarbons, and also contains heterocyclic compounds, emulsified water and trace elements (metals). [1] Minerals are found in a very wide concentration range; where the most abundant are Ni, V, and Fe, which are usually found in concentrations between 10 and 1000 ppm. Other metal elements often evoked in the context of their presence in oils, such as Pb, Sn, Co, Cu, Mo, Ti, and Zn, are in the 1-50 ppm range. [2,3,4]

The major constituents of the metal types in crude oil include metalloporphyrins that are primarily related to Ni, V, Fe, or Cu; poorly described and highly-tuned non-porphyrin species, and naphthenic acid salts that bind mainly Ca, Mg, Zn, and Ti but also potentially other elements. In petroleum, the mineral
varieties present can bind strongly with asphaltene by \( \pi-\pi \) connecting or they can be trapped in aggregates of asphaltene or macromolecular networks and often escape analysis. [5,6]

The process of determining the origin and composition of the crude oil, as well as the identification of some metallic elements (as impurities) in its composition is very important for determining its quality and further processing. The basic evaluation of ore consists of determining the quantity and quality of these components and elements such as (C, H, O as organic components) and (Fe, Ni, V as impurities) among others [7]. Attention and focus are given to identifying these trace elements because they pass in every step of the refining process and are accompanied with hydrocarbons, so they can cause many problems, where inorganic substances (impurities) accumulate on the parts of the equipment, causing problems and malfunctions, which necessitate the need to replace these parts of the equipment. There are some metallic elements and their components capable of forming acids that may cause problems such as corrosion, while other metallic elements may precipitate on hydrocarbon conversion catalysts and adversely affect their performance; besides, the presence of such trace elements may cause undesirable features and characteristics to appear. In addition, there are other reasons for this interest is that trace elements often give information and data related to geology and geography or to the origin and composition of petroleum.

Atomic absorption (AA) and inductively coupled plasma (ICP-AES) atomic emission spectroscopy currently are among the most widely used techniques and methods currently for the determination of trace elements and components in petroleum [8]. In addition, these techniques have some problems and constraints such as the use of expensive solvents, contamination with chemical reagents and the need for a method to digest the samples, and processing time, in addition to transporting the samples to the laboratory for examination and evaluation [9].

Laser-induced plasma spectroscopy (LIPS) is widely used for the qualitative and quantitative assessment study of varies elements and components. When the laser pulses are focused on a workspaces surface, a breakdown of the laser irradiated part of the target occurs. Based on the parameters of the laser beam, as energy, wavelength, pulse duration etc., and on the material parameters as physical and chemical properties of the sample [10-13]

In general, the success through LIPS-technique is due to the many features and benefits that make this analytical mechanism distinct and unique. Among these advantages are the ability to select multiple items at the same time, rapid response, remote selection, no prior preparation of samples to be examined, low cost of equipment, ease of use and examination and portability [14]. Through the use of LIPS-technique, it is possible to collect radiation in inaccessible places using other conventional analytical techniques; previous methods make this technique particularly advantageous for the evaluation of materials, for the analysis of hazardous materials, or for analysis in hostile environments and at high temperatures. Moreover, almost any type of sample can be analyzed, even if it is conductive or non-conductive and in any state of the material [15]. This technique relies on the use of a laser as a source of stimulation (to form plasma). The laser used in this technique is usually the Nd:YAG pulsed laser, however, the LIPS-technique also has some challenges, for example, when used for analysis of samples in the liquid state [16], due to the effect of the focal length that may affect the focus of laser beam, which reduces the reproducibility and sensitivity of the analysis results [17-18].

2. Experimental Methodology

The experimental arrangement of the LIPS set-up which was built is shown in the Figure (1). The system of experimental was designed by (Nd: YAG) pulsed laser, emitting 1064nm wavelength and changeable energy up to 2000 mj for each stroke of the laser and pulse duration 10ns with maximum pulse repetition rate is 10 Hz were used for LIBS-technique used for plasma excitation. The laser spot on the sample is 1 mm in diameter and its pulse energy is 500 mJ, measured by energy
meter. The working irradiance is 63.69 J/cm²; pulse repetition rate is 10(1/s). Where the beam of laser is focused and collected through a lens at focal distance is 7 cm. The plasma emissions are collected and transmitted to the spectrometer through an optical fiber placed 3 cm from the sample at 45°. The optical emission is collected of crude oil sample by lens and is focused on to optical fiber which deliver the plasma light to the entrance slit of spectrum analyzer (with wavelength range 320-740) nm which shows the spectral lines for the sample and then analyzed. The sample was mixed for 60 minutes by a stirrer at 30Cº by using a stirrer to be ready for the analysis process. This was done in order to achieve well homogenization of the sample composition. A drop of crude oil was poured on the glass slide of 12 cm² and left to settle for 30 minutes before execution the analysis, and this was done to confirm a fine distribution.

**Figure 1.** shows the illustration of the experimental setup.

3. **Results and Discussion**

3.1. **Comparison between the harmonic generation (HG) and fundamental wavelength to determine the metals lines**

In order to compare and determine the changes that can occur in determining the emission lines, the fundamental wavelength and harmonic generator technology (frequency doubled) in the process of plasma formation should be used and the parameters of the laser pulse must be determined and used on the sample surface. The results obtained from the emission spectrum lines are changed in determining the type of minerals, and thus the change in the emission intensity in the background. This difference is explained by the result when comparing using the fundamental wavelength technique and the harmonic generation technique to identify the heavy metals (HMs) present in crude oil. The intensity of the emission spectrum was recorded with the wavelength and compared using Microsoft Excel. Furthermore, Figures (2) and (3) shows a comparison of the crude oil-plasma emitted spectra in air and the recorded wavelengths. Figure (2) represents the 532nm second harmonic generator, at 10nm pulse duration, with different energy values from 200 -500 mJ while Figure 3 represents the fundamental wavelength of 1064 nm, with pulse duration of 10 nm, and energy of 500 mJ. On the other hand, figure (2) shows a too different intensity in each emission line, when using the wavelength of laser beam equal to 532 nm with different energy from 200 to 500 mj. It was noted that some lines have been saturated and other lines were very weak (not illustrated), therefore wavelength harmonic generation is not representing actual values of the spectral lines emitted by the heavy metals present, due to the absorption ability of those different elements in the crude oil sample.
At energy of 200 mj

At energy of 300 mj

At energy of 400 mj
5 At energy of 500 mj

**Figure 2.** The emission lines spectrum of plasma by using the wavelength of 532 nm with different laser energy

At energy of 500 mj

**Figure 3.** The emission lines spectrum of plasma at wavelength of 1064 nm and laser energy of 500 mj

3.2. *Optimization behavior of identification spectral lines for heavy metals*

The relationship between the considerations of the characteristics of the analytical lines of the crude is one of the factors that allows the evaluation of the quality of the crude oil, so that it locally adapts to the raw spectrum properties. The spectral lines were determined using mathematical software. A base correction has been made for each spectrum so that it can be compared to the National Institute of Standards and Technology (NIST) databases. In the following figures (4, 5 and 6) the detected emission lines spectra of the selected sample are shown. The emission lines characteristics of heavy metals were observed after determining the optimum state using an optical dielectric and at the selected spectral range from 320-740 nm. Figure (4) shows the detected emission line spectra of crude oil from southern Iraq without the use of optical isolator. It is noted that the lines cannot be clearly distinguished due to noise, while figure (5) below shows the raw spectrum produced using an optical insulator and figure (6) shows the same spectrum after treatment where the intensity of the emission spectrum was recorded with the wavelength and compared using Microsoft Excel. On the other hand, Figures (4) and (5) show very different wavelengths detected in each spectrum, when using the wavelength of the laser beam of 1064 nm with energy of 500 mJ but without optical isolator. It is clear that some lines were not compared to the standard due to the presence of greater electronic background (noise) of the sample compared to the optical isolator sample. Therefore, this spectrum does not represent the actual values of the spectral emission lines of existing heavy metals, due to the detection ability of different foreign wavelengths.
Figure 4. The emission lines spectrum of plasma before the treatment (without optical insulator)

Figure 5. The emission lines spectrum of plasma at 1064 nm wavelength and 500 mj energy with optical insulator

Figure 6. The emission spectrum line after treatment

3.3. Effect of the scan area of laser pulses on the induced electrons of heavy metals (Fe, Ni, V and etc...) in the emission plasma:
The emission spectrum lines for the induced electrons unique of Iron, Nickel and Vanadium metals are shown in figures (7), (8) and (9). Where the black line represents the scan area line. Referring to
fig.(7) the total spot area line is shown as reference standard which was approved in the final accounts at cumulative area of laser spots(A) and cumulative distance of the laser treatment line (D).

Five spot with different locals were selected to represent the scan area line this was adopted as reference stander of heavy metals analysis (Fe ,Ni , V and etc…) . The parameters used in the technique were of different values of area line spot rate (1,2,3,4 and 5) , spot size diameter of 800 µm , the energy is (500) mj , pulse period of (10) ns , focal length of 7 cm , laser pulse number of (10) 1/s and overlap 0%.

![Graph](image)

**Figure 7.** The emission spectrum lines for the induced electrons unique of Iron metal with the spot rate at cumulative A and D
Figure 8. The emission spectrum lines for the induced electrons unique of Nickel metal with the spot rate at cumulative A and D

Figure 9. The emission spectrum lines for the induced electrons unique of Vanadium metal with the spot rate at cumulative A and D
Figures (10a-b) to (12a-b) below show the rate effect of the scanning area line laser spots on the induced electrons of the analyzed metals, where figure A is for MI and figure B for M II for all these results obtained. In these figures two curves are revealed, the first represents the accumulated induced electrons and the second represents the unique induced electrons. It is noted from the figure that when increasing the rate the of the number of laser beams for the scanning area line, the number of induced electrons was increased, that is, new unique (non-repetitive) emitted spectral lines are discovered. This, in turn, affects the characteristics and accuracy of the analysis.

![Figure 10 A](image1.png)

**Identify induced electrons Fe I**

- Induced electrons
- Induced electrons total

![Figure 10 B](image2.png)

**Identify induced electrons Fe II**

- Induced electrons
- Induced electrons total

**Figure 10.** A,B The cumulative induced electrons number and the unique induced electrons of Fe I and Fe II with the cumulative number of the laser spots.
Figure 11. A,B The cumulative induced electrons number and the unique induced electrons of Ni I and Ni II with the cumulative area of the scan line.
4. Conclusions

A homogeneous sample that represents the real components of the original sample of crude oil is designed to obtain better results where the plasma spectrum resulting from the examination process through the use of an optical isolator. The optical isolator isolates the sample optically thus preventing the influence of resolving lines emitted by external light (noise). The emission lines being obtained clearer, dense and distinct, facilitate the process of obtaining spectral information more accurately, and thus the qualitative evaluation process is clearer and more accurate. It was observed that the choice of representation area plays a major role in the analysis process. Using a representative line with five laser points and an overlap of 0% to identify the unique induced electron was effective so the spectroscopy lines emitted by the laser-assisted plasma process...
contained most of the current analysis lines representing most of the minerals in the crude oil sample used. In order to obtain a qualitative evaluation process it was to identify all the emitted lines and identify all elements, especially heavy metals. Determining suitable (optimal) conditions for the examination process is an important process for obtaining more realistic and accurate analysis results. During the present work, best parameters (energy, plus duration, focal length as well as pulse repetition rate) were used to obtain the best plasma spectrum. As for the wavelength, of 1064 used was the best wavelength, other wavelengths did not give good result due to the difference in the amount of absorption of these wavelengths by the elements in the crude oil sample. Intensity of some emitted lines was Saturated while others lines were weak and blurred.

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