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Technical Note

Discriminating crude oil grades using laser-induced breakdown spectroscopy☆

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ABSTRACT

The analysis of crude oil using laser-based analytical techniques such as laser-induced breakdown spectroscopy (LIBS) has become of great interest to various specialists in different fields such as geology, petro-chemistry and environmental science. In this work, a detailed study is presented wherein the implementation of an efficient and simple LIBS technique to identify the elemental constituents of crude oil and to distinguish between different grades of petroleum crude oil is discussed.

Laser-induced plasma (LIP) technique has been used in this work for direct measurements of atomic, ionic and molecular species in dry crude oil samples with API gravities ranging between 18 and 36. The technique was implemented using the first harmonic of a pulsed Nd-YAG laser source. Atomic and molecular emission bands were observed, consisting of characteristic spectral lines of atoms and diatomic molecular bands, namely from C, H, Si, Na, Ca, Mg, AL, Fe, Ti, Mo, C_2 and CN. The intensities of high-resolution spectral lines for some atoms and molecules of elements such as Ca, Na, Fe, Mo, C_2 and CN were evaluated at different wavelengths along the obtained spectra. The molecular bands and the elemental spectral lines were used to assess the possibility of adopting the LIBS technique in differentiating between crude oil samples with different American Petroleum Institute (API) gravity values. The results indicate the presence of a distinct correlation between the API gravity values of the various oil samples and the spectral line intensities of the elements and some molecular radical constituents. In addition, the possibility of identifying the API gravity values of unknown oil samples is also indicated.

1. Introduction

Crude oil is considered a complicated mixture predominantly made of saturated aromatic hydrocarbons, minerals, emulsified water and hetero-nuclear compounds. Metals in crude oil can also exist in various organic and inorganic forms. One of the first organic molecules that were identified in crude oil is porphyrine (naturally occurring chemical species). The simplest porphyrine form is composed of four pyrrole molecules, joined together by a methane bridge (−CH=), and these are known as vanadyl tetrapyrrolic complexes. Metals can exist in other organic forms as well, which can be defined as non-porphyrine metals or organometallic compounds, and these exist as complexes, metallic soap or in the form of colloidal suspension [1]. Organometallic compounds of Ca, Cu, Cr, Mg, Fe, Ti and Mo can undergo adsorption via the water–soil interface and act as emulsion stabilizers. Potassium, magnesium, sodium and calcium sulfates and chlorides (salts) are considered as another form of metal combinations, which can occur in the water phase of oil emulsions or might be incorporated into crude oil during processing, transportation or storage [2]. Desalting operation is the first procedure in removing such metal combinations from crude oil. Emulsified water, which might be introduced into crude oil during transportation, or accumulate in the oil reservoir as a result of water contamination during secondary oil recovery, mainly contains carbonates and halides of alkaline and alkaline earth elements [1]. The physical properties, particularly specific gravity of the crude oil, play an influential role in the quality of petroleum, and thus affect global trade of petroleum. The specific gravity in this context is defined as the ratio of the mass of a given volume of oil at 15 °C to the mass of an equal volume of pure water at 15 °C. The specific gravity varies from 0.8 (45.3 API) for light crude oils to over 1.0 (less than 10 API) for heavy crude oils and bitumen [3]. API gravity, which is an arbitrary metric and a more popular one, is related to the inverse of the relative density of a petroleum liquid and the density of water (API = (141.5 / Specific Gravity at 60 °F) − 131.5) [4]. It is obvious from the relation that the API gravity of crude oil increases with a decrease in the specific gravity, and vice versa. The API gravity directly reflects the economic value of oil and it is also an important metric in shipping and volumetric calculations involving crude oil.

Considerable work has been done on the elemental analysis of petroleum crude oil since 1983. The evaluation of metals in crude oil

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requires pretreatment procedures during sample preparation wherein most of the errors originate. In addition, the processes are time-consuming, regardless of the analysis technique employed. Among these are atomic absorption spectrometry [2,5–8], chemical vapor generation [9], inductively coupled plasma spectroscopy [10–12], X-ray fluorescence spectrometry and chromatographic techniques [13,14]. These techniques are considered to be sensitive, but they share major drawbacks, namely they are all extensively time-consuming, require large sample volumes and are difficult to apply in-situ. Laser-induced breakdown spectroscopy (LIBS), on the other hand, has the advantage of providing a quick method for the detection and quantification of the constituents elements with very different samples forms and structures. This technique is also highly developed and matured and can thus be implemented in several different applications. LIBS is also more feasible for application since it has the advantage of being quasi-nondestructive and bias insensitive to almost all elements, irrespective of high or low atomic weight [15,16].

Most of the quantitative and qualitative work using the LIBS technique has been focused on solids and much less work has been carried out on liquids such as crude oil, which is the object of this study. Fichet et al. [17] have attributed the reduced applications of this technique in liquid analysis to the difficulty of generating plasma in liquid samples. This can result from many factors, one of which is the strong possibility of the laser pulse inducing bubbles within liquids that are not transparent to laser-induced plasma, which may affect the reproducibility of the results [18]. Such factors have been taken into account and the experimental setup used in this work has been designed to avoid optical damage and produce spectra with acceptable and reproducible signal to noise ratio.

The total metal content analysis was one of the earliest tools to be applied for investigating the elemental distribution patterns in crude oil. This mode of analysis on various wells with different asphaltene concentrations and viscosities showed that the contend of trace elements in oil decreases with increasing API gravity values, as lighter oils contain lesser polar compounds [1]. Previous studies that used LIBS in analyzing crude oil were aimed towards obtaining a better understanding of physical aspects of flame temperature, fuel composition [19–21], exhaust gas composition and equivalence ratio [22,23]. Ferioli et al. [24] used LIBS in a time-resolved study of spark-ignited engine exhaust and obtained measurements through the detection of C, O, N, and CN (a recombination product in the cooling plasma) spectral lines. Gondal et al. [25] used LIBS in Arabian light crude oil samples for identifying the concentration of their elemental constituents, such as Ca, Fe, Mg, Cu, Zn, Na, Ni, K and Mo, which were found to be in good agreement with values obtained by the more conventional inductive coupled plasma technique (ICP).

LIBS has been used for the detection of heavy and trace elements in petroleum that are well known for their short and long term health risks such as Cu, Ni, As, Be, Mo, Zn, Cr and Sb [26]. Recently, the characterization and quantification of trace elements in crude oil has been of major interest to geochemists. The determination of source rocks and basins can enable geochemists to act rapidly during oil production and refining in order to reduce environmental pollution and corrosion of pipe lines [27].

Portable LIBS system has been used by Fortes et al. [28] in order to analyze the similarities and/or differences between crude oil and specimens of five other fuel residues obtained from the spillage of the Prestige Oil Tanker which sank near the Galician coast. Their study found a remarkable difference between the chemical composition of crude oil and that of the fuel residues upon investigation of the intensity ratios of C/O, H/O, H/CN, H/C_2, H/C, C/N, C_2/CN and Mg/Ca.

In the current study, LIBS was used to study qualitatively the elemental composition of Egyptian crude oil samples collected from Ras Gharib petroleum fields and investigate any correlation between the variation of trace elements and the content of particular molecular bands (CN and C_2) in the collected samples and their calculated API gravity values. Addressing such correlation could be used as a discrimination tool between the oil samples and help to determine API gravity values of unidentified crude oil samples within the range of API gravity values used in this work, allowing for effective in-situ differentiation between high and low quality oil samples. In addition, analysis of trace metals in oil samples provides direct environmental and industrial implications and allows for the development of processes to rid the oil samples of the trace metal contaminations.

Table 1
General composition of crude oil.

Element	Weight percentage
Carbon	83.0–87.0%
Hydrogen	10.0–14.0%
Sulfur	0.1–2.0%
Nitrogen	0.05–1.5%
Oxygen	0.05–6.0%
Trace elements	<1000 ppm

2. Methodology and procedures

Six dry crude oil samples with different specific gravities were collected from Ras Gharib petroleum fields, located in the Eastern desert of Egypt, 300 km South East of Cairo on the Red Sea coast. The samples were collected from the top layer of the shore tanks, which were pretreated for purposes of dehydration, desalination and readying for shipping and further processing. The source for these samples is considered to be blended oil and is treated at West BAKR treatment plant after extraction from oil wells.

The treatment process is based on raising the temperature of crude oil at up to 80 °C–100 °C using three heat exchangers along with injection of a demulsifier. The oil undergoes the dehydration and desalination processes through an electrostatic dehydrator and an electrostatic desolater, respectively, in order to minimize the water and salt content, and is then pumped to the shore tanks. A Hydrometer was used to measure the specific gravities, and the API gravity values were obtained from the relevant relation. Water content was quantified by distillation; salt content by extraction; sulfur content by energy-dispersive X-ray fluorescence spectroscopy; kinematic viscosity by glass capillary viscometer and asphaltene content by direct extraction. All of the above analytical procedures were conducted at the Egyptian general petroleum company laboratory according to the American Society for Testing and Materials (ASTM) designations 1298, 4294, 445 and 95, and Institute Petroleum (IP) designations 77 and 143. The corresponding API gravity values were obtained from the standardized ASTM56 tables [29].

The selected samples, as previously described, were treated to minimize the water and salt content in order to identify the naturally occurring metals and those added during oil processing or from secondary oil recovery. Crude oils are complex structures consisting of lengthy chains of hydrocarbon molecules, where the major elemental constituents differ over narrow ranges of these hydrocarbon chains from one type of crude oil to another, as shown in Table 1 [30].

The crude oil samples in this work were analyzed using the LIBS technique without using any other sample pretreatment. Two droplets

Table 2
Specific gravity, API value, water content, salt content and asphaltene percentage of the oil samples investigated.

Samples	Specific gravity	API	W % volume	Salt content wt %	Asphaltene wt %
A	0.9437	18.45	0.05	0.008	8
B	0.9315	20.4	0.05	0.007	6.84
C	0.9135	23.4	0.05	0.005	7.7
D	0.8894	27.6	0.05	0.005	4.35
E	0.8478	35.4	0.05	0.004	3.01
F	0.8427	36.4	0.05	0.004	2.2