LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR EXPRESS IDENTIFICATION OF CRUDE OILS

IDENTIFICACIÓN DE PETRÓLEO CRUDO MEDIANTE ESPECTROSCOPIA DE PLASMA INDUCIDA POR LÁSER

F. G. Rendón-Sauz[a†], T. Flores-Reyes[a], C. Costa[b,c]

a) Instituto Politécnico Nacional, 89600 Altamira Tamaulipas, México; rsfabian12@gmail.com[†]
b) Departamento de Física, Escuela Politécnica Nacional, 170525, Quito, Ecuador.
c) Grupo Ecuatoriano para el Estudio Experimental y Teórico de Nanosistemas (GETNano), Diego de Robles y Vía Interoceánica, Quito, Ecuador.
† corresponding author

Compositional determination of crude oil as well as its API degrees are extremely important for its identification and subsequent processing. Currently, this information is obtained using laborious laboratory techniques, which require time and complex experimental infrastructure. In this study, we determined the presence of elements found in crudes extracted from different fields using the LIBS technique, and we present a method to quickly determine crude's quality based on the relationship between API degrees and the CN line's intensity, the later determined by LIBS.

Tanto la determinación composicional del petróleo crudo como el grado API son extremadamente importante para la identificación y ulterior procesamiento. Actualmente, esa información es obtenida utilizando técnicas de laboratorio laboriosas, que requieren tiempo e infraestructura experimental costosa. En este estudio, se determina la presencia de elementos en crudos obtenidos en diferentes regiones, aplicando la técnica LIBS, y se presenta un método para evaluar la calidad del crudo, basada en la relacion entre el grado API y la intensidad relativa de la línea CN.

I. INTRODUCTION

Identification of crude oil's origin, as well as the presence of certain elements in its composition, are important to determine its quality and for its further processing. An elemental analysis of crude consists on determining the presence and content of elements such as C, H, O, S, N, Ni, V, Fe, among others. The first five elements are part of the matrix while the rest are considered trace elements [1].

There is interest in trace elements because they may cause difficulties since they go through each step of the refining process along with hydrocarbons. Inorganic materials are deposited on the equipment causing malfunctions or even the need for equipment replacement. There are elements capable of forming acids that may cause corrosion, while metallic elements may deposit on hydrocarbon conversion catalysts and adversely affect their performance; besides, the presence of trace elements may cause undesirable properties. Another reason for this interest is that trace elements frequently provide information regarding the geography or geology of the crude's origin.

Currently, atomic absorption (AA) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) are the most used techniques for determining trace elements in petroleum [2]. However, these methods have some issues such as the use of expensive solvents, the need for sample digestion processes, the pollution with chemical reagents, the processing time and the need of moving samples to the laboratory [3].

LIBS is an atomic emission spectroscopy technique and it has been solidly established for rapid determination of the elemental composition of samples presented in any state of matter [4]. In the mid-80s, studies and applications of the LIBS technique in analytical chemistry were promoted due to the lower costs of laser systems and to the technological development of plasma detection devices such as the imaging optical detector or the intensified charge coupled device (ICCD). These advances, along with an important reduction of the instrumentation size, particularly of lasers and spectrometers, have led to the development of portable LIBS equipment, allowing a real-time and in situ analysis [5].

Generally, LIBS success is due to several advantages that make this analytical technique unique. Among these advantages is the possibility of determining multiple elements, the rapid response, the remote determination, the minimum sample treatment required, the attractive low instrumentation cost, its ease of use and portability [6]. With the LIBS technique is possible to collect radiation in places that would be inaccessible with other techniques, the previous makes this technique particularly attractive to the analysis of hazardous materials, materials at high temperatures or for the analysis in hostile environments. Besides, it is important to consider that almost any kind of samples can be analyzed, even if they are conductive or not and in any state of matter [7].

This technique is based on the use of a laser as excitation source. Commonly, the laser used for this technique is a Nd:YAG laser, which is a solid-state laser in which

the active medium is a transparent crystal, this crystal is doped with a small quantity of ionized neodymium which provides the lasing activity and optical pumping using a flash lamp. The laser pulse, focused on the sample, causes a dielectric breakdown of the sample without physical contact, producing a partially ionized gas known as plasma. Capturing the light emitted by the plasma allows the species detection.

However, the LIBS technique also presents some difficulties, for example, when used to analyze liquid matrices [8], because of the splashing effect that would affect the focal length of the laser beam, decreasing reproducibility and analysis sensitivity [9]. Despite this, there is a marked interest in applying this technique to liquid samples to have in situ multi elemental analyses, this has great relevance to environmental control and safety [10]. For this reason, there have been several proposals to improve the LIBS's analytical performance in liquid matrices [11], including nebulizer systems [12], double-pulse configurations [13], pre-concentrate systems [14], etc.

In this study, crude oil samples from Saudi Arabia, Algeria, the North Sea, Mexico and Venezuela were analyzed using LIBS. These samples had 34, 44, 38, 22 and 31 API (American Petroleum Institute degrees) respectively, in order to identify trace elements among hydrocarbons depending on the region where the samples were extracted from. Also, a calibration curve was made based on the relative intensity of the CN band and the API degree. Such correlation can be used to determine in situ the API degree of a certain unidentified sample.

II. EXPERIMENTAL DEVELOPMENT

II.1. Sample

Petroleum is a complex mixture containing hydrocarbons, small amounts of organic compounds such as sulfur and nitrogen, and small amounts of inorganic substances and metals. A crude elemental analysis consists in determining the presence and content of C, H, O, S, N, Ni, V, Fe, Na, Ca, K, etc. From the former elements, the first five ones are part of the matrix while the rest are considered trace elements [15].

In this study, we used crude oil samples from 5 regions located in 3 different continents. Every sample was provided by the Mexican Petroleum Institute (IMP). The sample's API degrees and its composition were known.

API degrees are relevant because they are intensity markers, which is a primordial aspect of establishing the crude's price and subsequent processing. Table 1 shows the classification of crude types according to its API degrees [16].

The samples were heated for 60 minutes with ultrasonic vibration at 65°C using a Branson 1510 ultrasonic equipment. This was done in order to obtain better emission spectra with well-defined spectral lines and a better signal-noise relation, as well as to reduce the splashing effect. Afterwards, the sample was placed on Macherey-Nagel MN615 absorbent

paper with 0.16 mm thickness. Using absorbent paper as a sample holder allows additional liquid absorption and homogenizes the sample's geometry, facilitating the laser's impingement.

Table 1. Crude oil classification according API gravity.

Crude	API degrees (°)
Extra heavy	Less than 1
Medium	22.0-29.9
Light	30.0-39.9
Super light	From 40 on

II.2. Experimental Set-Up

Fig. 1 shows a diagram of the experimental set-up. We used a LIBS 2000+ supplied by Ocean Optics, with a Nd:YAG laser which emits shots at a wavelength of 1064 nm with an adjustable energy of up to 250 mJ per shot and a pulse width of 8 ns. This system has a delay generator and a maximum pulse repetition frequency of 20 Hz. The detection system is a modular system including seven HR2000 spectrometers with resolution of 0.065 nm and 2048 pixels to sequentially cover a total spectral range of 200-980 nm.

The conditions in this study were the following: the energy of 239 mJ per shot, a 2 vs delay between the pulse and the reading to minimize the electronic background. The laser beam is focused through a lens with a focal distance of 7 cm. The plasma emission is collected and conveyed to the spectrometer through an optical fiber placed 3 cm from the sample in a 45° angle.
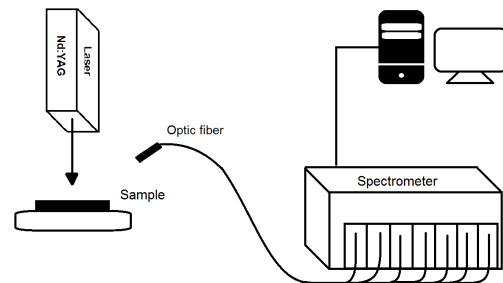

Figure 1. Schematic diagram of the experimental set up.

II.3. Spectra Treatment

Using the Mathematica 10 software, we carried out a baseline correction for each spectrum so that they could be compared in equal conditions. The method used was a moving average algorithm to minimize the differences between local minimum and maximum and soften the spectrum. Then, using interpolation between local minima, it produces a baseline model which will be used to remove the area under the curve, so that it locally adjusts to the characteristics of the raw spectrum. The emission line of H_α a 656.3 nm was used as a reference to normalize the spectra since it was a very well-defined line. The selected spectral range of interest was of 200-800 nm. Fig. 2 shows a LIBS spectrum of crude oil from the North Sea. The left picture shows the spectrum

before the treatment while the right picture shows the same spectrum after the treatment.
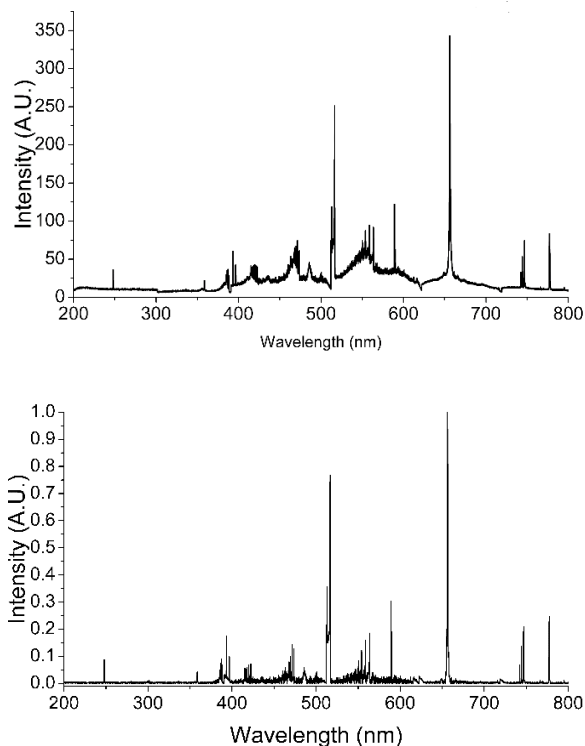

Figure 2. LIBS spectrum of typical sample a) before and b) after the data treatment.

II.4. Experimental Procedure

Filter paper was cut into pieces of 1×2 cm and then placed on the sample holder. A drop of crude oil, previously treated using ultrasound, was poured on the paper, it was left to settle for 1 hour before performing the analysis; this was done to ensure a good distribution.

Ten spectra were taken for each sample to have an averaged result. Separately, spectra were taken from a graphite pattern (Testbourne Ltd, 99 %), which was also analyzed under the same conditions.

Line identification was carried out using information from the National Institute of Standard and Technology, USA (NIST).

III. RESULTS AND DISCUSSION

III.1. Elemental analysis

Table 2 shows the results obtained from the elemental analyses made using LIBS, the spectra were taken from crude oil samples from different regions, and ordered by their wavelength. We identified spectral lines corresponding to elements such as Ca, N, Fe, Na, K and O, some of them belonging to the sample and other to the environment. On the other hand, we identified the emissions corresponding to C-N, C-C and CH bands; the corresponding characteristic lines are shown in Table 3.

Table 2. Elemental spectral lines observed when comparing spectra from graphite and from crude oil samples.

Element	Γ (nm)	Graphite	Saudi Arabia	Algeria	North Sea	Mexico	Venezuela
C I	247.86	x	x	x	x	x	x
V I	318.3					x	
Ca II	393.36	x	x	x	x	x	x
Ca II	396.84	x	x	x	x	x	x
V I	407.1					x	
Ca I	422.67	x	x	x	x	x	x
Ca I	430.25	x					
Ca I	443.57	x					
Ba II	455.4	x				x	
H_β	486.1		x	x	x	x	x
N I	500.5		x	x	x	x	x
Ca I	527.0	x				x	
Fe I	567.9	x	x	x			x
Na I	588.99	x	x	x	x	x	x
Na I	589.59	x	x	x	x	x	x
Ca I	610.2	x				x	
Ca I	612.2	x				x	
Ca I	616.2	x				x	
Ca I	643.9	x				x	
Ca I	646.2	x				x	
Ca I	649.3	x				x	
N I	648.53	x	x			x	x
H_α	656.3	x	x	x	x	x	x
Li I	670.79	x				x	
N I	742.4		x	x	x	x	x
N I	744.2						x
N I	746.83		x	x	x	x	x
K II	766.49	x	x	x		x	
K I	769.89	x				x	
O II	777.2	x	x	x	x	x	x

Peak identification is performed based on the comparison with the NIST's database and it is confirmed with previous reports.

Table 3. Molecular bands observed when comparing spectra from graphite and from crude oil samples.

Band	Γ (nm)	Graphite	Saudi Arabia	Algeria	North Sea	Mexico	Venezuela
C-N	358-359.2	x	x	x	x	x	x
C-N	385-389	x	x	x	x	x	x
C-N	415-422.7	x	x	x	x	x	x
C-H	428-432	x					
C-C	466.9-473.7	x	x	x	x	x	x
C-C	512.9-516.5	x	x	x	x	x	x
C-C	554.1-568.9	x	x	x	x	x	x

As was expected and as it has been previously reported [17], in the qualitative analysis of the spectra were lines corresponding to C, N, O, and H. These lines are characteristic of inherent elements composing crude oil or are due to the environment; for this reason, they are not important to identify the origin of each sample.

However, there are also lines that only appear in some samples. For example, the presence of Li is only detected in Mexican crude oil [18]. On the other hand, the Na line

shows a very different intensity in each simple, being the greatest the one corresponding to the Mexican crude oil, which comes from a region with limestone subsoil [19]. As has been reported previously, there is a relation between crude's composition and the subsoil's composition, being this one of the factors allowing to determine the origin of crude oil [20].

III.2. Correlation between molecular bands and API degrees

Determination of crude API degrees was developed by the American Petroleum Institute (API) to measure the relative density of different petroleum liquids, expressed in degrees. API gravity is graduated in degrees on a hydrometer instrument and was designed in a way that most values would fall between 10° y 70°. The formula used to obtain this effect is API Gravity = (141.5/SG at 60°F) - 131.5; in which SG is the specific gravity of the liquid, this complemented with the temperature, allows to determine the API degrees correlating them with data from (ad hoc) tables, with which the respective value of 60°F is obtained [21]. However, these calculations get complicated when a follow-up is required at variable pressure and temperature as the extraction is performed [22].

The LIBS technique, due to its portability, allows to carry out an express in situ analysis. This offers a new alternative for determining the API degree almost immediately, without having to carry the samples to the laboratory.

As it is known, API degree indicates the proportions of elements strange to the crude's chemical structure, such as metals. Nevertheless, the presence of these elements could be associated with the composition of the field's subsoil or it could be manifested in such reduced proportions that it would difficult its determination with a rapid technique such as LIBS in field conditions. In contrast, the emission associated with molecular bands like C-N is easily detected and, if there was a direct correlation with the API degree, it could serve as an immediate indicator.

Fig. 3 shows correlation curves between API degree, provided by the IMP, and the normalized value corresponding to the area under the CN molecular band at 385.3 nm in Fig. 3a and its intensity value observed in Fig. 3b.

III.3. Statistical Analysis

Crude oil samples from Saudi Arabia (SA), Algeria (AL), Mexico (MX), the North Sea (NS) and Venezuela (VN) were analyzed using the LIBS technique. 10 spectra were taken from each sample, and so 50 spectra were registered. Spectra were classified with the k-means method [23], using the open source statistical software PAST [24].

The k-means algorithm is a clustering method, which aims to separate m observations $x_1, x_2, \ldots, x_m$, in which x_i is a real vector of d dimensions and builds k groups, associating the

x_i vector to the j-th group. In order to make the classification, the k-means algorithm was parameterized with $k = 5$ groups.
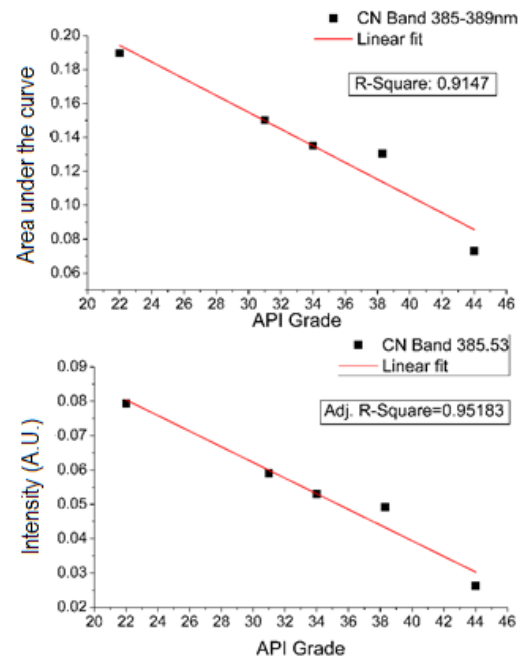

Figure 3. Correlation between API degree with respect to the line of the CN molecular band at 385.3 nm. Dependency is calculated regarding the a) normalized value of the area under the curve of the characteristic line b) normalized value of the relative intensity of the characteristic line.

Table 4 shows the result of this classification. Samples from Saudi Arabia (group 1), Mexico (group 2) and the North Sea (group 4) were correctly classified. However, some samples from Algeria (group 2) and Venezuela (group 5) were not. This indicates that the LIBS spectra had similarities that prevent a successful classification.

Table 4. Classification of crude oil samples from Saudi Arabia, Algeria, Mexico, North Sea and Venezuela.

Sample	Group	Sample	Group	Sample	Group	Sample	Group	Sample	Group
SA1	1	AL1	2	MX1	3	NS1	4	VN1	5
SA2	1	AL2	2	MX2	3	NS2	4	VN2	2
SA3	1	AL3	2	MX3	3	NS3	4	VN3	5
SA4	1	AL4	2	MX4	3	NS4	4	VN4	5
SA5	1	AL5	2	MX5	3	NS5	4	VN5	5
SA6	1	AL6	2	MX6	3	NS6	4	VN6	5
SA7	1	AL7	2	MX7	3	NS7	4	VN7	5
SA8	1	AL8	2	MX8	3	NS8	4	VN8	5
SA9	1	AL9	5	MX9	3	NS9	4	VN9	5
SA10	1	AL10	2	MX10	3	NS10	4	VN10	5

IV. CONCLUSIONS

Previous treatment using ultrasound is a rapid and effective method to prepare the samples to obtain high quality spectra, easy to interpret.

The LIBS technique allows to perform qualitative compositional analysis of crude oil in a fast way to identify

characteristic elements that could be associated with the field. On the other hand, API degrees show a direct correlation both with the line intensity associated with the CN band, and with de area under the curve of such line, this allows a rapid measure of this parameter.

The use of laser and compact spectrometers like the ones presented in this work proves the potential of this technique to perform qualitative compositional identification and rapid measure of API degree in field conditions.

V. ACKNOWLEDGEMENTS

REFERENCES

[1] R. C. Selley and S. A. Sonnenberg, Elements of Petroleum Geology, 3rd Ed. (R. C. S. A. Sonnenberg, New York, USA, 2014).

[2] V. Simanzhenkov and R. Idem, Crude oil chemistry (CRC Press, Amsterdam, Netherlands, 2003).

[3] R. S. Amais, C. D. Amaral, L. L. Fialho, D. Schiavo, and J. A. Nóbrega, Analit. Met. **6**, 4516 (2014).

[4] L. J. Radziemski, Spectrochim. Acta Part B **57**, 1109 (2002).

[5] F. C. Alvira, T. Flores, L. V. Ponce, and L. M. Osorio, Lat. Ame. Opt. and Phot. Conf. (Optical Society of America, 2014), p. LTh4A. 11.

[6] A. W. Miziolek, V. Palleschi, and I. Schechter, Laser induced breakdown spectroscopy (Cambridge University Press, London, United Kingdom, 2006).

[7] D. A. Cremers and A. K. Knight, Laser-Induced Breakdown Spectroscopy (Wiley Online Library, New York, USA, 2006).

[8] F. Al-Adel, M. Dastageer, K. Gasmi, and M. Gondal, J. Appl. Spectrosc. **80**, 767 (2013).

[9] J. Cáceres, J. T. López, H. Telle, and A. G. Ureña, Spectrochim. Acta Part B **56**, 831 (2001).

[10] S. Golik, O. Bukin, A. Il'in, E. Sokolova, A. Kolesnikov, M. Y. Babiy, Y. N. Kul'chin, and A. Gal'chenko, J. Appl. Spectrosc., 1 (2012).

[11] D. A. Cremers, L. J. Radziemski, and T. R. Loree, Appl. Spectrosc. **38**, 721 (1984).

[12] E. M. Cahoon and J. R. Almirall, Anal. Chem. **84**, 2239 (2012).

[13] A. De Giacomo, M. Dell'Aglio, F. Colao, R. Fantoni, and V. Lazic, Appl. Surf. Sci. **247**, 157 (2005).

[14] S. T. Järvinen, J. Saarela, and J. Toivonen, Spectrochim. Acta, Part B **86**, 55 (2013).

[15] C. Y. Reyes, J. A. Triguis, J. R. Cerqueira, N. C. Medeiros, I. C. Maciel, and O. M. C. de Oliveira, Cadernos de Geociências **12**, 84 (2016).

[16] O. C. Mullins, E. Y. Sheu, A. Hammami, and A. G. Marshall, Asphaltenes, heavy oils, and petroleomics (Springer Science & Business Media, Berlin, Germany, 2007).

[17] F. Rendón, A. Frías, A. Villarreal, T. Flores, L. Ponce, and G. Vázquez-Bautista, Proceedings of the 5th International Symposium on Experimental Mechanics and 9th Symposium on Optics in Industry (ISEM-SOI) 2015 (Springer, Mexico, 2017), pp. 181.

[18] L. Cedeno, L. Ordonez, and F. Pedraza, Información Tecnológica **14**, 51 (2003).

[19] T. Daubert and R. Danner, in Technical Data Book Petroleum Refining, (American Petroleum Institute, Washington DC, 1997).

[20] P. Mexicanos, Anuario estadístico (PEMEX, 1988).

[21] H. B. Bradley, Petroleum engineering handbook (Richardson, Texas, 1987).

[22] H. D. Beggs and J. Robinson, J. Pet. Technol **27**, 1 (1975).

[23] S. Lloyd, IEEE trans. on info. theory **28**, 129 (1982).

[24] Ø. Hammer, D. Harper, and P. Ryan, Palaeontol. Electr. **4** (2001).