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.

<table>
<thead>
<tr>
<th>Crude</th>
<th>API degrees (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extra heavy</td>
<td>Less than 1</td>
</tr>
<tr>
<td>Medium</td>
<td>22.0-29.9</td>
</tr>
<tr>
<td>Light</td>
<td>30.0-39.9</td>
</tr>
<tr>
<td>Super light</td>
<td>From 40 on</td>
</tr>
</tbody>
</table>

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.

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 Hα 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.

![Image](60x589 to 276x724)

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.

![Image](59x438 to 275x588)

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Graphite</th>
<th>Saudi Arabia</th>
<th>Algeria</th>
<th>North Sea</th>
<th>Mexico</th>
<th>Venezuela</th>
</tr>
</thead>
<tbody>
<tr>
<td>C I</td>
<td>247.86</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>V I</td>
<td>318.3</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca II</td>
<td>393.36</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Ca II</td>
<td>396.84</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>V I</td>
<td>407.1</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca I</td>
<td>422.67</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Ca I</td>
<td>430.25</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca I</td>
<td>443.57</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba II</td>
<td>455.4</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H β</td>
<td>486.1</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>N I</td>
<td>589.99</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Na I</td>
<td>589.59</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Ca I</td>
<td>610.2</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca I</td>
<td>612.2</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca I</td>
<td>616.2</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca I</td>
<td>643.9</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca I</td>
<td>646.2</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca I</td>
<td>649.3</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N I</td>
<td>648.53</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>H α</td>
<td>656.3</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Li I</td>
<td>670.79</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N I</td>
<td>742.4</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>N I</td>
<td>744.2</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N I</td>
<td>746.83</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>K II</td>
<td>766.49</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>K I</td>
<td>769.89</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O II</td>
<td>777.2</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Band</th>
<th>Graphite</th>
<th>Saudi Arabia</th>
<th>Algeria</th>
<th>North Sea</th>
<th>Mexico</th>
<th>Venezuela</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N</td>
<td>358-359.2</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>C-N</td>
<td>385-389</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>C-N</td>
<td>415-422.7</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>C-H</td>
<td>428-432</td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C</td>
<td>466.9-473.7</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>C-C</td>
<td>512.9-516.5</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>C-C</td>
<td>554.1-568.9</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

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
of the area under the curve of the characteristic line 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.

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

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.
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 the 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

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