Distinctive Features of Raman Spectroscopy of Crude Oils of the Absheron Peninsula

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Abstract

Raman spectroscopy provides useful information about hydrocarbon fluid inclusions in crude oils. In particular, the presence or absence of hydrocarbon functional groups may be qualitatively determined. In most oil spills situations, it is desirable to have more than one analytical technique for detecting of spilled oil to its suspected source. In this paper we present first results of Raman scattering spectra of crude oils taken from 6 Oil-gas Production Companies of Azerbaijan Republic.

Key words: Raman scattering, LIDAR, combinational light scattering, laser applications, oil pollution, laser spectroscopy, crude oil emission and scattering.

DOI 10.52171/2076-0515_2023_15_03_51_58

Received *10.05.2023*
Revised *18.09.2023*
Accepted *20.09.2023*

For citation:
Pashayev A.M., Valiyev N.A., Asgerov K.E., Musayev A.A., Mammadov I.Kh., Allahverdiyev K.R., Sadikhov I.Z.
[Distinctive Features of Raman Spectroscopy of Crude Oils of the Absheron Peninsula]
Herald of the Azerbaijan Engineering Academy, 2023, vol. 15, no. 3, pp. 51-58 *(in English)*

Herald of the Azerbaijan Engineering Academy
2023, vol. 15, no.3, pp. 51-58
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Abşeron yarımadasına məxsus xam neft nümunələrinin Raman səpilməsi spektrlərinin fərqləndirici xüsusiyyətləri

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Xülasə

Raman spektroskopiyası, xam neftin tərkibindəki karbohidrogen mayeləri barədə faydalı məlumatlar verir. Xüsusilə, karbohidrogen funksional qruplarının mövcud olması və ya olmaması bu metodla keyfiyyətli şəkildə müəyyən edilə bilər. Məlum olduğu kimi Neft dağılmaları ilə əlaqəli əksər hallarda, dağılmış neftin aşkarlanması və ehtimal olunan mənbənin müəyyənləşdirilməsi üçün birdən çox analitik metodun olması məqsədə uyğundur. Bu məqalədə biz Azərbaycan Respublikasının 6 neft qaz çıxarma idarəsinə məxsus xam neft nümunələrinin Raman səpilməsi spektrlərinin ölçülməsinin ilkin nəticələrini təqdim edirik.

Açar sözlər: Raman səpilməsi, LIDAR, İşığın Raman səpilməsi, lazerin praktiki tətbiqi, neft çirklənməsi, lazer spektroskopiyası, xam neftin şüalanması.

DOI 10.52171/2076-0515_2023_15_03_51_58

УДК 550.8.08

Отличительные характеристики рамановской спектроскопии сырой нефти Апшеронского полуострова

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Аннотация

Спектроскопия комбинационного рассеяния света дает полезную информацию о включениях углеводородных флюидов в сырой нефти. В частности, может быть качественно определено наличие или отсутствие углеводородных функциональных групп. В большинстве ситуаций, связанных с разливами нефти, желательно иметь более одного аналитического метода для обнаружения разлитой нефти и определения предполагаемого источника. В статье представлены первые результаты спектров комбинационного рассеяния сырой нефти, полученных от 6 нефтегазодобывающих компаний Азербайджанской Республики.

Ключевые слова: Рамановское рассеяние, ЛИДАР, комбинационное рассеяние света, использование лазеров на практике, нефтяное загрязнение, лазерная спектроскопия, эмиссия и рассеяние сырой нефти.

Introduction

Crude oil is very wide and diverse class of substances [1-5]. The complex nature of crude oil, may lead in complex chemical analysis method. In our previously published paper, we described KA-14 LIDAR developed at National Aviation Academy of Azerbaijan to detect oil spills on water surface of Caspian Sea and earth of Absheron peninsula [5-11].

According to existing literature 4 different techniques (infrared spectroscopy, fluorescence (FL), gas chromatography and low temperature luminescence) were used to identify oil spills on water surface and to establish spills source. FL spectra and identification of oil spills on Caspian Sea as measured by KA-14 LIDAR, developed at the NAA, were published by the authors of present artocle and the results have been described in [8-11].

Laser Raman spectroscopy is used in many scientific-research centers of world as a standard analytical method. At the same time as a tool in petroleum research, its role has been hindered by the high FL background. This FL background has such high intensity, that it is completely obscures any band due to Raman scattering (it is well known that intensity of Raman scattered bands is about 10-5 times less than intensity of excited light [12-16]).

In this paper we present the first results of *Raman* scattering spectra of crude oils taken from 6 *Oil-gas Production Companies (OGPC) of Azerbaijan Republic*.

Analysis of scientific and technical literature on the topic

The Raman method is widely use for the purpose of studying and confirming the composition of useful fossil migrations for obtaining oil spectra from different oil fields. The study showed that fats had similar molecular-mass regions, which were specific to a baseline region.

An analysis of the literature shows that Raman spectra of oils are observed in a wide range of the spectrum, including high-frequency. The most pronounced stripes of Raman bands are observed in the following wavelength: ~ 450 cm^{-1}, ~ 1350 cm^{-1}, ~ 1550 cm^{-1}, ~ 1600 cm^{-1}, ~ 1730 cm^{-1}, ~ 1770 cm^{-1}, ~ 1850 cm^{-1}, ~ 1950 cm^{-1} [1-4, 12, 14-16].

Compared to other methods, Raman spectroscopy facilitates the process of direct measurement in solid, liquid and gaseous media. The pattern has a number of advantages, such as special training and the absence of neutral to absorption strips.

Raman spectroscopy is widely used also for obtaining oil spectra from oil fields. When measuring the wavelength of λ = 532 nm in most substances are presented spectra in which radiation absorption occurs as a result of observation of FL, which is distinguished by wider maximums compared to the Raman signal.

To avoid FL effect, it is necessary to take measurements at a wavelength of λ=1064 nm or longer using a portable spectrometer. Measurements with a wavelength of λ = 1064 nm look promising for the analysis of crude oils by the Raman spectroscopy. Our measurements of Azerbaijanian crude oils by using the KA-14 LIDAR showed that the observed high intensity FL strongly quenches weak Raman spectra. In addition, we tried to perform measurements of Raman oil spectra using devices in the Laser Spectroscopy laboratory of the National Aviation Academy. Such devices include: *laser "Quantel Brilliant B" (main beams at λ = 532 nm, λ = 255 nm and λ=266 nm; •pulse duration-5 ns; •power 310 mJ, 170 mJ, and 60 mJ respectively; •MDR - 41 spectrometer, •photo detectors FEU - 62 and FEU - 100.

Unfortunately, the FL generated in the crude oils was extinguishing the expected Raman scattering spectrum (Figure 1).

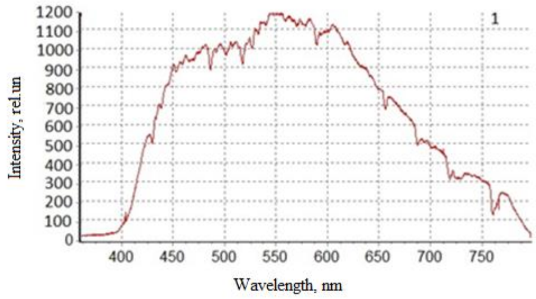

Figure 1 – Room temperature FL spectrum of crude oil of *Absheron OGPC (Pirallahi, Artem)*. Measurements were carried out with help of the *KA-14 LIDAR* developed at NAA. The spectrum is excited by the *CRF - 355* laser line of wavelength λ = 255 nm

In accordance with the above described, it was decided to carry out measurements on a special (manufactured in Japan) Raman installation located at the Institute of Physics of Azerbaijan National Academy of Sciences. This setup is performed using the excitation Spectra of YAG: Nd^{3+} laser second harmonic (λ = 514.5 nm).

Conclusion

Analysis of the available literature, calibration and maintenance of KA-14 LIDAR was carried out. An analysis of the available literature has led to the conclusion that the Raman spectra of crude oil is a fairly reliable method for creating Raman spectra of crude oil debris on water and earth surfaces and a Data Bank based on these spectra. The results given by the measurements carried out on the basis of the caliber are consistent with the results published in modern literature. The scientific and technical requirements of the research work put forward have been experienced and clarified. Thus, it was decided to measure the Raman spectra of crude oil samples from 12 OGPCs of Azerbaijan. On the basis of the project, separate spectral analysis of the extracted oils in different zones of Absheron peninsula and the creation of Raman spectra`s Data Bank of oils based on the data obtained are underway. The mentioned zones included 8 (eight) OGPCs belong to AzNeft (Azerbaijan) and 4 (four) Joint Ventures under AzNeft: OGPC: 1. Absheron; 2. Narimanov; 3. Oil Rocks; 4. Amirov; 5. Siyazan; 6. Tagiyev; 7. May 28; 8. Bibiheybat; Joint Ventures: 1. Balakhani Oil; 2. Muradkhanli Oil; 3. Surakhani Oil; 4. Binagadi Oil.

Measurement of Raman spectra by KA-14 LIDAR did not give any positive results. It was obviously to expect for this, since weak Raman scattering lines (10^{-5} degrees weaker from the intensity of the excitation laser) are screened with strong FL lines of oils (10^{-1} degree`s from the intensity of the excitation laser). Therefore, we decided to carry out the measurement of Raman spectra of oils using the Raman device available at the Institute of Physics of Azerbaijan National Academy of Sciences. Some of these first results is presented in Figures 2-7.

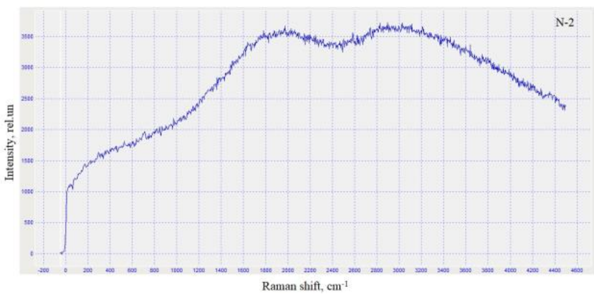

Figure 2 – Raman spectrum of crude oil of OGPC named after Tagiyev. The measurements were carried out by Raman spectra measurement equipment at the Institute of Physics Azerbaijan National Academy of Sciences. Spectrum was excited using YAG: Nd^{3+} laser's second harmonic (λ = 514.5 nm).

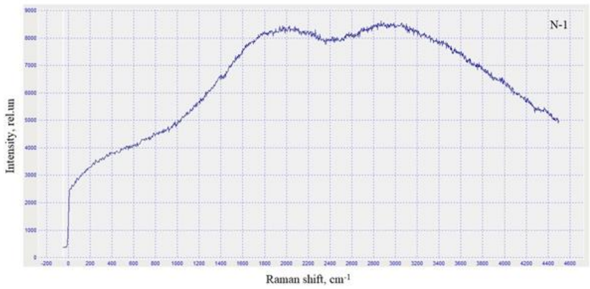

Figure 3 – Raman spectrum of crude oil of Lokbatan-BUTA OGPC. The measurements were carried out by Raman spectra measurement equipment at the Institute of Physics Azerbaijan National Academy of Sciences. Spectrum was excited using YAG: Nd^{3+} laser's second harmonic (λ = 514.5 nm).

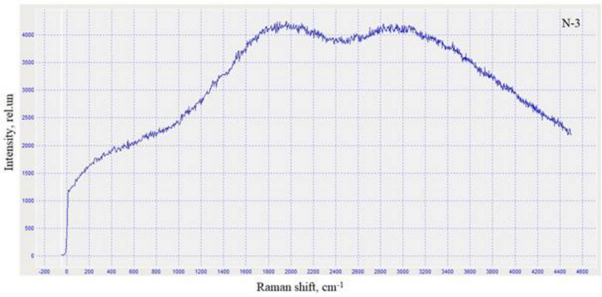

Figure 4 – Raman spectrum of crude oil of 28 May OGPC. The measurements were carried out by Raman spectra measurement equipment at the Institute of Physics Azerbaijan National Academy of Sciences. Spectrum was excited using YAG: Nd^{3+} laser's second harmonic (λ = 514.5 nm).

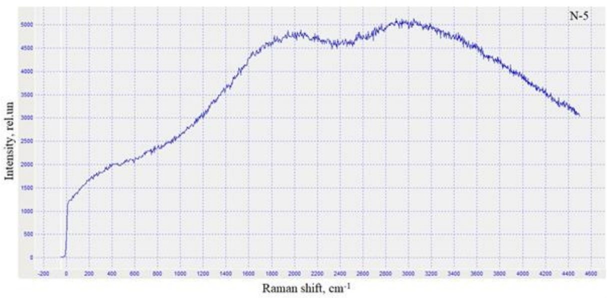

Figure 5 – Raman spectrum of crude oil of Bibiheybat OGPC. The measurements were carried out by Raman spectra measurement equipment at the Institute of Physics Azerbaijan National Academy of Sciences. Spectrum was excited using YAG: Nd^{3+} laser's second harmonic (λ = 514.5 nm).

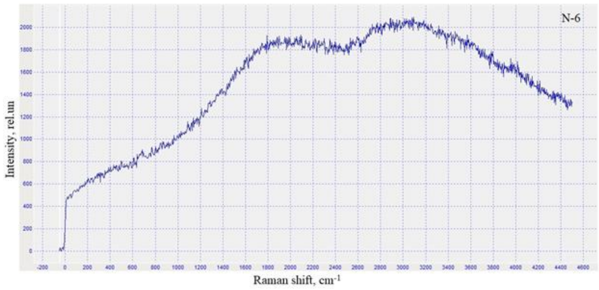

Figure 6 – Raman spectrum of crude oil of Narimanov OGPC. The measurements were carried out by Raman spectra measurement equipment at the Institute of Physics Azerbaijan National Academy of Sciences. Spectrum was excited using YAG: Nd^{3+} laser's second harmonic (λ = 514.5 nm).

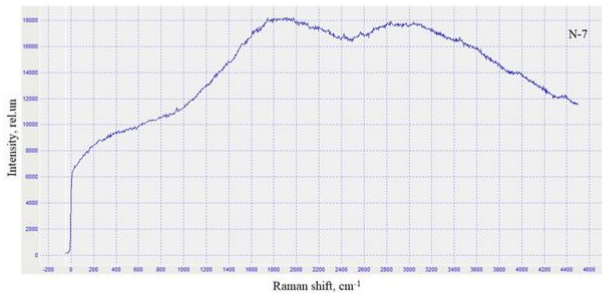

Figure 7 – Raman spectrum of crude oil of Oil Rocks OGPC (Neftjanie Kamni).
The measurements were carried out by Raman spectra measurement equipment at the Institute of Physics Azerbaijan National Academy of Sciences. Spectrum was excited using YAG: Nd^{3+} laser's second harmonic (λ = 514.5 nm).

As can be seen from Figures 2-7, the characteristic features of the Raman scattering spectra are observed as a weak wide bands in the spectral ranges of : •200 - 600 cm^{-1}, •1500-2300 cm^{-1} and •2400-3400 cm^{-1}.

The Raman spectra of crude oils of the remaining six OGPCs excited using YAG: Nd^{3+} laser's second harmonics (λ = 514.5 nm) are basically similar to those shown in Figures 2-7. Finally, it is worth noting that we plan to perform Raman scattering spectra of Azerbaijani oils using near-infrared laser lines to exclude a high-intensity FL background.

We contacted some colleagues in the Institute of Spectroscopy Russian Academy of Sciences and agreed on measurement questions. The equipment available in this organization (has a radiation wavelength of 1064 nm (1.16 eV)) excites Raman scattering spectra and significantly reduces the FL intensity of crude oil spectra.

One of preliminary results of Raman spectrum of crude oil taken from Lokbatan-BUTA OGPC is presented in Figure 8.

Finally, it is worth noting that we plan to perform Raman scattering spectra of Azerbaijani oils using near-infrared laser lines to exclude a high-intensity FL background. We contacted some colleagues in the Institute of Spectroscopy Russian Academy of Sciences and agreed on measurement questions. The equipment available in this organization (has a radiation wavelength of 1064 nm (1.16 eV)) excites Raman scattering spectra and significantly reduces the FL intensity of crude oil spectra. One of preliminary results of Raman spectrum of crude oil taken from Lokbatan-BUTA OGPC is presented in Figure 8. Finally, it is worth noting that we plan to perform *Raman* scattering spectra of *Azerbaijani* oils using near-infrared laser lines to exclude a high-intensity *FL* background. We contacted some colleagues in the *Institute* of *Spectroscopy Russian Academy of Sciences* and agreed on measurement questions. The equipment available in this organization (has a radiation wavelength of 1064 nm (1.16 eV)) excites *Raman* scattering spectra and significantly reduces the *FL* intensity of crude oil spectra. One of preliminary results of Raman spectrum of crude oil taken from *Lokbatan-BUTA OGPC* is presented in Fig. 8.

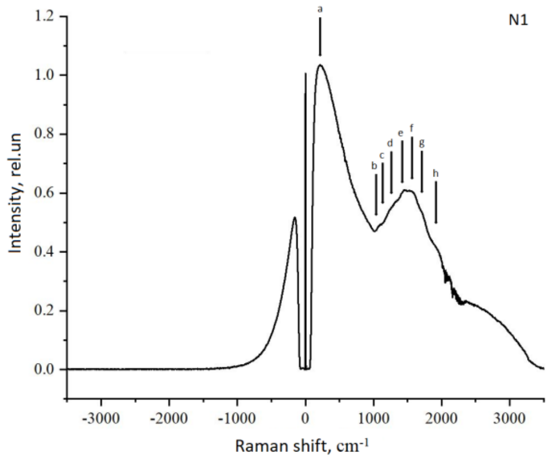

Figure 8 – Raman spectrum of crude oil of Lokbatan-BUTA OGPC. The measurements were carried out with the Raman installation, which is available at the Institute of Spectroscopy of Russian Academy of Sciences. The spectrum was excited by the YAG:Nd3+ laser (= 1064 nm). Horizontal axis- Raman shit, cm^{-1}. Vertical axis- intensity, rel. units

Frequency values of Raman scattering of crude oils obtained from the final processing of spectrum (Figure 8) is shown in Table 1.

Table 1 – Frequency values of *Raman* scattering of crude oils obtained from the final processing of spectrum (Figure 8)

Sample	Peak No1 (a) cm^{-1}	Peak No2 (b) cm^{-1}	Peak No3 (c) cm^{-1}	Peak No4 (d) cm^{-1}	Peak No5 (e) cm^{-1}	Peak No6 (f) cm^{-1}	Peak No7 (g) cm^{-1}	Peak No8 (h) cm^{-1}
Lokbatan - Buta OGPC	205	1090	1150	1200	1490	1570	1750	1950

Planned measurements in the Raman scattering spectra of crude oil from the remaining eleven organizations will allow the creation of a Data Bank of crude oils from Absheron peninsula of Azerbaijan.

Acknowledgments

The authors are indebted to the State Oil Company of Azerbaijan Republic (SOCAR) for financial support of present reserach in a frame of project “Creation of Raman Spectra Bank of Oil Extracted in Different Zones of Absheron Peninsula via LIDAR”.

Conflict of Interests

The authors declare there is no conflict of interests related to the publication of this article.

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