

SARA fraction measurements of Persian Gulf crude oil using LIF

spectroscopy based on analysis of variance (ANOVA)

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Graphical Abstract

Abstract

Crude oil is typically categorized into four main fractions: saturates, aromatics, resins, and asphaltenes, collectively referred to as SARA. To enable the rapid identification of these fractions, a novel on-site approach is introduced based on laser-induced fluorescence (LIF) spectroscopy. This method utilizes both the solvent (with dichloromethane, DCM) densitometry and quantum efficiency as key analytical parameters. Several crude oil samples are analyzed from different oilfields in the Persian Gulf, with optical parameters of interest i.e., peak concentration (C_p) and quantum efficiency (Q_E) giving by the experimental data. The relation between these parameters and crude oil fractions is attested through analysis of variance (ANOVA). Then, the predictive statistical models are developed to estimate the values of the crude oil fractions. The findings demonstrate that these predictive models exhibit high accuracy compared to the standard methods (ASTM D 6560 & ASTM D 4124). In fact, the proposed technique significantly reduces the testing time to less than 30 minutes.



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1. Introduction

Crude oil comprises approximately 17,000 distinct components, encompassing a wide variety of organic substances. Due to its highly intricate composition, conducting a comprehensive analysis of crude oil is nearly unfeasible [1,2]. As a result, crude oil components are typically grouped into four main categories: light fractions, known as Saturates and Aromatics, and heavy fractions, identified as Resins and Asphaltenes, abbreviated as SARA [3–7]. The heavy fractions are polar, environmentally persistent pollutants with complex structures that prevent the definition of a fixed chemical formula [8–13]. These fractions contain polycyclic aromatic compounds (PACs) with 3 to 9 aromatic rings, often incorporating elements like nitrogen, sulfur, and oxygen (NSO), as well as trace metals such as nickel and vanadium [14]. The toxicity and environmental persistence of PACs increase with a higher number of aromatic rings, greater molecular weight, and enhanced polarity. As a consequence, the precise quantification of crude oil fractions is crucial for both the petrochemical industry and environmental protection efforts.

Currently, various conventional techniques are utilized to measure SARA fractions, including the standard methods outlined in ASTM D-6560 (IP-143), ASTM D-2007, and ASTM D-4124 [15–17]. These methods are based on polarity as well as solubility of the components in a given solvent. However, it has certain disadvantages, including a long execution time (from 3 to 10 days), high solvent requirements, and low automation capability. These limitations have demonstrated the need for simpler, more efficient alternatives. One promising alternative addresses laser-induced fluorescence spectroscopy (LIFS), which addresses several of these challenges [18,19]. Nevertheless, accurately identifying crude oil fractions is difficult by LIFS alone due to the structural complexity of crude oil, the similarity of its fluorescent components, and the spectral overlap in LIF signals [20].

To overcome these restrictions, a novel hybrid method is introduced, which integrates LIFS with solvent densitometry technique alongside quantum efficiency analysis. Crude oil samples from various oilfields in the Persian Gulf are analyzed, and LIF signals are recorded in terms of different concentrations. Key optical parameters, namely peak concentration (C_p) and quantum efficiency (Q_E) are correlated with the SARA fractions according to the analysis of variance (ANOVA). As a result, robust predictive models are proposed for the assessment of crude oil fractions. The accuracy of the proposed method is validated through comparison with the standard ASTM D-6560 and ASTM D-4124 methods. This approach enables rapid, portable, on-site identification of crude oil fractions with high efficiency and precision.

2. Materials and methods

2.1. Crude oil samples

The Persian Gulf holds approximately 68% of the world's oil reserves and facilitates 60% of global oil transportation. Consequently, it is regarded as one of the most significant sources of marine pollution [2]. In this study, eight crude oil samples are collected from different oilfields within the Persian Gulf, including Kharg, Hendijan, Dorood, Reshadat, Foroozan, Resalat, Salman, and Azar. Fig. 1(a) presents a map highlighting the locations of the selected Iranian oilfields.

2.2. Standard methods: ASTM D 6560 & ASTM D 4124

The principal procedure in the standard methods relies on adsorption chromatography. Initially, asphaltene components are precipitated following the ASTM D-6560 (IP 143) procedure. In this step, crude oil is fractionated into asphaltene and maltene (comprising saturates, aromatics, and resins) using n-heptane and toluene solvents. The remaining maltene is then separated into three hydrocarbon fractions by making use of column chromatography, as specified by ASTM D-4124.

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Saturate and aromatic fractions are eluted using n-heptane and toluene, respectively. Finally, the SARA fractions are quantified as weight percentages in accordance with the ASTM D-6560 and ASTM D-4124 standard methods.

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2.3. Optical method: LIFS

Here, the crude oil samples are prepared in various concentrations ranging from 10^{-2} to 10^{-4} g/cm³ using dichloromethane (*DCM*) solvent with a density of 1.32 g.cm⁻³. The solvent is colorless and polar, with the chemical formula *CH*₂*Cl*₂ having a molar mass of 84.93 g.mol⁻¹. The cubic cuvettes (4×1×1 cm³) are filled with different concentrations taken from the samples of interest.

Laser-induced fluorescence spectroscopy (LIFS) is performed using a continuous-wave InGaN diode laser with a power of 110 mW and a wavelength of 405 nm. The fiber probe is set perpendicular to the incident laser beam. The fluorescence signals are recorded using an *AvaSpec (Avantes)* spectrometer, which operates over a wide range of 200–1100 nm. This spectrometer is equipped with a Czerny-Turner optical configuration, a 2048-pixel CCD array, and an optical resolution of 0.4 nm. Fig. 1 (b) depicts the LIFS setup using a right-angle array with a 405 nm excitation wavelength.



Fig. 1. (a) Location map of the Iranian oilfields of interest including (1) Azar, (2) Kharg, (3) Hendijan, (4) Dorood, (5) Reshadat, (6) Foroozan, (7) Resalat, and (8) Salman. (b) Schematic of a right-angle LIFS setup.

According to the conventional Beer-Lambert law, the fluorescence signal exhibits a linear relation with fluorophore concentration [21–23]. Nevertheless, at higher concentrations, deviations from this linearity occur due to resonance energy transfer. The concentration of the peak (C_p) is determined using empirical data obtained from the corresponding modified Beer-Lambert (MBL) plot. In this procedure, the fluorescence intensity at 490 *nm* is extracted from the LIF spectra at various concentrations. Subsequently, a plot of LIF intensity versus concentration is generated for the crude oil samples. The C_p value is directly obtained from the MBL plot according to the measured data.

Fluorescence quantum efficiency (Q_E) refers to the effectiveness of fluorescence emission, representing the energy lost by a substance that absorbs light through photon emission. It is typically defined as the ratio of the number of photons emitted to the number of photons absorbed. To determine the Q_E , the fluorescence intensity is plotted versus absorbance and the slope of the corresponding calibration curve allows for the calculation of the fluorescence quantum efficiency (%) for an unknown sample, as shown below [24]:

(1)

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$$Q_E = Q_R \left(\frac{G}{G_R}\right) \left(\frac{n^2}{n_R^2}\right) \times 100,$$

where $Q(Q_R)$ and $G(G_R)$ ascertain the quantum efficiency (of the reference) and the ratio of fluorescence intensity versus absorbance (as the reference), respectively. Furthermore, *n* and *n_R* represent the mean refractive indices of the test sample and the reference, respectively. In this study, Rhodamine 6G (RD6G) is selected as the reference fluorophore, with a known quantum efficiency of 0.95 [24]. The refractive index of the samples is measured to be 1.33 using an Abbe refractometer, while the refractive index of RD6G is obtained to be 1.36.

2.4. Analysis of variance (ANOVA)

Analysis of variance (ANOVA) is a statistical method that decomposes observed variance data into its various components. It is used for data sets with three or more groups to examine the interactions between dependent and independent variables. ANOVA evaluates the effect of the variable of interest on the mean of the statistical population. A P-value less than 0.05 indicates that the variable has a statistically significant impact on the population [25]. Here, ANOVA is utilized to investigate the relation between crude oil fractions and the corresponding optical parameters, based on R-square (R²). The statistical analysis is carried out using XLSTAT software, and a set of equations is developed to predict the SARA fractions.

3. Results and discussion

3.1. Standard methods: ASTM D 6560 & ASTM D 4124

Table 1 tabulates the values of SARA fractions for crude oil samples expressed as weight percentages. According to the prevalent trend in crude oil fractions, a decrease in the heavy compounds (asphaltenes and resins) results in an increase in the saturate fraction. It is important to note that the sum of the four fractions of crude oil equals unity where the oil fields are sorted from heavy to light crude oil.

No.	Oilfield	Saturate	Aromatic	Resin	Asphaltene
1	Azar	31.0	39.2	16.8	12.9
2	Kharg	40.9	33.0	13.9	12.2
3	Hendijan	48.9	25.7	16.5	8.9
4	Dorood	41.6	38.6	12.2	7.6
5	Reshadat	47.0	33.6	15.3	4.1
6	Foroozan	56.0	31.3	9.8	2.9
7	Resalat	58.6	30.1	9.1	2.2
8	Salman	63.4	26.9	8.3	1.4

Table 1. SARA fractionation results for different samples [wt%] [26].

3.2. Optical methods: LIFS

Fig. 2 (a and b) depicts the absorption and normalized LIF signal at 490 *nm* versus the concentration for samples of interest, respectively. The concentration of peak (C_p) is obtained by employing the experimental result from the MBL graph. Fig. 2 (c) illustrates the fluorescence intensity as a function of the absorbance. As previously mentioned, the quantum efficiency of the sample of interest can be determined by calculating the slope of this plot and applying Eq. (1). Fig. 3 represents the values of the measured optical parameters (C_p and Q_E) for eight crude oil samples in the bar chart.



Fig. 2. (a) absorption and (b) LIF intensity in terms of different concentrations for different samples of Persian Gulf at 490 *nm*. (c) LIF intensity versus absorption for different crude oil samples.



Fig. 3. Optical parameters including C_p and Q_E for the different crude oil samples.

3.3. Analysis of variance (ANOVA)

The SARA fraction abundances of all eight samples are given using the standard method. In contrast, the proposed method yields the C_p and Q_E parameters for each sample, as shown in Fig. 3. Table 2 tabulates the predicted relations and the correlation of optical parameters to reveal the dependence of the abundance of saturate, resin, and asphaltene fractions with the optical parameters. Subsequently, ANOVA is used to assess the statistical significance of the relations. The results confirm the correlation between the optical parameters and crude oil fractions, with P-values (Pr>F) less than 0.05. Overall, these relations predict the SARA fraction values which are linear in terms of the optical parameters.

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 Table 2. The predicted relations and the correlation of optical parameters

for saturate, resin, and asphaltene fractions.					
SARA fractions	Pr>F	Predicted relations [%]			
Saturate	0.01	$14605.1C_p + 123.3Q_E + 29.0$			
Resin	0.01	-2844.0Cp-69.3QE+19.5			
Asphaltene	0.007	-2103.7Cp-126.3QE+16.5			

Fig. 4. (a, b, and c) illustrate the optical results compared with the experimental values (standard methods: ASTM D 6560 & ASTM D 4124). The R-square values are found to be 81.5%, 80.5%, and 86.6% for the saturate, resin, and asphaltene fractions, respectively. These highlight the reliability of the proposed optical relations. It is important to note that the sum of the four fractions equals unity. Therefore, the aromatic fraction is determined from the other three fractions.



Fig. 4. Abundance percentage of optical model versus standard method for the fractions of (a) saturate, (b) asphaltene, and (c) resin taken from the oil fields of interest.

4. Conclusion

The solvent densitometry is used here to differentiate the crude oil samples taken from the Persian Gulf, using laser-induced fluorescence spectroscopy. At first, the optical parameters C_p and Q_E of the samples of interest have been. The correlation between these optical parameters and oil fractions is thoroughly examined using analysis of variance. The relationships are established to predict the values of crude oil fractions based on the optical parameters. The R-square values are found to be 81.5%, 80.5%, and 86.6% for the saturate, resin, and asphaltene fractions, respectively in order to verify reliability. As a consequence, the accuracy assessment of the given optical relationships is obtained and compared to the standard method. Eventually, this method benefits simplicity, cost-effectiveness as well as portability to reveal its potential as an alternative to the current standard methods for SARA assessment.

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Author contributions

F.A.N. conceived the idea, conceptualized the research, performed the experiments, interpreted the spectroscopy results, and wrote the paper. **P.P.** supervised the project, directed the research, and revised the manuscript. **A.R.R.** helped provide test samples and standard methods.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared

to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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