



## Research paper

# Evaluation of oil fingerprints similarity by a novel technique based on FTIR spectroscopy of asphaltenes: Modified moving window correlation coefficient technique



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## ABSTRACT

Investigation of oil fingerprints heterogeneities in different wells across the reservoir is a critical effort in various disciplines of geochemical studies. Exploring new, trustworthy, and straightforward techniques is an ongoing and interesting subject in the oil industry. In this paper, a novel procedure for oil fingerprints comparison by employing the structural characteristics of asphaltenes is suggested. For the first time, the modified version of the moving window correlation coefficient is proposed to resolve the drawbacks of the standard procedure and then implementing for comparison of oil fingerprints. This procedure is based on peak ratios calculated from the second derivative FTIR spectra of asphaltene samples. The results of this technique are summarized in a matrix with green, red and yellow cells based on the calculated values of the minimum correlation coefficient in all moving windows (MMWR) and the average of correlation coefficients in all moving windows (AMWR) regarding defined thresholds to better visualization of fingerprint similarity or dissimilarity between studied samples. The oil fingerprint similarities in the two case studies from the Dezful Embayment of southwest Iran were investigated to demonstrate the usefulness of this technique. Ten samples from different wells in the Qale Nar oil field and eight samples from the Shadegan oil field were studied. Results showed that crude oils in the Asmari reservoir from the Qale Nar field have a similar fingerprint and are homogenous. But crude oils in the Asmari reservoir from the Shadegan field involves several zones based on oil fingerprints similarity. Whole oil gas chromatography (WOGC) was performed for checking purposes. The proposed method based on FTIR spectra of asphaltene samples and their comparison with the modified moving window correlation coefficient can be regarded as a novel, reliable, and straightforward technique for oil fingerprint similarity assessment.

## 1. Introduction

Crude oil naturally comprises a complex mixture of many different compounds with specific characteristics. Thus, they are characterized by chemical group type analysis instead of individual molecular type characterization, which is difficult if not impossible (Ashoori, 2005; Tharanivasan, 2012). One of the most known group type analysis is the SARA separation which classifies crude oil into four different fractions (e.g., saturates, aromatics, resins, and asphaltenes) depend on solubility and polarity characteristics (Jiang et al., 2000; Ashoori, 2005; Hemmati-Sarapardeh et al., 2018). Asphaltenes involve an essential fraction of crude oils which a considerable number of studies have been dedicated to these compounds in the literature. Asphaltenes are a significant source of geochemical information in the crude oils and can be used to obtain oil fingerprints (Behar and Pelet, 1984, 1985; Christy

et al., 1991; Asemani and Rabbani, 2016; Riley et al., 2016).

Investigation of oil fingerprints in different wells across the reservoir is an efficient way to obtain valuable information about various phenomena such as reservoir filling, reservoir compartmentalization, petroleum basin development, petroleum mixing, secondary alterations of crude oils and so on (Larter and Aplin, 1995; Cubitt et al., 2004; Stainforth, 2004; Smalley and Muggeridge, 2010). In other words, assessing oil fingerprints across the reservoir provides a scientific interest and motivation to survey further the reason(s) of these homogeneities or heterogeneities and explore their origin(s). However some heterogeneities occur during filling of the reservoir such as different source rocks or source rock facies, gradual maturity of source rock, etc., other heterogeneities arise from in-reservoir processes such as water washing, evaporative fractionation, biodegradation, etc. (Larter and Aplin, 1995; Westrich et al., 1999; Rein and Schulz, 2007). These heterogeneities

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gradually disappear by mass transfer mechanisms, including gravitational and thermal segregation, molecular diffusion, and thermal convection (England et al., 1987). These mechanisms are naturally acting in the reservoir to equilibrate chemical composition and removing oil fingerprints heterogeneities. Also, it is vital to consider that the process of compositional equilibrium is long-term phenomena that take hundreds of thousands or millions of years to achieve a steady-state condition in fluid composition (England et al., 1987; Smalley and Muggeridge, 2010). Asphaltenes, as a heavy-end component of crude oil, are beneficial compounds in obtaining oil fingerprints.

Asphaltenes as a solubility class, which are insoluble in light normal alkanes and soluble in aromatic solvents, have a similar structural composition to the precursor of reservoir oil (Rubinstein et al., 1979; Behar and Pelet, 1984, 1985; Pelet et al., 1986; Lehne et al., 2009; Gray et al., 2011; Makeen et al., 2015; Hemmati-Sarapardeh et al., 2018). These compounds are not affected or little affected by secondary processes such as biodegradation, water washing, and so on (Rubinstein et al., 1979; Pan et al., 2002; Asemani and Rabbani, 2016; Chen et al., 2020). It has been proven that spectroscopy techniques, especially Fourier-transform infrared spectroscopy (FTIR), are entirely applicable to acquire a complete picture from the structural characteristics of asphaltenes (Yen et al., 1984; Christy et al., 1989; Sharma et al., 2007; Asemani and Rabbani, 2016, 2020; Carvalho et al., 2017). An efficient method should also be employed for comparison of structural characteristics of asphaltenes in oil fingerprint assessment studies. Moving window correlation coefficient has been suggested in the literature to distinguish highly similar oil samples (Chu et al., 2011; Li et al., 2013). But this technique suffers from several inherent drawbacks. In this paper, for the first time, a modified version of this technique is proposed to resolve these drawbacks. Then this method is utilized for comparison of oil fingerprints, which are obtained from structural characteristics of asphaltenes, across the studied fields.

The main goal of this paper is to propose a novel procedure for obtaining oil fingerprints and comparing them by the structural characteristics of asphaltenes and the modified moving window correlation coefficient technique, respectively. To achieve this goal, firstly, FTIR spectroscopy is used to investigate the structural characteristics of asphaltenes. Then, the modified moving window correlation coefficient technique is employed to disclose indistinct differences between samples. Finally, results are summarized in the similarity matrix to revealing the homogeneity or heterogeneity of oil fingerprints for the studied samples.

## 2. Geological setting

### 2.1. Qale Nar oil field

The Qale Nar field located in the northeastern part of Dezful Embayment, SW Iran (Fig. 1a). This region, as a part of the Zagros fold-thrust belt (ZFTB), is known as a crucial petroliferous place in the world, which comprises approximately 8% of world reserves (Bordenave and Burwood, 1995). The Asmari Formation with the dominant lithology of carbonate is the primary productive reservoir in this field. The Lower and Upper Asmari reservoirs are distinguished in the Shadegan field, but not in the Qale Nar field. The Gachsaran Formation has adequately sealed the Asmari reservoir in most of the Dezful Embayment fields. It is believed that Pabdeh and Kazhdumi Formations are the primary source rocks in the charging of reservoirs in this region (Fig. 2). The Pabdeh Formation with lower depth is an immature source rock in most areas of Dezful Embayment. Bordenave and Burwood (1990) showed that the Pabdeh Formation is a thick source rock with suitable maturity conditions to generate oil in the north-east of the Dezful region. The Qale Nar field comprises two relatively symmetrical anticlines (Fig. 1b).

### 2.2. Shadegan oil field

The Shadegan field situated in the central part of Dezful Embayment. This field has been formed as a single symmetrical anticline in which Asmari Formation and Bangestan group are producing reservoirs in this field (Fig. 1c). The Asmari Formation has two producing reservoir units, namely Lower and Upper Asmari, in the Shadegan field. This field likely sourced from the Kazhdumi Formation with little contribution of other source rocks. The former source rock has charged most of the oil fields in the Dezful Embayment, especially those located in the central and southern parts. This source rock made up of dark bituminous shale and limestone deposited in an intrashelf sealed depression (Fig. 2; James and Wynd, 1965; Bordenave and Burwood, 1995).

## 3. Materials and methods

### 3.1. Samples

Ten different samples from the Asmari reservoir in the Qale Nar field and eight samples from the Asmari reservoir (e.g., Upper and Lower Asmari reservoir units) in the Shadegan field were collected from the wellhead of different producing wells at atmospheric conditions. None of the wells has subjected to work over or any well treatments for more than two months before sampling, and wells have been producing for more than twenty years. Asphaltene deposition was not detected during sampling. The Qale Nar and Shadegan samples are listed in Table 1 and Table 4, respectively. The location of the studied wells is shown in Fig. 1b, and c. All samples were subjected to API gravity measurement, SARA analysis, whole oil GC, and FTIR spectroscopy was performed on asphaltene samples.

### 3.2. API gravity

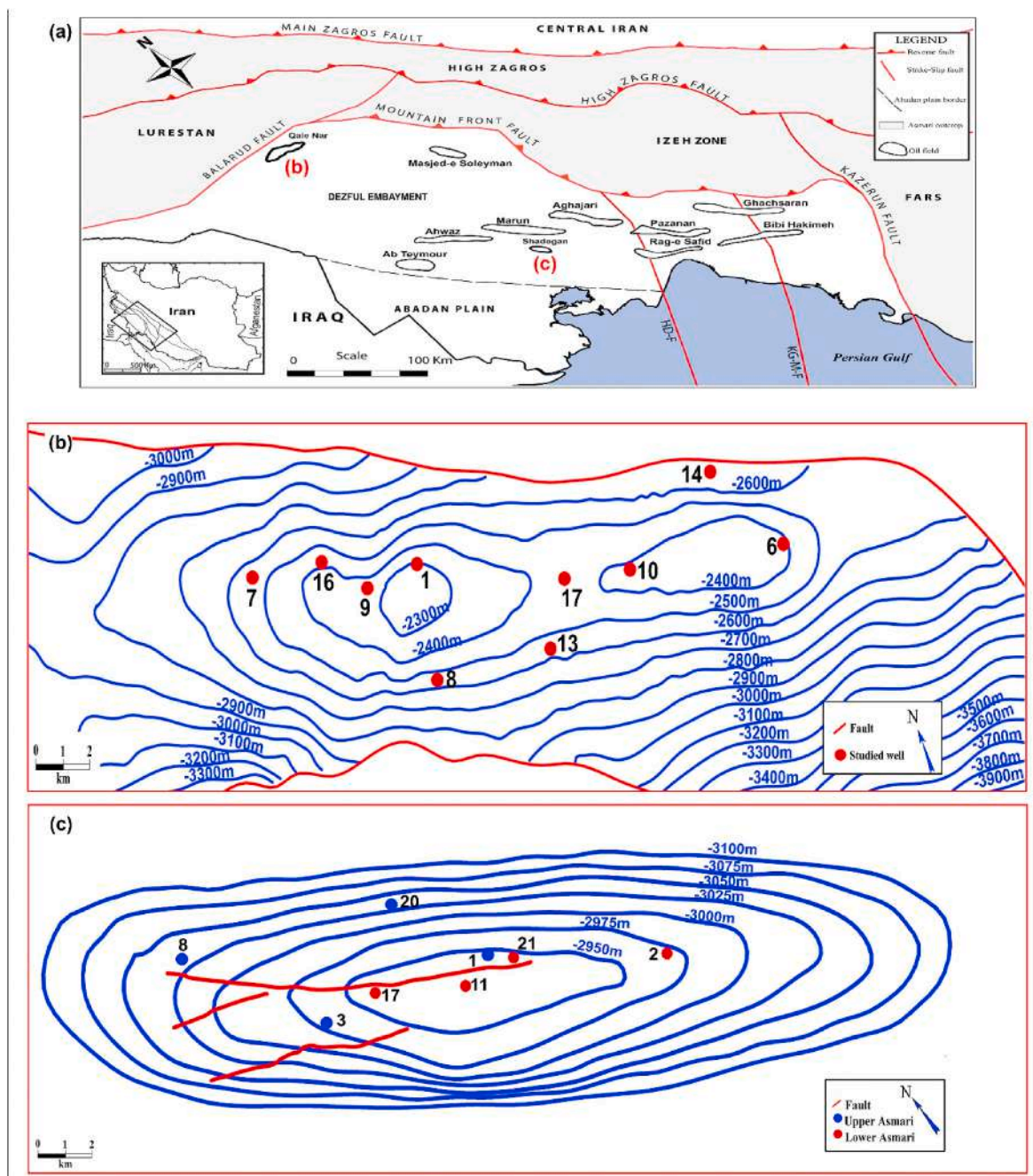
The density of oil samples was measured by Anton Paar DMA 4100 at the atmospheric conditions, and subsequently, their API gravity was calculated.

### 3.3. SARA analysis

Asphaltenes were precipitated from oil samples according to the D6560-17 standard (D6560, 2017). Initially, n-hexane was mixed with crude oils (30 ml: 1 g), and the mixture was refluxed for 1 h. The mixture stored in a dark place overnight. A filter paper recovered the precipitated materials, and the filtrate cake was washed by n-hexane under reflux to remove co-precipitated impurities from asphaltenes. Afterward, the pure asphaltenes were extracted by toluene. The toluene was removed, and samples were heated 100 °C for 30 min to obtain asphaltenes. Three remaining fractions of crude oils, namely saturates, aromatics, and resins, were extracted by fractionation of maltene (soluble part of crude oil in n-hexane). The chromatography column was packed by activated silica gel and used for fractionation. Firstly, saturates were eluted from the column by n-hexane, and subsequently, benzene was used to elution of aromatics, and finally, toluene/methanol (90/10) was utilized to recover resins.

### 3.4. Whole oil gas chromatography (WOGC)

1 µl of crude oil directly injected to HP 5890 Series II gas chromatograph for whole oil GC analysis. The GC equipped with a DB-1 capillary column (60 m × 0.1 mm and 0.25 mm film) and an FID detector, which operated at 350 °C. The carrier gas was helium with a constant flow of 1.6 ml/min. The column temperature programmed to hold for 5.0 min at 30 °C and then was risen to 320 °C at a rate of 3 °C/min and finally held for 20 min.



**Fig. 1.** a) Location map of different oil fields in the Dezful Embayment, SW Iran (modified after Farahzadi et al., 2019); b) contour map of the Qale Nar oil field on the top of the Asmari Formation; c) contour map of the Shadegan oil field on the top of the Asmari Formation. The solid circles in contour maps show the location of the study wells.

### 3.5. FTIR spectroscopy

Before recording FTIR spectra from asphaltenes, samples were mixed with KBr powder (1:100 wt: wt) and pressed to form into 13 mm pellets under pressure. FTIR spectra of asphaltene samples were obtained from pellets by Thermo Nicolet-Nexus 670 in the range of 4000 to 400  $\text{cm}^{-1}$  with 40 scans at 4  $\text{cm}^{-1}$  resolution. The repeatability of analysis and the identification thresholds for the moving window correlation coefficient technique was determined by six replication of one sample from each studied field. The QR-9 sample (from Qale Nar field) and the SG-1 sample (from Shadegan field) were subjected to replicate analysis of asphaltene extraction and FTIR spectroscopy.

#### 3.5.1. FTIR data pre-processing

The second derivative spectra were calculated from FTIR spectra to remove variation of baseline and reveal masked peaks or shoulders. It is noteworthy that peaks in the original spectra occur as valleys in the second derivative spectra. The differences of asphaltene amount, for different samples, during sample preparation were compensated via normalization of spectra. In this regard, each data point of the second derivative spectra was divided into root square of all data points (Gemperline, 2006). The second derivative spectra were obtained with GRAMS AI software, and normalization of spectra was carried out with OMNIC software. The generation of peak ratios and following calculation of the moving window correlation coefficient was performed via codes written in the MATLAB software.

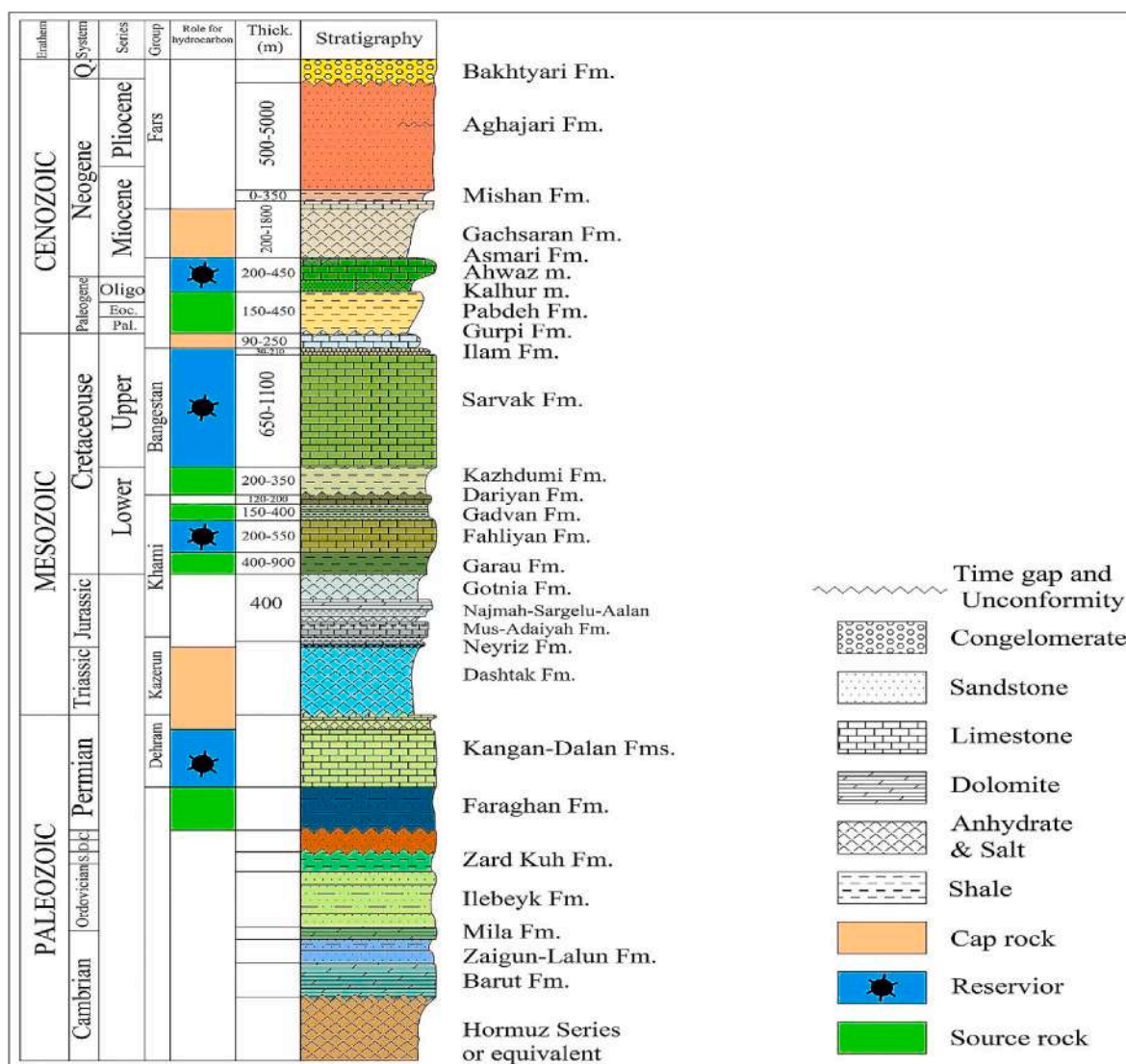


Fig. 2. General stratigraphic column of different formations and their petroleum system element in the Dezful Embayment (modified after Derikvand et al., 2018).

Table 1

API gravity and SARA analysis results for studied samples from the Qale Nar field.

| NO | Samples | API (°) | Saturate (wt%) | Aromatic (wt%) | Resin (wt%) | Asphaltene (wt %) |
|----|---------|---------|----------------|----------------|-------------|-------------------|
| 1  | QR-1    | 29.85   | 40.20          | 39.61          | 14.78       | 5.41              |
| 2  | QR-6    | 29.44   | 44.07          | 35.85          | 14.10       | 5.98              |
| 3  | QR-7    | 28.15   | 39.52          | 39.52          | 15.11       | 5.85              |
| 4  | QR-8    | 28.59   | 46.14          | 35.82          | 12.75       | 5.29              |
| 5  | QR-9    | 29.42   | 43.92          | 35.50          | 15.64       | 4.93              |
| 6  | QR-10   | 29.13   | 42.71          | 33.91          | 18.63       | 4.76              |
| 7  | QR-13   | 29.24   | 45.16          | 31.01          | 18.50       | 5.33              |
| 8  | QR-14   | 29.64   | 40.91          | 39.05          | 16.12       | 3.92              |
| 9  | QR-16   | 29.17   | 41.67          | 37.04          | 16.21       | 5.08              |
| 10 | QR-17   | 28.64   | 45.86          | 31.34          | 17.30       | 5.50              |

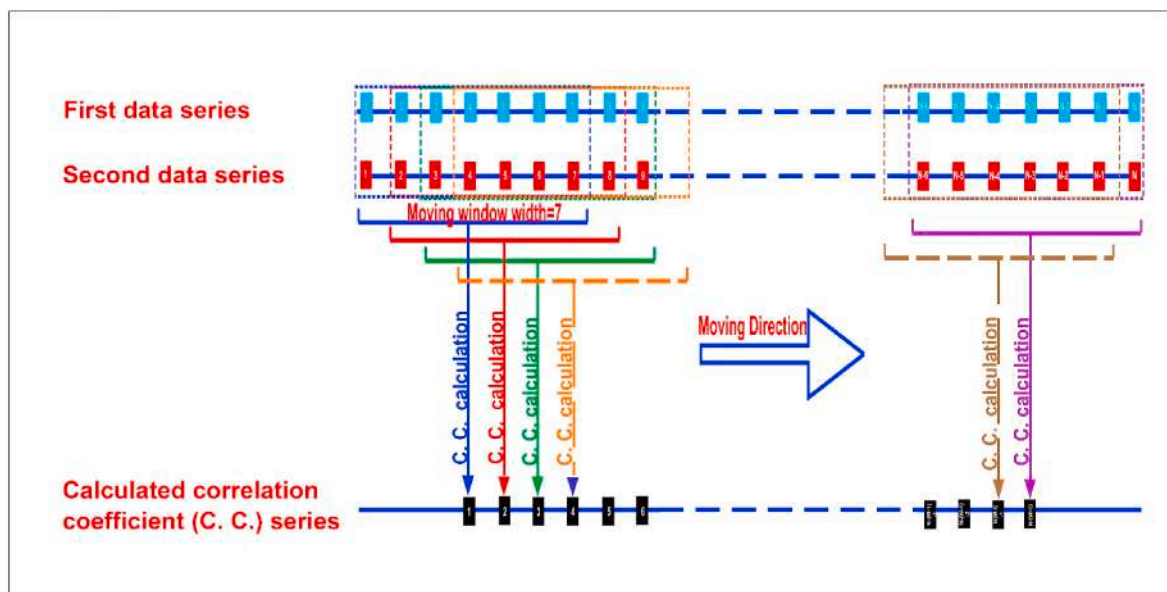
### 3.5.2. Moving window correlation coefficient technique

The oil fingerprint of different samples should be compared to reveal compositional homogeneities or heterogeneities. In this paper, oil fingerprints are obtained from asphaltenes due to their advantages regarding other light components of crude oil. Since the FTIR spectra of asphaltenes are representative of the molecular composition of these components, they can be directly used to obtain oil fingerprints. In this

regard, it is necessary to employ a precise technique that discloses even subtle changes between samples. The moving window correlation coefficient has been proven as an accurate technique in the investigation of highly similar samples (Chu et al., 2011; Li et al., 2013).

In this technique, the Pearson correlation coefficient is calculated in each successive spectral window instead of the whole spectra. Each window has a width of  $W$ , and the number of windows is  $N-(W-1)$ . Where  $N$  is the number of all spectral channels or data points. The calculated correlation coefficient in each window is attributed to the center of the window, so the window width should be an odd number. After each calculation, the window moves one point forward, and a new correlation coefficient is calculated for a new window. The number of calculated correlation coefficients is equal to the number of windows, and each window has  $(W-1)/2$  data points overlap with previous and next windows. The schematic of this technique is illustrated in Fig. 3. The intensity of the FTIR spectrum in different wavenumbers (spectral channels) is routinely used as an input data series for comparison of two samples by the moving window correlation coefficient technique.

The correlation coefficient provides a measure for the strength and direction of the relationship between two samples or spectra. Although the two identical spectra have a correlation coefficient equal to 1, the value of  $-1$  shows two spectra are entirely in a different direction, the peak in one spectrum is the valley with the same intensity and shape in



**Fig. 3.** Schematic of moving window correlation coefficient technique with seven points window width. The spectral channels of the FTIR spectrum, in the routine method, and the calculated peak ratios, in the modified method, for two studied samples are regarded as an input data series. The correlation coefficient is calculated for each window, and finally, a series of correlation coefficients are yielded.

another spectrum. As the differences between the two spectra increase, the value of the calculated correlation coefficient gets closer to zero, and in the complete different spectra approaches to zero. In other words, the zero value means two spectra have not any linear correlation.

However, one correlation coefficient is estimated for all data points in the traditional correlation coefficient technique, but N-(W-1) correlation coefficients are calculated in the moving window technique. Hence, the subtle differences which may be obscure in traditional methods will be revealed. In this technique, the calculated correlation coefficients in all windows (the correlation coefficients series) are compared with the defined threshold, and samples with one correlation coefficient lower than the threshold are regarded as different (Li et al., 2013).

### 3.5.3. Modified moving window correlation coefficient technique

Chu et al. (2011) employed a moving window correlation coefficient technique to compare an unknown crude oil with the database based on near-infrared spectra of crude oils. Li et al. (2013) applied this technique on the FTIR spectra of crude oils to distinguish highly similar samples. These authors used the spectral channel values (intensity of the FTIR or near-infrared spectrum in different wavenumbers) for performing this technique. Despite many inherent benefits of this procedure, but suffer from some drawbacks. The first drawback is the effect of baseline variation. This problem can be solved by utilizing second derivative spectra instead of the original spectra to remove the effect of baseline variation. The second drawback is that the technique is profoundly affected by little noises that may be occurred in the spectra, and these noises reduce the calculated correlation coefficient in the specific window(s) contain these noises. So, this situation may be mistaken with differences between samples since noises are random, and the amount of noises in two spectra may be different. Routinely, the authors limit the spectral range or wavenumbers range, which is used for the technique to solve this problem. For example, Li et al. (2013) used only 970–690  $\text{cm}^{-1}$  region of the FTIR spectrum in the moving window correlation coefficient technique. This solution causes high spectral data loss in the other regions of spectra (e.g., 4000–970  $\text{cm}^{-1}$ ). The third problem is associated with shifting in the bands for different samples. A little shifting in the maximum of bands can cause highly lowering the calculated correlation coefficient and interpreted as different samples.

For example, the C=C stretching in aromatics which routinely appears at 1600  $\text{cm}^{-1}$ , might be occurred in 1596  $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$  for two identical samples due to impact of Lorentz-Mie scattering and the Christiansen effect (Duyckaerts, 1959). In the common technique of moving window correlation coefficient because the maximum of two samples are not at the same wavenumbers, the calculated correlation coefficients for the specific windows include the spectral value of 1600  $\text{cm}^{-1}$  are largely lower than the expected for identical samples.

In this paper, a modified method was proposed to overcome the problems mentioned above and, at the same time, benefit from the advantages of the moving window correlation coefficient technique. In this manner, firstly, the spectra are converted to second derivative spectra to remove the effect of baseline variation and disclose the bands which had been masked in original spectra due to overlapping. Secondly, the maximum intensity of twelve valleys (a peak appear as a valley in the second derivative spectrum) in the whole range of the spectrum is selected. The most characteristics bands should be selected to better comparison of two samples. These bands are routinely 3052, 3014, 2958, 2923, 2850, 1727, 1600, 1460, 1375, 862, 808 and 746  $\text{cm}^{-1}$ . Thirdly, the peak ratios based on dividing the intensity of each band to intensity of other bands are generated ( $12 \times 11 = 132$  peak ratios). Finally, the moving window correlation coefficient technique is applied to this generated data series (132 peak ratios), and the results of this technique for assessment of oil fingerprints similarities are shown in the similarity matrix.

Two parameters are the most critical in performing a modified moving window correlation coefficient technique. These parameters include the size or width of the moving window and the identification thresholds for detecting identical or different samples. Replicates of one sample are used for determining these parameters. Initially, an arbitrary window width (for example, 9 points) is chosen, and correlation coefficients are calculated to find two replicates with the largest differences. Two replicates with the highest differences are used to calculate different series of correlation coefficients with a window width of 5–17 points with two intervals because the width necessarily should be odd. A series with the highest correlation coefficient shows the optimum window width. The correlation coefficient series with the window width lower and higher than the optimum size have lower correlation coefficients.

The repeatability in the FTIR spectra of samples is used to define the

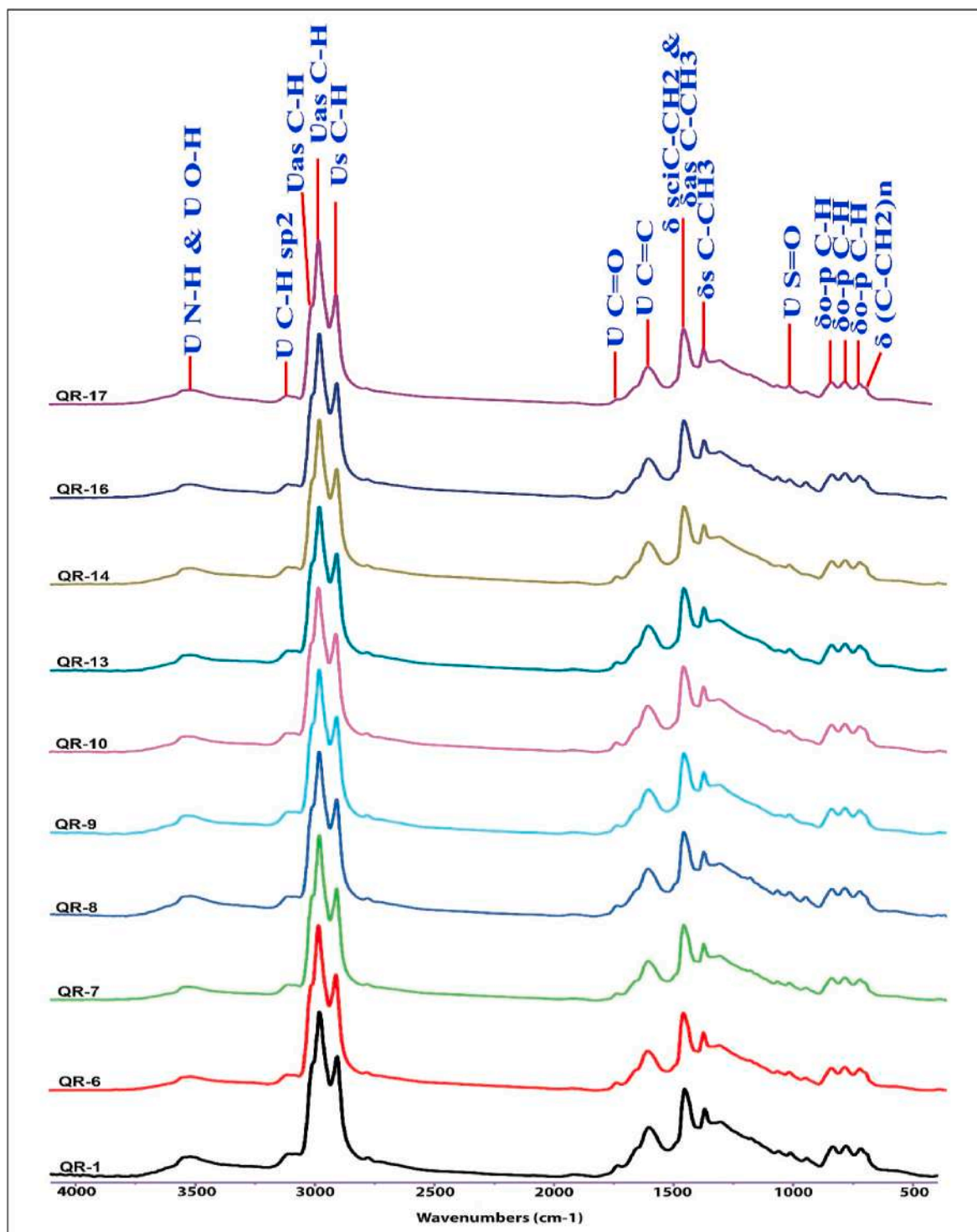


Fig. 4. a) FTIR spectra of asphaltenes for studied samples in the Qale Nar field. U: stretching,  $\delta$ : bending, o-p: out-of-plane, s: symmetric, as: asymmetric, sci: scissors.

threshold for distinguishing similar samples. Generally, more than five replications are suitable for obtaining thresholds. A modified moving window correlation coefficient technique with the optimum window size is performed for pairwise comparison of different replicates. The lowest value of the minimum correlation coefficient in all moving windows (MMWR) and the lowest value for an average of correlation coefficients in all moving windows (AMWR) for all replications are selected as the thresholds to distinguish identical samples.

Finally, the pairwise comparisons of studied samples are

summarized in a matrix named as a similarity matrix to better visualization of pairwise comparison of samples. Three colors of green, yellow, and red, similar to traffic light, are used to color each cell based on the MMWR and AMWR values for two specific samples relative to the defined thresholds. However, the green color shows both the MMWR and AMWR are higher than the thresholds, and two studied samples are similar. The red color shows the opposite of green color, in which both values are lower than the thresholds, and samples are different. If one of the values is higher and the other is lower than the

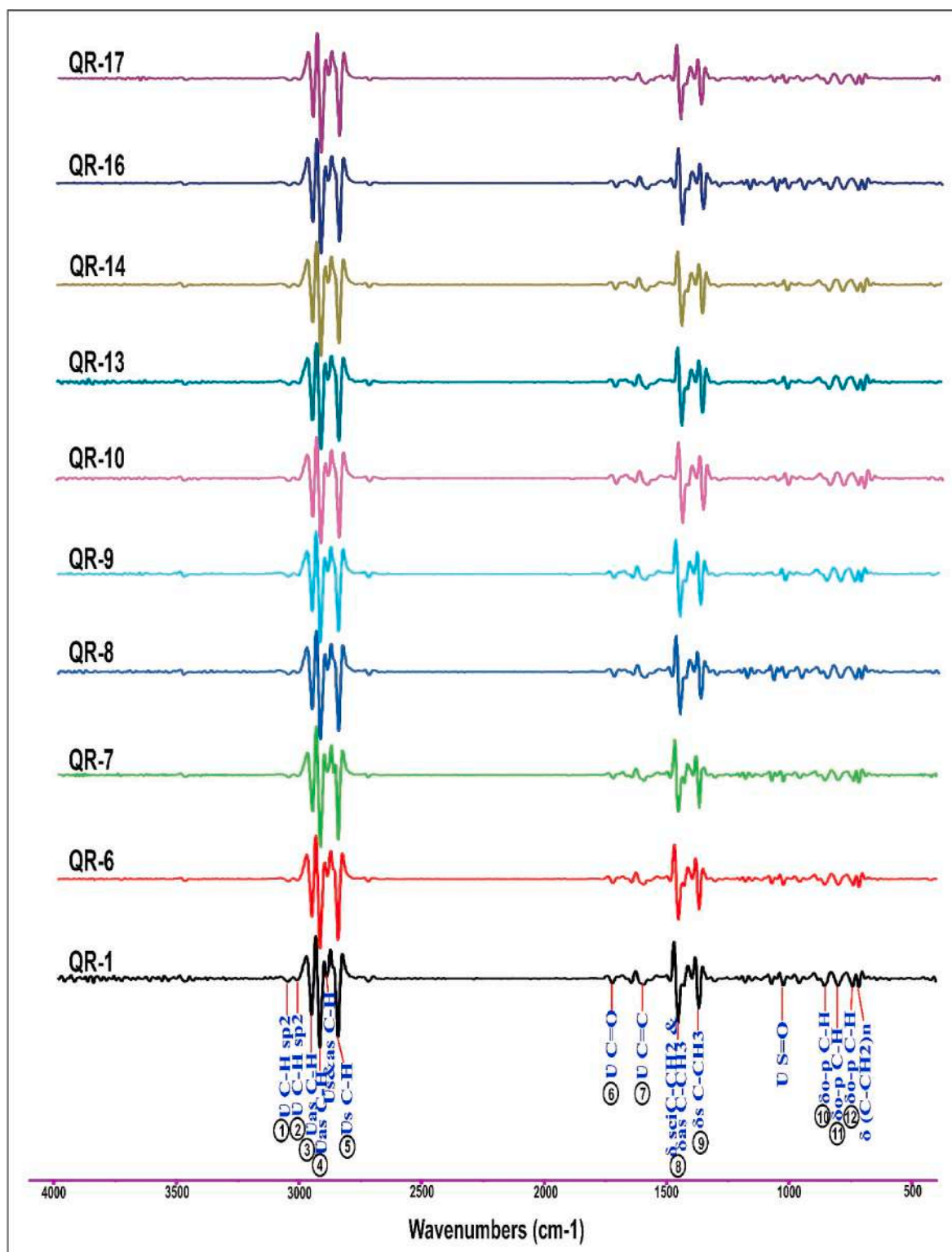


Fig. 5. Normalized second derivative FTIR spectra of asphaltenes for studied samples in the Qale Nar field. Twelve selected bands for the modified moving window correlation coefficient technique are marked in the spectra. U: stretching,  $\delta$ : bending, o-p: out-of-plane, s: symmetric, as: asymmetric, sci: scissors.

thresholds, the cell is colored by yellow, which means that limited similarity exists between two samples and should also be checked by other techniques. The optimum window width and the thresholds should be determined for each sample batch separately.

## 4. Results and discussion

### 4.1. Case study I: Qale Nar oil field

#### 4.1.1. Bulk properties of oil samples

SARA analysis and API results are listed in Table 1. The API gravity

**Table 2**

Results of pairwise comparisons of six replicates for the QR-9 sample to determine identification thresholds in the Qale Nar field.

| Sample | Duplicates             | Min correlation coefficient in all moving windows (MMWR) | Max correlation coefficient in all moving windows | Average of correlation coefficients in all moving windows (AMWR) |
|--------|------------------------|----------------------------------------------------------|---------------------------------------------------|------------------------------------------------------------------|
| QR-9   | 1&2                    | 0.9598                                                   | 0.9999                                            | 0.9855                                                           |
|        | 1&3                    | 0.9813                                                   | 0.9998                                            | 0.9948                                                           |
|        | 1&4                    | 0.9697                                                   | 0.9999                                            | 0.9894                                                           |
|        | 1&5                    | 0.9866                                                   | 0.9999                                            | 0.9959                                                           |
|        | 1&6                    | 0.9635                                                   | 0.9998                                            | 0.9866                                                           |
|        | 2&3                    | 0.9711                                                   | 0.9996                                            | 0.9853                                                           |
|        | 2&4                    | 0.9805                                                   | 1.0000                                            | 0.9969                                                           |
|        | 2&5                    | 0.9642                                                   | 1.0000                                            | 0.9934                                                           |
|        | 2&6                    | 0.9769                                                   | 1.0000                                            | 0.9960                                                           |
|        | 3&4                    | 0.9491                                                   | 0.9994                                            | 0.9842                                                           |
|        | 3&5                    | 0.9681                                                   | 0.9999                                            | 0.9886                                                           |
|        | 3&6                    | 0.9375                                                   | 0.9994                                            | 0.9799                                                           |
|        | 4&5                    | 0.9893                                                   | 1.0000                                            | 0.9980                                                           |
|        | 4&6                    | 0.9988                                                   | 1.0000                                            | 0.9997                                                           |
|        | 5&6                    | 0.9884                                                   | 1.0000                                            | 0.9969                                                           |
| Total  | Min of each column     | 0.9375 <sup>a</sup>                                      | 0.9994                                            | 0.9799 <sup>b</sup>                                              |
|        | Max of each column     | 0.9988                                                   | 1.0000                                            | 0.9997                                                           |
|        | Average of each column | 0.9723                                                   | 0.9998                                            | 0.9914                                                           |

<sup>a</sup> Threshold of the minimum correlation coefficient in all moving windows (MMWR).

<sup>b</sup> Threshold of the average of correlation coefficients in all moving windows (AMWR).

of samples varies from 28.15 (QR-7) to 29.85 (QR-1). Among the different fractions of SARA analysis, the saturate fraction has the highest value, and other fractions show a descending order of aromatics, resins, and asphaltenes, respectively. In the asphaltene content, the QR-14 (3.92%) has the lowest amount, and the QR-6 (5.98%) has the highest amount. The changes in asphaltene content have a narrow range, and the difference between the highest and lowest content equal to 2.06%. The range of differences for other fractions is higher than asphaltenes, for example, 8.6%, 6.62%, 5.88% for aromatics, saturates, and resins, respectively. The changes in the content of different fractions for various wells are due to differences in depth of studied zone in each well and the effect of gravity segregation.

#### 4.1.2. Assignment of FTIR spectra

The second derivative spectra were used in this study to remove the effect of baseline variations. Bands and shoulders in the raw spectra appeared as valleys in the second derivative spectra. Although most of the bands are overlapped in the raw spectra, and few peaks appear, in the second derivative spectra, the overlapped bands and shoulders are resolved and help to the thorough study of spectra. For example, the C–H stretching in the polynuclear aromatic compounds appears as a single band at about 3050 cm<sup>-1</sup> in the raw FTIR spectra. This band resolves to the two separate valleys at about 3052 and 3014 cm<sup>-1</sup> in the second derivative spectra (Asemani and Rabbani, 2020). The raw and second derivative FTIR spectra of asphaltenes for studied samples in the Qale Nar field are shown in Fig. 4 and Fig. 5, respectively. The visual appearance of different samples is relatively similar, and small differences related to the relative height of different peaks can be seen.

The 3052 and 3014 cm<sup>-1</sup> bands, in the second derivative spectra, are due to C–H stretching in the polynuclear aromatic compounds. Due to overlapping, only one peak at 3050 cm<sup>-1</sup> appears in the raw spectra,

|       | QR-1   | QR-6   | QR-7   | QR-8   | QR-9   | QR-10  | QR-13  | QR-14  | QR-16  | QR-17  |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| QR-1  | 1*     | 0.9676 | 0.9685 | 0.9764 | 0.9821 | 0.9741 | 0.9729 | 0.9836 | 0.9859 | 0.9740 |
|       | 1**    | 0.9934 | 0.9926 | 0.9932 | 0.9968 | 0.9931 | 0.9950 | 0.9962 | 0.9956 | 0.9941 |
| QR-6  | 0.9676 | 1      | 0.9724 | 0.9566 | 0.9847 | 0.9794 | 0.9921 | 0.9882 | 0.9669 | 0.9706 |
|       | 0.9934 | 1      | 0.9928 | 0.9888 | 0.9964 | 0.9945 | 0.9991 | 0.9974 | 0.9940 | 0.9916 |
| QR-7  | 0.9685 | 0.9724 | 1      | 0.95   | 0.9742 | 0.9711 | 0.9736 | 0.9830 | 0.9633 | 0.9895 |
|       | 0.9926 | 0.9928 | 1      | 0.9929 | 0.9924 | 0.9928 | 0.9925 | 0.9947 | 0.9949 | 0.9975 |
| QR-8  | 0.9764 | 0.9566 | 0.95   | 1      | 0.9662 | 0.9830 | 0.9710 | 0.9674 | 0.9946 | 0.9737 |
|       | 0.9932 | 0.9888 | 0.9929 | 1      | 0.9891 | 0.9958 | 0.9909 | 0.9927 | 0.9986 | 0.9954 |
| QR-9  | 0.9821 | 0.9847 | 0.9742 | 0.9662 | 1      | 0.9748 | 0.9913 | 0.9861 | 0.9837 | 0.9759 |
|       | 0.9968 | 0.9964 | 0.9924 | 0.9891 | 1      | 0.9930 | 0.9981 | 0.9967 | 0.9946 | 0.9930 |
| QR-10 | 0.9741 | 0.9794 | 0.9711 | 0.9830 | 0.9748 | 1      | 0.9899 | 0.9937 | 0.9878 | 0.9871 |
|       | 0.9931 | 0.9945 | 0.9928 | 0.9958 | 0.9930 | 1      | 0.9966 | 0.9978 | 0.9964 | 0.9969 |
| QR-13 | 0.9729 | 0.9921 | 0.9736 | 0.9710 | 0.9913 | 0.9899 | 1      | 0.9919 | 0.9856 | 0.9763 |
|       | 0.9950 | 0.9991 | 0.9925 | 0.9909 | 0.9981 | 0.9966 | 1      | 0.9985 | 0.9956 | 0.9935 |
| QR-14 | 0.9836 | 0.9882 | 0.9830 | 0.9674 | 0.9861 | 0.9937 | 0.9919 | 1      | 0.9745 | 0.9880 |
|       | 0.9962 | 0.9974 | 0.9947 | 0.9927 | 0.9967 | 0.9978 | 0.9985 | 1      | 0.9957 | 0.9964 |
| QR-16 | 0.9859 | 0.9669 | 0.9633 | 0.9946 | 0.9837 | 0.9878 | 0.9856 | 0.9745 | 1      | 0.9780 |
|       | 0.9956 | 0.9940 | 0.9949 | 0.9986 | 0.9946 | 0.9964 | 0.9956 | 0.9957 | 1      | 0.9959 |
| QR-17 | 0.9740 | 0.9706 | 0.9895 | 0.9737 | 0.9759 | 0.9871 | 0.9763 | 0.9880 | 0.9780 | 1      |
|       | 0.9941 | 0.9916 | 0.9975 | 0.9954 | 0.9930 | 0.9969 | 0.9935 | 0.9964 | 0.9959 | 1      |

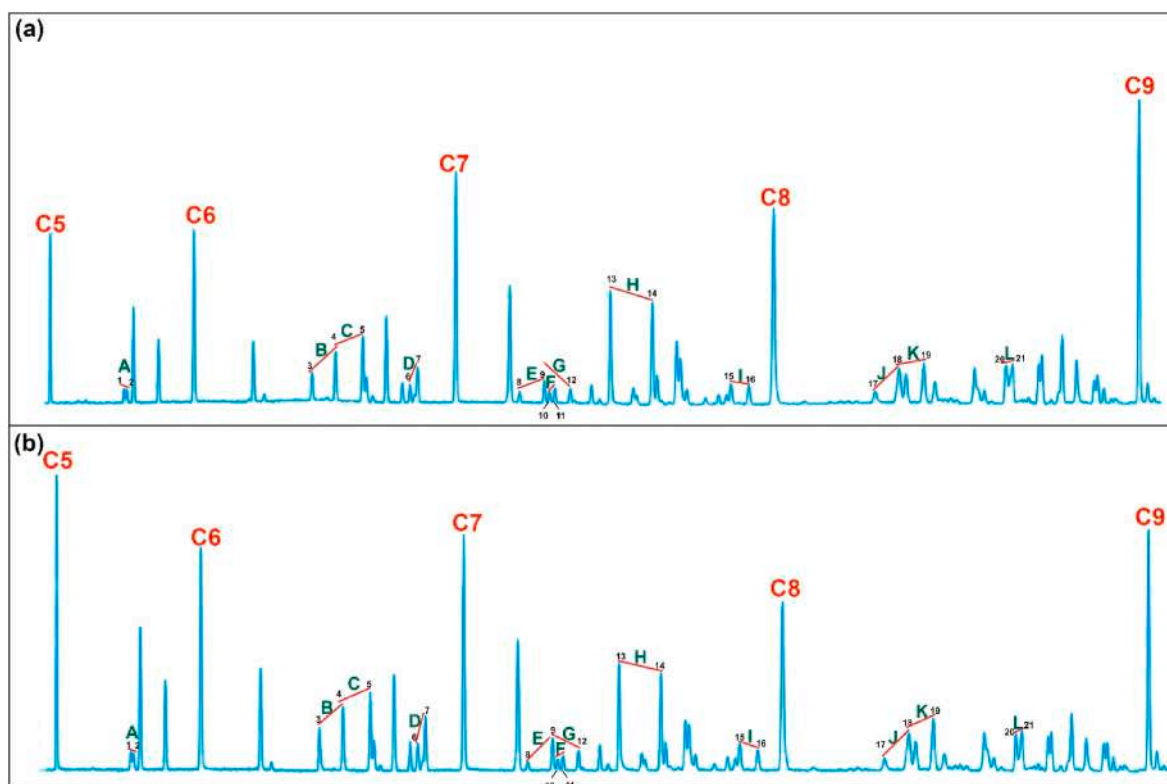
\* MMWR  
\*\* AMWR

Similarity in fingerprint

Dissimilarity in fingerprint

Limited similarity in fingerprint

**Fig. 6.** Similarity matrix from pairwise comparison of fingerprints for studied wells in the Qale Nar field. Relative comparison of the MMWR and AMWR values with the defined thresholds is the basis of each cell color. MMWR: the minimum correlation coefficient in all moving windows, AMWR: the average of correlation coefficients in all moving windows. The defined thresholds for the MMWR and AMWR are 0.9375 and 0.9799, respectively, in the Qale Nar field. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 7.** WOGC chromatogram in n-C5 to n-C9 region for representative samples: a) QR-1 and b) QR-6; to show different ratios used to compare oil fingerprints in the Qale Nar field. A: Peak No. 1/Peak No. 2; B: Peak No. 4/Peak No. 3; C: Peak No. 4/Peak No. 5; D: Peak No. 7/Peak No. 6; E: Peak No. 9/Peak No. 8; F: Peak No. 9/Peak No. 12; G: Peak No. 11/Peak No. 10; H: Peak No. 14/Peak No. 13; I: Peak No. 15/Peak No. 16; J: Peak No. 18/Peak No. 17; K: Peak No. 19/Peak No.18; L: Peak No. 20/Peak No.21.

**Table 3**

Chemical identification of selected inter-paraffin peaks for oil fingerprint comparison between studied samples in n-C5 to n-C9 region.

| Peak No. | Chemical identification           |
|----------|-----------------------------------|
| 1        | Cyclopentane                      |
| 2        | 2,3-dimethylbutane                |
| 3        | Benzene                           |
| 4        | Cyclohexane                       |
| 5        | 2-methylhexane                    |
| 6        | 1,3-dimethyl-, trans-cyclopentane |
| 7        | 1,2-dimethyl-, trans-cyclopentane |
| 8        | 1,1,3-trimethyl-cyclopentane      |
| 9        | 2,5- dimethylhexane               |
| 10       | Ethyl-cyclopentane                |
| 11       | 2,4- dimethylhexane               |
| 12       | 1,2,4-trimethyl-cyclopentane      |
| 13       | Toluene                           |
| 14       | 2-methylheptane                   |
| 15       | 2-trans-ethylmethyl cyclopentane  |
| 16       | 1-trans-2-dimethyl cyclohexane    |
| 17       | 2,6-dimethyl heptane              |
| 18       | Ethyl-cyclohexane                 |
| 19       | 1,1,3-trimethyl cyclohexane       |
| 20       | m-xylene                          |
| 21       | p-xylene                          |

but in the second derivative spectra, two valleys are apparent. The 2958 and 2923  $\text{cm}^{-1}$  bands are assigned to the asymmetric stretching of methyl and methylene, respectively. Two lower wavenumber bands in 3000–2750  $\text{cm}^{-1}$  region, e.g., 2870 and 2850  $\text{cm}^{-1}$ , are attributed to symmetric stretching of methyl and methylene, respectively. The C–H stretching of the methine groups appears between symmetric and asymmetric bands at the 2897  $\text{cm}^{-1}$ . It should be noted that curve

fitting discloses five bands evidently in this region (Asemani and Rabbani, 2020). In the studied samples, one of the bands (e.g., 2870  $\text{cm}^{-1}$ ) is not evident and appears as a small shoulder beside the 2850  $\text{cm}^{-1}$  band in some samples (Fig. 5). Although the C=O stretching in the carboxylic acids and esters occurs at about 1730  $\text{cm}^{-1}$ , the C=C stretching in aromatics (ring mode) appears at 1600  $\text{cm}^{-1}$ . A band at 1460  $\text{cm}^{-1}$  can be assigned to  $\text{CH}_3$  asymmetric bending,  $\text{CH}_2$  scissors, or both of them, and the 1376  $\text{cm}^{-1}$  band is due to  $\text{CH}_3$  symmetric bending vibration. The band appeared at the 1030  $\text{cm}^{-1}$  is attributed to the sulfoxide group stretching (Lin-Vien et al., 1991; Smith, 1998; Pavia et al., 2008; Asemani and Rabbani, 2020). Bands in the region below 900  $\text{cm}^{-1}$  are related to C–H out of plane bending (wagging) vibration of aromatic rings. These bands are utilized to determine the number of substitutions in the benzenes. Yen et al. (1984) stated that the aromatic rings with penta-substitution give rise bands in the  $880 \pm 20 \text{ cm}^{-1}$ , with tetra-substitution at  $830 \pm 30 \text{ cm}^{-1}$ , with tri-substitution at  $780 \pm 20 \text{ cm}^{-1}$ , with di-substitution at  $740 \pm 20 \text{ cm}^{-1}$ , and with mono-substitution at  $700 \pm 20 \text{ cm}^{-1}$ . Hence, the 862, 808, and 746  $\text{cm}^{-1}$  bands are related to penta-substitution, tetra- substitution, and di-substitution aromatic rings in the studied samples. The Band at 723  $\text{cm}^{-1}$  is due to rocking vibration by methylene in straight-chain alkanes with more than four carbons (Pavia et al., 2008).

#### 4.1.3. Oil fingerprint similarity assessment

##### 4.1.3.1. FTIR spectra of asphaltenes

**4.1.3.1.1. Determination of optimum moving window width and identification thresholds.** Two replicates with the most significant differences, from six replicates of the QR-9 sample, were selected to determine the optimum window width in the Qale Nar field. Results show that a series of correlation coefficients calculated by the window width of 13 points have higher values regarding window width with larger and lower sizes. The correlation coefficients increased from 5

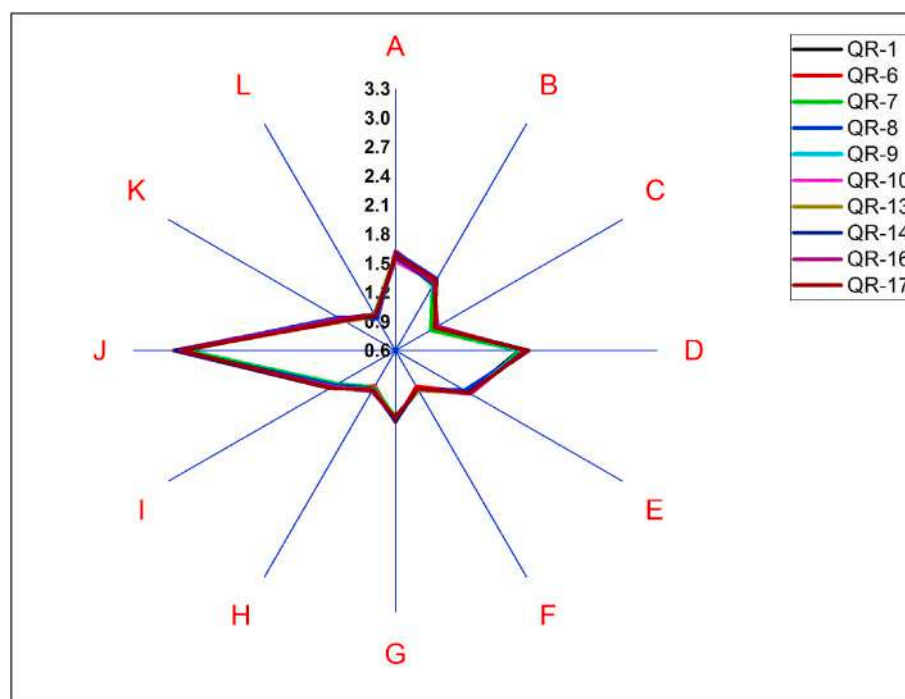


Fig. 8. Polar plot of calculated peak ratios from the WOGC chromatograms in n-C5 to n-C9 region for studied samples from the Asmari reservoir in the Qale Nar field.

Table 4

Bulk characteristics of studied samples in the Shadegan oil field.

| NO | Samples | Reservoir Unit | API (°) | Saturate (wt%) | Aromatic (wt%) | Resin (wt%) | Asphaltene (wt%) |
|----|---------|----------------|---------|----------------|----------------|-------------|------------------|
| 1  | SG-1    | Upper Asmari   | 29.39   | 46.06          | 41.46          | 10.94       | 1.54             |
| 2  | SG-2    | Lower Asmari   | 30.38   | 48.25          | 40.78          | 9.77        | 1.2              |
| 3  | SG-3    | Upper Asmari   | 26.69   | 42.64          | 38.91          | 12.26       | 6.2              |
| 4  | SG-8    | Upper Asmari   | 22.15   | 34.67          | 42.83          | 14.78       | 7.72             |
| 5  | SG-11   | Lower Asmari   | 30.53   | 45.78          | 40.43          | 12.49       | 1.3              |
| 6  | SG-17   | Lower Asmari   | 28.99   | 44.93          | 38.9           | 9.86        | 6.3              |
| 7  | SG-20   | Upper Asmari   | 22.3    | 35.64          | 41.82          | 15.21       | 7.34             |
| 8  | SG-21   | Lower Asmari   | 30.9    | 47.69          | 40.43          | 10.89       | 1                |

points width until 13 points, and then the correlation coefficients decreased with increasing the window width. Hence, the window width of 13 points was selected for the Qale Nar field.

The pairwise comparison between six replicates of the QR-9 sample was carried out by the modified moving window correlation coefficient to define identification thresholds. The results of these pairwise comparisons are summarized in Table 2. In the Qale Nar field, 0.9375 was chosen as the MMWR threshold to define similar samples. In addition to this parameter, 0.9799 was determined as the AMWR threshold for the identification of identical samples. However, the samples with similar fingerprints show the MMWR and AMWR higher than the threshold; the samples with different fingerprints have the MMWR and AMWR lower than the threshold. When one of the MMWR or AMWR was smaller than the threshold, this situation is a sign of limited similarity between samples, and it is also proposed to check their condition with other techniques.

**4.1.3.1.2. Oil fingerprinting by the modified moving window correlation coefficient technique.** Ten samples across the Asmari reservoir in the Qale Nar field were subjected to investigation by the modified moving window correlation coefficient technique. The similarity matrix for the Qale Nar oil field is shown in Fig. 6, which illustrates the comparison between different samples. The MMWR and AMWR for each pair of wells were calculated and are shown in the matrix. As all of the comparisons between different samples show the MMWR and AMWR values higher than the thresholds, all cells of the matrix have a green

color. This pattern signifies that oil fingerprints in all wells are similar. Hence, the Asmari reservoir in this field does not show any oil fingerprint heterogeneity.

**4.1.3.2. Oil fingerprinting by whole oil gas chromatography (WOGC).** The WOGC technique is a known technique to obtain oil fingerprints, which is commonly called a GC fingerprinting method in the geochemistry studies. This technique is mainly based on the light-end fractions (e.g., saturates and aromatics) of crude oil (Hwang et al., 1994). All studied wells in the Qale Nar field were subjected to WOGC analysis. Twelve peak ratios from selected inter-paraffin peaks in n-C5 to n-C9 region were calculated to reveal similarities or dissimilarities in oil fingerprints across the Qale Nar field (Fig. 7 and Fig. 1S§). The identification of peaks was accomplished based on retention times and comparing them to those published in the literature (Walters and Hellyer, 1998; Márquez et al., 2016, 2017). The chemical identification of peaks is listed in Table 3. The polar plot of these peak ratios is illustrated in Fig. 8. The star diagram shows that all samples have a similar trend, and the relative differences between samples in each of the calculated ratios are lower than 5%. Thus, all samples share identical fingerprints. These results are along with previous results from the heavy-end fraction of oils. Hence according to both light-end and heavy-end fractions of crude oils, all studied wells across the Asmari reservoir have similar fingerprints in the Qale Nar oil.

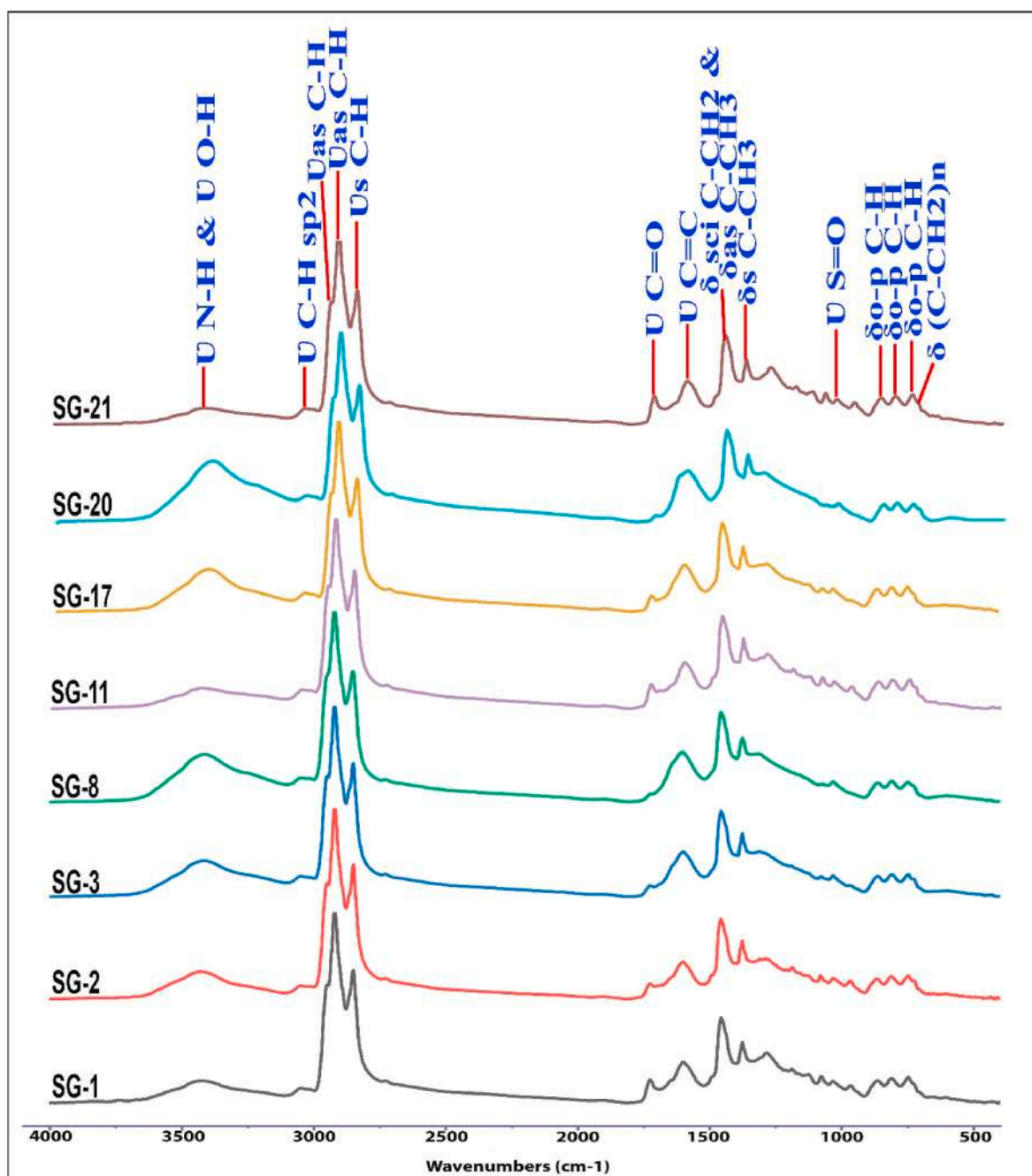


Fig. 9. FTIR spectra of asphaltenes for studied samples in the Shadegan field. U: stretching,  $\delta$ : bending, o-p: out-of-plane, s: symmetric, as: asymmetric, sci: scissors.

## 4.2. Case study II: Shadegan oil field

### 4.2.1. Bulk properties of oil samples

Bulk characteristics of eight samples from the Upper and Lower Asmari reservoir units in the Shadegan field are listed in Table 4. Saturate fraction has the highest value regarding other fractions, except for SG-8 and SG-20 samples. This fraction changes from 34.67% (SG-8) to 48.25% (SG-2). Aromatic, resin and asphaltene content ranges between 38.9 and 42.83%, 9.77–15.21%, 1–7.72%, respectively. API gravity shows a linear trend with saturate content and a reverse trend with asphaltene content. The minimum value of API is 22.15 for the SG-8 sample, which has the lowest saturate and highest asphaltene content. The maximum API value (30.9) belongs to the SG-21 sample with the lowest value of asphaltene.

### 4.2.2. Assignment of FTIR spectra

The raw and second derivative FTIR spectra of asphaltene fraction for studied samples in the Shadegan field are depicted in Fig. 9 and Fig. 10, respectively. Figs. 9 and 10 illustrate that samples have some differences in the height of bands, but the position of peaks is the same. The assignment of peaks is similar to those mentioned in section 4.1.2.

### 4.2.3. Oil fingerprint similarity assessment

#### 4.2.3.1. FTIR spectra of asphaltenes

4.2.3.1.1. Determination of optimum moving window width and identification thresholds. Two replicates of the SG-1 sample with the most significant differences (e.g., SG-1-1 and SG-1-4) were selected, and a modified moving window correlation coefficient with different window width was applied. The window widths were ranged from 5 points to 17 points with 2 points interval. The calculated correlation

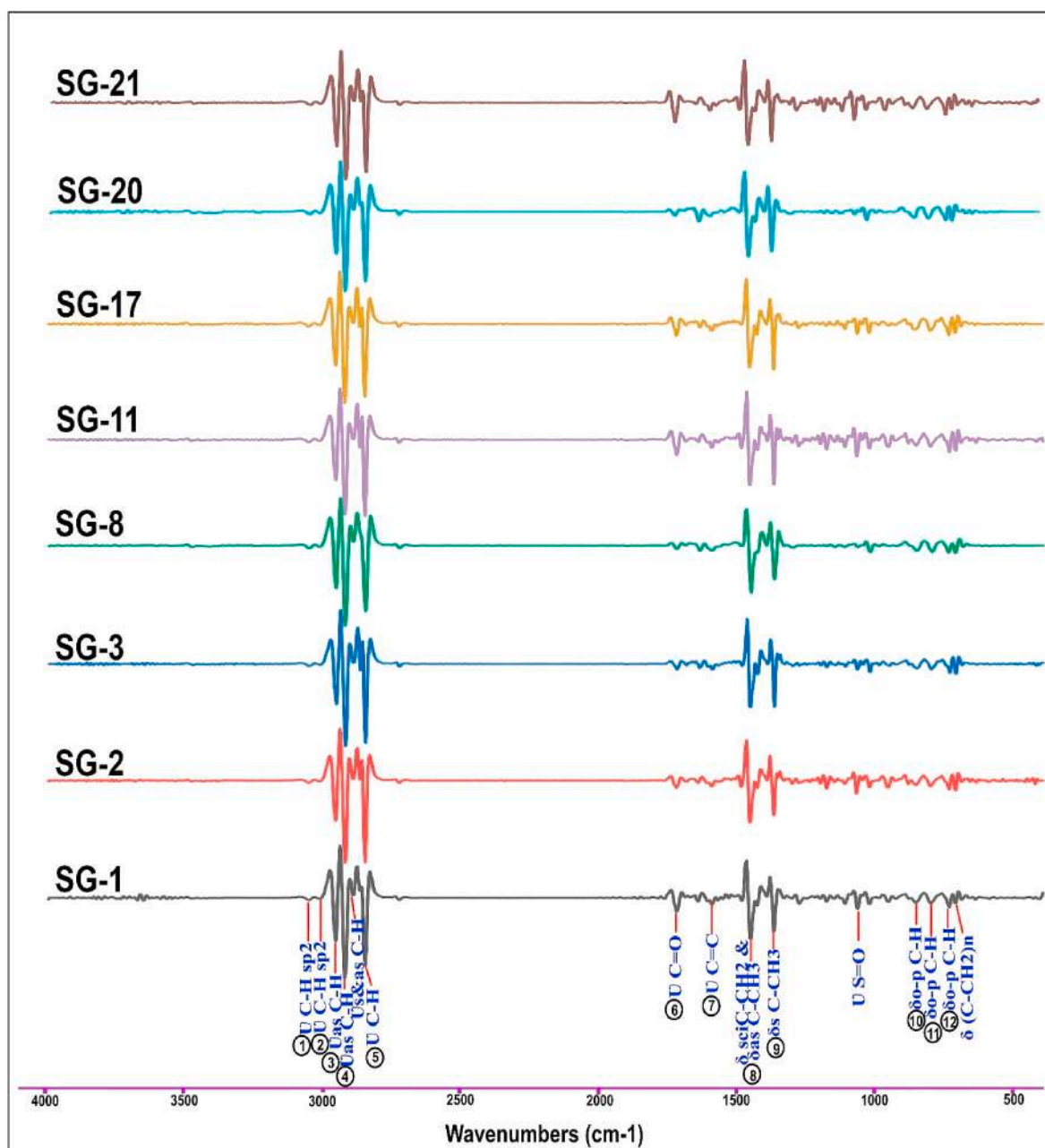


Fig. 10. Normalized second derivative FTIR spectra of asphaltenes for studied samples in the Shadegan field. Twelve selected bands for the modified moving window correlation coefficient technique are marked in the spectra. U: stretching,  $\delta$ : bending, o-p: out-of-plane, s: symmetric, as: asymmetric, sci: scissors.

coefficients showed that the 13 points window width has the maximum values. The correlation coefficients increased from 5 to 13 points and decreased from 13 to 17 points. Hence the optimum window width of 13 points was selected for the Shadegan field. The thresholds for MMWR and AMWR were calculated from pairwise comparison of different replicates of the SG-1 sample. The results of these comparisons are summarized in Table 5. The 0.9379 and 0.9881 were assigned to the threshold of the MMWR and AMWR, respectively.

**4.2.3.1.2. Oil fingerprinting by the modified moving window correlation coefficient technique.** Eight samples from two productive reservoir units, namely Upper and Lower Asmari, were evaluated by the modified moving window correlation coefficient technique to assess oil fingerprints similarity in the Shadegan field. The MMWR and AMWR for each pairwise comparison of samples were calculated, and results are summarized in the similarity matrix (Fig. 11). It is apparent at first glance that some heterogeneities are evident in the Shadegan field.

When looking into details, the relationship and similarity between each pair of wells are disclosed. According to results, each of the Upper and Lower Asmari reservoirs includes three zones based on oil fingerprints similarities and dissimilarities (Fig. 12). The SG-8 and SG-20 samples have similar fingerprints and belong to UAS- I zone (Fig. 12a). The SG-3 and SG-1 samples have different fingerprints from each other. These samples are also different from the SG-8 and SG-20 samples. The SG-3 and SG-1 samples situate in the two different zones, namely UAS-II and UAS-III zones, respectively (Fig. 12a). The Lower Asmari reservoir contains three zones based on fingerprints homogeneities and heterogeneities of samples (Fig. 12b). The SG-17 has a different fingerprint from other samples and includes in LAS-I zone. The LAS-II zone contains the SG-11 and SG-21 samples, which have a similar fingerprint with each other. The SG-2 sample, with a different fingerprint from other samples, attributes to LAS-III zone (Fig. 12b). The SG-1 sample from the Upper Asmari reservoir has a similar

**Table 5**

Results of pairwise comparisons of six replicates for the SG-1 sample to determine identification thresholds in the Shadegan field.

| Sample | Duplicates             | Min correlation coefficient in all moving windows (MMWR) | Max correlation coefficient in all moving windows | Average of correlation coefficients in all moving windows (AMWR) |
|--------|------------------------|----------------------------------------------------------|---------------------------------------------------|------------------------------------------------------------------|
| SG-1   | 1&2                    | 0.9927                                                   | 1.0000                                            | 0.9984                                                           |
|        | 1&3                    | 0.9460                                                   | 1.0000                                            | 0.9932                                                           |
|        | 1&4                    | 0.9379                                                   | 1.0000                                            | 0.9912                                                           |
|        | 1&5                    | 0.9807                                                   | 1.0000                                            | 0.9972                                                           |
|        | 1&6                    | 0.9786                                                   | 1.0000                                            | 0.9941                                                           |
|        | 2&3                    | 0.9528                                                   | 1.0000                                            | 0.9939                                                           |
|        | 2&4                    | 0.9451                                                   | 1.0000                                            | 0.9909                                                           |
|        | 2&5                    | 0.9943                                                   | 1.0000                                            | 0.9990                                                           |
|        | 2&6                    | 0.9936                                                   | 1.0000                                            | 0.9977                                                           |
|        | 3&4                    | 0.9912                                                   | 1.0000                                            | 0.9985                                                           |
|        | 3&5                    | 0.9669                                                   | 1.0000                                            | 0.9927                                                           |
|        | 3&6                    | 0.9640                                                   | 1.0000                                            | 0.9911                                                           |
|        | 4&5                    | 0.9605                                                   | 1.0000                                            | 0.9898                                                           |
|        | 4&6                    | 0.9576                                                   | 1.0000                                            | 0.9881                                                           |
|        | 5&6                    | 0.9895                                                   | 1.0000                                            | 0.9981                                                           |
| Total  | Min of each column     | 0.9379 <sup>a</sup>                                      | 1.0000                                            | 0.9881 <sup>b</sup>                                              |
|        | Max of each column     | 0.9943                                                   | 1.0000                                            | 0.9990                                                           |
|        | Average of each column | 0.9701                                                   | 1.0000                                            | 0.9943                                                           |

<sup>a</sup> Threshold of the minimum correlation coefficient in all moving windows (MMWR).

<sup>b</sup> Threshold of the average of correlation coefficients in all moving windows (AMWR).

fingerprint with the SG-11 and SG-21 samples from the Lower Asmari. These three samples located in the crest of the Shadegan anticline.

**4.2.3.2. Oil fingerprinting by whole oil gas chromatography (WOGC).** The WOGC technique was performed to complement and validate the results of the modified moving window correlation coefficient technique. The height of inter-paraffin peaks was used to calculate peaks ratios for oil fingerprinting. Twelve peaks ratios were calculated from n-C5 to n-C9 region to disclose oil fingerprints similarities and dissimilarities (Fig. 13, Figs. 2S and 3S). The chemical identification of selected samples is listed in Table 3. These peak ratios were plotted in the polar diagrams to the comparison of fingerprints between samples (Fig. 14). Fig. 14a illustrates that some differences exist between samples in the Upper Asmari. The SG-8 and SG-20 samples have identical trends and values. The SG-1 and SG-3 samples show different patterns from other samples in the Upper Asmari reservoir. Similar to the Upper Asmari, three distinct patterns are evident in the fingerprints of the Lower Asmari samples (Fig. 14b). The SG-11 and SG-21 samples show a similar trend, and their values in all of the peak ratios are relatively identical. The SG-2 and SG-17 samples show different trends from each other and other samples in the Lower Asmari. These results are similar to those obtained from the modified moving window correlation coefficient technique of asphaltene samples. The SG-1 has a similar value and trend with the SG-11 and SG-21 samples. Furthermore, the WOGC results showed that the SG-2 and SG-3 are different from each other, and this conclusion complemented the result of FTIR spectroscopy, which had shown limited oil fingerprint similarity. Thus, according to both light-end and heavy-end fractions of crude oils, the Upper and Lower Asmari reservoirs have heterogeneous fingerprints in the Shadegan field.

However, faults are likely the main reason for fingerprint

heterogeneity between the UAS-II and other zones (e.g., UAS-I and UAS-III), dissimilarities between the UAS-I and UAS-III zones are not related to faults. Also, the fingerprints heterogeneities in the Lower Asmari reservoir do not obey the pattern of faults. The Asmari Formation is accounted for a naturally fractured reservoir (NFR), which induced fractures as a result of compressional stresses are the main cause of its reservoir quality. The distribution of compressional stresses is not always even in all parts of the reservoir, and their patterns cause various fracture networks in different parts of the reservoir (Paredes et al., 2015). Hence, variation in the fracture network in different parts of the Asmari reservoir (Upper and Lower) in the Shadegan field is likely the main reason for the oil fingerprints heterogeneities. The stress concentration and fracture intensity are higher in the crest than the flank of the anticline. The pattern of defined zones in the Asmari reservoir follows this model. The wells located in the crest has different oil fingerprint from those situated in the flank of the anticline.

## 5. Conclusions

The main conclusions of this paper are summarized as the following:

- The moving window correlation coefficient provides a series of correlation coefficients instead of one general correlation coefficient for two data series.
- The proposed modified procedure resolved the drawbacks of the common version of the moving window correlation coefficient technique. In this procedure, the peak ratios calculated from the second derivative FTIR spectra are used as an input data series instead of spectral channels for each sample. This procedure is beneficial for oil fingerprint similarity assessment and revealing subtle differences between oil fingerprints. In this paper, the structural characteristics of asphaltene were employed to obtain oil fingerprints.
- Results show fingerprint similarity in the Asmari reservoir of the Qale Nar field. But, three distinct fingerprints were recognized in each of the Upper and Lower Asmari reservoirs from the Shadegan field.
- The routine technique of whole oil gas chromatography was performed to check and complement the obtained results. This technique completely corroborated the results of FTIR spectroscopy of asphaltene.
- Variation in the fracture networks due to uneven compressional stresses distribution across the Asmari reservoir is the likely reason for fingerprint heterogeneities in the Shadegan field.
- The finding of this paper revealed that the modified moving window correlation coefficient method and FTIR spectra of asphaltene are regarded as a novel, trustable, cost-effective, easy to interpretation technique for oil fingerprint similarity assessment.

## CRedit authorship contribution statement

**Morteza Asemani:** Methodology, Formal analysis, Writing - original draft, Writing - review & editing. **Ahmad Reza Rabbani:** Supervision, Methodology, Writing - original draft. **Hashem Sarafdokht:** Resources.

## Declaration of competing interest

The corresponding author confirms on behalf of all authors that there have been no involvements that might raise the question of bias in the work reported or in the conclusions, implications, or opinions stated.

|       | SG-1   | SG-2   | SG-3   | SG-8   | SG-11  | SG-17  | SG-20  | SG-21  |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| SG-1  | 1*     | 0.8876 | 0.7780 | 0.5647 | 0.9848 | 0.9285 | 0.5962 | 0.9568 |
|       | 1**    | 0.9834 | 0.9707 | 0.9192 | 0.9949 | 0.9851 | 0.9327 | 0.9959 |
| SG-2  | 0.8876 | 1      | 0.9609 | 0.8387 | 0.8574 | 0.9287 | 0.8639 | 0.7304 |
|       | 0.9834 | 1      | 0.9855 | 0.9566 | 0.9871 | 0.9800 | 0.9649 | 0.9720 |
| SG-3  | 0.7780 | 0.9609 | 1      | 0.8821 | 0.7371 | 0.8794 | 0.8993 | 0.5830 |
|       | 0.9707 | 0.9855 | 1      | 0.9720 | 0.9637 | 0.9863 | 0.9795 | 0.9521 |
| SG-8  | 0.5647 | 0.8387 | 0.8821 | 1      | 0.5083 | 0.6909 | 0.9854 | 0.3587 |
|       | 0.9192 | 0.9566 | 0.9720 | 1      | 0.9147 | 0.9400 | 0.9960 | 0.8931 |
| SG-11 | 0.9848 | 0.8574 | 0.7371 | 0.5083 | 1      | 0.9273 | 0.5545 | 0.9758 |
|       | 0.9949 | 0.9871 | 0.9637 | 0.9147 | 1      | 0.9806 | 0.9284 | 0.9955 |
| SG-17 | 0.9285 | 0.9287 | 0.8794 | 0.6909 | 0.9273 | 1      | 0.7443 | 0.8635 |
|       | 0.9851 | 0.9800 | 0.9863 | 0.9400 | 0.9806 | 1      | 0.9536 | 0.9866 |
| SG-20 | 0.5962 | 0.8639 | 0.8993 | 0.9854 | 0.5545 | 0.7443 | 1      | 0.3906 |
|       | 0.9327 | 0.9649 | 0.9795 | 0.9960 | 0.9284 | 0.9536 | 1      | 0.9087 |
| SG-21 | 0.9568 | 0.7304 | 0.5830 | 0.3587 | 0.9758 | 0.8635 | 0.3906 | 1      |
|       | 0.9959 | 0.9720 | 0.9521 | 0.8931 | 0.9955 | 0.9866 | 0.9087 | 1      |

\* MMWR  
 \*\* AMWR

Similarity in fingerprint (Green)  
 Dissimilarity in fingerprint (Red)  
 Limited similarity in fingerprint (Yellow)

Fig. 11. Similarity matrix resulted from pairwise comparison of fingerprints for studied wells in the Shadegan field. MMWR: the minimum correlation coefficient in all moving windows, AMWR: the average of correlation coefficients in all moving windows. The defined thresholds for the MMWR and AMWR are 0.9379 and 0.9881, respectively, in the Shadegan field.

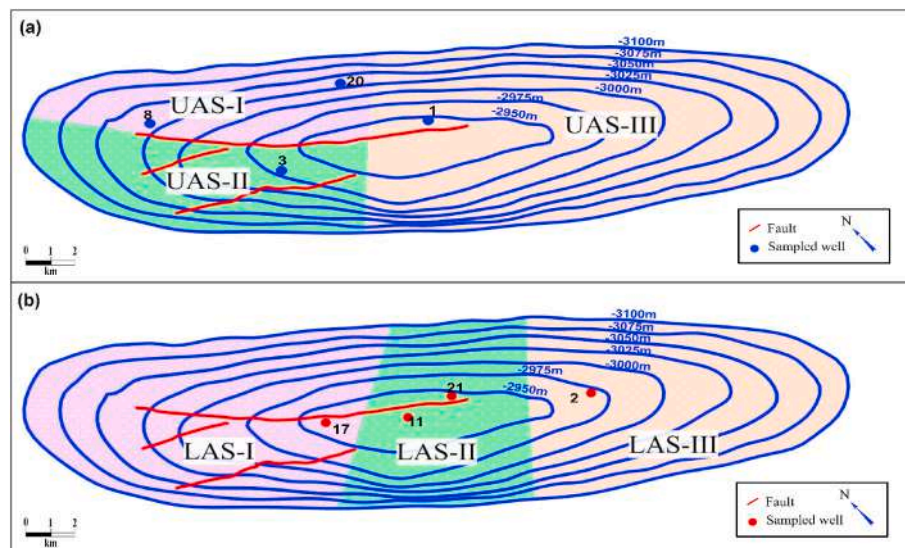
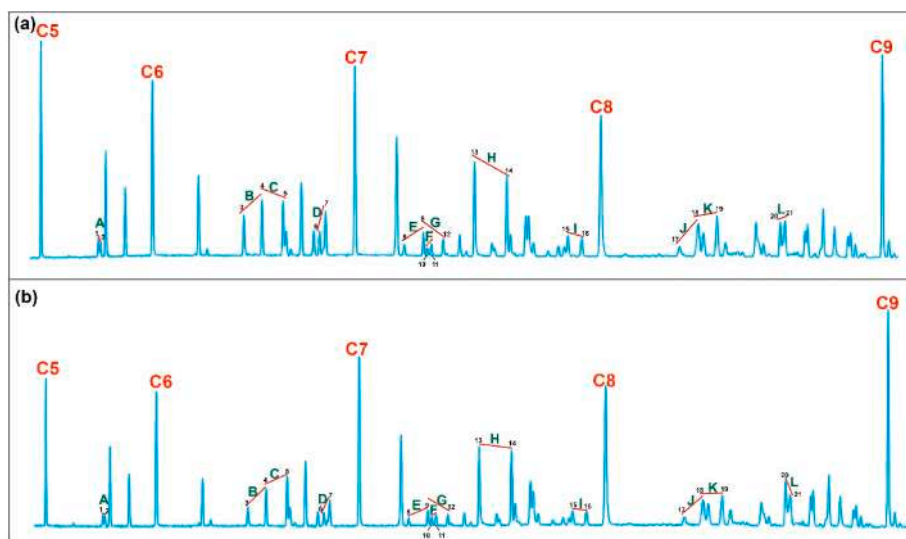


Fig. 12. Schematic of different zones based on similarity and dissimilarities of oil fingerprints. a) Upper Asmari reservoir, b) Lower Asmari reservoir.

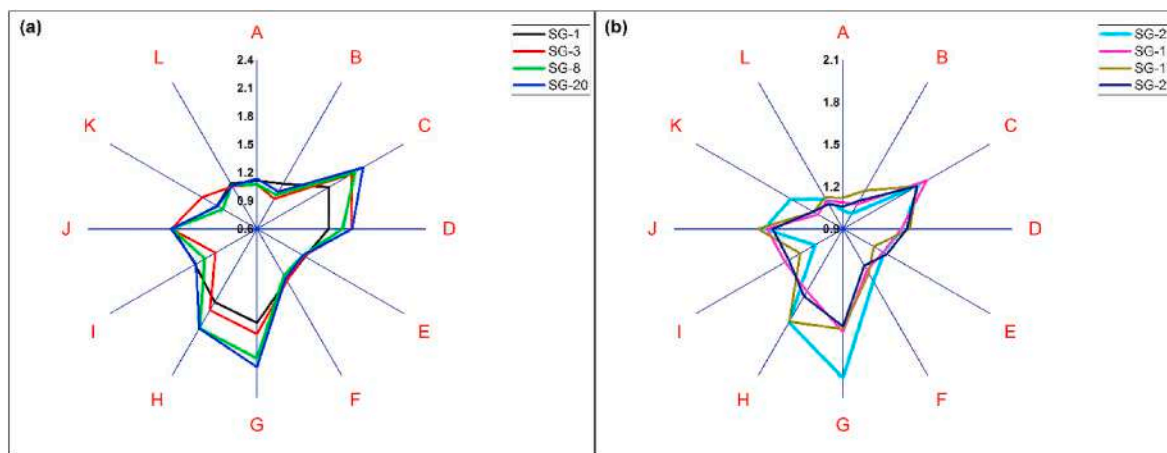
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**Fig. 13.** WOGC chromatogram in n-C5 to n-C9 region for representative samples: a) SG-1 and b) SG-2; to show different ratios used to compare oil fingerprints in the Shadegan field. A: Peak No. 1/Peak No. 2; B: Peak No. 4/Peak No. 3; C: Peak No. 4/Peak No. 5; D: Peak No. 7/Peak No. 6; E: Peak No. 9/Peak No. 8; F: Peak No. 9/Peak No. 12; G: Peak No. 11/Peak No. 10; H: Peak No. 14/Peak No. 13; I: Peak No. 15/Peak No. 16; J: Peak No. 18/Peak No. 17; K: Peak No. 19/Peak No. 18; L: Peak No. 20/Peak No. 21.



**Fig. 14.** Polar plots of calculated ratios from WOGC chromatograms in n-C5 to n-C9 region to compare fingerprints. a) Upper Asmari reservoir and b) Lower Asmari reservoir.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpetgeo.2020.104542>.

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