

Oil-oil correlation by FTIR spectroscopy of asphaltene samples

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ABSTRACT: In this paper, a new technique with easy interpretation, low cost, and reliable results is presented for oil-oil correlation purpose. In this technique, the structural characterization of asphaltene, because of its structural similarity with kerogene and resistance to secondary processes (e.g., migration, biodegradation, thermal maturity, and so on), was considered as a correlation parameter and asphaltene structure similarity in different oil samples is the basis of geochemical correlation. FTIR spectroscopy was applied to detect and compare asphaltene structures with each other. The four oil samples from different oil fields in the Iranian sector of the Persian Gulf were investigated by FTIR spectroscopy and introduced indexes that represent structural characteristic of asphaltene enabled us to perform geochemical correlation. To validation of this technique, the other common geochemical techniques (e.g., stable carbon isotope and biomarkers) were applied to geochemical correlation. These techniques completely supported and complemented the results of the asphaltene FTIR spectroscopy technique. The results of these three techniques show genetic relationships among these 4 oil samples and indicated that these oil samples belong to two distinct oil families. The First oil family originated from carbonate rich source rock and the second oil family was sourced from calcareous shale source rock.

Key words: Fourier transform infrared (FTIR) spectroscopy, oil-oil correlation, asphaltene, Persian Gulf, Iran

1. INTRODUCTION

The geochemical correlations are comparisons between oil-oil and/or crude oils and bituminous extracts of source rocks are used to determine if there is a genetic relationship between them based on molecular composition. Correlations are accomplished by comparing elemental, molecular, and isotopic parameters using techniques such as gas chromatography (GC), gas chromatography with mass spectrometry (GC/MS), and carbon isotope ratio determination (IRGC/MS) (Engel and Macko, 1993). In general, asphaltene are characterized by fused aromatic rings, aliphatic side chains, and polar heteroatoms-containing functional groups. In the last few years asphaltene have become of immense interest for exploration techniques, since it was reported that they possess structural features of the related source rock kerogens. This is because the use of asphaltene from crude oils may help to overcome the lack of source rock samples in basin analysis when reliable predictions for the generation of hydrocarbons are required (Lehne,

2008). Pelet et al. (1986) proposed that asphaltene are structural equivalents of kerogens, and that only their solubility allows them to migrate in petroleum. Thus, oil asphaltene are considered to be reservoir fragments of the source rock kerogen (Pelet et al., 1986).

In this paper, the molecular structure of asphaltene was considered as a correlation parameter and structure characterization of asphaltene was done by FTIR spectroscopy to compare asphaltene structures and performing geochemical correlation. In the past, FTIR spectroscopy of crude oils (whole oil not asphaltene) has been employed as a new tool in reservoir compartmentalization (Permanyer et al., 2002), but, this paper presents new application of FTIR spectroscopy on solving geochemical issues. FTIR spectroscopy gives reliable information, including the paraffinicity or aromaticity of the samples, the relative proportion of carbonyl and/or carboxyl groups versus aliphatic compounds, information on the existence and abundance of various functional groups in the samples, the abundance of aromatic nuclei and oxygen-containing groups relative to aliphatic chains, and the degree of condensation in the polyaromatic compounds (Permanyer et al., 2002, 2005, 2007; Griffiths and de Haseth, 2007). In a word, this technique gives structural characterization of samples.

The main objectives of this paper are: 1) introducing the structural characterization of asphaltene by FTIR spectroscopy, as a new and reliable technique for correlation purposes, 2) application of FTIR spectroscopy to evaluate genetic relationships of 4 crude oil samples collected from the north part of the Persian Gulf, and 3) utilization of stable carbon isotope and biomarker data for support and complement the results of FTIR spectroscopy.

2. GEOLOGICAL SETTING

The Persian Gulf is structurally a foreland basin filled by terrigenous clastics transported from adjacent regions and carbonate sediments generated across the ramp surface (Alavi, 2004). This Basin is the richest region of the World in terms of hydrocarbon resources. According to different estimates, this basin contains 55–68% of recoverable oil reserves and more than 40% of gas reserves of the world. The biggest Gas field in the World (South Pars/North Dome) is also located in the Persian Gulf. The Iranian part of the Zagros Range

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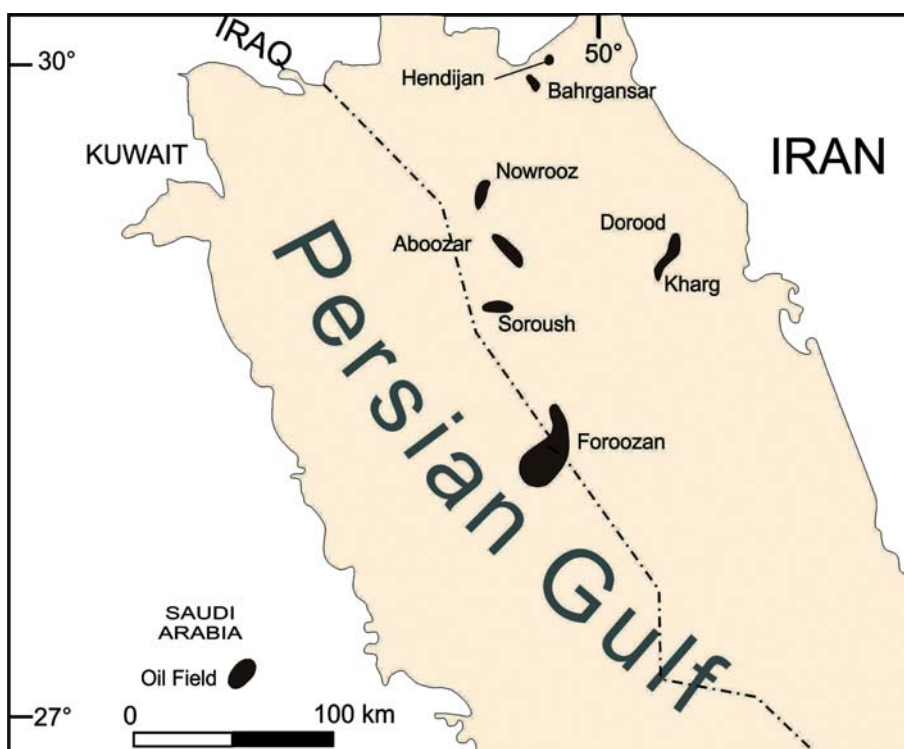


Fig. 1. Location map of oil fields in the Persian Gulf. The Foroozan, Dorood, Bahregansar, and Hendijan are the oil fields that were sampled.

and the Persian Gulf accounts for 10.9% and 16% of the world's proven oil and gas reserves (Soleimany, 2010). There are six main petroleum reservoir target horizons with different ages in the Zagros Range and the Persian Gulf. The youngest is in Cenozoic (Asmari Formation), then there are three major reservoir targets in Mesozoic (Sarvak, Fahliyan and Surmeh Formations), while the oldest is in the Upper Paleozoic–lower Mesozoic horizon (Dalan and Kangan Formations).

Four produced crude oil samples were collected from the Sarvak and Fahliyan (Yamama) Formations throughout oil fields in the NW part of the Persian Gulf. The Sarvak Formation consists of thick bedded to massive carbonate sediments and shows good porosity and permeability. This formation is one of the significant reservoir rocks in the Zagros Fold and the Persian Gulf. The age of this formation is Late Cretaceous (Cenomanian–Turonian). The Fahliyan (Yamama) Formation consists of coarse-grained carbonate. This formation shows good porosity and permeability and is a good reservoir rock in the Zagros Range and in the NW Persian Gulf. The Fahliyan (Yamama) formation is Early Cretaceous (Neocomian) in age (Ghazban, 2007).

For this study, two produced oil samples (DY and FY) were collected from the Fahliyan (Yamama) Formation in the Dorood and Foroozan oil fields, and two produced oil samples (BS and HS) were also collected from the Sarvak Formation in the Hendijan and Bahregansar oil fields from NW of the Persian Gulf (Fig. 1). In the following section, sample preparation and analysis methods are described.

3. MATERIAL AND METHODS

The oils were analyzed for API gravity with an Anton Paar DMA5300M density meter. The first step in performing SARA separation is removing asphaltenes. Asphaltenes were extracted from crude oils according to the standard test procedure that named IP-143, with some modification and using n-pentane as a precipitation solvent (IP 143/01, 2012). Crude oil samples were heated to approximately 80 °C and cooled at room temperature. Approximately 5 mg of each oil sample was placed in a flask with a capacity of 250 mL. N-pentane solvent was also added to the test portion in the flask at a ratio of 25 mL to each 1 g of oil sample. The mixture was boiled and refluxed for 60 min. At the end of this period, the flask was removed, cooled, closed with a stopper, and stored in a dark place for 150 min. Filter paper (Whatman Grade 42 with 125 mm diameter) was placed in a funnel, the content of the flask decanted into filter paper, and then the residue in the flask transferred with successive quantities of hot n-pentane. After that, the filter paper and contents were removed from the funnel and placed in the reflux extractor and refluxed by n-pentane at rate of 4 drops/s from the end of the condenser for an extraction period until a few drops of n-pentane from the bottom of the extractor left no residue on a glass slide, and then refluxing continued by 60 mL of toluene until all the asphaltenes were dissolved from the paper. The contents of the flask (asphaltene plus toluene) were transferred to a clean and dry evaporating vessel (the flask washed out with successive small quantities of toluene to a total not exceed-

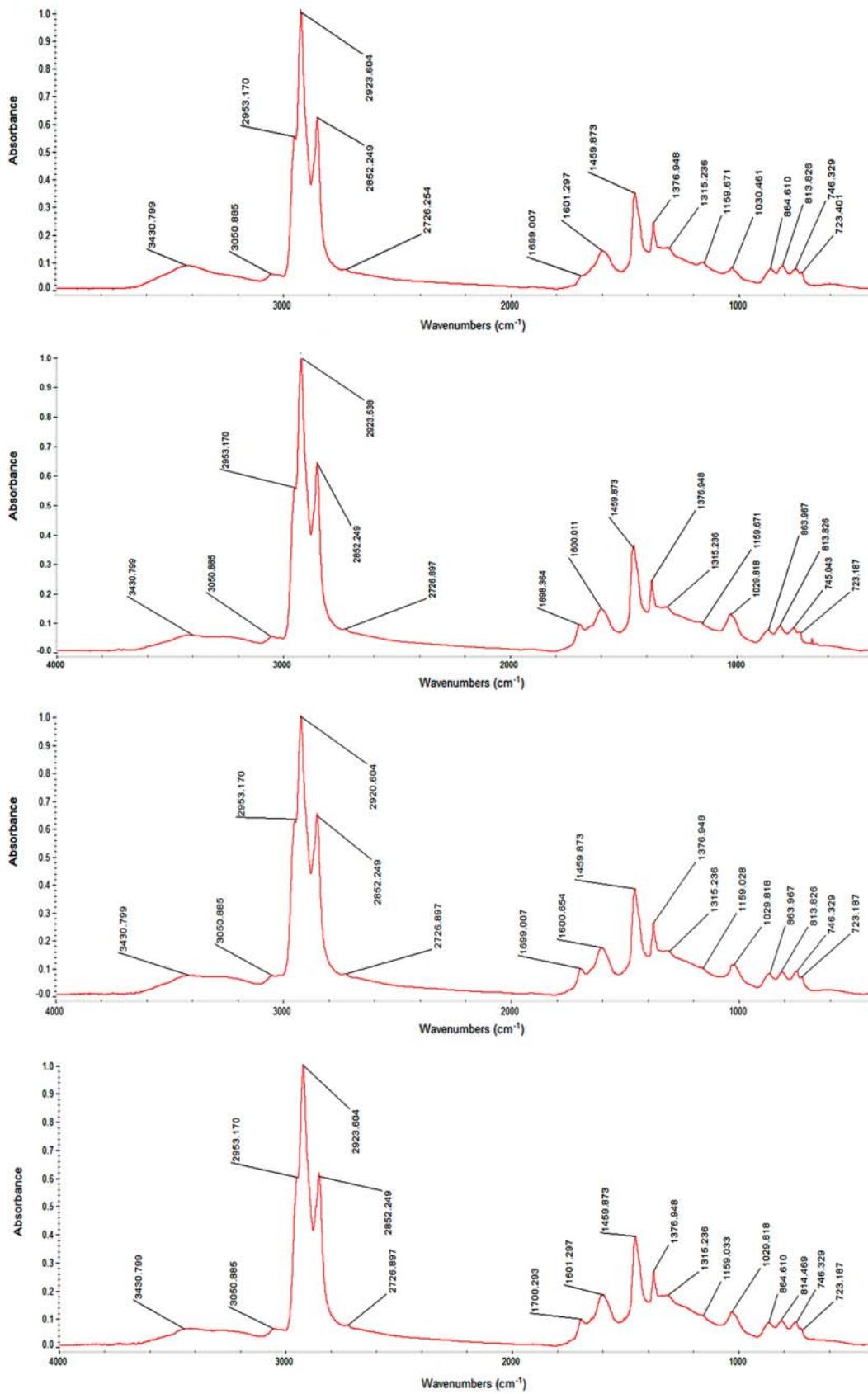


Fig. 2. IR spectrum of asphaltene samples after normalizing. (a) IR spectrum of DY sample, (b) IR spectrum of FY sample, (c) IR spectrum of HS sample, and (d) IR spectrum of BS sample.

ing 30 mL). The toluene was removed by evaporation in a boiling water bath. The dish and contents were dried in an oven at 100 °C for 30 min. Finally, the dish was cooled in the cooling vessel for 60 min and weighed. Asphaltenes were stored in small plastic containers (to prevent absorption of moisture) until subsequent tests were performed.

After the asphaltenes were removed, other fractions of crude oil (Saturate, Aromatic and Resin) were separated by using column chromatography. The adsorption column was prepared by alumina and silica gel. The saturate compounds were washed out from the column by adding n-pentane to the top of the column and allowing all of n-pentane effluent to drain from the column. The remaining fractions were washed out by adding toluene to separate aromatic compounds and toluene/methanol in a proportion of 90/10 for resin compounds. The weight of each fraction is reported as a percentage.

Fourier transform infrared spectroscopy (FTIR) is a technique that deals with the infrared region of the electromagnetic spectrum, and is used to obtain an infrared spectrum from solid, liquid or gas samples in the mode of absorption or transmittance (Griffiths and de Haseth, 2007). In this study, MID Infrared Spectroscopy was used which refers to using infrared radiation with wave numbers ranging from 4000

cm^{-1} to 400 cm^{-1} . In MID-IR region, there are many strong fundamental rotational-vibrational molecular transitions and making this an extremely useful region of the electromagnetic spectrum to determine structural information about the investigated samples. The spectrums were recorded in absorption mode by Thermo Nicolet-Nexus 670 in range of 6000 cm^{-1} to 600 cm^{-1} , with 40 scans at a resolution of 4 cm^{-1} . To obtain the FTIR spectrum, 20 mg of asphaltene samples were ground with mortar and pestle and then mixed with 200 mg potassium bromide (KBr) which had been powdered previously. The resulting compound was compressed under high pressure and the result was a KBr pellet that was inserted into a holder in the spectrometer to record the spectrum. In order to better compare, all of the spectra should be normalized (Doumenq et al., 1991). The normalization process was done based on asymmetrical stretching of the C–H bond in CH_2 that was seen in all spectra at 2923 cm^{-1} . Resulting spectra are shown in Figure 2. All samples had the same appearance and general pattern but different peak height. Interpretations of all peaks in the spectrums are given in Table 1.

Different indexes that represent the structural and functional features of asphaltene samples are calculated on the basis of peak areas. Peak areas are measured from valley to

Table 1. Interpretation of all peaks are observed in the spectra of asphaltene samples

The best-known modes of vibrational motion in a molecule are the stretching and bending modes. In any group of three or more atoms, which two of them are identical, there are two mode of stretching that named symmetric and asymmetric. In general, asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibrations; also, stretching vibrations occur at higher frequencies than bending vibrations. The terms scissoring, rocking, wagging, and twisting are commonly used in the literature to describe different types of bending. The more description about vibrational modes is beyond the scope of this paper and can be find in the following references. In the following, interpretation of picks that was seen in the infrared spectrum, according to their wavenumbers, is described in the table.

Picks	Interpretations	References
3430 cm^{-1}	A broad and weak band due to O–H and N–H stretching	
3050 cm^{-1}	A small band due to C–H stretching in aromatic compounds (= C–H or sp^2 C–H stretching)	
2953 cm^{-1}	Asymmetrical stretching of C–H bond in CH_3 ($U_{\text{as}} \text{CH}_3$) and stretching of C–H bond in alkanes.	
2923 cm^{-1}	Asymmetrical stretching of C–H bond in CH_2 ($U_{\text{as}} \text{CH}_2$)	
2852 cm^{-1}	Symmetrical stretching of C–H bond in CH_3 ($U_{\text{s}} \text{CH}_3$) and asymmetrical stretching of C–H bond in CH_2 ($U_{\text{as}} \text{CH}_2$)	
2726 cm^{-1}	Stretching of C–H bond in aldehyde hydrogen	
1700 cm^{-1}	Stretching of C=O bond in secondary amides	
1600 cm^{-1}	Stretching of C=C bond in aromatic rings	
1460 cm^{-1}	Symmetrical bending of C–H in CH_2 ($\delta_{\text{s}} \text{CH}_2$), asymmetrical bending of C–H in CH_3 ($\delta_{\text{as}} \text{CH}_3$), and asymmetrical stretching of C=C bond in aromatic rings	Interpretations were done based on these references: Derrick et al., 1999; Mayo et al., 2003; Stuart, 2004; Silverstein et al., 2005; Field et al., 2008; Pavia et al., 2009.
1376 cm^{-1}	Symmetrical bending of C–H bond in CH_3 ($\delta_{\text{s}} \text{CH}_3$)	
1315 cm^{-1}	Bending of C–H bond in CH_3 (wagging and twisting bending) and stretching of C–O bond in carboxylic acid	
1159 cm^{-1}	In plane bending of C–H bond in aromatic compounds	
1030 cm^{-1}	Stretching of S=O bond in sulfoxides	
864 cm^{-1}	Out of plane bending of C–H bond in aromatic compounds	
814 cm^{-1}	Out of plane bending of C–H bond in aromatic compounds	
744 cm^{-1}	Out of plane bending of C–H bond in aromatic compounds	
724 cm^{-1}	Out of plane bending of C–H bond in aromatic compounds and bending (rocking type) of C–H in CH_2 (this pick indicate straight chain alkanes with 4 or more carbon atoms)	

valley (Permanyer et al., 2002). The following indexes were calculated with regard to peaks area ratio. To achieve accurate values, the peak areas were calculated three times with a maximum 0.001 difference, and then the indexes were calculated based on the average of these 3 values. Some of these indexes that were used for structural and chemical comparison of asphaltene samples are described below:

Aliphatic index: $(A_{1460} + A_{1376})/A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{2953} + A_{2923} + A_{2862}$, which represents all aliphatic compounds present in a sample.

Long chain index: $A_{724}/(A_{1460} + A_{1376})$, which represents straight chain alkanes with 4 or more carbon atoms in a sample.

Aromatic index: $A_{1600}/(A_{814} + A_{743} + A_{724})$, which represents all aromatic compounds present in a sample.

Substitution 1 index: $A_{864}/(A_{864} + A_{1376})$, which represent benzene structures that share one H, which attach to C atoms of the benzene ring, with other structures. Polyaromatic compounds with low condensation have a Substitution 1 index greater than their Substitution 2 index.

Substitution 2 index: $A_{814}/(A_{864} + A_{814} + A_{743})$, which represent benzene structures that share three H, which attach to C atoms of the benzene ring, with other structures. Polyaromatic compounds with high condensation have a Substitution 2 index greater than their Substitution 1 index.

In the above indexes, "A" refers to the peak area in the absorption spectrum and the subscript number represents the number of waves whose that peak is seen in the absorption spectrum.

The stable carbon isotope analyses were performed using the Finnigan Delta Plus mass spectrometer. The stable carbon isotope data are presented in the δ -notation relative to V-PDB standard (Coplen, 1994), with the analytical precision estimated to be $\pm 0.2\%$.

Saturate and aromatic fractions were used for biomarker analysis. The analysis was performed by an Agilent 7890A gas chromatograph equipped with an Agilent 7683B automatic sampler that has an on-column injection chamber and a fused silica capillary column (60 m length and 0.25 mm internal diameter). Helium gas was used as a carrier gas and 5 β -cholane used as a standard. Table 2 shows selected bio-

marker parameters that were used in this study.

4. RESULTS AND DISCUSSION

Asphaltenes extracted from oil have close structural similarities to their precursor, kerogen, and this structural signature is preserved during petroleum migration (Behar and Pelet, 1985; Peters et al., 1999; Di Primio et al., 2000; Bazin and Gucci, 2001). Consequently, the structural characteristics of these oil fractions can be considered as a correlation parameter and it can be deduced that asphaltenes from different reservoirs with similar structure are genetically related. For oil-oil correlation, the structure of asphaltene samples should be compared with each other. It is apparent that comparison should be done on the basis of compounds that are predominant in asphaltene structures. The structure of asphaltene varies in different crude oils and different chemical structures were suggested in different investigation. Nonetheless, asphaltenes in different crude oils share some similar features; they are characterized by fused aromatic rings, aliphatic side chains, and polar heteroatom-containing functional groups (Koots and Speight, 1975; Groenzin and Mullins, 2000; Spiecker et al., 2003). Since aromatic and aliphatic compounds are significant and fundamental structures in asphaltenes, comparison of asphaltene structures with each other should be done based on these compounds. To validate these facts from geochemical point, the different indexes that introduced and calculated by FTIR data was compared with stable carbon isotope data. Different factors affect on value of stable carbon isotope but two of the most important factor are number of elements and type of bonds (single, double or triple bonds) presents in that compound and later factor have greater effect on carbon isotope value. For examples enrichment of ^{13}C isotope in methane is less than ethane. If we neglect the minus sign, the ethane has a smaller value than methane. On the other hand, enrichment of ^{13}C isotope in compounds with triple bonds is more than single bonds compounds with same number of elements. Indexes introduced by FTIR data represent the relative amounts of specific compounds in asphaltene. For example, aliphatic index represent amount of aliphatic compound in asphaltene. So according

Table 2. Selected saturate and aromatic biomarker ratios for samples were investigated in this study

Samples	DBT/Phenanthrene	Pristane/Phytane	C29H/C30H	C35HS/C34HS	Steranes/Terpanes	Gam/C31HR	C30DiaH/C30H	C29H/C30H	C28BNH/C30H	C24Tet/C23t	C26t/C25t	C24t/C23t	C22t/C21t	C19t/C23t	C27 Dia/(Dia + Reg)	Ts/(Ts + Tm)	MPI-1	MPI-2
FY	2.28	0.77	1.36	1.15	0.17	0.00	0.03	1.36	0.02	1.37	0.48	0.29	0.94	0.25	0.01	0.30	0.78	0.99
DY	2.92	0.64	1.53	1.01	0.16	0.04	0.01	1.53	0.01	1.51	0.38	0.25	1.09	0.17	0.10	0.19	0.65	0.89
BS	0.90	0.86	0.57	1.03	0.38	0.30	0.04	0.57	0.06	0.72	0.51	0.60	0.38	0.08	0.54	0.40	0.81	0.83
HS	0.98	0.68	1.00	0.85	0.29	0.37	0.03	1.00	0.03	1.32	0.63	0.53	0.58	0.26	0.36	0.34	0.80	1.03

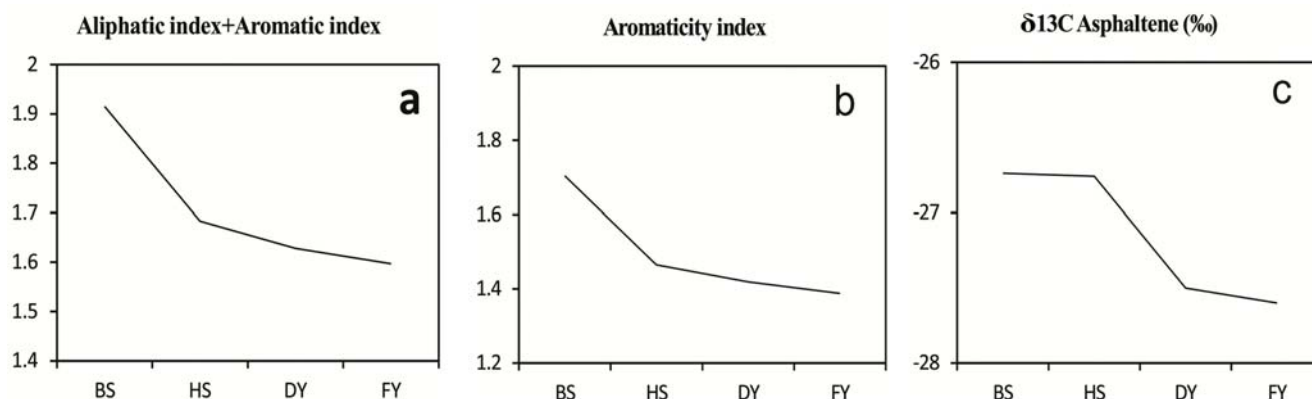


Fig. 3. (a) Aromatic and aliphatic indexes summations for different asphaltene samples, (b) aromatic index for different asphaltene samples, (c) stable carbon isotopic ratio for different asphaltene samples. The comparison of an aromatic index with stable carbon isotopic ratio shows that the isotopic ratio becomes less negative as the aromatic index increases.

these facts, if relative amounts of aromatics compound in first asphaltene sample is more than second sample, the relative value of isotope (with neglecting minus sign) in first sample is less than second sample. Different indexes were compared with isotope data of asphaltenes and summation of aromatic and aliphatic indexes showed a logical relationship with the isotopic data of asphaltenes (Fig. 3). This figure illustrates that when the value of aromatic and aliphatic indexes summations increase, the value of the isotope ratio becomes large (with neglecting minus sign) and aromatic and aliphatic compounds in the asphaltene structure could have the most significant effect on the relative value of the isotopic ratio. In other measures, the value of aromatic index solely was compared with the isotopic ratio value (Fig. 3b). This figure also shows the relationship that observed in Figure 3a. Finally, it can be deduced that the aromatic and aliphatic compounds are the most abundant structures in asphaltenes, and the aromatic compounds have a greater abundance than aliphatic compounds (i.e., the aromatic compounds have a more effect on the isotope ratio) and other compounds have less frequency than these compounds, because, have little effect on isotope value.

According above, structural characteristics of asphaltene samples were compared with each other based on aromatic and aliphatic compounds. These results are completely compatible with the structures proposed for asphaltenes in the literature. Indeed, the aromatic compounds form the core of the asphaltene samples, and the aliphatic compounds, form a side branches of the aromatic cores. These facts indicate that asphaltene structural similarity should be taken based on aromatic and aliphatic compounds.

The aliphatic index and long chain index represent amount of aliphatic compounds. The first index indicate the relative amount of whole aliphatic compounds in asphaltenes and long chain index indicate the aliphatic compounds with straight chain alkanes with 4 or more carbon atoms in asphaltenes. The cross plot of long chain index vs. aliphatic index was used

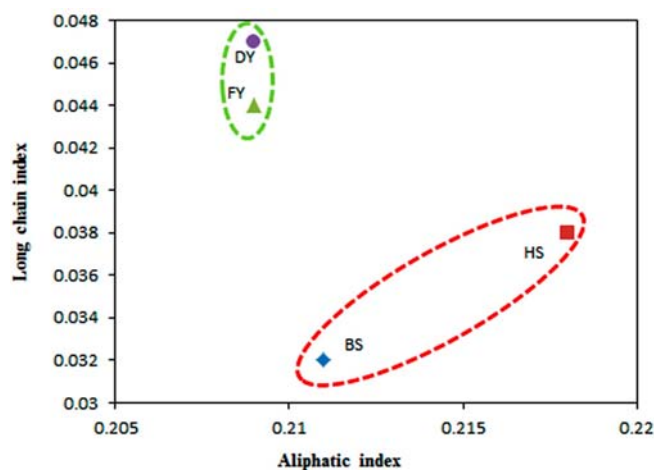


Fig. 4. The long chain index vs. aliphatic index for different asphaltene samples to compare asphaltene structures based on aliphatic compounds.

for comparing asphaltene structures based on aliphatic compounds (Fig. 4).

The aromatic, substitution 1 and substitution 2 indexes represent relative amount of aromatic compounds in asphaltenes. The relative amount of aromatic compounds in asphaltene can be seen in aromatic index. The substitution 1 and substitution 2 indexes indicate benzene structures that share one and three H with other structures, respectively. Actually, substitution 1 and substitution 2 indexes represent condensation degree of poly-aromatic compounds, which present in the nuclei of asphaltenes. The cross plots of substitution 1 and substitution 2 vs. aromatic index were used to compare asphaltene structures with regard to aromatic compounds (Fig. 5).

According to the similarity in relative amount of aliphatic compounds in long chain index vs. aliphatic index crossplot, there are two oil families. The first family including Foroozan (FY) and Dorood (DY) samples and the second family including Bahregansar (BS) and Hendijan (HS) samples (Fig. 4). For

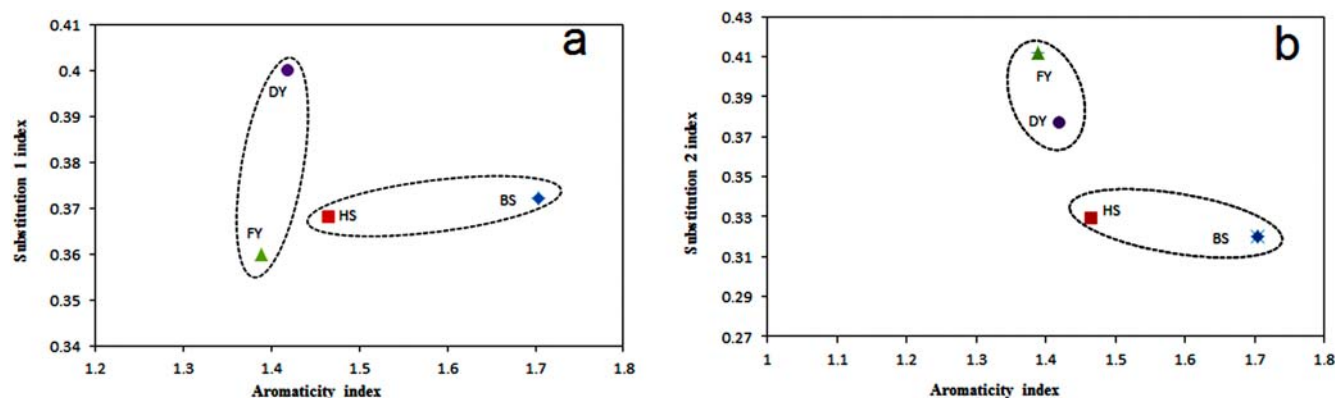


Fig. 5. Comparison of asphaltene structures based on aromatic compounds. (a) Substitution 1 index vs. aromatic index; (b) Substitution 2 index vs. aromatic index for different asphaltene samples.

comprehensive comparison, aromatic compounds should also be considered. Figure 5 illustrates aromatic compounds comparison, and this figure shows the same results as does Figure 4. These defined oil families, whose members have a similar asphaltene structure, have same genetic relationships, and each family has its own specific source rock. To validate and complement the obtained results, the other common geochemical techniques were used. These techniques are carbon isotope ratios and biomarker parameters.

Carbon isotope ratios depend on the depositional environment, type of kerogen, migration pathways as well as oil types and the age of the source rocks. They can be used to determine a genetic relationship between numbers of oil samples (Galimov, 1973; Galimov, 1985; Rabbani and Galimov, 2000; Galimov and Rabbani, 2001; Rabbani and Kamali, 2005; Rabbani, 2008; Rabbani et al., 2014). Table 3 shows the bulk composition of the studied oils in terms of NSO, saturates, aromatics, API and stable carbon isotopes. The lowest content of asphaltene compounds (3.1%) were monitored in the Foroozan crude oil with 37.3° API, whereas the other oil samples with an API gravity of (21.7–25°) show total content of asphaltene fraction of about 6.4–14.8%. The content of the polar fraction of the crude oils does not exceed 29.6% (Fig. 6). Saturated and aromatic hydrocarbon $\delta^{13}\text{C}$ values range from -27.40‰ to -28.33‰ and -27.20‰ to -27.63‰ , respectively, suggesting that all the oils were derived from algal dominated marine organic matter. The shapes and trends of stable carbon isotope type curves (Stahl, 1977), can be used to identify the relationship between different crude

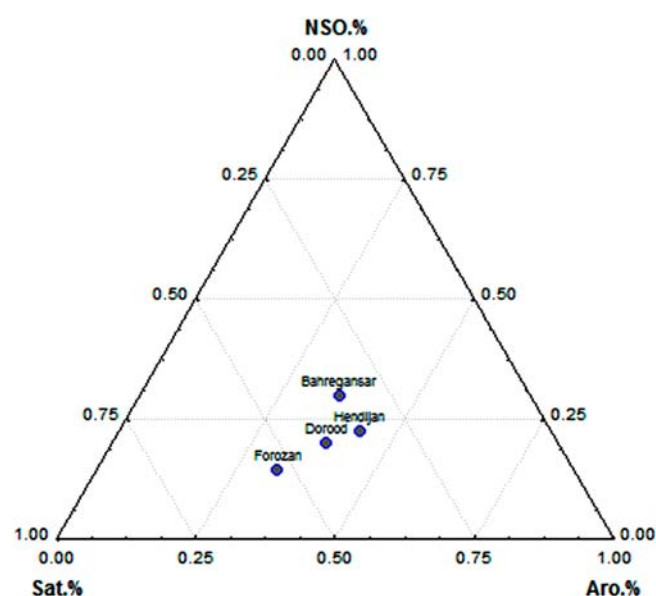


Fig. 6. Ternary diagram showing the compound class distribution of the studied crude oils.

oils. The isotopic curves of the studied saturate, whole oil, aromatic, resin and asphaltene fractions were used for correlation and comparing with results of asphaltenes FTIR spectroscopy (Fig. 7).

The similarity in trend of isotope ratios suggests the similar genetic relationships. Figure 7 illustrates two oil families that each family has a similar trend. The first family included

Table 3. Bulk oil composition, API gravity, GC and carbon isotope data for crude oil samples

Samples	Oil Field	Reservoir	API	Sat. (%)	Aro. (%)	Res. (%)	As. (%)	Stable carbon isotopes, $\delta^{13}\text{C}$ (‰)				
								Sat.	Oil	Aro.	Res.	Asp.
BS	Bahregansar	Sarvak	21.8	34.40	36.00	14.80	14.80	-28.30	-27.60	-27.30	-27.10	-27.20
HS	Hendijan	Sarvak	21.7	34.20	43.30	16.20	6.30	-27.60	-27.50	-27.40	-27.20	-27.50
DY	Dorood	Yamama	25	41.6	38.6	12.2	7.6	-27.4	-27.2	-27.2	-26.9	-27.5
FY	Foroozan	Yamama	37.3	53	32.5	11.4	3.1	-27.2	-27.2	-27.2	-27.2	-27.6

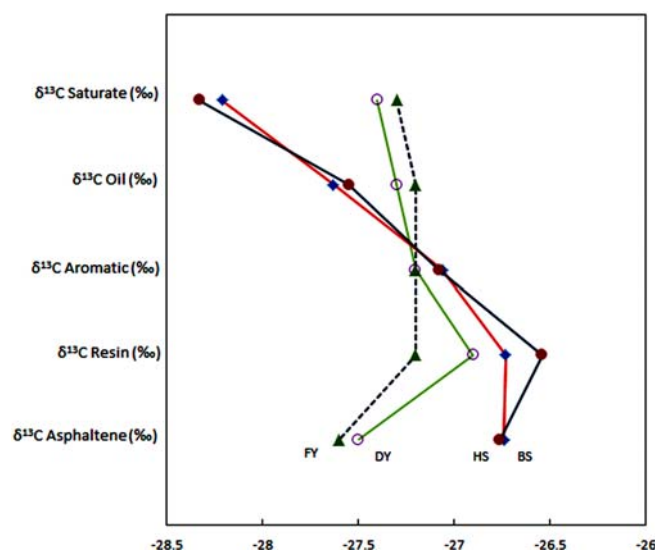


Fig. 7. Galimov curves for different oil samples. According to trend similarity, the figure shows two oil families.

Foroozan (FY) and Dorood (DY) samples and the second family included Bahregansar (BS) and Hendijan (HS). So, members of each oil family are genetically related and have

its own specific source rock. These Results are completely equivalent with FTIR technique. So, these oil samples are belong to two oil families.

The other common techniques in geochemical studies are biomarker parameters that were applied in this paper. Biomarkers are complex molecular fossils derived from once living organisms (Peters et al., 2005). Because these biological markers can be measured in oils as well as in source rock bitumen, they provide a tool to correlate oil families and to relate oils with source rocks. Thus biomarkers provide information on the organic matter in the source, environmental conditions during deposition and burial, thermal maturity experienced by a source rock or crude oil, degree of biodegradation, and sometimes the age of organic matter (Peters et al., 2005).

DBT/Phenanthrene vs. Pristane/Phytane and Steranes/Terpanes vs. C27Dia/(Dia + Reg) cross plots that are standard established curves in geochemical studies, was used for diagnosing the depositional environment and source rock lithology (Fig. 8). Biomarker parameters indicate that the studied oils belong to two main genetic groups. The Figures 8a and b show that the Foroozan (FY) and Dorood (DY) samples originated from carbonate source rock deposited in an

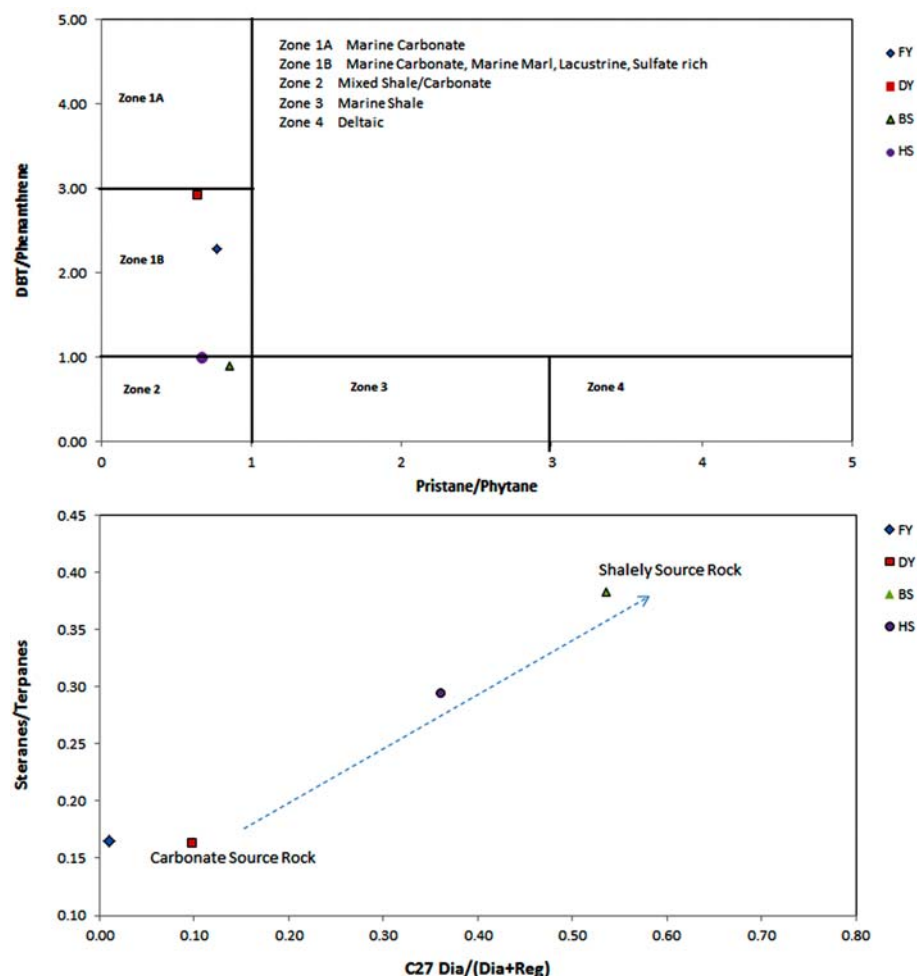


Fig. 8. Cross plot of dibenzothiophene/phenanthrene (DBT/P) vs. pristane/phytane (Pr/Ph) ratio and Steranes/Terpanes vs. C27 Dia/(Dia + Reg) for studied oil samples from the NW of the Persian Gulf.

anoxic environment, while the Bahregansar (BS) and Hendijan (HS) samples originate from marine or calcareous shaley source rock. These results are completely similar with results of isotope data and FTIR spectroscopy of asphaltene samples. In order to final validation and complementation, the star diagram technique were applied.

One of the most common techniques for correlation is using different biomarker parameters in polygon curves that called a star diagram. Figure 9 shows star diagrams for the samples that were investigated in this study. Star diagrams using

biomarkers ratios (Steranes/Terpanes, Gam/C31HR, C29H/C30H, C24Tet/C23t, C24t/C23t, C22t/C21t, and C19t/C23t) show that relative amount of these parameters make a shape that are similar for same genetic samples. The shape of star diagrams for Foroozan (FY) and Dorood (DY) samples are the same and Bahregansar (BS) and Hendijan (HS) are also similar. So, the same two oil families determined that was resulted from other techniques like FTIR spectroscopy of asphaltenes, Isotope data, and biomarker parameters (Fig. 9).

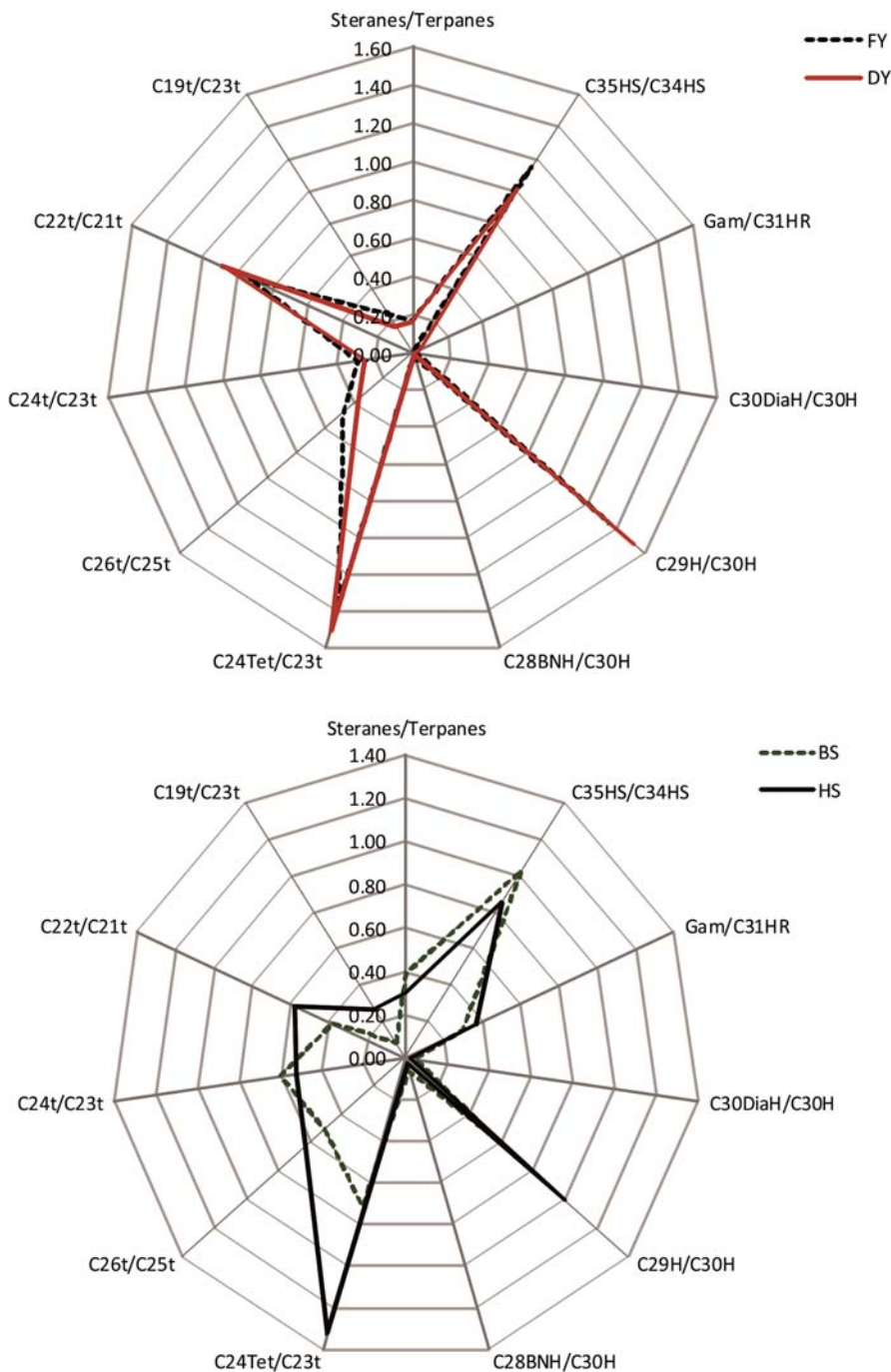


Fig. 9. Star diagrams of different oil groups in the studied area.

5. CONCLUSION

In this paper, structural characteristics of asphaltenes was considered as a parameter for correlation of crude oils and from this point have several advantageous like structure similarity with kerogene and unaffected and/or little affected by secondary process (e.g., migration, biodegradation, thermal maturity, and so on). One of the simplest ways for asphaltene structural characterization is FTIR technique, which, was employed in this paper and reliable information from structural characteristics of asphaltene was resulted. The resulted data by FTIR enabled us to perform crude oil correlation. To validation and complementation, the other common geochemical techniques (e.g., stable carbon isotope and biomarkers) were employed. According results of three techniques (e.g., FTIR spectroscopy, carbon isotope data, and biomarkers data), the investigated crude oil samples from different oil fields in the Persian Gulf show that these oils comprise two independent oil families. The first oil family consists of the Dorood and Foroozan oil samples, and the second oil family consists of the Bahregansar and Hendijan samples. So, we can introduce the FTIR spectroscopy of asphaltene samples as a new technique to performing geochemical correlation.

REFERENCES

- Alavi, M., 2004, Regional stratigraphy of the Zagros Fold-Thrust Belt of Iran and its proforeland evolution. *American Journal of Science*, 304, 1–20.
- Bazin, D. and Gucci, L., 2001, Soft X-ray absorption spectroscopy in heterogeneous catalysis. *Applied Catalysis A: General*, 213, 147–162.
- Behar, F. and Pelet, R., 1985, Pyrolysis-gas chromatography applied to organic geochemistry: Structural similarities between kerogens and asphaltenes from related rock extracts and oils. *Journal of Analytical and Applied Pyrolysis*, 8, 173–187.
- Coplen, T.B., 1994, Reporting of stable hydrogen, carbon, and oxygen isotopic abundances. *Pure Applied Chemistry*, 66, 273–276.
- Derrick, M.R., Stulik, D., and Landry, J.M., 1999, *Infrared Spectroscopy in Conservation Science*. The Getty Conservation Institute, Los Angeles, 235 p.
- Di Primio, R., Horsfield, B., and Guzman-Vega, M.A., 2000, Determining the temperature of petroleum formation from the kinetic properties of petroleum asphaltenes. *Nature*, 406, 173–176.
- Doumenq, P., Guiliano, M., and Kister, M.K., 1991, Approche méthodologique directe et continue du processus d'oxydation des bitumes par spectroscopie infrarouge à transformée de Fourier. *Analytica Chimica Acta*, 242, 137–141.
- Engel, M.H. and Macko, S.A., 1993, *Organic geochemistry: principles and applications*. Plenum Press, New York, 861 p.
- Field, L.D., Sternhell, S., and Kalman, J.R., 2008, *Organic Structures from Spectra* (Fourth edition), John Wiley & Sons Ltd., Chichester, 453 p.
- Galimov, E.M., 1973, *Carbon isotopes in oil-gas geology*. National Aeronautics and Space Administration, Washington, D.C., 395 p.
- Galimov, E.M., 1985, *The Biological Fractionation of Isotopes*. Academic Press, Orlando, 261 p.
- Galimov, E.M. and Rabbani, A.R., 2001, Geochemical characteristics and origin of natural gas in southern Iran. *Geochemistry International*, 39, 780–792.
- Ghazban, F., 2007, *Petroleum geology of Persian Gulf*. Tehran University and National Iranian Oil Company, Tehran, 707 p.
- Griffiths, P.R. and de Haseth, J.A., 2007, *Fourier Transform Infrared Spectrometry* (Second edition). Wiley-Interscience, Hoboken, 529 p.
- Groenzin, H. and Mullins, O.C., 2000, Molecular Size and Structure of Asphaltenes from Various Sources. *Energy & Fuels*, 14, 677–704.
- IP 143/01, 2012, Standard Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products. ASTM International, United States of America.
- Koots, J.A. and Speight, J.C., 1975, Relation of Petroleum Resins to Asphaltenes. *Fuel*, 54, 182–188.
- Lehne, E., 2008, *Geochemical study on reservoir and source rock asphaltenes and their significance for hydrocarbon generation*. Ph.D. Thesis, Technische Universität Berlin, Berlin, 255 p.
- Mayo, D.W., Miller, F.A., and Hannah, R.W., 2003, *Course notes on the interpretation of infrared and Raman spectra*. John Wiley & Sons, Inc., New Jersey, 567 p.
- Pavia, D.L., Lampman, G.M., Kriz, G.S., and Vyvyan, J.A., 2009, *Introduction to Spectroscopy* (4th Edition). Brooks/Cole Publishing Company, Belmont, 656 p.
- Permanyer, A., Douifi, L., Dupuy, N., Lahcini, A., and Kister, J., 2002, FTIR and SUVF spectroscopy as an alternative method in reservoir studies: Application to Western Mediterranean oils. *Fuel*, 84, 159–168.
- Permanyer, A., Douifi, L., Lahcini, A., Lamontagne, J., and Kister, J., 2005, FTIR and SUVF spectroscopy applied to reservoir compartmentalization: a comparative study with gas chromatography fingerprints results. *Fuel*, 81, 861–866.
- Permanyer, A., Rebufa, C., and Kister, J., 2007, Reservoir compartmentalization assessment by using FTIR spectroscopy. *Journal of Petroleum Science and Engineering*, 58, 464–471.
- Peters, K.E., Fraser, T.H., Amris, W., Rustanto, B., and Hermanto, E., 1999, *Geochemistry of crude oils from Eastern Indonesia*. American Association of Petroleum Geologists Bulletin, 83, 1927–1942.
- Peters, K.E., Walters, C.C., and Moldowan, J.M., 2005, *The biomarker guide*. Volume 2, Biomarkers and isotopes in petroleum systems and Earth history (Second edition). Cambridge University Press, Cambridge, p. 475–1155.
- Pelet, R., Béhar, F., and Monin, J.C., 1986, Resins and asphaltenes in the generation and migration of petroleum. *Organic Geochemistry*, 10, 481–498.
- Rabbani, A.R. and Galimov, E.M., 2000, Geochemical identification of oil source formations in southern Iran. *Geochemistry International*, 38, 1198–1206.
- Rabbani, A.R. and Kamali, M.R., 2005, Source rock evaluation and petroleum geochemistry, offshore SW Iran. *Journal of Petroleum Geology*, 28, 413–428.
- Rabbani, A.R., 2008, Geochemistry of crude oil samples from the Iranian sector of the Persian Gulf. *Journal of Petroleum Geology*, 31, 303–316.
- Rabbani, A.R., Kotarba, M.J., Baniasad, A.R., Hosseiny, E., and Wieclaw, D., 2014, Geochemical characteristics and genetic types of the crude oils from the Iranian sector of the Persian Gulf. *Organic Geochemistry*, 70, 29–43.
- Silverstein, R.M., Webster, F.X., and Kiemle, D.J., 2005, *Spectrometric identification of organic compounds* (7th Edition). John Wiley & Sons, Ltd, New York, 502 p.
- Soleimany, B., 2010, *Reactivation of deep seated folds in northwest Persian Gulf*. Ph.D. Thesis, University of Barcelona, Barcelona, 242 p.

- Spiecker, P.M., Gawrys, K.L., Trail, C.B., and Kilpatrick, P.K., 2003, Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 220, 9–27.
- Stahl, W.J., 1977, Carbon and nitrogen isotopes in hydrocarbon research and exploration. *Chemical Geology*, 20, 121–149.
- Stuart, B., 2004, *Infrared spectroscopy: fundamentals and applications*. John Wiley & Sons Ltd., Chichester, 224 p.
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