

SIGNIFICANCE OF SPECTROSCOPIC CHARACTERIZATION FOR DETERMINING DEPOSITIONAL ENVIRONMENT OF ORGANIC MATTER IN SOME DEVONIAN SHALE

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Abstract

The aim of this paper is to show the possibilities of applying the quick FTIR molecular vibrational spectroscopy with ATR technique and UV-Vis spectroscopy to determine the depositional environment of organic matter in shale with its infrared and ultraviolet spectra. The technique is employed for 20 shale rock samples of the Timah Tasoh (TT) formation (Lower Devonian), which was collected from the Sanai Hill A located at Kampung Guar Jentik, Beseri District, Perlis, Malaysia. Spectroscopic characterization was carried out to explore the hydrocarbon distribution and type of humic substances present in these shales. The FTIR spectra of the shale samples from TT formation are divided into three zones, -OH groups stretching vibration, Alkyne C-H bending bands in aliphatic hydrocarbons and the absorption spectrum of aromatic OPCH stretching and aromatic IPCH stretching bands. In this paper, particular attention is devoted to the OPCH bending vibrations between 690 and 900 cm^{-1} . The absorbance values of aromatic OPCH, in shale of TT formation, is in the range of 0.11-0.19. In terms of the E4/E6 ratio which was treated with methanol and DCM, TT formation shows the dominance of humic acid within the samples. The E4/E6 ratio treated with methanol and DCM in TT Formation ranges from 0.78 to 1.31 and 0.98 to 1.67 respectively. Alkyl naphthalenes have found in all samples of FTIR spectra at 690 cm^{-1} (w), 775 cm^{-1} (s), 795 cm^{-1} (s) and 832 cm^{-1} (w) bands in OPCH bending vibrations, suggesting their sourcing mainly from terrestrial organic matter. Humic acid presence in TT formation shale supports the FTIR results and indicates that the organic matter in these shales contains plant derived hydrophilic minerals i.e. terrestrial in origin.

Keywords: *Spectroscopy; Depositional environment; Organic matter; Shale; Humic acid.*

1. Introduction

FTIR spectroscopy is a frequently used technique capable of differentiating the hydrocarbon functional group in shale or coal [1]. The functional groups of aromatic and aliphatic hydrocarbons can be determined. This can be done through the vibrational characteristics of their structural, chemical bonds. The use of ATR accessories, by those using very hard crystals (like germanium, silica, zinc selenide and diamond) characterized by their range of hardness values and optical properties, has further advanced the use of FTIR in soils, shale, and coal [2]. Dilution with KBr is no longer necessary, reproducibility is increased, and the nondestructive nature of this analysis allows the sample to be re-used for other analyses. Like FTIR, UV-Vis is increasingly employed for in-field applications [3-5] for laboratory studies of crude oils and in determining the type of humic substance [6-7]. For the organic chemist, UV-Vis is mostly concerned in conjugated systems with electronic transitions; the intensities and positions of the absorption band largely depend on the specific system under consideration [8].

Alkyl naphthalenes are widespread constituents of geological and geochemical materials. They are commonly found in oils and various types of sedimentary rocks such as shales and coals [9-12]. It has been suggested that alkyl naphthalenes are derived mainly from the de-functionalization of terpenoids, so they have the potential to provide information about their

precursor, as well as depositional environment [9-15]. However, the presence of the alkyl naphthalenes by using FTIR spectra in shale rocks has not been commonly carried out. In the present study, shales were collected from the Timah Tasoh (TT) Formation located at Sanai Hill. There is a lack of data available on literature that focused on the spectroscopic characterization of the shales in the TT formation. Furthermore, spectroscopic methods such as UV-Vis and ATR-FTIR have been used in the evaluation of liquid petroleum yield of hydrocarbon source rocks [16-18]. However, the spectroscopic analysis used for the origin of organic matter in the source or reservoir rocks have received very little attention to date. Therefore, the objective of the present study is to use spectroscopic analysis and obtain the hydrocarbon distribution and humic substance type, which will determine the source depositional environment of organic matter in shale.

2. Study area

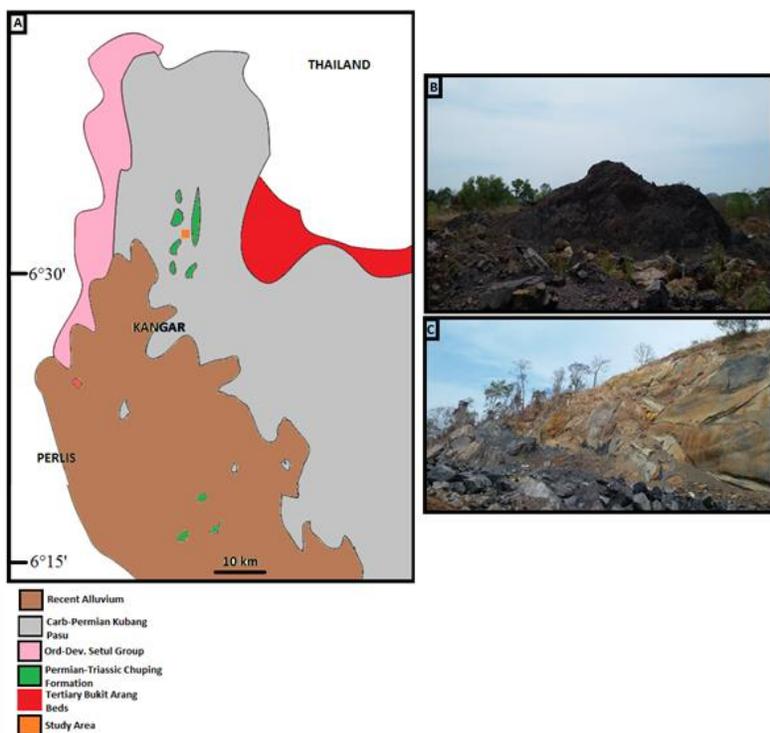


Figure 1. Study area. (A) General Geological Map of Perlis. (B,C) Timah Tasoh Shale beds from Kampung Guar Jentik outcrops

The Timah Tasoh Formation conformably overlies pelagic limestone of the Silurian Mempelam Limestone and ranges between 5 to 40 m in thickness. It comprises dark to mudstone, with occasional cherts. The Timah Tasoh Formation exposed at Sa-nai Hill A, B and C, Hutani Aji and Pulau Langgun, Langkawi [19-20]. In the present study shale from Timah, Tasoh formation has been collected from Sanai Hill A (Figure 1). At the North East of Hutani Lipur Bukit Ayer in Kampung Guar Jentik, Berseri District, Perlis of Peninsular Malaysia, just south of Timah Tasoh Dam, the study area is located. It is about 16 km north of Kangar. The samples were collected from the outcrop which is located at the coordinates of 6°33'18.00"N 100°12'24.00"E (Fig. 1).

3. Samples and methods

At the Timah Tasoh formation, 20 samples of shale were handpicked through channel sampling by using the method mentioned in [21] from exposures that were not weathered. All samples were ensured that weathered exposures are removed by eliminating the surface material. The rock samples were all air dried to remove any moisture present in the sample. Colors of shale are varying from medium light gray to dark. All samples were crushed into fine grains (2mm). Coning and quartering sub-sampling method were used to homogenize all of the samples; this is to ensure that the samples are homogenized and reduce bias results as well as increased the accuracy of the data [22]. These samples were then used to carry out spectroscopic characterization by using Attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR) and Ultraviolet-Visible Spectroscopy (UV-Vis).

Infrared measurements were made using a Cary 660 Series FTIR Spectrometer equipped with PIKE MIRACLE diamond attenuated total reflectance spectroscopy (ATR). Data collection

was done using the Resolutions Pro software package which was also used for background and automatic baseline correction of all spectra. Spectra were acquired at transmittance mode from 16 coadded scans between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} , then area normalized prior to further analysis. The limit of detection of the instrument is 0.08%. Background scans were collected using the same settings as the sample analyses. Replicate spectra collected on selected samples showed consistent peak positions and absorbance intensities. The data collected was further analyzed using the software called Essential FTIR. The area percentage of hydrocarbon functional groups was calculated by summing the absorbance intensities between the respected wavelength [23].

The ultraviolet-visible (UV-Vis) is used in analytical chemistry. The main purpose for UV-Vis is mainly to study the E4/E6 ratio. E4 is determined at the absorption frequency of 465 nm, and E6 is determined at the absorption frequency of 665 nm. For identifying the type of humic substance dichloromethane and dichloromethane: methanol was used as a solvent. Both chemical reagents and solvents had a high degree of purity and were used without prior purification. The spectra in the UV-VIs were obtained according to procedures described in Cunha *et al.* [24]. This study evaluated the nature of humic material by determining the E4/E6 ratio. The U.S. EPA method 3550 was used. 2.0g of each sample was weighed and treated with 8ml of methanol each. Later, 3 minutes of ultrasonic stirring was carried out followed by 5 minutes of centrifugation. The extraction of each of the 10 samples was analyzed using Shimadzu UV-3150 UV Vis Spectrophotometer by placing the liquid samples in quartz cells. The range of the scanning wavelength was 400 nm- 700 nm.

4. Results

4.1. Ultraviolet-Visible spectroscopy

It is suggested that the values of the relationship E4/E6 for humic acid are smaller than 5.0 and between 6.0 and 8.0 for fulvic acids [24]. In term of the E4/E6 ratio which was treated with methanol and DCM, TT Formation shows the dominance of humic acid within the samples (Table 1). The value of E4 and E6 that are treated with methanol and DCM are range from 0.05 to 2.91, 0.04 to 2.73 and 0.08 to 1.98, 0.06 to 2.22 respectively. Almost equal values of E4 and E6 also indicate the presence of humic acid in TT Formation. The E4/E6 ratio treated with methanol and DCM in TT Formation ranges from 0.78 to 1.31 and 0.98 to 1.67 respectively (Table 1).

Table 1. UV-Vis results of shale from TT Formation treated with methanol and DCM

Sample	Absorbance in methanol			Absorbance in DCM			Sample	Absorbance in methanol			Absorbance in DCM		
	E4	E6	E4/E6	E4	E6	E4/E6		E4	E6	E4/E6	E4	E6	E4/E6
TT-1	2.91	2.73	1.07	0.12	0.11	1.11	TT-11	1.87	1.66	1.13	0.24	0.22	1.08
TT-2	0.14	0.11	1.26	0.22	0.13	1.67	TT-12	2.64	2.47	1.07	0.21	0.21	0.98
TT-3	0.50	0.46	1.08	0.21	0.14	1.51	TT-13	0.39	0.32	1.23	0.21	0.17	1.20
TT-4	0.10	0.08	1.21	0.23	0.23	0.97	TT-14	0.27	0.23	1.14	0.79	0.78	1.01
TT-5	0.81	0.73	1.11	0.15	0.14	1.05	TT-15	0.05	0.04	1.26	0.15	0.12	1.24
TT-6	1.12	1.02	1.09	1.58	1.50	1.05	TT-16	0.05	0.04	1.31	0.13	0.11	1.23
TT-7	2.38	2.09	1.14	0.68	0.80	0.85	TT-17	0.04	0.03	1.23	0.13	0.11	1.24
TT-8	0.40	0.33	1.21	1.98	2.22	0.89	TT-18	0.04	0.06	0.78	0.14	0.11	1.22
TT-9	0.76	0.62	1.23	0.72	0.74	0.98	TT-19	0.11	0.09	1.19	0.08	0.07	1.26
TT-10	1.62	1.50	1.08	0.10	0.07	1.46	TT-20	0.95	0.91	1.04	0.08	0.06	1.29

4.2. Fourier transform infrared spectroscopy

The ATR-FTIR analysis was conducted to characterize the functional groups in the shale. The FTIR spectra of the shale samples from TT Formation is divided into three zones, -OH groups stretching vibration, Alkyne Aliphatic =C-H bending in Aliphatic hydrocarbons and the absorption spectrum of Aromatic In plane C-H (IPCH) bending and Aromatic out-of-plane C-H (OPCH) bending (Table 2 and Figure 2).

Table 2. Functional groups identified through FTIR spectra of the shale in the TT formation

Samples	Alkyne APH 700–600 =C–H bend- ing Absorbance	Aromatic bending 900–690 Out-of-plane C–H bending Absorbance	Aromatic bending 1275–1000 In-plane C–H bending Absorbance	Aromatic C=C stretch- ing 1430-1650 Absorbance	-OH Stretching 3600-3000 Absorbance
TT-1	0.069	0.112	0.159	0.011	0.015
TT-2	0.098	0.153	0.225	0.013	0.020
TT-3	0.150	0.182	0.266	0.016	0.023
TT-4	0.134	0.173	0.247	0.010	0.016
TT-5	0.097	0.129	0.195	0.007	0.014
TT-6	0.145	0.191	0.268	0.013	0.018
TT-7	0.133	0.171	0.253	0.020	0.015
TT-8	0.142	0.177	0.251	0.016	0.018
TT-9	0.141	0.162	0.234	0.017	0.018
TT-10	0.155	0.197	0.280	0.020	0.023
TT-11	0.162	0.195	0.274	0.021	0.024
TT-12	0.134	0.144	0.210	0.018	0.021
TT-13	0.147	0.179	0.252	0.020	0.018
TT-14	0.119	0.127	0.202	0.023	0.015
TT-15	0.089	0.158	0.225	0.037	0.020
TT-16	0.104	0.191	0.266	0.034	0.021
TT-17	0.069	0.131	0.302	0.120	
TT-18	0.098	0.125	0.262	0.133	
TT-19	0.150	0.158		0.037	
TT-20	0.134	0.191		0.034	

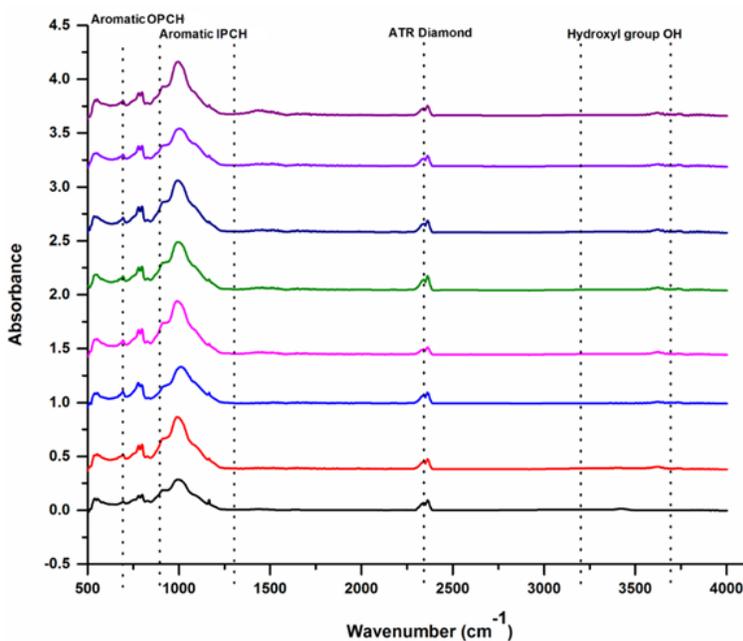


Figure 2. FTIR spectra of few shale samples from the TT Formations in the wavenumber 4000-500 cm^{-1} , showing the Aromatic OPCH bending bands, Aromatic IPCH bending bands, ATR Diamond and -OH stretching bands



The critical region of the infrared spectrum for assessing alkyne C-H bending bands in aliphatic hydrocarbon is 600-700 cm^{-1} . Aromatic OPCH bending appears in the regions 900–690 cm^{-1} and Aromatic in plane C-H bending observed in the region of 900-1250 cm^{-1} . Intensity peak of free OH-compounds is detected in the region of 3700–3200 cm^{-1} [25-28]. All samples of shale in TT Formation contains alkyne C-H bending bands, aromatic in plane C-H bending and Aromatic OPCH bending (Figure 2). The absorbance values of aromatic OPCH, aromatic IPCH and aromatic C=C stretching in shale of TT Formation are in the range of 0.11-0.19, 0.15-

0.30 and 0.007-0.133 respectively (Table 2). Only one aliphatic hydrocarbon functional group (Alkyne APH) has identified through FTIR spectra. The absorbance values of Alkyne APH in shale of TT Formation is in the range of 0.069-0.162 (Table 2). This study is focused on aromatic hydrocarbons to determine the source depositional environment of organic matter. Therefore, particular attention is given to Aromatic OPCH bending bands.

5. Discussion

5.1. Humic acid and its relation to the source of organic matter

Humic acid is one of the organic constituents of oil shale. It has been considered to be a major kerogen precursor, which in turn can be a major petroleum precursor [29]. Humic acid deposited in shale as the death of thick growth of vegetation, it accumulated in large piles, and as geological time passed, it was buried from rock and mudflows and deposits of sand and silt. The weight of the overflow compacted or compressed out all the moisture, and what remains today is a deposit of dried, prehistoric plant derivatives. Therefore, the presence of humic acid in TT formation shale indicates that these shales contain plant derived hydrophilic minerals which are very small in size compared to metallic minerals which come from the ground up rocks and soil. It is suggested that a higher degree of aromaticity of humic acid in shale was evidenced by lower E4/E6 ratio [24]. Therefore, we predicted that four samples (TT-15-18) of TT formation, which shows relatively low absorbance values of E4/E6 (Table 2), indicating the degree of aromaticity is much higher in these samples as compared to other samples.

5.2. Alkyl Naphthalenes and its relation to the source of organic matter

Some of the aromatic compounds found in crude oils and sediments are believed to have been derived from a modification of biologically produced compounds such as steroids and terpenoids. Steroids give rise to substituted phenanthrenes, and terpenoids appear to produce alkylnaphthalenes. The processes by which higher plant triterpenoids in sediments are converted into aromatic hydrocarbons have been proposed to commence with loss of the C-3 oxygen functionality, followed by sequential aromatisation from the A ring through to the E ring the ultimate products of this process would, therefore, be tetracyclic and pentacyclic aromatic hydrocarbons [30]. Alkyl naphthalenes are derived from various precursor compounds and their composition change with increasing thermal maturity. However, alkyl naphthalenes are often abundant in oils and sedimentary organic matter which have undergone biodegradation or thermal cracking. Alkyl naphthalenes generally occur in terrestrial oils and rocks in higher concentrations than in marine oils and rocks, suggesting their sourcing mainly from terrestrial organic matter [31].

5.3. The 700-900 cm^{-1} region

Usually, aromatic hydrocarbons are dominated by the OPCH ($700\text{-}900\text{ cm}^{-1}$) bend vibrations [32-33]. Correlations for substituted benzene rings may be applied to polynuclear aromatic compounds, but the known absorption regions for the OPCH bending vibrations must be broadened. The ranges are as follows: 4 adjacent hydrogens--($720\text{-}780\text{ cm}^{-1}$), 3 adjacent hydrogens--($780\text{-}800\text{ cm}^{-1}$), 2 adjacent hydrogens--($800\text{-}910\text{ cm}^{-1}$), 1 hydrogen--($860\text{-}910\text{ cm}^{-1}$). Although the pattern is fairly complex, these bands can be identified as the strongest in this region. Weak and medium bands are no indication as to the type of substitution. The absorption bands of the studied shale in this region are listed in Table 3 [34].

Naphthalenes substituted in the 1-position showed a doublet at 800 and 780 cm^{-1} which can be attributed to three and four adjacent hydrogen atom vibrations. When substituents are in the 2-position, the expected band at 900 cm^{-1} for a single hydrogen atom is weak. The 900 cm^{-1} band varies in strength with the number of single hydrogen atoms present and is very strong when they are in the 9,10-position [35].

Table 3. Distribution of aromatic out of plane banding bonds in TT shale samples

Sample	Data	Aromatic out of plane banding			
		Pentylnaphthalene (C ₁₅ H ₁₈)			
TT-1	Wavenumber (cm ⁻¹)	694.74	778.97	798.11	827.52
	Absorbance	0.08	0.14	0.14	0.09
TT-2	Wavenumber (cm ⁻¹)	694.39	778.82	797.80	827.17
	Absorbance	0.11	0.19	0.20	0.12
TT-3	Wavenumber (cm ⁻¹)	694.46	778.78	797.39	827.17
	Absorbance	0.13	0.23	0.25	0.14
TT-4	Wavenumber (cm ⁻¹)	694.07	778.70	797.23	827.37
	Absorbance	0.14	0.22	0.23	0.12
TT-5	Wavenumber (cm ⁻¹)	693.24	777.24	795.42	829.69
	Absorbance	0.11	0.19	0.17	0.05
TT-6	Wavenumber (cm ⁻¹)	694.19	778.17	797.04	827.80
	Absorbance	0.15	0.25	0.26	0.13
TT-7	Wavenumber (cm ⁻¹)	74.06	58.53	57.34	80.05
	Absorbance	0.13	0.23	0.24	0.10
TT-8	Wavenumber (cm ⁻¹)	694.35	778.17	796.96	827.72
	Absorbance	0.13	0.23	0.24	0.12
TT-9	Wavenumber (cm ⁻¹)	694.07	778.10	796.92	827.83
	Absorbance	0.13	0.21	0.22	0.11
TT-10	Wavenumber (cm ⁻¹)	694.23	778.74	797.31	827.68
	Absorbance	0.15	0.25	0.26	0.14
TT-11	Wavenumber (cm ⁻¹)	694.23	778.66	797.23	827.52
	Absorbance	0.15	0.24	0.26	0.14
TT-12	Wavenumber (cm ⁻¹)	694.07	778.74	797.43	827.48
	Absorbance	0.11	0.18	0.19	0.10
TT-13	Wavenumber (cm ⁻¹)	694.19	777.98	796.92	828.11
	Absorbance	0.14	0.24	0.24	0.12
TT-14	Wavenumber (cm ⁻¹)	694.07	778.06	797.04	828.26
	Absorbance	0.11	0.19	0.19	0.08
TT-15	Wavenumber (cm ⁻¹)		779.01	798.54	830.76
	Absorbance		0.07	0.08	0.07
TT-16	Wavenumber (cm ⁻¹)		778.97	798.62	831.15
	Absorbance		0.08	0.09	0.08
TT-17	Wavenumber (cm ⁻¹)		777.90	797.88	830.15
	Absorbance		0.11	0.11	0.08
TT-18	Wavenumber (cm ⁻¹)		778.54	798.03	831.23
	Absorbance		0.09	0.10	0.07
TT-19	Wavenumber (cm ⁻¹)	693.96	778.58	796.88	826.37
	Absorbance	0.14	0.21	0.22	0.12
TT-20	Wavenumber (cm ⁻¹)	694.31	777.94	796.81	827.80
	Absorbance	0.16	0.27	0.29	0.14

In the present study, alkyl naphthalenes (pentylnaphthalenes) confirms by the presence of two strong and two weak bands in the OPCH (700-900 cm⁻¹) bend vibration region [34]. These are 690 cm⁻¹ (w), 775 cm⁻¹ (s), 795 cm⁻¹ (s) and 832 cm⁻¹ (w). The absorbance range of strong bands, i.e. 795 and 775 cm⁻¹ bands in TT shales between the range of 0.29-0.08 and 0.27-0.07 respectively. Weak bands of pentylnaphthalenes at 695 and 832 cm⁻¹ between the range of 0.16-0.08 and 0.14-0.05 respectively (Table 2, Fig. 3). 690 cm⁻¹ bands were absented in TT15-18 samples only (Table 2, Fig. 3). However, 710 cm⁻¹ band can be seen in these samples which show, might be 690cm⁻¹ bands were shifted due to the actual frequency shift of a single absorption band or alternatively by the relative intensity changes of overlapped bands [36]. It has also observed that the absorbance values of pentylnaphthalenes in these four samples are relatively very low as compared to all other samples (Table 2).

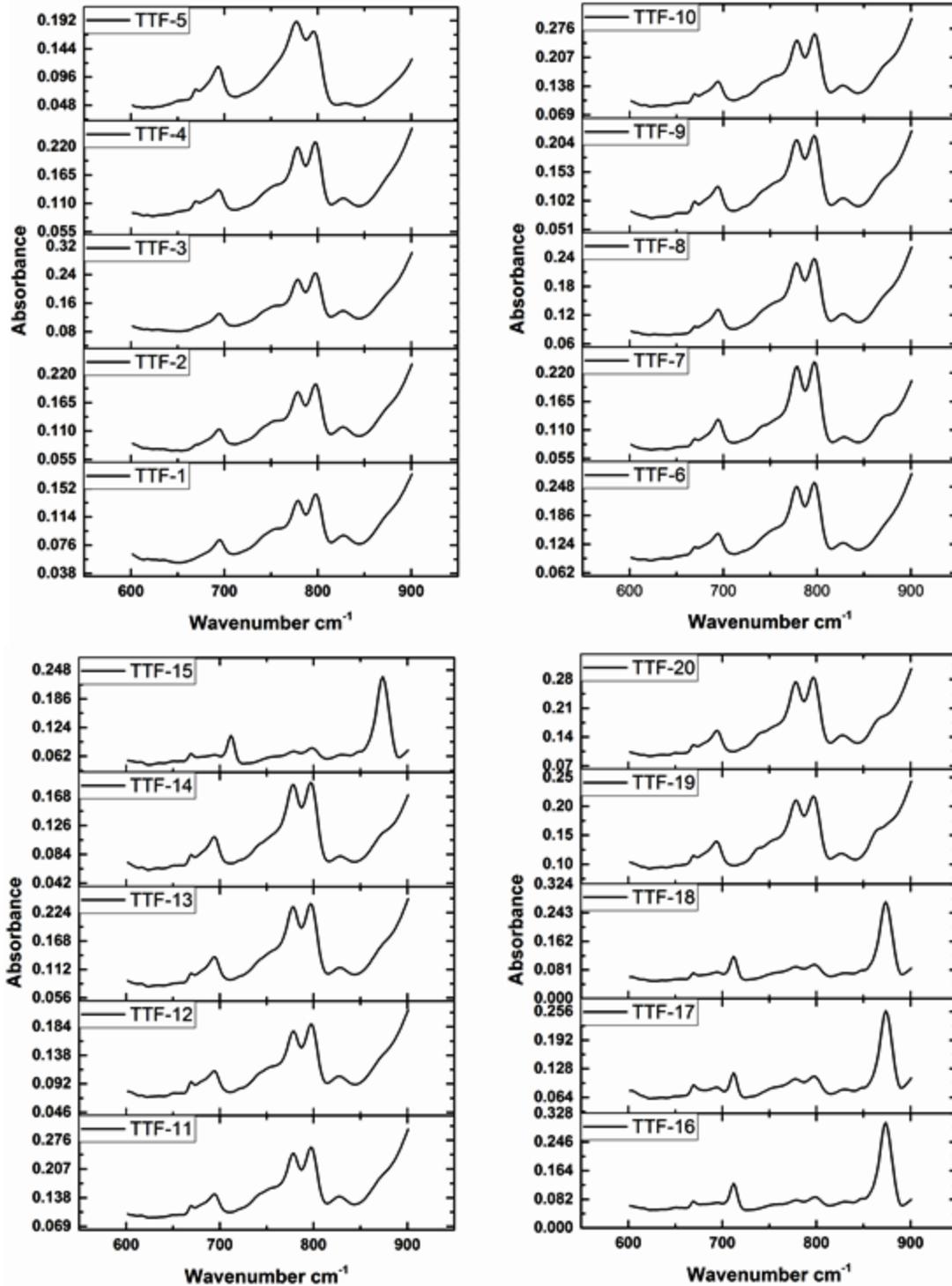


Figure 3. FTIR spectra of TT shale showing Aromatic OPCH region

6. Conclusions

The study showed the significance of spectroscopic techniques to determine the source depositional environments of organic matter in shale. Three divisions have been made in FTIR spectra of the shale samples from TT Formation: -OH groups stretching vibration, Alkyne C-H bending bands in Aliphatic hydrocarbons and the absorption spectrum of Aromatic OPCH and

Aromatic IPCH. Alkyl naphthalenes have found in all the samples of FTIR spectra at 695 cm^{-1} (w), 775 cm^{-1} (s) and 795 cm^{-1} (s) and 832 cm^{-1} (w) bands in OPCH bending vibrations, suggesting the terrestrial origin of organic matter. The E4/E6 ratio treated with methanol and DCM in TT Formation shows the dominance of humic acid. Presence of humic acid also indicates that the organic matter in these shales is terrestrial in origin. Only four samples (TT-15-18) show relatively low absorbance values of both humic acid and pentylnaphthalenes in FTIR and UV-Vis spectra.

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