

Determination of Absorption and Fluorescence Spectrum of Iraqi Crude Oil

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Abstract: The fluorescence spectroscopy (FS) is increasingly used in petroleum technology due the availability of better optical detection techniques, because FS offers high sensitivity, good diagnostic potential, and relatively simple instrumentation. Absorption and fluorescence spectrum of crude oil was studied at room temperature using optical path cuvette 1 cm. In this work, the absorption spectra were scanned (190-1100) nm while the emission spectra were obtained at different excitation wavelengths (266, 337, 420, and 488) nm. Crude oil was diluted by absolute ethanol to prepare different concentrations of crude oil. Ethanol as a solvent was used to dilute crude oil to obtain a solution transparent and the light could be transmitted. This work considers as an additional spectroscopic tool to develop into a fast responsive system for charchtrize the crude oil.

Keywords: Fluorescence Spectroscopy, Crude Oil, UV-Vis Spectroscopy

1. Introduction

Crude oil is a simply unprocessed oil found deep beneath the earth's surface. It can range in color from clear to black and can be found as a liquid or solid. Overall properties of crude oil are dependent upon their chemical composition and structure. Generally, all crude oil is made up of hydrocarbon compounds. The main hydrocarbons in crude oil are aliphatic, aromatic, and asphaltenic compounds [1].

Methods of optical absorption spectroscopy are increasingly being used for the analysis of crude oil because they offer high speed, low cost, non-contact, non-destructive testing options, desirable for environmental protection, and process control, or oil exploration purposes. The absorption behavior of crude oil strongly depends on the wavelength range employed. In particular, UV-Vis absorption of crude oils is due to the presence of a wide range of cyclic aromatic compounds, including asphaltenes, with the intensity and the spectral properties of this absorption being directly related to chemical composition [2].

Fluorescence has been extensively used in the petroleum

industry for analysis and classification of different crude oil samples. This field attempt to connect typical fluorescence parameters (intensity, emission wavelength, and lifetime) to physical characteristics of the crude oil such as chemical composition and density (API gravity) [3]. Stelmaszewski [4, 5] study the identification of oil by fluorescence method. Also, he studied the application of fluorescence in detection of petroleum pollutants, determination of oil in water concentration, determination of particular polycyclic aromatic compounds, and identification of oil contaminants. Ryder used steady state and time resolved fluorescence method to study emission spectrum of petroleum [6]. Steffens studied the fluorescence characteristics of solutions containing fixed amount of Nujol pure oil and different concentrations of Brazilian crude oil [7]. Evdokimov and Losev, analyze a possibility of UVVA characterization for fingerprinting of various types of crude oils and describe some effects of crude oil dilution on optical absorbance [8]. Goncalves employed absorption and fluorescence techniques to study aggregation process in asphaltenes solutions [9].

Ethanol C₂H₅OH, (also called ethyl alcohol), is a volatile,

colorless liquid. Nearly all the ethanol used industrially is a mixture of 95% ethanol and 5% water, which is known simply as 95% alcohol. Although pure ethyl alcohol (known as absolute alcohol) is available, it is much more expensive and is used only when definitely required [10]. When crude oil and ethanol mixed under vigorous shaking, ethanol extract hydrocarbons from crude oil while the heavy components remain at the bottom.

For the mixture, absorption in the visible range are well known and less intense than crude oil. Moreover using excitation in the visible range it is possible to access only crude oil absorption and consequently only crude oil emission. The possibility of using fluorescence to detect crude oil was reported in the early 1970s [11].

In this work, absorption and fluorescence spectra at

different excitation wavelengths of different concentrations of Al- Nassiriya crude oil were measured and identified.

2. Materials and Methods

The crude oil samples were obtained from Al- Nassiriya Oil Field to perform fluorescence and absorption measurements. It was necessary to extract crude oil to obtain a transparent solution to the incident light and for this reason ethanol was chosen as a solvent. Five crude oil samples were diluted with ethanol for the measurements, the different dilution are shown in Table 1. The chemical analysis of Al- Nassiriya oil was carried out by Oil Research and Development Center/Ministry of Oil in Iraq; the most salient data is shown in Table 2.

Table 1. Crude Oil Samples.

Sample	Ethanol (ml)	Crude Oil (ml)	Total Volume (ml)	Concentration v%
1	5	1	6	16.6
2	5	2	7	28.5
3	5	3	8	37.5
4	5	4	9	44
5	5	5	10	50

Table 2. Al- Nassiriya Crude Oil Properties.

S. No	Properties	Results	ASTM test method
1	Kin. Viscosity, cSt, 100° F (37.8°C), min	4.369	D445
2	Kin. Viscosity, cSt, 100° F (37.8°C), min		D445
3	Kin. Viscosity, cSt, 210° F (98.9°C), min	3.855	D445
4	Specific Gravity, 60° F (15.6°C), max	0.888	D1298
5	Flash point, (°C), min	22	D93
6	Distillation Temp. 90% Point, (°C), max	370	D86
7	Pour point, (°C), max	-12	D97
8	Cold Filter Plugging Point	-18	D6371
9	Ash, ppmw, max Wt%	2.2 Wi %	D482
		Total= 17.93	
10	Trace Metal Contaminants, ppmw, max	Al= 0.03 Cd= 0.15 Cu= 0.13	
11	Sodium plus Potassium	Na=0.51 ppm Ca = 4.2 ppm K= 4 ppm	See Note below
12	Lead	0.075 ppm	
13	Vanadium (untreated)	0.57 ppm	
14	Vanadium (treated 3/1 Wt. ratio Mg/V)	0.91	
15	Calcium	4.2 ppm Fe=7.2ppm Se =17.9 ppm Ni =0.02 ppm Cr =0.002 ppm Al =0.03 ppm	
16	Other Trace Metals above 5 ppmw	Zn =1.2 ppm Na =0.51 ppm K =4 ppm Cd =0.15 ppm Co =0.003 ppm Mn =0.05 ppm	
17	Filterable Dirt, mg/ 100ml, max	6.8	D2276
18	Water & Sediment, Vol. %, max	0.0	D2709/D1796
19	Water Content, Vol. %, max	0.0	D95
20	Thermal Stability, Tube No., max		D1661
21	Fuel Compatibility, Table No., max. (50/50 mix with second fuel)		D1661
22	Wax content, Wt%	2.2	D524/D189
	Wax Melting Point, °F		

S. No	Properties	Results	ASTM test method
23	Carbon Residue Wt % (10% Bottoms) max		
	Direct Pressure Atomization		
	Carbon residue, Wt. % (100% sample) max Air Atomization, Low pressure		D 524/D 189
	Carbon Residue, Wt % (100% sample), Air Atomization, High Pressure	70.46%	
	Gross Heat of combustion, Btu/lb		D 4809/D 240
24	Distillation range (Not no Residuals)	10%	D 86
		20%	C:H:N
		30%	83:11:1.02
		40%	
		50%	
		60%	
		70%	
		80%	
25	Sulfur, Wt. % max	2.1%	D 129 / D 4294
		0.49	D 5291
26	Nitrogen, Wt. %, max	29.53	D 482
27	Total ash ppm w, max.	6.8	D 5452 / D 2276
28	Filterable dirt mg/100 ml	2.5 psi	Relevant standard D323
29	Reid vapor pressure (RVP) At 37.8°C	2.6	Relevant standard
30	Asphaltene W %		

3. Apparatus

UV-Vis double beam PC scanning spectrophotometer was used for all absorbance measurements. All measurements were made at room temperature. Samples were analyzed in reduced volume by using 1 cm (1.5 mL total) quartz cuvette with ethanol blank in the reference position.

Varian Cary Eclipse fluorescence spectrophotometer was used for emission measurements. Fluorescence is measured using an excitation source placed at 90° to the detector. Excitation radiation is provided by a Xenon flash lamp. The Xenon flash lamp flashes up to 80 times per second and has a pulse width of approximately 2 to 3 microseconds. This light is then focused through a lens onto the excitation entry slit, then passes through an excitation monochromator and into the sample. The resulting fluorescence passes through an emission monochromator and is detected by a photomultiplier.

4. Results

4.1. Absorption Measurements

In Fig. 1, the absorption of ethanol was taken in order to study the spectrum of the solvent. Ethanol has an absorption band at 337 nm. The absorption spectrum of 16.6% crude oil in ethanol is shown in Fig. 2. The spectrum exhibits a maximum absorbance around 400 nm and a broad band with more than 100 nm. This represents the numerous of hydrocarbon compounds in the crude oil. The absorbance at ~ 400 nm related to $n-\pi^*$ transition indicated the double bound components in the crude oil. Figure 2 also shows the comparison between the spectra of ethanol and 16.6% crude oil. By looking to the intensity of absorbance, it is shown that the spectrum of ethanol is negligible compare to crude oil. Figure 3 shows absorption spectra of different diluted-

samples of crude oil. More dilution led to obtain higher absorbance since more light can be transmitted. However, the absorbance spectrum does not change at high concentration of crude oil (> 28.5%). For that, diluted samples less than 16.6% are preferred to study and characterize the crude oil.

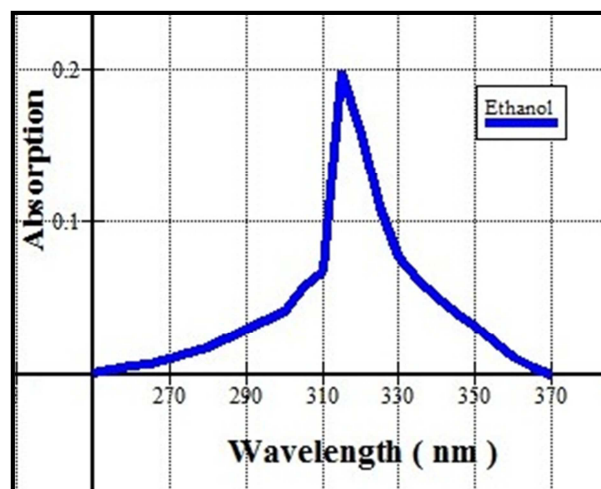


Fig. 1. Absorption spectrum of ethanol.

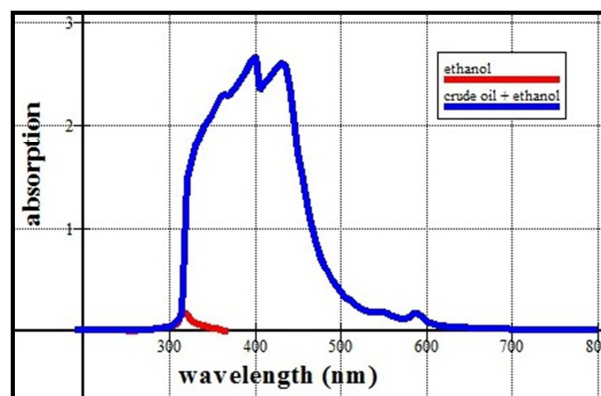


Fig. 2. Absorption spectra of crude oil diluted with ethanol and ethanol.

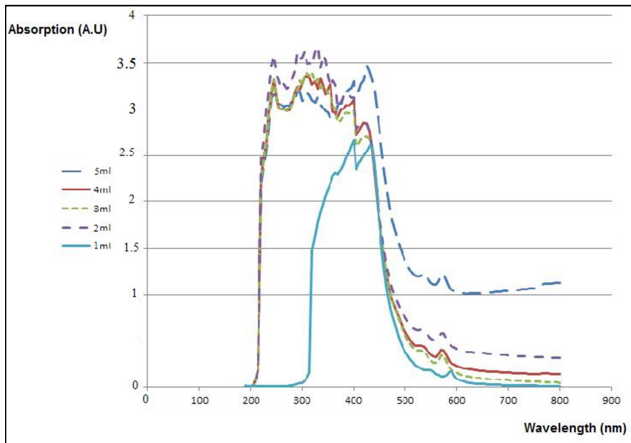


Fig. 3. Absorption spectra of different diluted-samples of crude oil.

4.2. Fluorescence Measurements

Figure 4 shows the fluorescence spectra of diluted crude oil excited at 266 nm. In this case, the emission bands around 515 nm were appeared, the emission band decrease with the increase of oil concentration.

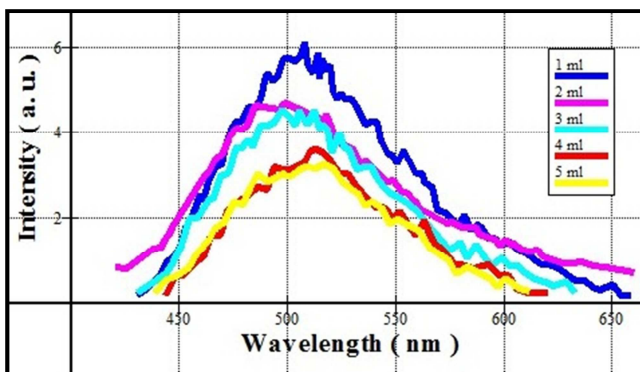


Fig. 4. Fluorescence spectra of diluted oil excited at 266 nm.

In contrast to absorbance study, the increase in oil concentration show a decrease in the emission intensity due to decreasing in the light penetration.

Fig. 5 shows the fluorescence spectra of diluted oil excited at 337 nm. In this case the emission band around 515 nm can be observed. A blue shift of 10 nm was occurred at concentration < 37.5% comparing to figure 1. This could be related to the effect of polar solvent (ethanol).

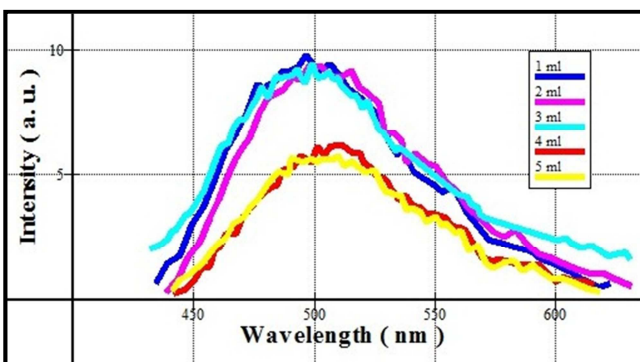


Fig. 5. Fluorescence spectra of diluted oil excited at 337 nm.

Figures 6 and 7 show fluorescence spectra of diluted oil excited at 420 and 488 nm respectively, fluorescence spectra appear around 480 and 525 nm respectively, which decrease with the increase in oil concentration. In figure 6, a blue shift of 25 nm was occurred compare to figure 4 and 5. This is in contrast of other researcher [10, 11]. On other hand, figure 7 shows a red shift of 10 nm was appeared when the oil excited at 488 nm compared to 337 and 226 nm.

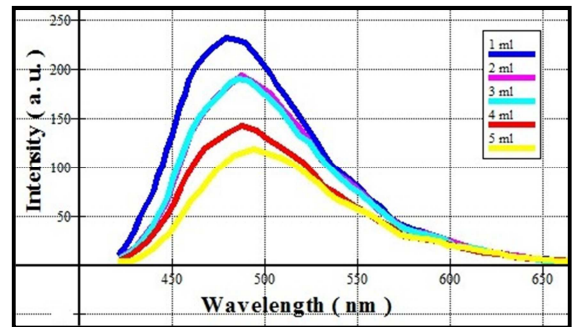


Fig. 6. Fluorescence spectra of the samples excited at 420 nm.

Energy transfer process is responsible for long wavelength shift and broadening in spectral band emission. Simultaneously a quenching process reduces emission intensity, the same effect was observed by other authors using solvents as benzene, cyclohexane and n-heptane [10].

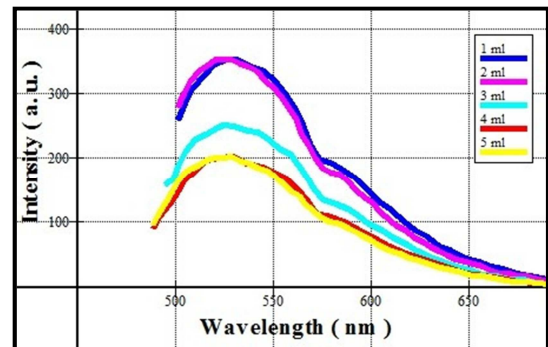
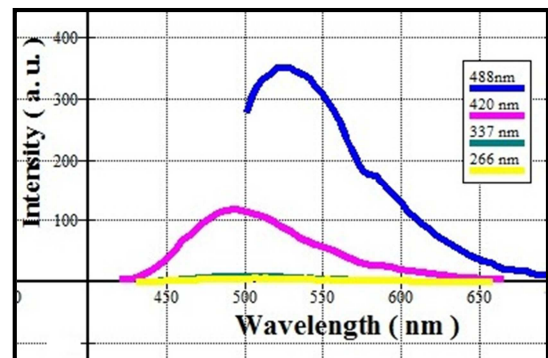
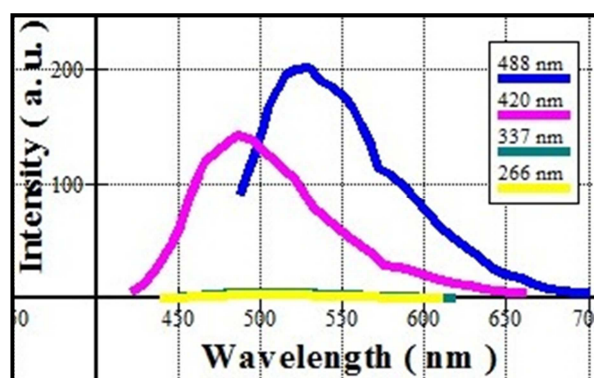


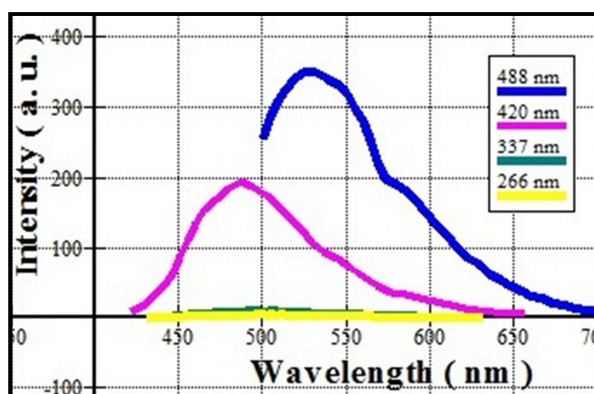
Fig. 7. Fluorescence spectra of the samples excited at 488 nm.

Figure 8 shows the fluorescence spectra at 226, 337, 420 and 488 nm for different oil concentrations. The samples A to E has the same behavior when excited at 266, 337, 420 and 488 nm.

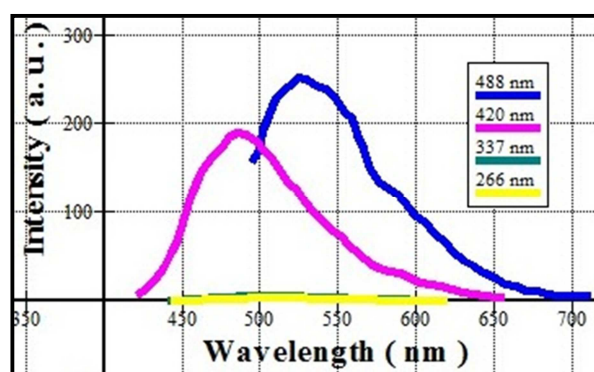




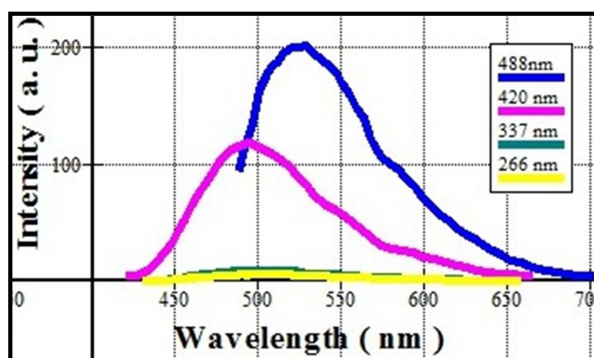
B



C



D



E

Fig. 8. Fluorescence spectra of diluted crude oil in Ethanol, (A) 16.6%, (B) 28.5%, (C) 37.5%, (D) 44%, (E) 50% excited at (266, 337, 420 and 488) nm, respectively.

5. Conclusions

Absorption and fluorescence characteristics of crude oil were studied, ethanol was used to extract and dilute the crude oil for light penetration. Absorption spectra of crude oil are occurred between 320 to 465 nm at different concentration of oil.

Crude oil excited using ultraviolet wavelengths emitted in the visible wavelength, while excited the samples in the visible wavelength resulting fluorescence in the visible range with longer wavelength.

In general, due to low absorption of crude oil in the ultraviolet range, the fluorescence intensity is very low. While the high absorption in the visible range causing an increase in the fluorescence intensity. When the oil concentration increases a reduction in the fluorescence occur due to the effect of quenching particles.

Acknowledgment

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