

# Characterization of Petroleum Crude Oils using Laser Induced Fluorescence

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## Abstract

The use of laser induced fluorescence (LIF) spectroscopy to characterize crude oil has privileges compared to conventional techniques in terms of reducing the size of sample, rapidity of measurements, high sensitivity and simplicity of sample handling and possibility of *in situ* measurements. The fluorescence radiation emitted from crude oil is the result of the interaction between the aromatic compounds and the electromagnetic radiation. The fluorescence spectra and their intensities are directly affected by the chemical composition and physical properties of the investigated samples. Important fluorescent information might be lost with the use of a single excitation wavelength, but might be obtained using other excitation wavelengths and thus enhancing the technique's discrimination capability between different crude oil samples. For this reason, fluorescence spectra in the present work were obtained using four types of CW lasers as excitation sources. Five dry crude oil samples with American Petroleum Institute (API) gravities between 18 and 44 were diluted to 5 mg/l using chlorinated solvent. The excitation of the samples was performed using diode pumped solid state lasers (DPSS) emitting at 266 nm, 405 nm, 532 nm and an argon ion laser at 488 nm. The present work introduces for the first time the usage of laser induced fluorescence spectroscopy in the characterization of Egyptian crude oils. The results revealed the dependence of the emitted fluorescence on the physical and chemical properties of the oil samples including the API gravity, viscosity, sulphur and asphaltene contents. Thus, it is feasible to make use of LIF as a simple and fast spectrochemical analytical technique in differentiating between different types of crude oil.

**Keywords:** Laser induced fluorescence; Crude petroleum; API gravity; Chlorinated solvent

## Introduction

Petroleum is considered as a complex mixture of hydrocarbons compounds that are essentially composed of carbon and hydrogen in a wide variety of molecular arrangements. These hydrocarbons are divided into three main classes – alkanes, cycloalkanes and aromatics. Their average range in crude oil is  $C_5H_{12}$  to  $C_{18}H_{38}$  along with heteroatom-containing, oxygen, nitrogen and sulfur. In addition to the previous contents, petroleum oil contains trace amounts of metals such as iron, nickel, copper and vanadium [1,2]. The physical properties, particularly specific gravity, of the crude oil play a big role in the global petroleum trading. It is defined as the ratio of the mass of a given volume of the oil at 15°C to the mass of an equal volume of pure water at the same temperature. It varies from 0.8 (45.3 API) for the lighter crude oils to over 1.0 (less than 10 API) for heavy crude oil and bitumen [3]. API gravity which is an arbitrary figure and more popular term, can be defined as the inverse measure of the relative density of a petroleum liquid and the density of water with the formula  $(API = (141.5 / \text{Specific Gravity at } 60^\circ F) - 131.5)$  [4]. It is clearly seen from the previous relation that the API gravity of the oil increases with the decrease of the specific gravity and vice versa. The API gravity term reflects directly the economic value of the oil and it is also an important factor in shipping and volume calculations

The analysis of crude oil using fluorescence techniques is used some decades ago to investigate the presence of petroleum in the logging soil, drill cutting, cores and soil samples using ultraviolet light [5]. There is a recent expansion on the utilization of fluorescence based measurements as a qualitative guide in the assessment of crude oil's the maturity in bulk and in hydrocarbon fluid inclusion (HCFI). Oil-bearing fluid inclusions (FI) are small samples, usually <5  $\mu\text{m}$  in radius, of pore fluid trapped during the crystallization of minerals such as quartz, feldspar and carbonate [6]. Laser-induced fluorescence (LIF)

spectroscopy is of great importance for environmental monitoring. Besides outstanding sensitivity and good selectivity, particular advantages of the LIF technique include the capabilities for *in situ* and remote sensing analysis. The contamination of water or soil with petroleum products (oils) represents a major environmental risk. Since most petroleum products exhibit distinct native fluorescence it was of big motive to apply LIF analysis for the detection and characterization of oils in environmental compartments.

The combination of LIF instrumentation with geotechnical drilling equipment for real-time subsurface detection of oil pollutions was pioneered by Lieberman et al. [7]. Several studies focused on adopting remote fluorosensors that can be usable in estimating the fluorescence life times and the emission spectra of crude oils on contaminated soil and sea water surfaces [8-11].

The fluorescence emission from crude oils is basically dependent on the presence of cyclic aromatic hydrocarbons [12], and could be described by the emitted radiation in a transition between the two lowest singlet states. The oil's aromatic compounds dissolved in the solvent can be excited directly by wide range of light radiation and undergo  $\Pi$ -electron transitions. There will be no competing processes, if the molecule can remain in lowest excited state,  $S_1$  for  $10^{-12}$  to  $10^{-9}$  seconds

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or longer as the situation will be suitable enough for the molecule to fluoresce. Fluorescence exists when there is a transition from the zero vibrational level of the first excited state to one of the vibrational levels of the ground state [8,13,14]. Since the crude oil is abundant of versatile fluorescent chromophores, the emitted fluorescence spectra are affected by the oil chemical composition, physical properties and rely on the excitation source that is employed [15].

Generally speaking, intense narrow emission bands with small Stokes shifts are the major characterization emission for light oils (high API gravities), while oils with low API gravities (heavy oils) are characterized by less intense broad bands with higher Stokes shifts [16,17].

Energy transfer and quenching effects are considered the major players for determining the emission behavior of petroleum oils. They are very considerable factors due to the fact of the relatively high abundance of quenchers and fluorophores that are found naturally in crude oils [18].

Quenching takes place when a crude oil constituent decreases the fluorescent intensity for the excited fluorophore. Oxygen molecule is considered the most common quenching constituent. The excited sample transfers excitation energy to a quencher molecule, leading to the de-excitation of the sample and producing an excited quencher molecule. A fluorescent signal is recorded when the excited quencher molecule is a fluorescent species, otherwise, it will be diminished [19].

It was crucial to dilute the crude oil samples for having a transparent solution to transmit incident light for performing fluorescence assessments and to decrease the effect of non radiative processes. Steffens et al. diluted crude oil samples using NUJOL solvent of concentrations between 0.05% (500 ppm) and 0.005% (50 ppm) showed high fluorescence intensity upon using 350, 450, 532 nm excitation sources [20].

Another factor that affects the fluorescence spectra is the kind of the used solvent. Hydrocarbons are dissolvable in a wide variety of solvents. Solvents can be classified according to their chemical structure. Up to 90% of solvents are synthesized from crude oil. The procedure could be in a petrochemical manufacturing site or closely related to the oil refinery process. The other solvents can be synthesized by using coal, natural gas and biomass or other raw materials. Refinery distillation can separate many hydrocarbon solvents which are subjected to further purification and treatment. Some are synthesized from olefins [21]. According to the carbon backbone type the hydrocarbon molecules, hydrocarbon solvents could be further divided into three sub-groups, which are aliphatic, aromatic and paraffinic solvents families [22]. Low molecular weight aliphatic solvents are molecules containing more than four carbon atoms such as pentane, hexane, heptane and higher which are more suitable in fluorescence application than aromatic solvents which are not preferred because of their inherent fluorescence.

Oxygenated solvents have carbon, hydrogen and oxygen atoms. They are synthesized via series of chemical reactions from olefins (derived from oil or natural gas), leading to many other sub-groups including; esters, ketones, alcohols, ethers, glycol ethers and glycol ether esters which are capable of dissolving the aromatic portion without extracting asphaltene nor other heavy fractions [22,23].

Another solvents – chlorinated hydrocarbon – which are polar aprotic organic compounds containing at least one covalently bonded chlorine atom such as methylene chloride, chloroform, carbon tetrachloride or trichloroethane [24]. This group is characterized by

its strength and ability in dissolving the aromatic portion with the extraction of asphaltene and other heavy fractions which has polar organic compounds that contain variable functional groups with O, N and S atoms. The strength of such solvents is coming from its dielectric constant which is 9.1 and tends to have large dipole moment (1.6 D) for instance methylene chloride. One can define the solvent's dielectric constant by the solvent's ability to reduce the field strength of the electric field surrounding a charged particle immersed in it and its ability to reduce the solute's internal charge [25].

The present work focuses on the qualitative analysis and the characterization of crude oils with wide range of API and other physical and chemical properties using laser induced fluorescence as a simple, fast and accurate spectrochemical analytical technique.

## Materials and Method

Five dry crude oil samples with different specific gravities were collected from Ras Gharib petroleum fields, located in the Egyptian eastern desert, 300 km south east of Cairo on the red sea coast. Some of the samples chemical and physical characteristics which may have an effect on the fluorescence behavior were predetermined. For instance hydrometer method was used to determine the specific gravities, sulfur content was identified by energy – dispersive X-ray fluorescence spectroscopy, kinematic viscosity was obtained using glass capillary viscometer and asphaltene content was obtained by extraction. All of the above analytical methods were performed according to the American Society for Testing and Materials (ASTM) designations 1298, 4294, 445 and Institute Petroleum (IP) designation 143 respectively. The corresponding API gravities were obtained from the standard tables ASTM56 [26]. 50 mg/l from each sample was prepared in 250 ml measuring flask using methylene chloride as a solvent, each at a time and homogenous solutions were obtained after vigorous shaking. The used solvent does not have any fluorescence behavior at the wavelengths of interest. The dilution step was crucial for getting a solution transparent to laser light and to reduce self-absorption effects. The laser beam is focused into one end of an optical fibre while the other end of the fibre delivers the beam onto one side of a 10 mm thickness quartz cuvette filled with the diluted oil sample.

Since, important fluorescent information might be lost with the use of a single excitation wavelength, but might be obtained using other excitation wavelengths and thus enhancing the technique's discrimination capability between different crude oil samples. Four optical excitation sources have been used throughout the present study involving methylene chloride as a solvent. They include a continuous wave (CW) argon ion laser (American laser company USA – ARJ – MED. INC, class 3b) delivering laser light of 4.8 mW power at 488 nm wavelength, (CW) DPSS violet laser (100 mW power at 405 nm), (CW) DPSS UV laser (5 mW power at 266 nm) and a CW DPSS green laser (2 mW power at 532 nm). The emitted fluorescence is collected from 90° via another fibre used to deliver the fluorescent light to the spectrometer (USB2000 FLG, Ocean Optics, USA). Acquisition and analysis of the spectra obtained from the spectroscopic system is accomplished using the commercial Spectra Suit software (Ocean Optics, USA). Utilising computer software (Origin, Origin Lab. Corp., USA, Version 8) to process and normalize all the spectra. The typical Laser induced fluorescence setup is described in more details in previous publication [27].

Solvents have different extraction efficiencies. The choice of solvents is determined by many factors such as cost, spectral qualities, method regulations, extraction efficiency, toxicity, and availability. Oil samples dissolved in methylene chloride can be examined by various excitation

wavelengths and the experiments were done after taking all the safety requirements when dealing with such solvent from wearing goggles and gloves.

This is due to the advantageous properties of methylene chloride as its high extraction efficiency, low cost, and specification by many state regulatory methods[28] and in extracting most of the chromophores present in the crude oil compared to cyclohexane (results are not shown). Methylene chloride is, however, highly volatile, which makes it difficult to store samples and to prepare standards [9].

The used solvent was excited separately by the used excitation sources in order to determine whether it fluoresces at such wavelengths. Neither spectral lines nor bands have been detected in the spectral region of interest that will be adopted for the later measurements. Thus it was certain that the emitted fluorescence originated from the oil samples under investigation.

## Results and Discussion

The major physical and chemical parameters of crude oil samples under investigation are summarized in Table 1 where the specific gravity, sulfur, asphaltene contents and the viscosity are determined by using ASTM.

As mentioned before fluorescence is a phenomenon in which certain compounds, containing molecular arrangements generally referred to as chromophores, emit fluorescent radiation when excited by incoming light of certain wavelengths. The chromophores are contained in hundreds of different compounds. Asphaltenic aromatic and resin fraction of crude oil fluoresce in the ultraviolet and visible portion of the electromagnetic spectrum when interact with radiation of the proper excitation wavelength. According to Karpicz et al. ultraviolet wavelengths (300-400 nm) are primary used as an excitation wavelength for oils that emit fluorescence in the visible range with wavelength 400 to 600 nm [10]. The hydrocarbon structure of the oil samples is one of the detrimental factors affecting the emitted fluorescence characteristics. The incorporation of additives as well as the used solvents affects also the fluorescence properties of the oils.

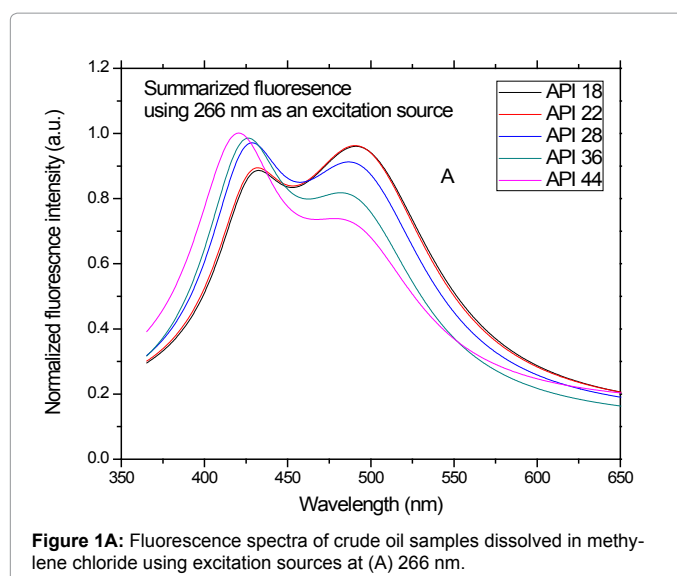
The main objective of using powerful solvent such as methylene chloride is to make sure that most of the fluorescent chromophores in the oil samples - asphaltene fraction for instance - have been dissolved which could then be excited by suitable excitation sources and hence could enhance the discrimination between different types of crude oils.

The emission spectra profile for heavy and light oil samples for each figure are nearly similar with broader, lower fluorescence emission bands intensities for light oils (high API gravity) than those of lower API gravity (heavier oils) where the fluorescence spectra profile tends to be stronger.

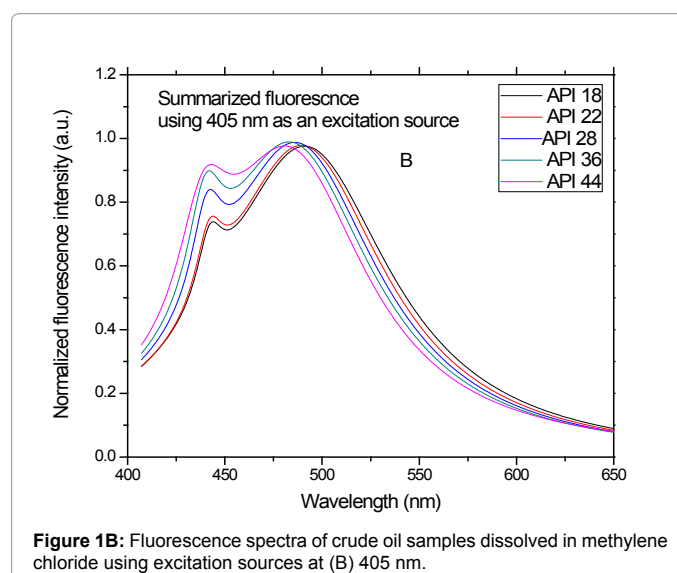
Figures 1A and 1B represents the fluorescence spectra obtained from a series of five crude oil samples diluted by methylene chloride solvent and excited by lasers of 266 nm and 405 nm wavelengths. The

| Samples | Specific gravity | API   | Sulfur wt % | Viscosity c.st | Asphaltene wt % |
|---------|------------------|-------|-------------|----------------|-----------------|
| A       | 0.9437           | 18.45 | 4.1         | 229            | 8               |
| B       | 0.9212           | 22.1  | 3.55        | 29.8           | 7.7             |
| C       | 0.8853           | 28.35 | 2.9         | 25.3           | 4.35            |
| D       | 0.8428           | 36.1  | 1.2         | 2.95           | 2.2             |
| E       | 0.8058           | 44.1  | 0.23        | 2.3            | 0.5             |

**Table 1:** Chemical composition, API gravities and viscosities of the crude oil samples used in the present study.



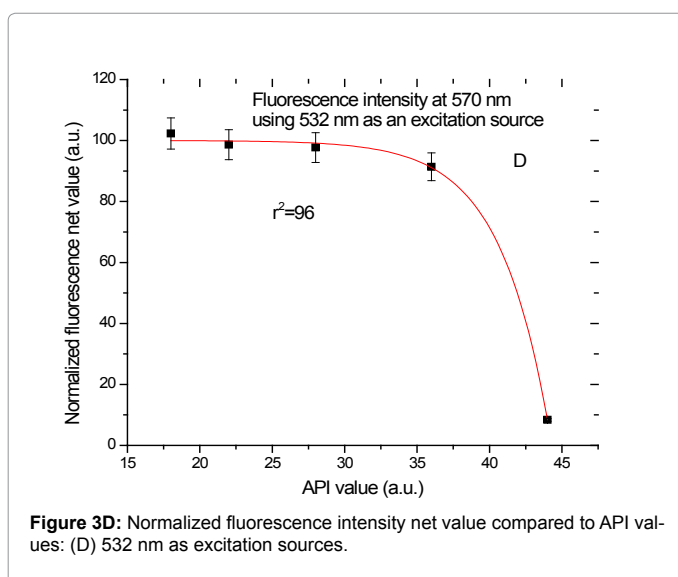
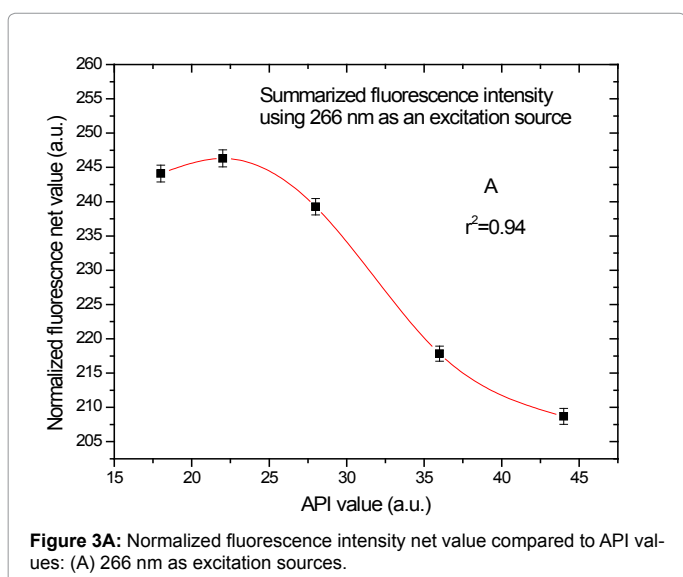
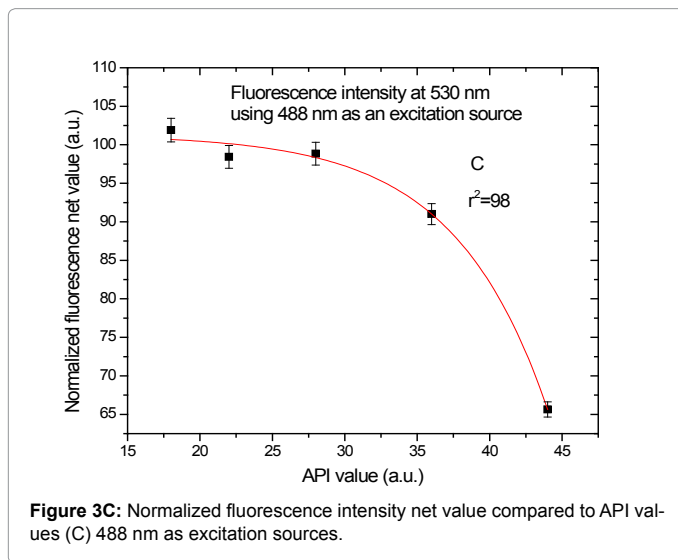
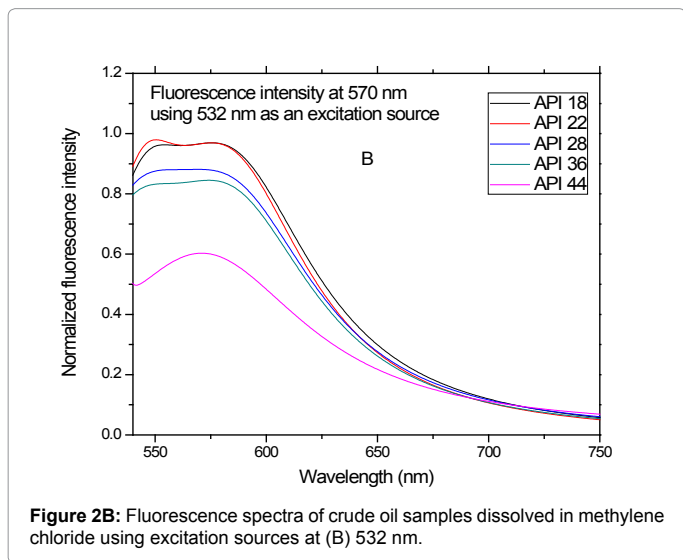
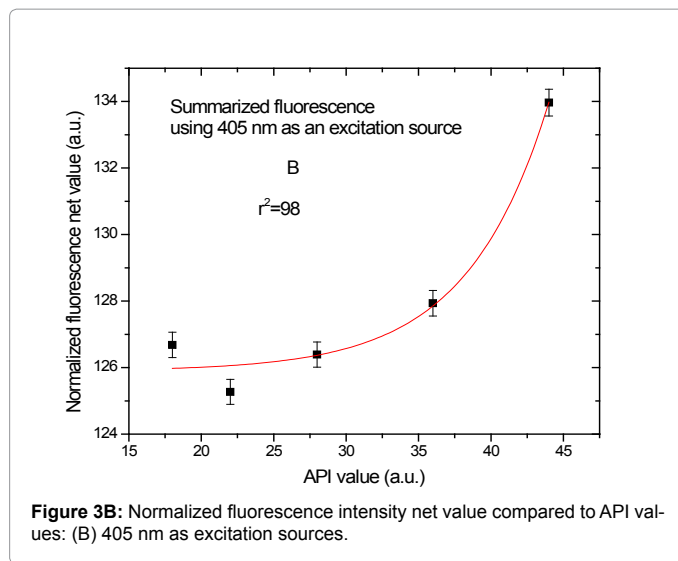
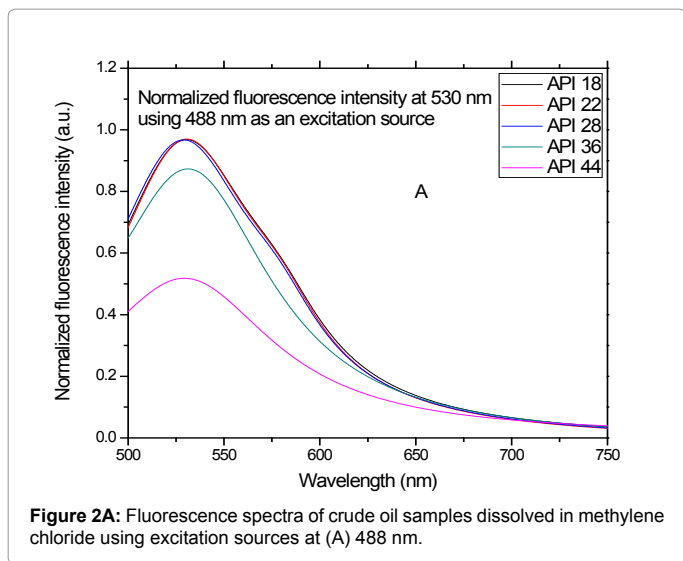
**Figure 1A:** Fluorescence spectra of crude oil samples dissolved in methylene chloride using excitation sources at (A) 266 nm.

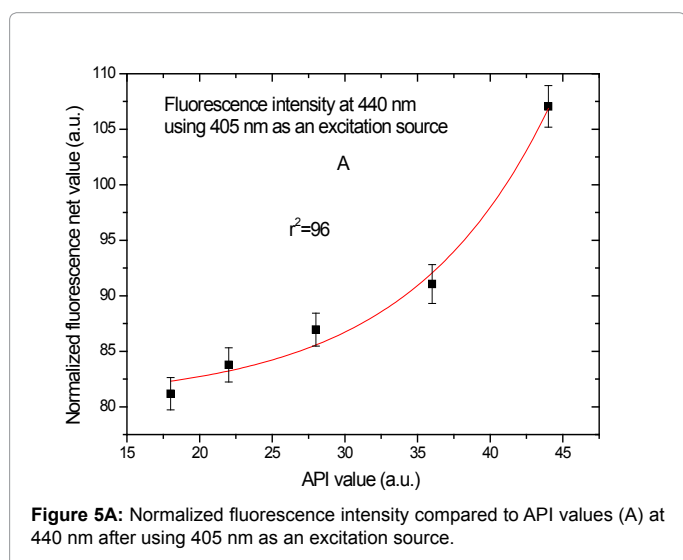
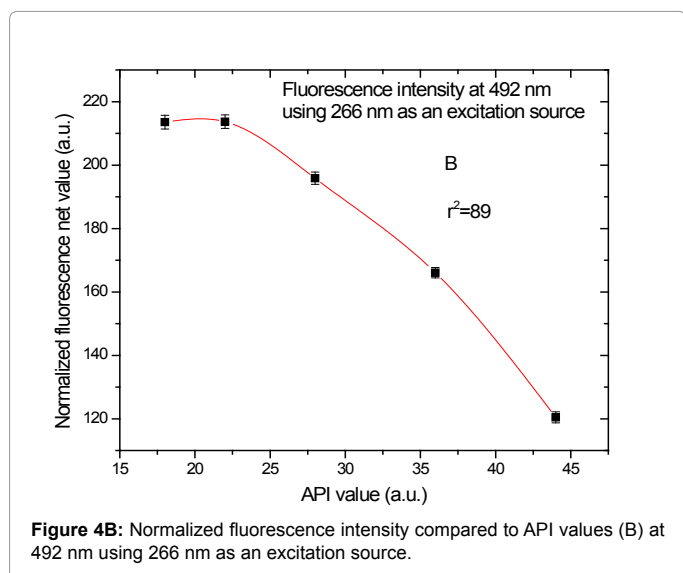
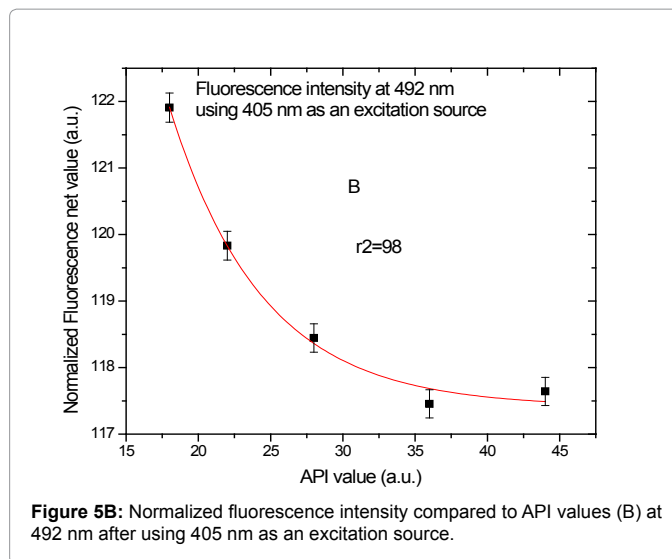
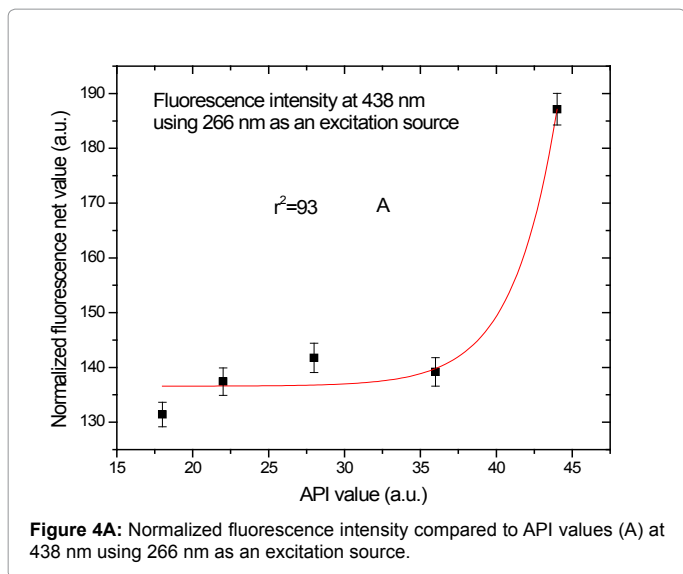


**Figure 1B:** Fluorescence spectra of crude oil samples dissolved in methylene chloride using excitation sources at (B) 405 nm.

intensities of the fluorescence bands for most samples are close to each other. The samples excitation with 266 nm led to two fluorescence emission peaks near 410 nm and 490 nm, while those excited by 405 nm gave two fluorescence emission peaks near 430 nm and 490 nm. The 490 nm fluorescent peak for light oils (high API) is lower than those of heavy oil (low API) which tend to be narrower. Surprisingly, the fluorescence behavior - upon using the mentioned excitation sources - of the oil samples is reversed before 450 nm, where the light oils tend to give higher intensity spectral lines than heavy oils do.

Figures 2A and 2B shows the emission spectra obtained from the above mentioned crude oil samples diluted by methylene chloride solvent as well but upon using 488 nm and 532 nm as excitation sources. The emission peaks in this case were near 530 and 570 nm respectively and the light oils tend to give less intense and broader spectral bands than heavy oils do. It is worth mentioning that upon using 488 as an excitation source, it couldn't resolve emission peaks of oils with close API values. This could be explained by increasing the rate of energy transfer in the samples excited with 266, 405 than 488 nm laser sources.





Apparently, from the above figures a correlation can be obtained between the API values of oil samples and the emitted fluorescence as shown in Figures 3A-5B. The intensity of emitted fluorescence before 450 nm, decreases exponentially with the decrease of API values, however this relation is reversed after 450 nm, where the intensity of the emitted fluorescence increases exponentially with the decrease of the oil samples' API values.

The excitation of diluted crude oil samples using different laser sources in the ultraviolet and visible portion led to fluorescence emission in the visible portion range from 400 nm-600 nm as observed by many authors [10-20]. Before 450 nm, the emission spectra of oils with high API gravity (light oils) can be described as strong fluorescence emission with relatively narrow bands than that for heavier oils (lower API gravity) where there is a red shifted weaker and broader fluorescence emission. These changes in fluorescence emission can be attributed to the fact of the presence considerable amounts of materials that have the ability of quenching non-radiatively fluorescence in heavy oils, resulting in low fluorescence intensities and the higher concentration of fluorophores leads to higher rate of energy transfer resulting in broadening of the emitted spectrum. As the petroleum oil gets denser, the concentration of large polycyclic aromatic Hydrocarbons (PAH) increases. These molecules have small band gaps, and higher collisional quenching rates, than those in light oils.

On the contrary, oils with high API gravity (light oils) are having more diluted fluorophore concentrations that tend to reduce the rates of energy transfer with consequently a narrower emission bands.

This overall trend has been reversed after 450 nm with the use of methylene chloride as a solvent, where the trend of the heavy oils (low API gravity) can be described as strong fluorescence relatively narrow emission bands than that of lighter oils (higher API gravity) whereby the fluorescence emission spectra are red shifted, broader and overall weaker.

Methylene chloride is characterized by its strength and ability in dissolving the aromatic portion with the extraction of asphaltene and other heavy fractions. From Table 1 the asphaltene fraction that is composed of high molecular weight and polarity components is anticipated to have big fractions of materials which are having the capability of quenching fluorescence. The asphaltenic content has

as well large chromophores which are more abundant in heavy oils compared to light ones. These large chromophores absorb a big part of the emitted energy and emitting fluorescence at longer wavelength above 450 nm with more intense bands for the heavy oil. According to a previous spectroscopic investigation of purified porphyrin fractions, the chromophore that may absorb at the 450 nm range could be attributed to the Soret band of vanadyl porphyrins, with a molecular composition of  $C_{32}H_{36}N_4O_2V$  [29,30].

Ryder et al. in another series of experiments have found that oils of big asphaltene concentrations are tending to have short lifetime. This was with the exception of oil with API gravity 20 where they have been found to having longer lifetime with an asphaltene percentage of 7.5% [31]. These fluorescence emission behavior differences can be attributed to the fact that light oils tend to contain fewer molecules of small bandgaps absorbing, which non-radiatively quench fluorescence leading to the observed lower fluorescence emission. Upon using strong solvent like methylene solvent with heavy oil samples that are rich in Asphaltene fractions, fluorophores of large band gaps are having the ability of transferring energy to large numbers of smaller band gaps molecules. The observed higher fluorescence intensities can be attributed to that high rate of energy transfer.

But the change in the shape and intensity of the emitted fluorescence with changing the excitation source is expected due to the change in the excited fluorophore, quencher concentration and the rate of energy transfer. The same effect has been observed in the literature by using solvents as benzene, cyclohexane and n-heptane.

However, other components of the oil may mask this trend by the high degree of scattering mainly through collisional quenching.

## Conclusion

Laser induced fluorescence can be adopted through various methodologies for the identification and discrimination between crude oil. In the present study, we have clearly shown the LIF capabilities in the discrimination between different Egyptian crude oil samples with different API gravity values. Moreover, with minimal sample preparation and without sample destruction, it is possible to determine the API value of unknown sample within the range of the current work. Yet, there are still further considerations in adopting such technique In situ for efficient, quick and robust technique for quantitative and qualitative analysis of crude oil. The nowadays miniaturization with the same time developed energy outputs and effective detectors favors the expanding of such noninvasive technique in the oil industry and related fields.

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