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Application of Fluorescence to the Study of Crude Petroleum

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Abstract Crude petroleum oils are complex mixtures of different compounds (mainly organic), which are obtained from an extensive range of different geological sources. The fluorescence of crude petroleum oils derives largely from the aromatic hydrocarbon fraction, and this fluorescence emission is strongly influenced by the chemical composition (e.g., fluorophore and quencher concentrations) and physical characteristics (e.g., viscosity and optical density) of the oil. 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. In this work we analyzed crude petroleum at different dilution in Nujol, a transparent mineral oil. The main objective of this work was to verify the possibility to measure crude oil emission spectroscopic without use of volatile solvents. The mixtures of nujol with different -crude oil concentrations were measured with a 10 mm optical path cuvette thus simplifying the fluorescence spectroscopy signal detection. The emission spectra were obtained by exciting the samples with a 400 W Xenon lamp at 350 nm, 450 nm and 532 nm. The emissions of the samples were collected perpendicularly with the excitation axis.

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Introduction

In the petroleum industry, the characterization of crude oil is a key factor for improved optimization of the refining process. Spectroscopic techniques have gained relevance for this purpose because of their potential to give rapid responses containing valuable information related to the intrinsic chemical characteristics of each analyzed sample.

Petroleum oils are mixtures of aliphatic, aromatic, and high molecular weight organic compounds [1]. Due to this heterogeneity, chemical analysis is generally complex. Petroleum oils are typically characterized using liquid chromatography, separating into saturates, aromatics, resins, and asphaltenes [2, 3]. Each of these components can be further characterized by the use of Gas Chromatography–Mass Spectrometry (GC–MS) which provides unambiguous identification of individual components.

Infrared (IR, both mid-IR, MIR, and near- IR, NIR) spectroscopies are the most widely used in spectroscopic techniques for crude oil analysis. The simplicity of sample handling and the rapidity of the analysis have facilitated the development of new ways to determine the physical-chemical properties of petroleum products (gasoline, kerosene, diesel, etc.). In spite of its good signal/noise ratio, rapid response, simplicity and low cost, IR still presents several limitations, such us the overlapping of absorption bands and saturation of the signal due to the high absorbance of dense sample such as crude petroleum.

Another technique that is gaining importance in the petrochemical field is fluorescence spectroscopy, due to its sensitivity and selectivity. Fluorescence has been exten-

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sively used in the petroleum industry for the analysis and classification of different petroleum samples and reviews describing the basis of the technique and its inherent advantages and disadvantages can be found in the literature [4–8]. Factors such as the specific chemical composition (concentration of fluorophores and quenching species) and physical (viscosity and optical density) influence emission intensity and wavelength. In the case of heavy oils, fluorescence emission is generally broad, very weak, and has short lifetimes, whereas lighter oils have narrower more intense emission bands, and longer lifetimes [9, 10]. The nature of the emission is governed by the complex interplay between energy transfer and quenching caused by the high concentrations of fluorophores and quenchers in petroleum oils. The complexity of crude oils usually prevents the resolution of any specific chemical component in terms of individual emission parameters

Several different solvents can be used to dilute crude oil to obtain a solution transparent to transmit light [5]. Nerveless organic solvents are highly flammable, depending on their volatility. Exceptions are some chlorinated solvents like dichloromethane and chloroform. Mixtures of solvent vapors and air can explode. Many solvents can lead to a sudden loss of consciousness if inhaled in large amounts is the case of chloroform. Nujol is a brand of mineral oil used in infrared spectroscopy. It is a heavy paraffin oil so it is chemically inert and has a relatively uncomplicated IR spectrum. It density is 0.838 g/mL at 25 °C. The empirical formula of Nujol is essentially the alkane formula $C_nH_{(2n+2)}$ where n is very large. Crude oil and nujol can be mixed in a uniform phase under vigorous shacking. Absorption and emission in the UV and visible range are well knowing and less intense than crude oil emissions. Moreover using excitation in the visible range it is possible to access only crude oil absorption and consequently only crude oil emission.

Remote sensing techniques, such as Light Detection and Ranging with lasers (Lidar) can be able to detect oil spills and even potential oil exploration areas. By the measurement of oil thickness the value of absorption coefficient for many samples and in a wide wavelength band (300–600 nm) should be known ad hoc or be inferred at laboratory scale. Also by knowing the crude oil emission spectra can be possible to identify the oil origin and its quality [11].

In the past few years Brazil has changed from oil user to oil producer due the discovery of many deep sea oil reserves and it has started a large scale exploration program which requires sophisticated techniques to identify and detect oil spills in a duct network of many thousand of kilometers. Therefore this first approach is to start an additional spectroscopic tool to develop into a fast responsive system to oil leaks and spills in the handling of crude oil transport and on-site refining.

Materials and methods

The crude oil sample was obtained from Bacia de Campos Region, located in the Brazilian continental shore, close to the State of Rio de Janeiro, between latitudes 21° and 23° S.

To performe fluorescence measurements it was necessary to dilute crude oil to obtain a solution transparent to transmit ligth. For this reason it was chose Nujol oil that is a solvent relatively free of absorption bands at 350, 450 and 532 nm, wavelengths used to excited crude oil. Six oil samples of the crude class in progressive dilutions in Nujol were used for the measurements. Mixtures were shaken vigorously to obtain uniform solutions. The different concentrations prepared samples are showed in Table 1.

The absorption spectra of all samples were measured at room temperature in the range 200 nm–2,500 nm using a Varian Spectrometer Cary 17 D. The emission spectra were obtained by exciting the samples (1 mm thickness) with a 150 W Xenon lamp. The emissions of the samples were analyzed with a 0.5 m monochromator (Spex) and a PMT detector. The signal was amplified with an EG&G 7220 lock-in and processed by a computer. Sample cells in the 100 mm were used in the absorption and emission experiments. Emissions were also analyzed in a Horiba Fluorolog 3 fluorimeter. The wavelengths used are 350 nm, 450 nm and 532 nm.

Results

According Karpicz et. al. [12] oils are typically excited using ultraviolet wavelengths (300–400 nm) and fluoresce in the visible wavelength range from 400 to 600 nm. The compound's Carbon Structure will determine their fluorescent properties. The incorporation of additives will also affect the fluorescence properties of oils. Figure 1 is a graph taken from showing different types of refined crude oils and crude oil products, each with its corresponding emission wavelength. The difference in crude oil fluorescence is primarily due to the refinement process.

Crude oil compositions vary widely. They can have dramatically varied compositions in the C_5–C_{40} carbon range such as relative amounts of paraffinic, aromatic and

Table 1 Concentration of oil in Nujol

Sample	Concentration (%)
1	0.005
2	0.010
3	0.015
4	0.020
5	0.030
6	0.050

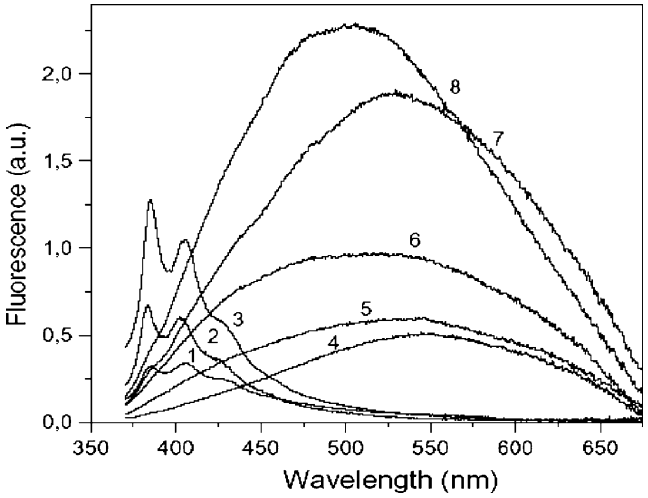


Fig. 1 Emission wavelength of refined crude oils and crude oil products [12]

asphaltenic compounds, differences in the n-alkane distributions and unresolved complex mixtures, and different relative ratios of isoprenoids to normal alkanes. Refined petroleum products are obtained from crude oil [13].

In Fig. 2 it is possible to observe Nujol optical properties. In Fig. 2a we observe that Nujol has absorption band at 350 nm but at 450 and 532 nm the absorption is negligible. However, the excitation of Nujol in these wavelengths results in emission bands around 420 and 500 nm, as it is possible to see at Fig. 2c. Adding crude oil to Nujol solution the absorption window shifts to red linearly to oil concentration enhancement.

In the Fig. 3 is showed the fluorescence for the different proportions between crude oil and Nujol samples excited at 350 nm. In this case we observe two emission bands around 400 and 550 nm, both ones characteristics to crude oil emission. The emission band at 550 nm decrease with the increase of oil concentration.

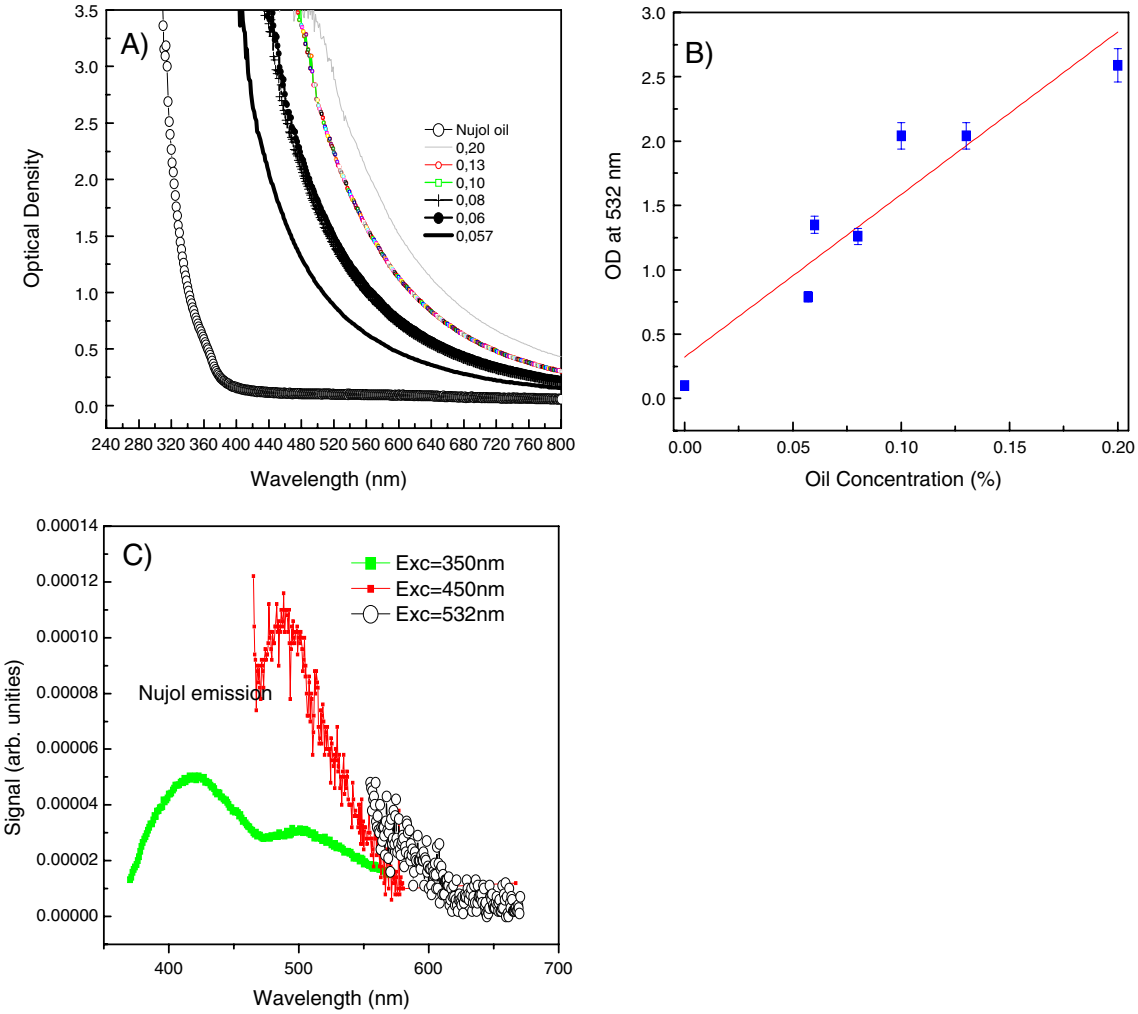


Fig. 2 **a** Optical absorption of Nujol and crude oil—Nujol solution in proportions 0.20, 0.13, 0.10, 0.08, 0.06 and 0.05; **b** Optical density at 532 nm in function of oil concentration; **c** Nujol emission under excitation at 350, 450 and 532 nm

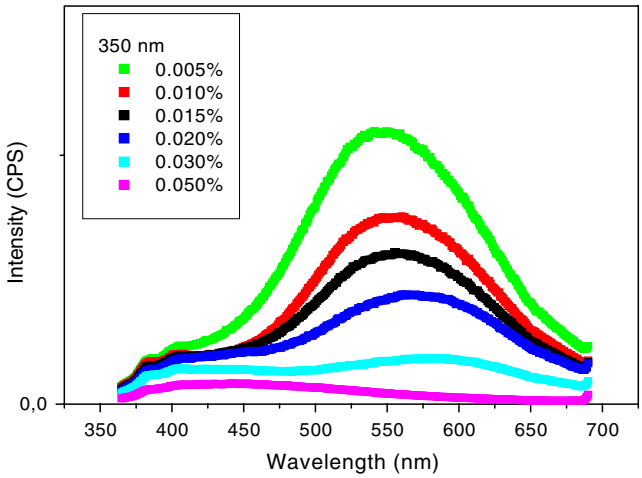


Fig. 3 Fluorescence spectra of the samples excited at 350 nm

It is possible to see that the increase in oil concentration depict a decrease in the emission intensity. The development was expected because with more oil concentration more difficulty light penetrates at the sample. It can to be seeing also in the Figs. 4 and 5, which have the same development.

When radiation of one wavelength is absorbed by a molecule with the appropriate molecular structure, it can be remitted at a higher wavelength (lower energy). Crude oil also contains fluorescent molecules [14].

In the Fig. 4 is showed the fluorescence for the different samples excited at 450 nm. In this case a emission band around 560 nm can be observed and shift to red and decrease with the increase in the oil concentration.

In the Fig. 5 is showed the fluorescence for the different samples excited at 532 nm. For this excitation, the emissions appear around 660 nm and also shifts to red and decrease with the increase in oil concentration.

Energy transfer process is responsible for red shift and broadening in emission spectral band. Simultaneously a quenching process reduces emission intensity. The same effect was observed by other authors using solvents as benzene, cyclohexane and n-heptane [5].

The Fig. 6 shows the fluorescence spectra of 350, 450 and 532 for different oil concentrations.

In this figure it can to be seeing that the samples “a” to “e” has the same development when excited at 350, 450 and 532 nm, except the last one “f” that is different, possible because the higher oil concentration. That is, with the increase in the sample concentration the rate emission decreased.

This work could be important when the focus is in the use of an active optical method. The fluorescence Lidar is promising because of its high capability of active sensing to positively distinguish the oil from the water or biological substances. Fluorescence is strongly indicative of the presence of oil. Research and development of fluorescensor have been conducted many investigators [15, 16].

By our results we observe that higher concentrated samples present different shape of emission spectra that those presented for lower concentrated ones. This method can be applied to determine concentration of oil in ambiental pollution.

This experiment can be help interpretations in Lidar research. In the case of Lidar experiments a film of oil is formatted in the water surface. Knowing the emission shape observed in the laboratory is possible to identify the quantity of oil presented in a determinate area.

According Measures [11], in most oil-spill situations, the fluorescence from the oil film will be much stronger than the background water fluorescence, so that there is unlikely to be any problem in detecting the oil. By our results we can affirm that crude oil from Bacia de Campos region is a heavy oil and emission profile suggest composition similar to German crude oil.

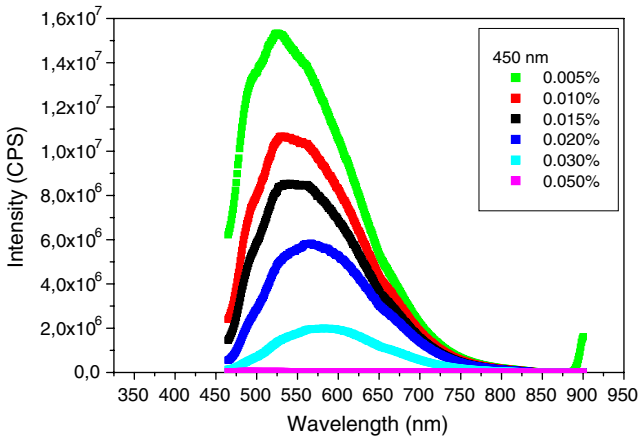


Fig. 4 Fluorescence spectra of the samples excited at 450 nm

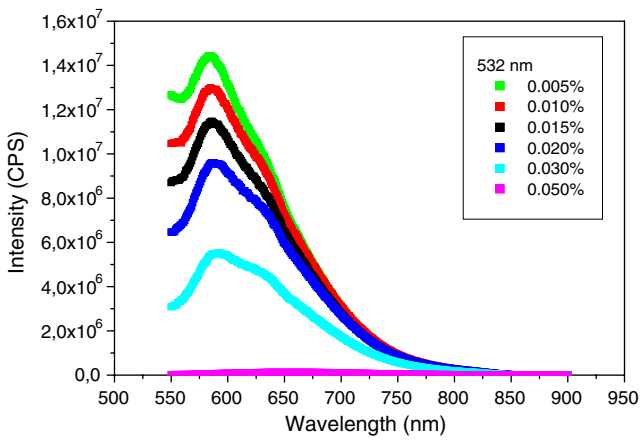


Fig. 5 Fluorescence spectra of the samples excited at 532 nm

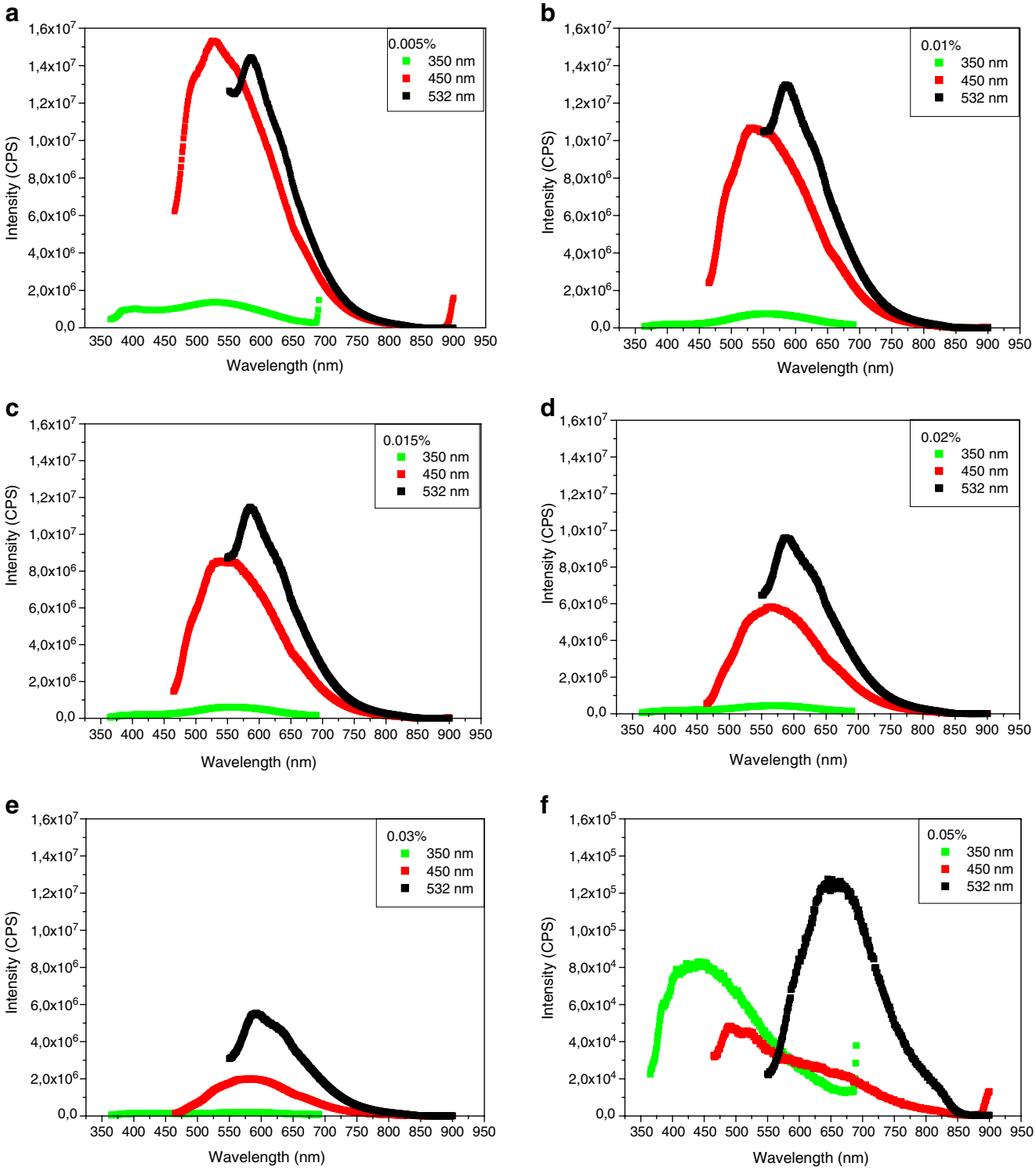


Fig. 6 Fluorescence spectra of samples with crude oil in Nujol: **a**) 0.005%, **b**) 0.010%, **c**) 0.015%, **d**) 0.020%, **e**) 0.030%, **f**) 0.050%, excited at 350 nm, 450 nm and 532 nm

Conclusions

Due to its sensitivity and selectivity, fluorescence spectroscopy is increasingly used in petroleum technology.

It was studied the fluorescence characteristics of solutions containing fixed amount of Nujol pure oil and different concentrations of crude oil. Nujol was used to solute the crude oil allowing light penetration. The goal of

this experiment was to obtain an experimental method to measure easily the oil fluorescence upon excitation at wavelengths compatible if that ones used in Lidar research. The results show an effective means to obtain rapidly distribution of crude oil concentration. When the oil concentration increases occurs a displacement in the wavelength possible because the higher oil concentration.

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