



APPLICATION OF FLUORESCENCE SPECTROSCOPY FOR SPECTRAL DISCRIMINATION OF CRUDE OIL SAMPLES

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Abstract. Spectroscopic techniques have been extensively used in the petroleum industry for the characterization of crude oils. The present article shows the results of the application of fluorescence techniques for the analysis of the density of Brazilian crude oil samples. Fluorescence emission spectra of crude oil consist of relatively broad bands in the visible region (from ca. 350 to 650 nm), the intensities of which tend to accompany the API grade. Synchronous Fluorescence Spectroscopy (SFS) was performed with a wavelength interval of 50 nm starting the excitation at 450 nm. Time-Resolved Fluorescence Spectroscopy (TRFS) showed that the fluorescence lifetime is related to the API value, lighter oils with higher API exhibiting a longer lifetime. The present results demonstrate that fluorescence spectroscopy is useful in the characterization of complex samples like crude petroleum.

Keywords: fluorescence; spectroscopy; crude oil; synchronous fluorescence; time-resolved fluorescence

1. 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.

Infrared (IR, both mid-IR, MIR, and near-IR, NIR) spectroscopies are the most widely used 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 addition, some studies have shown good results for the prediction of the distillation properties of crude oil. IR spectroscopy has been extensively used in the analysis, identification and characterization of heavy crude oils (Hannisdal, et al., 2005), medium crude oils (Falla et al., 2006; Abbas, et al., 2006; Hidajat and Chong, 2000), gasolines (Fodor, 1996; Lysaght, 1993), distillation products (Chung et al., 1999 ; Kim et al., 2000), hydrocarbons (Mille et al., 1985; Reboucas, et al., 2007) and gas condensates (Van Agthoven, et al., 2002). In spite of its good signal/noise ratio, rapid response, simplicity and low cost, IR presents several limitations, typical problems encountered with this technique being the

overlapping of absorption bands and saturation of the signal due to the high absorbance of crude petroleum.

Another technique that is gaining importance in the petrochemical field is fluorescence spectroscopy, due to its sensitivity and selectivity. Fluorescence has been extensively 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 (Ellingsen and Fery-Forgues, 1998). The current focus of work in this field is to attempt to relate typical fluorescence parameters (intensity, emission wavelength, lifetime) to physical characteristics of the crude oil, such as chemical composition and density (API gravity).

In this work, we have utilized different modes of fluorescence spectroscopy (conventional steady-state, synchronous and time-resolved) to examine and compare their potential for correlating basic properties of crude Brazilian petroleum samples, in terms of their API gravity.

2.1. Total Fluorescence Spectroscopy (TFS)

Although the spectra look rather simple, complex samples like crude oil that contain several absorbing and emitting species actually have very complex fluorescence emission spectra. Thus, upon changing the excitation wavelength, different species can be excited selectively and the emission spectrum can change accordingly. In TFS, an excitation wavelength is selected and the emission is recorded over the wavelength range of interest. A new excitation wavelength is chosen and the emission range is scanned again. TFS data are thus usually presented as a three-dimensional map of the fluorescence intensity (z-axis) as a function of the excitation and emission wavelengths (x- and y-axes, respectively). Rayleigh and Raman scattering of the excitation light by the sample usually result in artifact signals along two diagonals of the map (at $x=y$, corresponding to the coincidence of the excitation and emission wavelength; and at $y = x + C$, where C is determined by the vibrational

mode dominant in the Raman scattering). These artifact signals do not contain any information about the sample and can be a source of error unless adequately removed from the data. TFS has been used for crude oil and product analysis and for the determination of crude oil pollution in water (Dudelzak et al., 1991; Liping et al., 2005). However, the procedure is relatively time-consuming, which is a clear limitation for its application in industrial processes.

2.2. Synchronous Fluorescence Spectroscopy (SFS)

Another approach similar to TFS is SFS. In SFS, however, both the excitation and emission wavelengths are scanned simultaneously during acquisition. At the beginning of the analysis, the starting excitation (λ_{exc}) and emission (λ_{em}) wavelengths and an initial wavelength difference $\Delta\lambda$ are selected. After each scan, $\Delta\lambda$ is increased and the scan repeated. SFS data provide a three-dimensional response surface for the fluorescence intensity. SFS spectral features are usually sharper than the corresponding conventional fluorescence spectra due to the compression of spectral bandwidth and do not present the artifacts due to Rayleigh and Raman scattering. SFS has several advantages relative to standard fluorescence spectroscopy for the analysis of complex samples such as crude oil and its derivatives (Wakeham, 1977) and has been extensively used for the analysis of crude oils, petroleum products and aromatic hydrocarbons, as well as for oil spill identification, gasoline adulteration control, crude oil classification and petroleum photodegradation studies (Patra and Mishra, 2002a, Patra and Mishra, 2002b, Guangjun et al., 2006.).

2.3. Time-Resolved Fluorescence Spectroscopy (TRFS)

This is the newest fluorescence technique to be applied in the petrochemical industry. The method uses a pulsed excitation source and measures, either directly or indirectly, the decay of the fluorescence intensity as a function of time after the pulse. The most important parameter in this technique is the

fluorescence lifetime or the average time that the molecule remains in the excited state before decaying to the ground electronic state by the emission of fluorescence. Excited species with different fluorescence spectra and/or different lifetimes will emit with different intensities at different times. TRFS data can be conveniently represented as a three-dimensional map of the fluorescence intensity as a function of emission wavelength and time for each excitation wavelength. For crude oils, the fluorescence lifetime was found to be very dependent on the API gravity (Quinn et al., 1988). TRFS has been used by several groups for petroleum characterization and classification (Hegazi et al., 2005, Hegazi and Hamdan, 2002, Hegazi et al., 2001) and TRFS maps have been applied with success in the identification of petroleum products such as kerosene, gasoline and diesel fuel (Saitoh and Takeuchi, 2006).

3. MATERIALS AND METHODS

3.1. Crude Petroleum Samples

The sample database consisted of crude petroleum samples (medium density) from a Brazilian refinery (REVAP, Petrobras). Laboratory analysis on these samples provided the required physical properties (API gravity) and fluorescence spectra measurements (TFS, SFS and TRFS) were carried out on these samples. Algorithms for the proper representation of crude oil spectra were implemented in MatLab programming language.

3.2. Apparatus

The densities of the samples were measured in g/cm^3 with a Model DMA 4500/5000 Densimeter (Anton – Paar) to obtain the API degree.

Both conventional fluorescence and TFS emission spectra were recorded on a Hitachi Model F-4500 fluorimeter. The working parameters for conventional spectra were an excitation wavelength of 337 nm and an emission range from 350-650 nm (5 nm intervals) with 5.0-nm excitation and 2.5-nm emission slits with a scan rate of 60 nm/s. For

TFS, the excitation range was 230–600 nm (5-nm intervals) and the emission range 300–750 nm (5-nm intervals) with 5.0-nm slits and a scan rate of 1200 nm/min. For SFS, a Perkin Elmer Model LS50 fluorimeter was employed with excitation from 250–650 nm, 15-nm excitation and 10 nm emission slits and a scan rate of 500 nm/min. An Edinburgh Instruments Model LP900 laser flash photolysis spectrometer operated in the fluorescence mode was utilized for the TRFS measurements. Samples were excited with 5-ns pulses of the third harmonic (355 nm; power of 40 mJ/s) of a pulsed Nd-YAG laser.

4. RESULTS AND DISCUSSIONS

The conventional steady-state emission spectra (obtained by employing a fixed excitation wavelength of 337-nm) of several crude oils are presented in Figure 1. As mentioned above, the fluorescence spectra of crude oil typically consist of a broad band in the visible region, from ca. 350 to 650 nm, which reflects the overlapping of the emission from the different fluorophores present in the system.

These spectra illustrate the tendency of the fluorescence emission intensity to accompany the API grade. In general, light crude oils exhibit somewhat stronger fluorescence emission bands than heavier oils and the emission of the latter tends to be weaker and red-shifted. This difference in behavior is due to the nature of the fluorophores present in each case and the greater or lesser contribution of reabsorption and quenching to the emission process. When an excited organic molecule emits light as fluorescence, part of this light can be reabsorbed by other molecules present in the mixture, resulting in increased emission at longer wavelengths. In addition, a variety of other physical and chemical processes can accelerate the decay of an excited state. These processes include excited state reactions, energy transfer, complex-formation and collisional quenching by species such as molecular oxygen or metal ions. In heavy crude oils with a higher density, the quenching processes are more pronounced, as indicated by

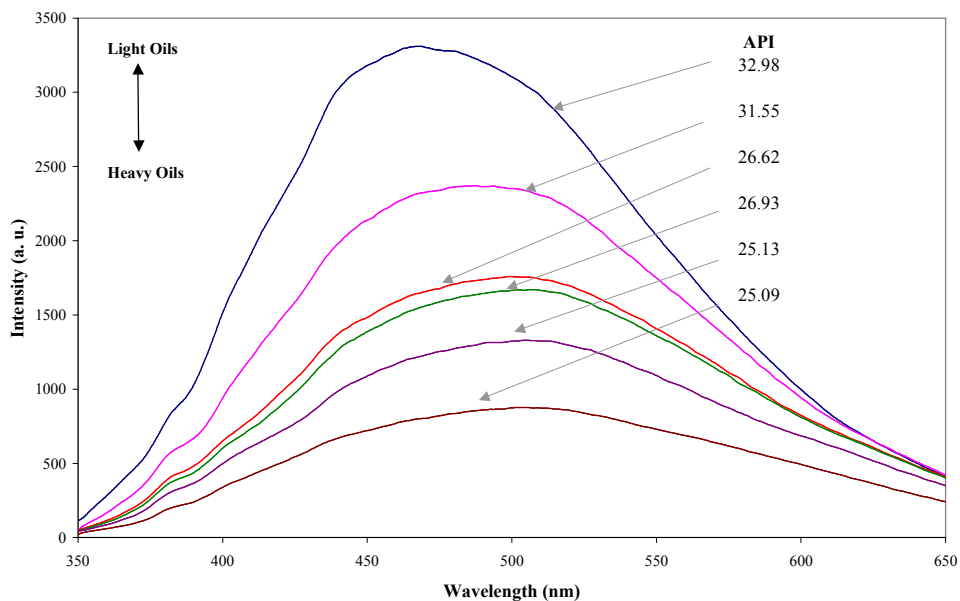


Figure 1. Fluorescence emission spectra of crude oil samples with different API values, indicated for each sample.

the reduction in the fluorescence intensity (Figure 1) for the heavier crude oils. Moreover, energy transfer processes, which result in a shift of the spectrum to longer wavelengths (lower energies), are also more prominent (Figure 1) in the lower API grade samples.

Two samples that differ significantly in their API grade were selected from the sample subset above to illustrate the results obtained by the other fluorescence techniques. The TFS

results for these two samples are depicted in Figures 2 and 3. Prior to use of the TFS data in modeling, the artifact peaks due to Rayleigh and Raman scattering (clearly visible as two diagonal swaths in the contour maps) were mathematically excised from the fluorescence data. This permits a more realistic comparison of modeling results between TFS and SFS or TRF. After removal of the scattering artifacts, the general trend observed in the topographical

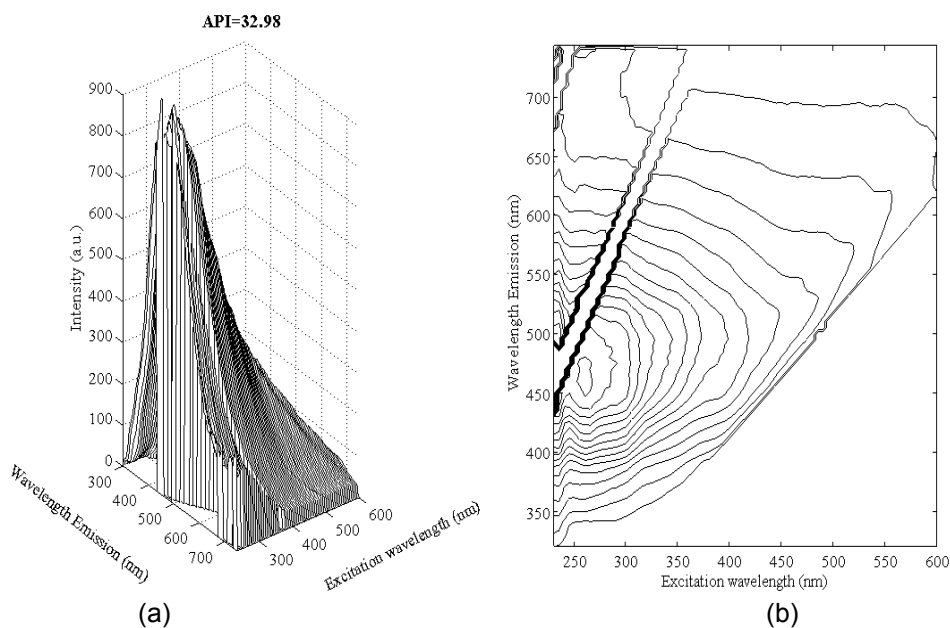


Figure 2. Total Fluorescence Spectra of the crude oil sample of Figure 1 with the highest API value (a) 3D topographical diagram (b) contour map.

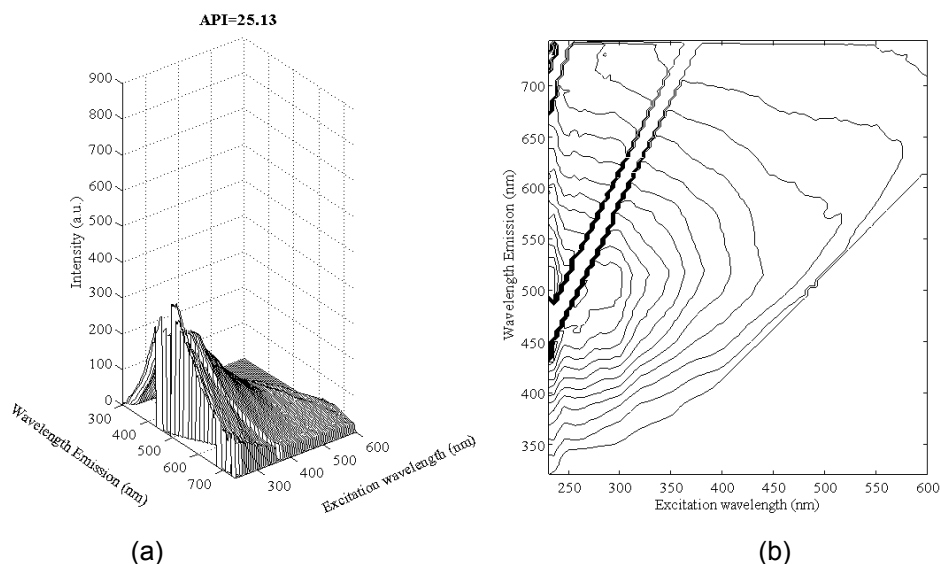


Figure 3. Total Fluorescence Spectra of the crude oil sample of Figure 1 with the lowest API value (a) 3D topographical diagram (b) contour map.

diagrams is, as in the conventional spectra, higher fluorescence intensity at the higher API grade. The contour maps also nicely show the red-shift in the emission maximum due to enhanced energy transfer in the heavier crude oil. Thus, the emission maximum of the high API crude oil is centered near 460 nm, while that of the heavy crude oil with low API is broader and shifted out to ca. 500 nm.

The synchronous fluorescence spectra of these samples are shown in Figures 4 and 5. The trend of a net decrease in intensity for the heavier crude oil observed in TFS is also evident in SFS. However, unlike TFS, the SFS spectra do not contain the scattering artifacts and the spectral maps have better defined contours with shoulders that might contain valuable information for the classification and characterization of crude oil.

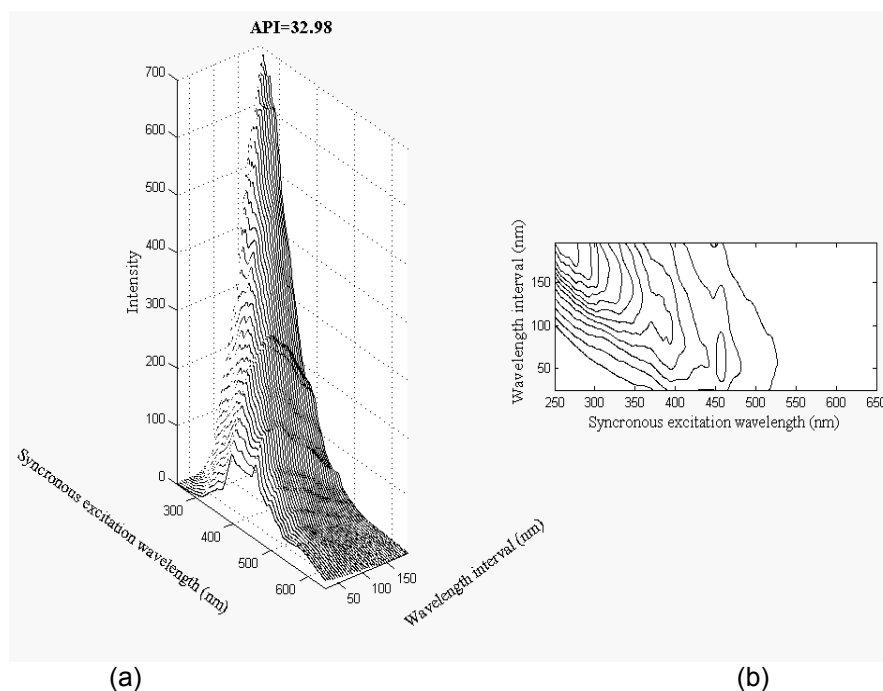


Figure 4. Synchronous Fluorescence Spectra of the crude oil sample with the highest API value (a) 3D topographical diagram (b) contour map.

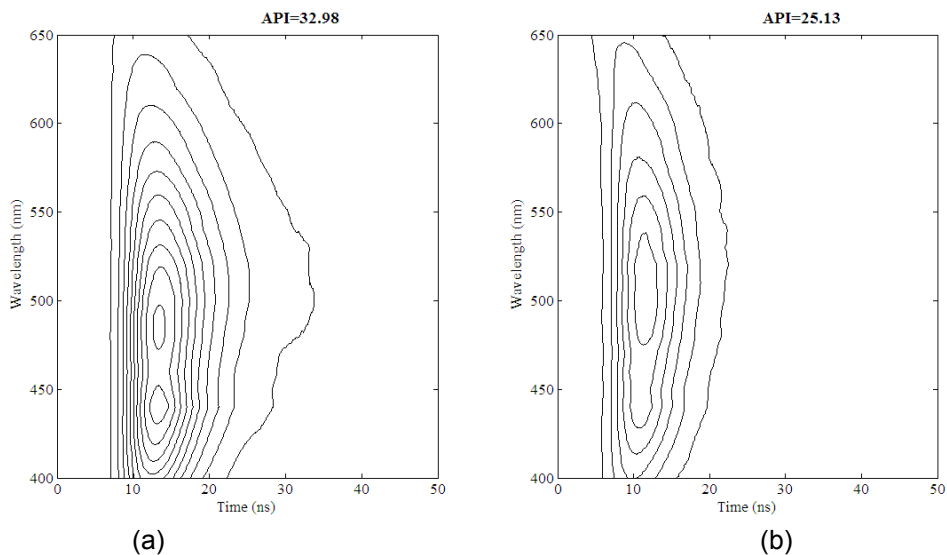


Figure 7. Contour maps for Time-Resolved Fluorescence Spectra of the (a) lighter crude oil and (b) heavier crude oil samples of Figure 6.

Figure 5. Synchronous Fluorescence Spectra of the crude oil sample with the lowest API value (a) 3D topographical diagram (b) contour map.

The time-resolved fluorescence spectra (TRFS) of these two samples, Figures 6 and 7, show that the fluorescence lifetime is also related to the API value. The fluorescence lifetime of the heavier petroleum is shorter than that of the lighter petroleum. Since quenching reduces the lifetime, this provides direct

experimental support for our previous inference, based on the relative fluorescence intensities and the red-shift of the emission (also present in Figures 6 and 7), that quenching processes are more predominant in heavier crude oils than in lighter ones.

From a modeling point of view, the

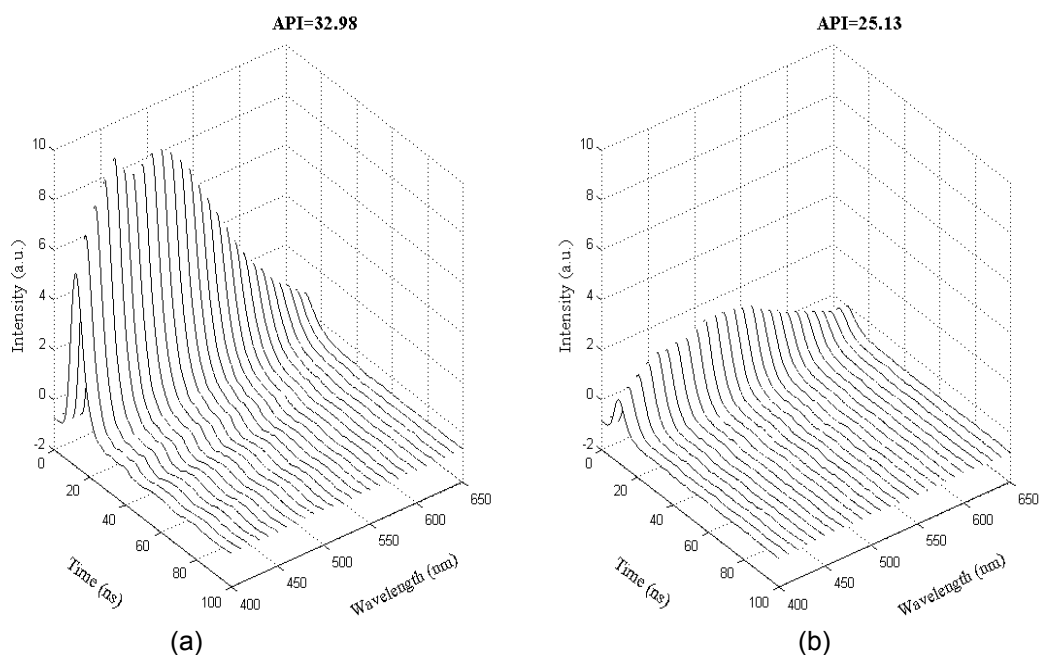


Figure 6. 3D topographical diagrams for Time-Resolved Fluorescence Spectra of (a) lighter crude oil and (b) heavier crude oil.

possibility of recording the emission spectrum at different times has several advantages. Since emitting species have different lifetimes, this technique might permit one to discriminate to some extent between the overlapping emissions of the various emitting species present in crude oil, potentially providing much more information than is available from TFS and SFS alone.

5. CONCLUSIONS

Fluorescence spectroscopy is capable of providing important information from samples as complex as crude oil. TFS is the easiest technique to implement, but has several limitations when the fluorescence signal or fluorescence intensity map is to be used to develop predictive models, since Rayleigh and Raman scattering can make major contributions to the signal. If the wavelength interval and slit widths are judiciously chosen, SFS avoids the scattering artifacts of TFS and provides better defined contour maps with pronounced shoulders that seem to be characteristic of each sample. TRFS provides the additional dimension of time and has the potential of providing direct indications of the importance of quenching processes and of time-resolving the emission from different fluorophores present in the petroleum sample. Nonetheless, relative to TFS or SFS, the application of TRFS in industry for the online and remote characterization and classification of crude oils would be more complex and much more expensive.

In summary, further studies using the various fluorescence techniques combined with multivariate calibration should be performed in order to confirm the potential of fluorescence as a spectroscopic tool for the development of prediction models applicable in industry.

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