

EPR and Fluorescence Spectroscopy in the Photodegradation Study of Arabian and Colombian Crude Oils

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EPR and fluorescence spectroscopy were used to evaluate the degradation of crude oils of different origins that were submitted to photochemical weathering under tropical conditions. The EPR spectra obtained showed signals of the paramagnetic species: the vanadyl VO^{2+} ion and organic free radicals. A decrease in linewidth of free radical signals was observed for both oils irradiated for 100 hours with sunlight of 350 W/m^2 . The reduction in the linewidth of the free radical of 9.8% in Arabian oil and 18.5% in Colombian oil, as well as the decrease in radical numbers, indicated photochemical degradation, especially in Colombian oil. The linewidth narrowing corresponding to free radicals in the irradiated oils occurred due to the rearrangement among radicals and aromatic carbon consumption. The irradiated oils showed a reduction in the relative intensity of fluorescence of the aromatics with high molecular mass, polar aromatics, and asphaltene. The fluorescent fraction was reduced by 61% in Arabian oil and 72% in Colombian oil, corresponding to photochemical degradation of crude oil aromatic compounds.

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1. INTRODUCTION

Some mechanisms have been proposed for the removal of hydrocarbons from the sea. For low molecular weight volatile components, evaporation or desorption from seawater followed by photooxidation in the air is thought to be the dominant process. For the remaining nonvolatile components, microbiological consumption and photochemical degradation were invoked. In tropical waters, which receive a high solar flux and are nutrient depleted, thus reducing microbiological productivity, photochemical processes may be as important as biological degradation [1]. Aromatic (naphthalenes, fluorenes, dibenzothiophenes, and phenanthrenes) and saturated fractions of petroleum were reduced by 40% and 70%, respectively, when Arabian light crude oil was subjected to microbial degradation. Crude oil components that were recalcitrant to biodegradation were degraded by sunlight irradiation [2].

Petroleum is formed by the thermal degradation of kerogen and may also contain large amounts of asphaltene [3]. Asphaltenes are macromolecular compounds, comprising polyaromatic nuclei linked by aliphatic chains or rings of

various lengths and sometimes by functional groups [4–6]. They appear to differ in size, with a statistically identical distribution of aromatic nuclei and linking units. Recent evidence suggests that asphaltenes may be considered as small “soluble” fragments of kerogen, as they share comparable structures [7–10]. Asphaltenes from rock extracts, and the corresponding kerogens, contain the same constituent macromolecular units [6]. A consequence of this compositional similarity is that asphaltenes and kerogen undergo parallel evolutions during burial heating. Coal may be regarded as a special type of kerogen, derived mainly from terrestrial organic matter [11, 12]. Each of these materials is comprised mainly of carbon, hydrogen, oxygen, nitrogen, and sulphur [3].

An interesting characteristic of the coal and asphaltene fraction of crude oils is the presence of stable free radicals [13]. Garif'ianov and Kozyrev [14] were the first to briefly mention the presence of unpaired electrons in crude oils. Petroleum and related materials such as heavy oils, asphalt, pitch, coal tar, tar sands, kerogen, and oil shale have been studied by EPR [15]. Asphaltenes are a problem in the production of heavy crude oils due to their tendency to flocculate

and precipitate during oil production and refinement [16]. Over the last few years, the need for a more efficient exploitation of heavy feedstocks has led to an increasing interest in the elucidation of the molecular structure of asphaltenes in order to understand their behavior in thermal and catalytic processes.

Fluorescence spectroscopy has been applied directly to crude oil or to asphaltene solutions and the absorption/emission behaviors of such a multicomponent system have been studied in detail [17–19]. In the petroleum industry fluorescence analysis is routinely used as an indicator of the presence of crude oil, but this technique can be also used to explore structural information regarding asphaltene molecules, such as the condensation of aromatic rings from the differences in intensities and positions of the fluorescence bands.

EPR is a useful method for the investigation of paramagnetic species. The EPR spectra of crude oils show the signals of two different paramagnetic centers, namely, the vanadyl group VO^{2+} and the free radical [20, 21]. Vanadyl compounds produce EPR signals with the anisotropic g factor and hf splitting. The characterization of crude oil has been achieved using this signal. Petroleum asphaltene contains three fundamental types of aromatic complexes with vanadyl, as well as organic radicals ($g = 2.0027\text{--}2.0037$) of 10^{18} spins/g [22]. EPR studies on asphaltene free radicals associated with unpaired π electrons stabilized by resonance in a large aromatic ring system are not numerous, even if the radical species and the problems involved in the analysis are similar to those found in coal and other carbonaceous materials [13–15, 20–23].

In the present study, EPR and fluorescence spectroscopy were used in order to evaluate the photodegradation of crude oils of different origins when these are submitted to tropical weathering. In these experiments the following crude oils were used: Arabian petroleum (Arabian light crude oil), because it is the oil that most circulates around the world in tankers, and Colombian petroleum (Cusiana crude oil) because this oil was spilled in an accident that occurred at the Presidente Getúlio Vargas refinery, Araucária, Paraná, Brazil.

2. EXPERIMENTAL SECTION

The crude oils used for this study were supplied by the Brazilian oil company, PETROBRAS. The preparation and irradiation methodology of crude oils was described by Guedes et al. in 2003 [21]. For each irradiated sample a nonirradiated control was used. The samples were irradiated by exposure to sunlight in the yard of the Chemistry Department of the Universidade Estadual de Londrina ($23^\circ 18' 45''$ S, $51^\circ 11' 15''$ W), Paraná, Brazil. The mean intensity of solar irradiation corresponded to 350 W/m^2 measured by the Meteorological Institute of Paraná (SIMEPAR, Brazil). After exposure of the crude oil films over water, the phases were separated by centrifugation and collected for analysis. The experiments were performed in duplicate to guarantee the reliability of the results.

EPR experiments were performed at X-band (9.5 GHz) microwave frequency and at a magnetic field modulation of

TABLE 1: Weight percentage of asphaltene and heteroatoms in the crude oils.

Oil	Asphaltene	Sulfur	Nitrogen
Arabian	0.01	1.7	1.09
Colombian	0.09	0.17	19.6

100 kHz in a Varian E-109 spectrometer at room temperature. Cr^{3+} :MgO ($g = 1.9797$) was used as a g marker and the Varian strong pitch signal as a spins counter standard. The microwave frequency was accurately read with an HP 5352 B frequency counter. Petroleum was introduced into 4 mm quartz EPR tubes. A “cavity baseline,” that is, an EPR spectrum of the empty cavity, was obtained and revealed no signal. The magnetic field of the EPR instrument was calibrated periodically against a standard sample.

Synchronous fluorescence scans (SFS) were recorded with petroleum in dichloromethane at a dilution of 1 to 1000 v/v using a quartz cell. The spectra at 90° -angle sample geometry were obtained from commercial fluorimeter, Shimadzu RF-5301PC equipment with photon counting. The wavelength interval, $\Delta\lambda$, between λ_{em} and λ_{ex} , was 20 nm with a 1.0 nm bandpass.

Some basic information on weight percentages of asphaltenes and heteroatoms present in the crude oils are shown in Table 1.

3. RESULTS AND DISCUSSION

Organic free radicals are present in the asphaltene fraction of oils, but little is known regarding their molecular nature due to the multiplicity of molecular structures that cause the appearance of an unresolved single line with a width between 4 and 6 Gauss [24]. The g parameter is sensitive to the chemical neighborhood of the unpaired electron, although asphaltenes (heavy oil fractions) demonstrate characteristics of a mixture of free radicals. These radicals are associated with a delocalized π system stabilized by resonance in polyaromatic centers. The g values are dependent on the content of heteroatoms (N , O , and S) and on the aromatic carbon fraction [25].

The EPR spectra were obtained for Arabian and Colombian crude oils. The signals of the paramagnetic species of Arabian petroleum are shown in Figure 1. The g value determined for the free radical signal was 2.0033 ± 0.0001 for Arabian petroleum and 2.0030 ± 0.0001 for Colombian petroleum. One possible interpretation for the g values observed corresponds to neutral radicals of carbon or nitrogen [4]. Thus, Arabian petroleum should have a lower percentage of aromatic carbon than Colombian petroleum, in which the percentage of heteroatoms should be higher. However, it is also possible that a difference in the distribution of the anisotropy in both the g value and the hyperfine coupling constants of the two samples produces a difference in the spectral shape, which could cause a small variation in the g value feature [26]. It is interesting to observe that this variation could result in increased localization of the electron on the heteroatom.

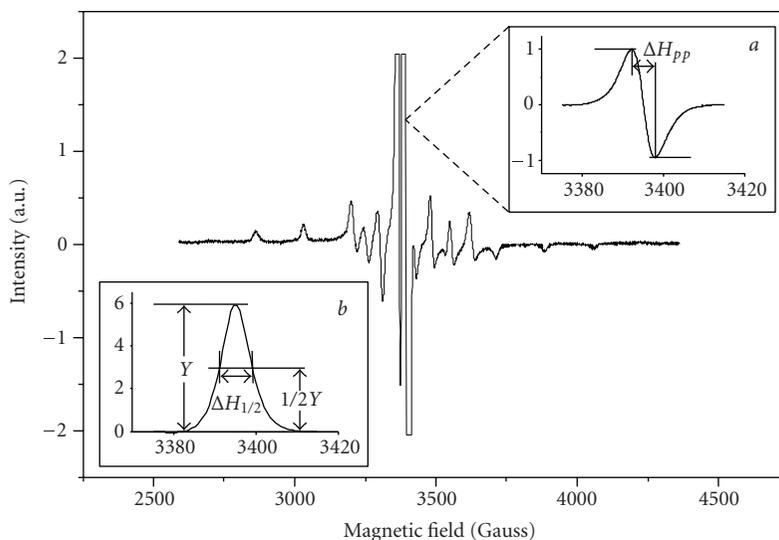


FIGURE 1: EPR spectrum of Arabian light crude oil at room temperature (gain = 1.0×10^4). (a) EPR spectrum of the free radical (gain = 2.0×10^3). ΔH_{pp} is peak-to-peak linewidth. (b) EPR line integration of the free radical. $\Delta H_{1/2}$ is linewidth at half-height.

No changes were observed in the free radical g -values in petroleum by exposure of the samples (irradiated and nonirradiated) to sunlight.

In petroleum asphaltenes, the hyperfine interaction is generally between the electron spin delocalized in an aromatic π orbital and the nuclear magnetic moments of H attached to the aromatic C . The linewidth broadening of the free radical cannot be attributed unequivocally to the unresolved hyperfine structure of the EPR spectrum. The effects of the aromaticity and the different degrees of substitution in the linewidth and the lineshape probably overlap, and a different number of spins could also contribute to the linewidth by dipolar interaction [24]. There are most likely a number of chemically distinct radicals, and each one of these different radicals also has a range of chemical environments and conformations, in such a manner that the variation in linewidth is not simply due to a variety of radicals but also to the distribution of these radicals in the crude oils. In addition, the mobility of radicals in petroleum is relatively low because of the high viscosity of these compounds, consequently, there will also be some contribution to the linewidth from the anisotropic components of the g tensor [26].

The linewidth ΔH_{pp} or peak-to-peak separations of the EPR derivative peaks (Figure 1(a)) and the linewidth $\Delta H_{1/2}$ or full width at half-height in EPR absorption peak (Figure 1(b)) of the free radical signal were 5.2 ± 0.1 and 7.8 ± 0.1 Gauss for Arabian petroleum and 5.3 ± 0.1 and 7.9 ± 0.1 Gauss for Colombian petroleum, respectively. The line shape parameter ($R_s = \Delta H_{1/2}/\Delta H_{pp}$) was 1.5 ± 0.1 for both crude oils. Line shapes are intermediate between Gaussian ($R_s = 1.18$), when instrumental or random statistical effects are most important and Lorentzian ($R_s = 1.72$), when lifetime effects dominate [27]. The EPR lines of the free radicals showed asymmetry around g , as revealed by Di Mauro et al. [26], and showed a tendency towards Lorentzian. Montanari et al.

determined R_s for seven asphaltenes obtained from different crude oils [25], the values were similar to those calculated here for petroleum.

Solar irradiation did not alter the linewidth of the signal corresponding to the free radical within a few hours of exposure of the oil films. A decrease in the ΔH values was observed for both oils in samples irradiated for 100 hours (Figures 2 and 3). The reduction in linewidth from 5.1 to 4.6 Gauss (9.8%) in Arabian oil and from 5.4 to 4.4 Gauss (18.5%) in Colombian oil indicates photochemical degradation of the crude oils under solar light.

In agreement with Scotti and Montanari [24], the g -values obtained by EPR for free radicals were found to be lower when the aromatic carbon fraction was larger, in the asphaltene of several crude oils registered by NMR. The fact that Arabian oil ($g = 2.0033$) presents a heteroatom weight percentage of 2.79%, smaller than Colombian oil (19.77% wt), and the fact that nitrogen and sulfur are located mainly in the aromatic systems in petroleum indicate that this oil is less aromatic than the Colombian oil ($g = 2.0030$). Another important fact obtained by EPR is that Colombian oil presents 19.6% wt of nitrogen and since this heteroatom is related mainly with porphyrinic and nonporphyrinic systems in petroleum asphaltenes, it is possible to affirm that the oil of Colombian origin has a larger asphaltene fraction than Arabian oil.

The spin relative counts of the free radical signal in crude oils indicated a reduction of 12% in this paramagnetic species in irradiated Arabian oil, while in irradiated Colombian oil this corresponded to 35% after 100 hours under solar light. In the nonirradiated samples (control) the spin counts revealed an increase of 16% and 9% in radicals in Arabian and Colombian oils, respectively, indicating that the photochemical process is capable of degrading the aromatic components present in petroleum.

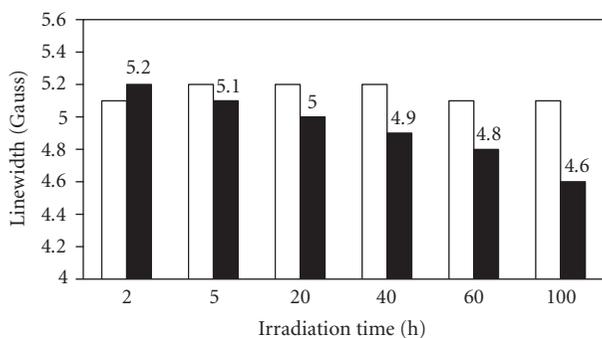


FIGURE 2: Variation of the linewidth of the free radical versus sun-light irradiation time for Arabian petroleum. Filled columns represent the irradiated samples and blank columns represent the nonirradiated samples.

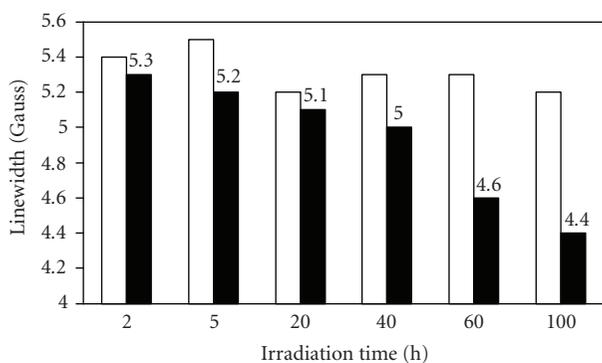


FIGURE 3: Variation of the linewidth of the free radical versus sun-light irradiation time for Colombian petroleum. Filled columns represent the irradiated samples and blank columns represent the nonirradiated samples.

The degradation of crude oils can be observed by a reduction in the amount of free radicals related to spin counts and to linewidth narrowing of the EPR signal of these paramagnetic species, which react with atmospheric oxygen and can be extinguished during the exposure of crude oils to solar light.

There was no significant variation in the ΔH values for the free radicals in the nonirradiated samples. The line shape parameter was determined in the EPR spectra and showed no modification in relation to the value obtained before irradiation.

It is possible to affirm that the narrowing of the EPR line corresponding to free radicals in the irradiated oils was due to the rearrangement among the radicals present. The electromagnetic source, in the case of the solar light, with chemical modification properties in relation to some substances, can break links that result in the generation of free radicals, which upon suffering rearrangements or recombinations can produce other chemical species different from the precursory compounds.

The photochemical degradation of crude oils was also characterized by synchronous fluorescence scan [28]. This

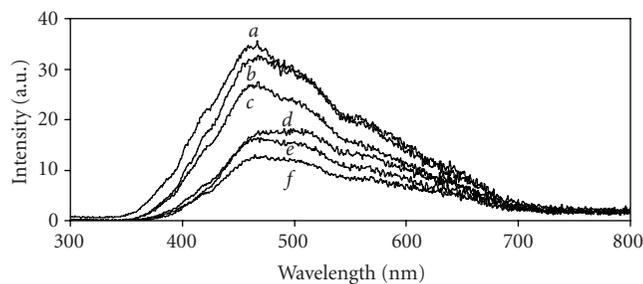


FIGURE 4: Synchronous fluorescence spectrum ($\Delta\lambda = 20$ nm) of Arabian petroleum. Irradiation times: (a) 0 h, (b) 2 h, (c) 20 h, (d) 40 h, (e) 60 h, and (f) 100 h.

possibility was achieved by scanning both the monochromators simultaneously, a process called spectroscopy SFS.

The ability to analyze a complex multicomponent mixture without resorting to tedious separation procedures is extremely useful for routine analysis. Single-wavelength fluorescence measurement is limited in its ability to analyze complicated multi-component samples when they have severely overlapping emission and/or excitation spectra. This can be overcome using SFS, where the overlapping of spectra can be minimized. Lloyd and Evelt's first application of SFS was in the field of forensic science [29–32]. The development of SFS-based methods for the analysis of PAHs (polycyclic aromatic hydrocarbons) in solution without a pre-separation procedure has been a topic of interest in the past few years. The SFS characteristics of chrysene, perylene, dibenz[a,c]anthracene, and coronene were studied in aqueous and aqueous micellar media [33]. Synchronous fluorescence methods were used to determine selected polynuclear aromatic hydrocarbons in a coal liquid (solvent-refined coal) product without a pre-separation step [34].

It was found that the aromatic, polar, and asphaltenic fractions present in petroleum are fluorescent [35]. In studies with petroleum, fluorescence is a sensitive indicator of photochemical transformation [36]. It is known that the photodegradation of petroleum begins with light absorption generating a singlet oxygen and/or free radical [37]. Petroleum contains aromatic hydrocarbons known to generate singlet oxygen, which are intermediates for the photooxidation of crude oil. Free radical reactions involve hydrogen abstraction and the formation of hydroperoxy radicals. Free radicals can be generated in water by photochemical electron transfer and this mechanism may be important in the oil-water interface [1].

The oil films dispersed in water and irradiated with sunlight showed decreased fluorescence intensity at all wavelengths from 350 to 700 nm (Figures 4 and 5). In the visible spectrum there was a strong reduction in the emission intensity of aromatic polycyclic hydrocarbons of low and high molecular mass, polar aromatics, and asphaltene. The typical emission of the constituent fractions of crude oil was shown by Nicodem et al. [35].

The fluorescent areas of the samples exposed to sunlight were determined and the relative percentages are listed

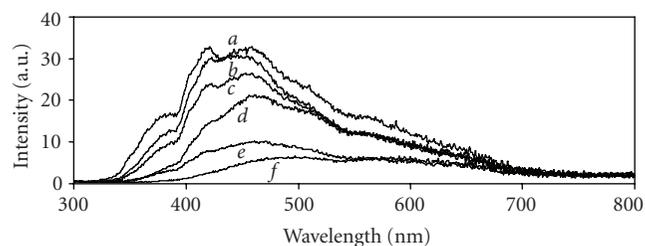


FIGURE 5: Synchronous fluorescence spectrum ($\Delta\lambda = 20$ nm) of Colombian petroleum. Irradiation times: (a) 0 h, (b) 5 h, (c) 15 h, (d) 20 h, (e) 60 h, and (f) 100 h.

TABLE 2: Fluorescence percentage of the oils calculated through the integrated area of the spectra corresponding to the irradiated samples.

Irradiation time	Integrated area of fluorescence	
	Arabian oil	Colombian oil
Nonirradiated	100%	100%
2 h	90%	99%
5 h	79%	94%
20 h	73.5%	79%
30 h	56.5%	65.5%
40 h	54%	54%
60 h	48%	37%
100 h	39%	28%

in Table 2. Considering the calculation of the fluorescence spectra area of Arabian and Colombian oils, before and after 100 hours of irradiation with medium intensity of solar light about 350 W/m^2 impacting the samples, it was observed that fluorescence was reduced by 61% in Arabian oil and by 72% in Colombian oil, corresponding to the photochemical degradation of the aromatic components of crude oils. The fluorescent fraction of Colombian oil was more sensitive to photochemical degradation.

The decay in fluorescence intensity at 500 nm, the typical wavelength of the asphaltene emission in petroleum, during the photochemical degradation of the oils followed the tendency represented in Figure 6. Fluorescence was reduced at the ratio of 1 : 2.5 for Arabian oil and at the ratio of 1 : 4 for Colombian oil, after 100 hours of irradiation under tropical conditions. The photochemical degradation of the correspondent fraction was observed by fluorescence spectroscopy.

In the 400 nm region, where the emission zone of the petroleum polar fraction begins, that is, aromatic containing heteroatoms [35], fluorescence was reduced at the ratio of 1 : 5 for Arabian oil and of 1 : 16 for Colombian oil after 100 hours of irradiation. The results showed, once again, that Colombian oil was more affected by the consequences of photodegradation.

Fluorescence spectroscopy and EPR are important techniques used to characterize the photochemical weathering of petroleum. The oils studied in the present investigation were

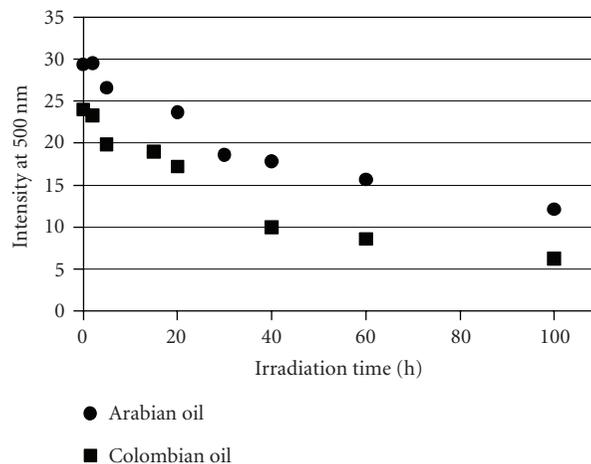


FIGURE 6: Fluorescence intensity at 500 nm versus sunlight irradiation time. Circles represent Arabian oil and squares represent Colombian oil.

significantly affected by the action of sunlight under tropical conditions, especially Colombian oil. These spectroscopy techniques can be further explored and, consequently, applied in the monitoring of petroleum weathering and its by-products in environmental matrixes whenever accidents occur or routine operations result in oil spill. The period of permanence of toxic and refractory aromatic components of petroleum in aquatic systems can be evaluated not only through quantitative chromatographic methods, but also using nondestructive and more economical qualitative methods.

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