

Photochemistry of petroleum

I. Systematic study of a brazilian intermediate crude oil

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Received 15 May 1996; accepted 9 June 1998

Abstract

The photochemical weathering of a crude Brazilian petroleum as a film over sea-water by sunlight has been studied using a combination of analytical tools including elemental analysis, GC, UV-VIS, IR, Fluorescence, and NMR. Fluorescence intensity decreased rapidly upon irradiation, whereas only slight weathering could be observed by GC and IR even after 100 h of exposure to full tropical sunlight. The other methods used did not reveal observable changes in petroleum composition. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: petroleum; photochemistry; photodegradation; petroleum weathering; fluorescence

1. Introduction

It is estimated that 3.2 million tons of petroleum enters the world oceans each year, mostly as a result of human activities (Clark, 1989). Oil films or slicks are formed and transformed by a combination of physical, photochemical, and biological processes. Associated physical changes such as evaporation, dissolution, dispersion and spreading, with accompanying changes in density, viscosity, and interfacial tension, have been extensively studied (Seymour and Geyer, 1992) and modeled (Mackay and McAuliffe, 1988) in order to predict oil movement following a spill. Biological transformations have also been extensively studied (National Academy of Sciences, 1985; Larson and Berenbaum, 1988) in connection with the impact of spilled oil on the sea shore

ecosystem, and in order to understand the eventual fate of spilled oil.

Photochemical processes, in contrast, have been little studied and are not well understood. For example there exist parameters that can be used to evaluate the physical and biological weathering of oils (Atlas et al., 1981; National Academy of Sciences, 1985; Boehm et al., 1987), but no index for photochemical weathering has been proposed. Nevertheless, in the last 10 years it has been recognized that photochemical processes play an important role in petroleum slick weathering (Payne and Phillips, 1985; Bongiovanni et al., 1989). It is now well established that solar irradiation affects oil emulsion stability (Payne et al., 1987; Mackay and McAuliffe, 1988) and water solubility (Jordan, 1991). Although photochemically induced physical changes in petroleum characteristics are easily measured, the chemical changes responsible are much less well understood (National Academy of Sciences, 1985).

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The large variations found in petroleum composition provide a partial explanation for our lack of understanding since photochemical weathering would be expected to vary with the physical and chemical properties of the oil. Perhaps a more fundamental reason for our lack of understanding of this important phenomenon resides in the relative lack of research on the photochemical degradation of petroleum (Nicodem et al., 1997). Much of the existing research does not allow the unequivocal separation of biological and photochemical processes. In many cases conditions are used that do not simulate environmental conditions (for example, the use of short wavelength UV lamps), or involve petroleum fractions, or model compounds. While these studies can give useful information on possible reactions, they do not replace photochemical studies of crude petroleum under natural or simulated natural conditions. There have been several very good studies of petroleum dispersed or 'dissolved' in water (Literathy et al., 1989; Ehrhardt and Weber, 1991; Ehrhardt et al., 1992), but the photochemistry in water may be very different from the photochemistry on water. For petroleum in water, the oil–water interface is important and light will be absorbed at this interface, while for petroleum on water, light will be absorbed mainly at the oil–air interface and the photochemistry is expected to occur in a relatively non-polar environment. Of the few known studies of crude petroleum films on seawater in which photochemical transformations can be separated from other weathering processes, three are restricted to the oxidation of the sulfur containing constituents (Burwood and Speers, 1974; Patel et al., 1979; Lamathe, 1982). Another three papers are mainly concerned with alterations in interfacial tension and the formation of mousse (Thingstad and Pengerud, 1983; Desmaison et al., 1984; Daling et al., 1990), and only one looks at petroleum composition (Daling et al., 1990). All of these studies utilize temperate climate conditions. There has been a report (Watkinson and Griffiths, 1987) of the photochemistry of petroleum films under tropical conditions, but this study does not eliminate biological transformations and uses the special condition of absorption on membranes.

Even considering related photochemical research, the number of publications is still small and it is difficult to compare results, which sometimes con-

flict due to the fact that different oils and analytical techniques are used.

A greater knowledge of the photochemical transformations therefore seems warranted. In tropical sea conditions, where the solar intensity is high and biological processes are impeded by lack of nutrients, photochemical processes may be a major contributor to petroleum degradation (Ehrhardt et al., 1992). Furthermore, photochemical processes may also be important to the subsequent biological consumption of oil (Nicodem et al., 1997). For these reasons, it was decided to study the photochemical alteration of films of a crude Brazilian petroleum, using natural sunlight under tropical conditions, in order to obtain more information on the photochemistry of petroleum under these conditions.

2. Experimental

The petroleum used in this study was from the Brazilian Campos offshore oil field in the state of Rio de Janeiro, and was a gift of the Brazilian oil company, PETROBRAS. In all experiments 5 ml of petroleum was floated over 20 ml of sea water. The resulting oil film was 0.7 mm thick. Petri dishes with pyrex lids were used. This pyrex transmits 75% at 295 nm and 85% at 300 nm and does not appreciably attenuate sunlight. Its use is common practice for samples with considerable absorption in the UVA and visible portions of the solar spectrum (Anba-Lurot et al., 1995; Lartiges and Garrigues, 1995). Samples were irradiated by exposure to sunlight on the chemistry building roof on cloudless days from 10 AM until 4 PM, and were stored in the dark in a freezer at -15°C between irradiations until the total number of hours was accumulated. Although storage at room temperature gave the same results, this precaution was taken to insure that there was no biological degradation on extended storage during cloudy periods. For every irradiated sample there was a non-irradiated blank which was treated in the same way except that a black cover plate was used to eliminate irradiation. Following irradiation, the two phases were separated by centrifugation and the oil samples were stored in the dark at -15°C while awaiting analysis.

Elemental analysis (CHN) was run on a Perkin Elmer 2400 CHN. Absorption spectra were obtained in dichloromethane using a Varian-Cary 1E UV-VIS spectrophotometer. Fluorescence spectra were recorded in dichloromethane at a dilution of 1 to 1000 v/v using a SPEX Fluorolog 2 Model F111XI with photon counting. Analyses were front face synchronous with 20 nm offset between excitation and emission monochromators and a bandpass of 1.0 nm.

Infrared spectra were obtained using a Nicolet 740-FT-IR on samples deposited as films between NaCl plates. The petroleum sample was applied without dilution.

Gas liquid partition chromatographic analysis utilized a Hewlett-Packard 5890 II instrument with on-column injection at 310°C. A 20 m by 0.3 mm – 54 column was used with hydrogen as carrier gas. Column temperature was programmed from 40°C to 300°C.

Proton NMR spectra were obtained at 300 MHz in deuterio-chloroform using a Varian Gemini-300. Carbon 13 NMR spectra were also obtained in deuterio-chloroform using a Bruker DRX-300.

3. Results and discussion

The alterations in composition produced by solar irradiation were investigated using elemental analysis (CHN), gas liquid partition chromatography (GC), electronic absorption spectrometry (UV-VIS), fluorescence emission spectrometry, infrared spectrometry (IR), proton nuclear resonance spectroscopy (^1H NMR), and Carbon 13 nuclear resonance spectroscopy (^{13}C NMR). These methods individually

and collectively give information on the types and distribution of petroleum components. Individual methods are discussed separately followed by general conclusions.

3.1. Elemental analysis (CHN)

The results of the elemental analysis for irradiation times from 0 to 100 h are given in Table 1. Before irradiation, the sum of the percent of carbon and hydrogen is $97.78\% \pm 0.58\%$ leaving only 2.22% for other elements such as nitrogen, sulfur, and oxygen. Nitrogen was also measured (column 4) and gave 2.25%, but the nitrogen measurement consistently gave large errors (in this case 1.70%) perhaps due to the low concentrations of nitrogen that were being measured. An independent measurement on a different instrument gave C 86.30%, H 12.60%, N 0.26%, and S 0.49% which leaves only 0.35% for other elements, chiefly oxygen (Fernandes, 1994).

As can be seen from Table 1, the percentage of carbon and hydrogen is the same, within experimental error, for zero and 100 h of irradiation. The remaining percentage starts at 2.22% and terminates at 2.44% with no systematic fluctuation in between. Within experimental error it is concluded that even after 100 h of solar irradiation, this petroleum does not show increased incorporation of oxygen (less than 1%). Other methods (vide infra) do show that the petroleum has become more oxidized, but the actual percentage of added oxygen must be low.

Previous studies involving CHN have given mixed results, in several cases, ‘photochemically’ weathered petroleum showed an increased oxygen content (Sydnes et al., 1985; Ducreux et al., 1986; Daling et

Table 1
CHN Analysis of petroleum

Irradiation time (h)	Percentage of C	Percentage of H	Percentage of N	Number of measurements
0	85.42 ± 0.49	12.36 ± 0.09	2.25 ± 1.70	4
2	85.50 ± 0.43	12.42 ± 0.10	1.07 ± 0.67	3
5	85.19 ± 0.49	12.41 ± 0.23	0.93 ± 0.60	3
20	85.54 ± 1.05	12.37 ± 0.45	1.94 ± 1.78	4
40	85.34 ± 0.70	12.18 ± 0.49	2.10 ± 1.76	4
60	85.19 ± 1.61	12.13 ± 0.60	2.80 ± 2.05	5
100	85.42 ± 0.57	12.14 ± 0.22	1.68 ± 0.89	5

al., 1990), while in others it did not (Jordan, 1991; Tjessem et al., 1984). These studies are not directly comparable with present results or with each other, since different crude oils, weathering times, and irradiation conditions were used.

Three explanations can be put forward for the results observed in this study: (1) the rate of photochemical oxygenation may be so slow that 100 h provides insufficient time for significant oxygen incorporation, (2) oxygenated compounds are formed but migrate into the aqueous phase, or (3) the process of oxidation produces low molecular weight oxidized components which are volatile and therefore lost. Migration of polar oxygenated photoproducts into the water column has been previously observed (Scheier and Gominger, 1976; Griffin and Calder, 1977; Larson et al., 1979; Ostgaard et al., 1987), as has the formation of volatile ketones and aldehydes (Ehrhardt and Weber, 1991).

The experimental setup used here does not allow the determination of volatile photoproducts, and water solubilities were not determined as part of this study. In a separate project using the same petroleum, it was found that polar organics are indeed formed and migrate into the water phase (Fernandes, 1994), however, the quantity (0.02%) is very small and cannot explain the lack of oxygenation.

3.2. Gas liquid partition chromatography (GC)

The main feature of the GC chromatographs shown in Fig. 1a–d is the progressive loss of the lower boiling components and the maintenance of the progression typical of linear alkanes. The loss of the lower boiling components due to evaporation is a general weathering process (Mackay and McAuliffe, 1988; Seymour and Geyer, 1992; Lee, 1991) and is expected to occur here since the samples were covered but not sealed. These results are reasonable considering that in this study biological transformations are not observed and the linear alkanes are resistant to photochemical transformation.

The ratio of linear *n*-octadecane to phytane has been used as an indicator of biological weathering (National Academy of Sciences, 1985; Boehm et al., 1987) since the branched hydrocarbon phytane is resistant to biological degradation. However, it has been found that branched hydrocarbons are readily

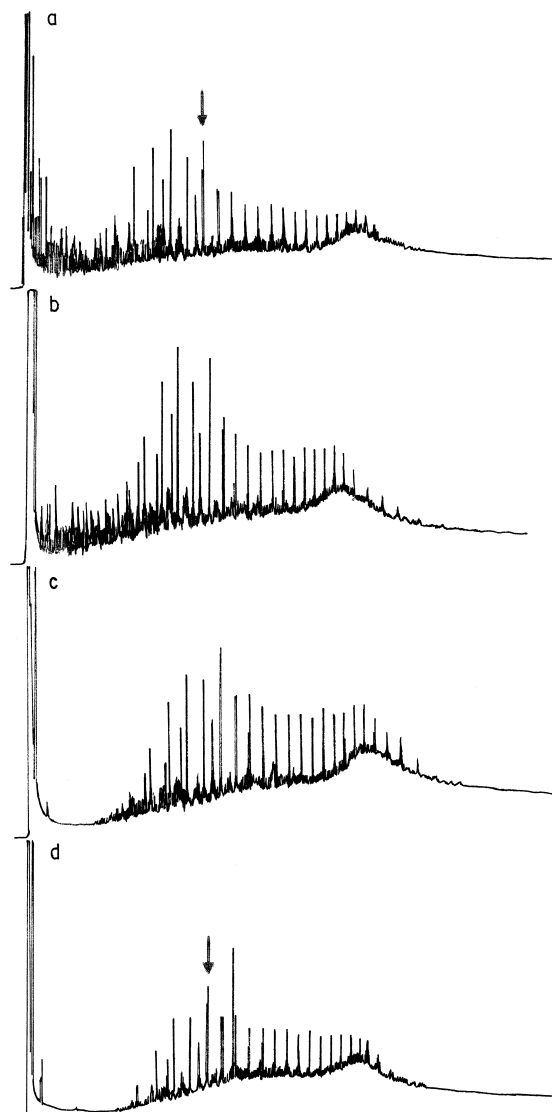


Fig. 1. Gas liquid partition chromatogram of crude petroleum after (a) 0 h of irradiation, (b) 5 h, (c) 60 h, (d) 100 h. The arrow refers to the peak due to pristane.

photo-oxidized in seawater and in the presence of a sensitizer. For example, pristane (Rontani and Giusti, 1987) and 3,6-dimethyloctane (Rontani and Giusti, 1988) are converted to ketones and alcohols. Petroleum contains components capable of acting as sensitizers (Sydnes et al., 1985; Lichtenthaler et al., 1989) and this could, in principle, also be occurring here. If branched hydrocarbons such as phytane and

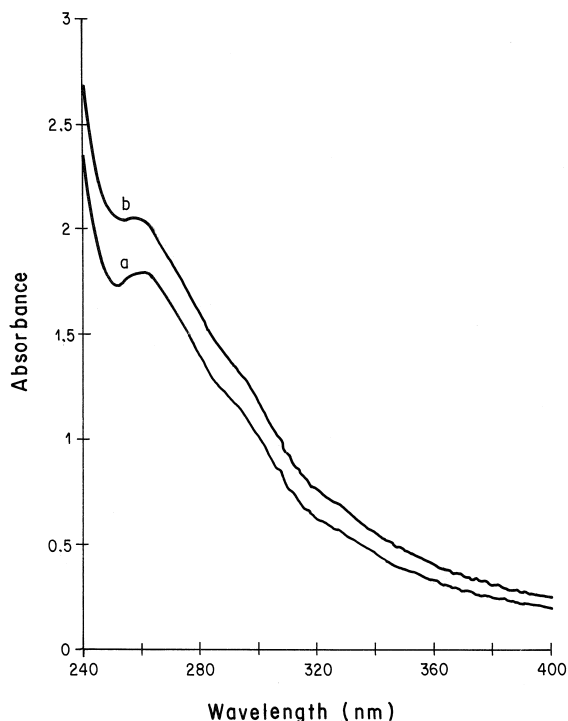


Fig. 2. UV absorption spectrum of petroleum diluted 1 to 10,000 in CH_2Cl_2 . (a) 0 h irradiation, (b) 100 h.

pristane were preferentially lost through photochemical processes, the utility of the ratio of linear to branched hydrocarbons as an indicator of biological transformation would be compromised.

The concentration of pristane was therefore measured relative to *n*-heptadecane (C_{17}). The location of pristane in the GC spectrum was determined by co-injection and it is known that C_{17} elutes slightly before pristane (Reed, 1977). The C_{17} to pristane ratio for non-irradiated petroleum was 0.646. Analysis of petroleum irradiated 100 h gave 0.664 for this ratio. The change in this ratio is within the error for this type of analysis and is entirely too small to show a clear effect even after 100 h with this petroleum. Since in this study biological processes are not observed, this result indicates that photodegradation of pristane is not important for the exposure times used here.

3.3. Electronic absorption spectrometry (UV-VIS)

The relatively structureless UV-VIS-NIR absorption spectrum of this petroleum is typical for petroleum (Mullins et al., 1992). The UV portion of the absorption spectrum is shown in Fig. 2. There is

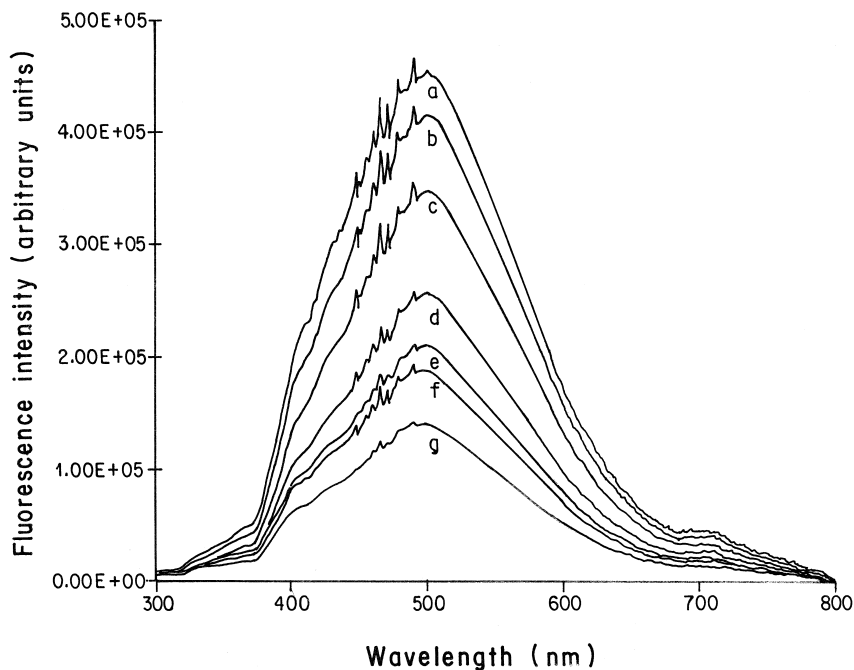


Fig. 3. Synchronous fluorescence spectrum of petroleum with irradiation times (in hours) of (a) 0, (b) 2, (c) 5, (d) 20, (e) 40, (f) 60, (g) 100.

an absorption maximum at 260 nm with a long wavelength tail. In the UV, the spectral shape remains relatively constant following irradiation but the intensity increases slightly after 100 h of irradiation. The simplest explanation for this increase involves the same process of evaporation of the lower boiling components seen using GC. The loss of the lighter aliphatics, which do not absorb, and the lower boiling monoaromatic components, which absorb only weakly in the spectral range analyzed, would result in an increased concentration of those components with absorption beyond 240 nm.

3.4. Fluorescence

Fig. 3 shows the synchronous fluorescence spectra of the petroleum as a function of irradiation time. There is a significant decrease in fluorescence intensity after only 5 h of irradiation. The non-irradiated blank, on the other hand, remained relatively constant. The total peak area for irradiated and non-

irradiated petroleum samples are compared in Fig. 4. It is evident from this figure that the major processes leading to the loss of fluorescence are photochemical.

The relatively rapid initial decrease in fluorescence intensity is followed by a much slower decline which may indicate that some fluorescent components are much more reactive and are preferentially destroyed, as has been suggested for oil in water dispersions (Literathy et al., 1989), but it could also be partially caused by physical alterations in the film with time. Evaporation of the lighter fractions and possibly photochemical polymerization (Thominette and Verdu, 1984) would increase the viscosity and could impede bimolecular oxidations such as the reactions of singlet oxygen.

It might be expected that certain aromatic petroleum constituents would be preferentially transformed and that the synchronous spectra would show alterations in relative intensity with irradiation. This is, however, not observed. The ratio of the maximum

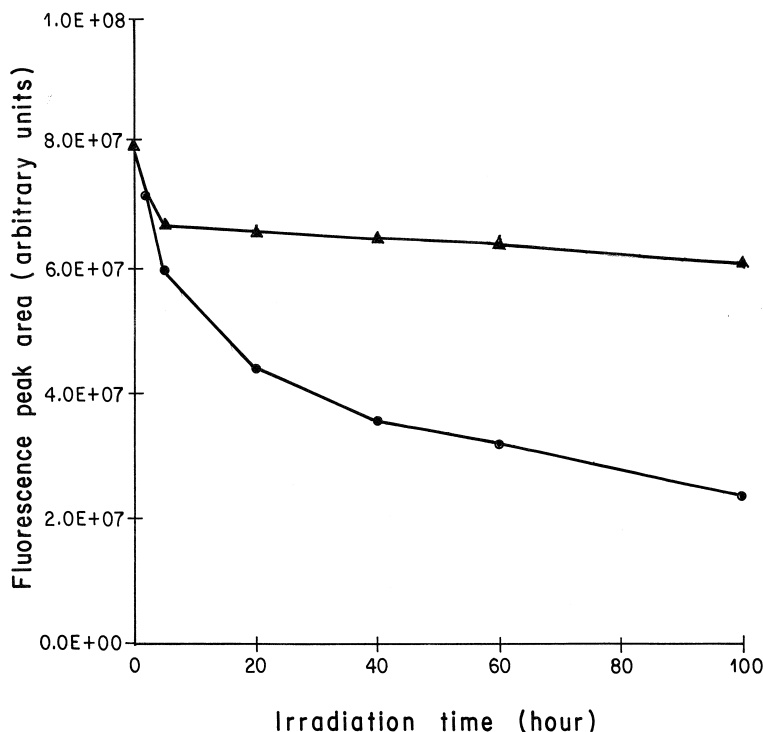


Fig. 4. Total integrated fluorescence intensity from 300 to 800 nm for petroleum samples diluted 1 to 1000 as a function of irradiation time. Triangles are for the non-irradiated blanks, circles are the data for irradiated samples.

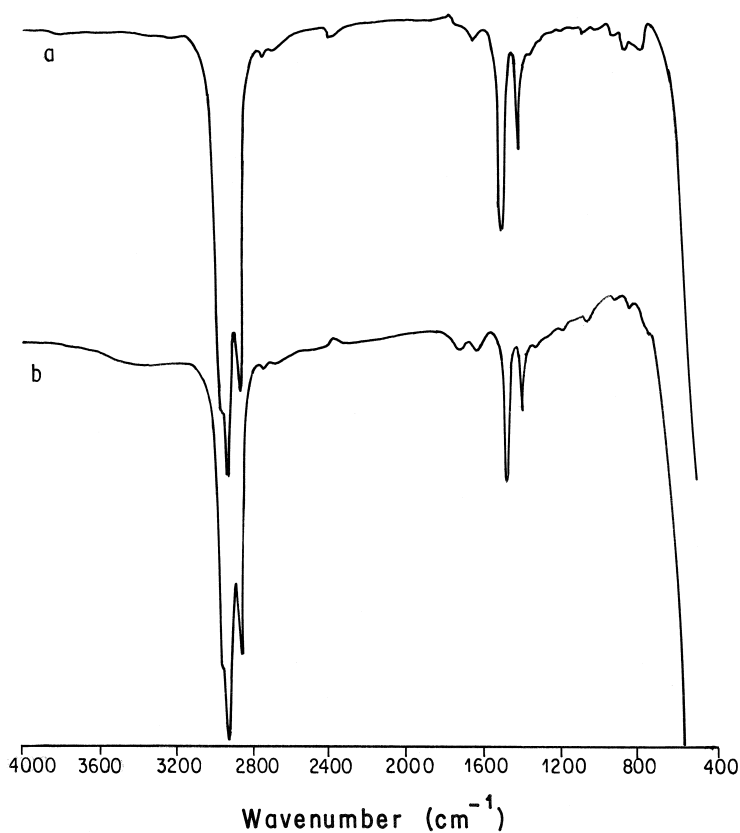


Fig. 5. FT-IR spectrum of petroleum as a film on NaCl. Spectrum (a) before irradiation, spectrum (b) after 100 h of solar irradiation.

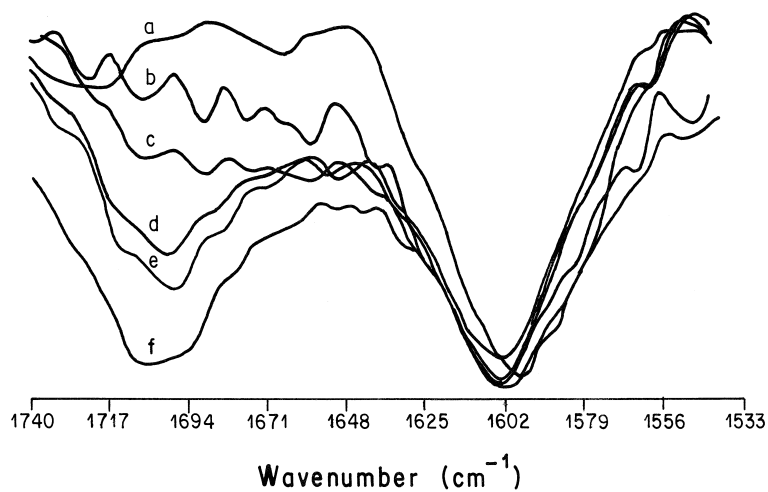


Fig. 6. FT-IR spectrum of the 1600–1740 cm^{-1} region as films on NaCl. Relative intensity of the 1700 cm^{-1} region in relation to the 1602 cm^{-1} absorption as a function of irradiation time in hours. (a) 0, (b) 5, (c) 20, (d) 40, (e) 60, (f) 100.

intensity at 500 nm to the intensities at 400, 600, and 700 nm are the same for the non-irradiated sample (0 h) and the sample irradiated for 100 h.

The integrated fluorescence intensity after 100 h is only 39% of the initial intensity. In the same time period there is a slight increase in absorption (Fig. 2) so the reduction in fluorescence cannot be due to decreased absorption. The implication is that a major portion of the fluorescent fraction has suffered transformation into co-absorbing and relatively non-emitting components.

3.5. Infrared spectrometry (IR)

The infrared spectrum of petroleum irradiated for 100 h is compared to non-irradiated petroleum in Fig. 5. It can be seen that although the overall spectra are very similar, the irradiated sample does show decreased absorption in the 700–900 cm^{-1} region and some increased absorption in the 3400, 1700, and 1100 cm^{-1} regions. The increased absorption is indicative of absorptions due to OH, carbonyl, and C–O bonds, respectively.



Fig. 7. FT-IR spectrum of the 950–1200 cm^{-1} region as films on NaCl. Intensity of absorption as a function of irradiation time in hours. (a) 0, (b) 5, (c) 20, (d) 40, (e) 60, (f) 100.

Table 2
 ^1H NMR Analysis of petroleum

Irradiation time	Percentage of aliphatics ^a	Percentage of polar ^b	Percentage of aromatic ^c
0	90.8	5.4	3.7
5	86.3	7.3	6.3
20	89.1	6.5	4.3
40	90.0	6.5	3.5
60	93.2	4.2	2.6
100	91.5	5.5	3.0

^a Integrated area of proton absorption between 0 and 2 ppm.

^b Integrated area of proton absorption between 2 and 4 ppm.

^c Integrated area of proton absorption between 6 and 9 ppm.

The development of the absorption around 1700 cm^{-1} is shown in Fig. 6, which shows the region between 1540 and 1740 cm^{-1} . With continued irradiation, an absorption centered around 1700 cm^{-1} develops. In this case, the constant absorption at 1602 cm^{-1} due to aromatic ring vibrations (Conley, 1966) could be used to scale and superimpose the spectra so that the growing-in of the 1700 cm^{-1} band could be clearly seen. This new band corresponds to the absorption due to carbonyl or carboxyl stretching (Conley, 1966).

The band in the region from 950 to 1200 cm^{-1} is shown in Fig. 7. The initial weak absorptions at 960, 1030, 1085, and 1170 cm^{-1} are characteristic of n-alkane and substituted benzenes. These absorptions are gradually submerged by a broad absorption in the same region which increases with irradiation time. This is the region of absorption of the C–O bond in alcohols, ethers, esters, and acids, and the simplest explanation for the increased absorption involves the formation of carbon–oxygen bonds due to photochemical oxidation. Non-irradiated samples do not show this increased absorption.

The C=O bond absorption at 1700 cm^{-1} and C–O bond absorptions in the region of 1100 cm^{-1} are strong absorptions and can be observed even when the concentrations of the species absorbing are small. The weak increase observed would seem to indicate that, albeit slowly, the petroleum film is becoming more oxidized.

3.6. Proton nuclear resonance spectroscopy (^1H NMR)

The proton NMR of this petroleum is dominated by aliphatic CH_3 , CH_2 , and CH absorptions in the 0

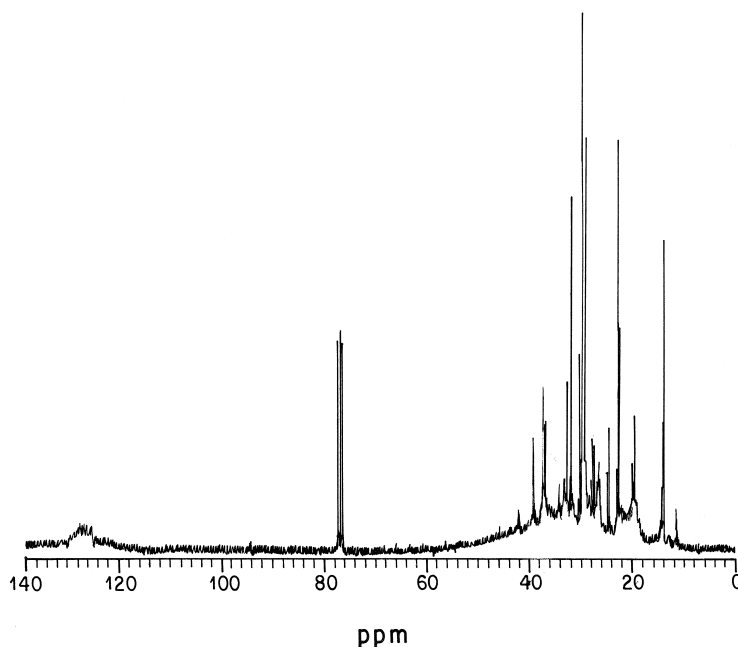


Fig. 8. Carbon 13 NMR spectrum, in CDCl_3 , of the crude petroleum used in this work.

to 2 ppm region, as is the case for most petroleum samples. The absorptions in the 2 to 4 ppm region characteristic of hydrogen linked to heteroatoms (N, S, O), and the absorption in the 6 to 9 ppm region characteristic of aromatic protons are much less intense. The intensities in these three spectral regions were integrated and the results are presented as percentage values in Table 2. Although there are some variations in the values, the initial (0 h) and final (100 h) percentages are essentially the same, and it is concluded that the variations reflect the precision of the method. No significant alteration was observed in either the percent of aromatic or heteroatom protons.

3.7. Carbon 13 nuclear resonance spectroscopy (^{13}C NMR)

The Carbon 13 NMR spectrum of non-irradiated petroleum is shown in Fig. 8. The strong absorption between 76.5 and 78 ppm is due to solvent (CD_3Cl). The low field absorptions between 10 and 50 ppm are due to aliphatic sp^3 carbons while the weak absorptions between 100 and 160 ppm are due to aromatic sp^2 carbons. The ratio of the integration of the sp^2 to sp^3 area is 0.242 for the non-irradiated petroleum. This value does not represent the actual ratio of sp^2 to sp^3 carbon since the intensities of carbon 13 absorptions are not equal for different types of carbon (Breitmaier and Voelter, 1987). A ^{13}C NMR spectrum taken of a sample of petroleum irradiated for 60 h did not show any obvious alteration except that the ratio of sp^2 to sp^3 carbons had increased slightly to 0.278. This increase could indicate that aliphatic carbons are being oxidized to carbonyl (sp^2) carbons. The change is so small, however, that it may be within experimental error, and in any case confirms that there is little, if any, change in overall structure.

4. Conclusions

Even after 100 h of solar irradiation, this intermediate crude petroleum shows no discernable chemical alterations as measured by CHN, GC, UV-VIS, and NMR analyses. Using IR, slight changes can be

observed, with the formation of carbonyl or carboxyl and C–O functions, but the overall spectra before and after irradiation are still very similar.

In contrast, the fluorescence emission intensity decreases rapidly and is only two fifths of its initial intensity after 100 h of irradiation. This rapid conversion of fluorescent aromatic components into non-fluorescent aromatic derivatives occurs even when no oxygen incorporation can be observed.

It is generally believed that the reduction of fluorescence intensity is due to the formation of oxygenated derivatives which are less fluorescent, as has been observed on irradiation of petroleum derivatives in the aqueous phase (Ehrhardt and Knap, 1989; Ehrhardt et al., 1992). The present results are difficult to explain in this way, but it is possible that the low levels of oxidation observed here could be responsible for the diminished fluorescence. If oxygenation preferentially oxidized high molecular weight aromatics, then low levels of oxygenation would transform a large percentage of the fluorescing aromatics into nonfluorescing aromatic derivatives. The petroleum used in this study contains about 20% aromatics (Fernandes, 1994). If these are the fluorescing components (e.g., if the polar and asphaltene fractions are relatively non-fluorescing) and the average molecular weight of this fraction is 320 Da, then preferential oxidation of these components would require incorporation of 0.5% of oxygen. This would oxidize half of the aromatics and reduce the fluorescence intensity by half. This might be a reasonable possibility if the main oxidative pathway involved specific singlet oxygen addition to the larger multi-ring aromatics.

A second possibility involves the phototransformation of aromatics by non-oxidative pathways. It is known that at high concentration, aromatics such as anthracene and benzantracene dimerize to products with greatly reduced fluorescence (Bouas-Laurent et al., 1980), and this may be occurring in this case. At the present time the reason for this large decrease in fluorescence is unknown, and further work will be necessary to resolve this issue. In any case, if photochemically induced reduction of fluorescence is equally rapid for other types and samples of petroleum, then fluorescence may provide a sensitive method for observing photochemical weathering of petroleum.

Acknowledgements

We would like to thank the Brazilian Oil company central research center CENPES/PETROBRAS for the oil and seawater samples used in this research and for help with NMR spectra. We thank Dr. Rosane San Gil for help with collection and analysis of the NMR spectra and LADETEC-UFRJ for help with the GC analysis. We also acknowledge financial support from the 'Conselho Nacional de Desenvolvimento Científico e Tecnológico' (CNPq), the 'Financiadora de Estudos e Projetos' (FINEP), and the Fundação Universitária José Bonifácio.

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