ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 155 (2003) 243–252

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photochemical transformations of water-soluble fraction (WSF) of crude oil in marine waters

A comparison between photolysis and accelerated degradation with TiO_2 using GC–MS and UVF

Roberta L. Ziolli [a,*], Wilson F. Jardim [b]

[a] Departamento de Química da Pontifícia Universidade Católica do Rio de Janeiro, Rua Marquês de São Vicente,
225 Gávea, 22453-900 Rio de Janeiro, RJ, Brazil
[b] Instituto de Química da Universidade Estadual de Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil

Received 25 October 2002; accepted 4 November 2002

Abstract

Changes in the chemical nature of the water-soluble fraction (WSF) of crude oils caused by photolysis and heterogeneous photocatalysis using TiO_2 were investigated by gas chromatography–mass spectrometry (GC–MS) and ultraviolet fluorescence spectrophotometry (UVF). Two Brazilian crude oil samples with different concentrations of WSF (45 and 15 $mg\,C\,l^{-1}$) were studied. Photochemical driven reactions were investigated under UV-Vis irradiation in the absence and in the presence of the photocatalyst. The presence of aromatic hydrocarbon in the WSF before irradiation, resulting from crude oil slick solubilization on seawater, was confirmed by chromatograms that showed a series of low molecular weight aromatic hydrocarbons together with a unresolved complex mixture (UCM). However, in the irradiated WSF these compounds were not detected. After 6 days photolysis period, WSF from both crude oils did not show peaks of aromatic compounds, whereas the presence of long chains unsaturated hydrocarbons as well as sulfur compounds were detected. In contrast, when TiO_2 was employed, complete photodegradation of both crude oil samples in the WSF occurred after very short light exposure periods (1–2 days). Quantitative data were also obtained and discussed here. The results reinforce photodegradation as an effective weathering process for the transformation of dissolved crude oil fraction, particularly in high solar radiation environments. Complete degradation in a short period of time was only made possible by heterogeneous photocatalysis.

Keywords: Crude oil; Photolysis; Heterogeneous photocatalysis; TiO_2; WSF

1. Introduction

Despite the fact that in most natural water bodies the photic zone is only a small fraction of the surface layer, this sunlighted environment is very dynamic under both biological and chemical aspects. Photochemical degradation mediated by sunlight is a important pathway for transformation of crude oil in tropical seawater, specially when the oil is rich in aromatics (resistant to further biodegradation). Since chromophores are abundant in crude oils, many of the transformations are the result of direct photochemical processes. Another important photomediated process occurs only in the presence of catalysts. Natural catalyst comprehends a wide variety of compounds, including humic substances as well as the surface of many metal oxides, such as titanium dioxide (TiO_2) particles [1]. The mechanisms involved in the degradations using TiO_2 have been discussed in the literature although there is controversies [2]. It is supposed that this process allows an accelerated degradation of the organic compounds due to the use of the catalyst, TiO_2, and also probably due to photo-oxidation enhancement of the assimilation of intermediary metabolites. Through a better knowledge of these photochemical aspects, it is possible to make reasonable assessment on the behavior (and ecotoxicology) of the water-soluble fraction of crude oil in surface seawater.

Gas chromatography (GC) is one of the chromatographic methods most widely used to separate and quantify total and individual hydrocarbons present in the WSF [3–5]. Similarly, identification of petroleum compounds using GC–MS has been reported in studies of biomarkers [6,7]. Wang and Fingas [8] presented a review on the analytical aspects

---

* Corresponding author. Tel.: +55-21-3114-1824;
fax: +55-2-1224-29-66.
E-mail addresses: rlziolli@rdc.puc-rio.br (R.L. Ziolli),
wfjardim@iqm.unicamp.br (W.F. Jardim).

1010-6030/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00397-0

related to hydrocarbons in oils, petroleum products and oil-spill-related environmental samples by GC–MS. There are also many reports on the use of GC–MS in the quantification and identification of the oil hydrocarbon photodegradation products [9–12]. Fluorescence spectrophotometry has also been used to monitor very low concentrations of oil in seawater. In a number of studies, UVF was the technique used to measure the total oil concentration in extracts of WSF [13,14].

In this paper, photoreactions of the water-soluble fraction of two different Brazilian crude oils were investigated, using GC–MS. This was performed in order to compare the photochemical behavior not only due to photolysis, but also under more drastic conditions of heterogeneous photocatalysis using TiO_2.

2. Experimental

All glassware was washed with diluted detergent and then thoroughly rinsed with hot tap water, followed by distilled water, and finally, Milli-Q pure water. They were oven-dried and subsequently washed with acetone and twice with re-distilled dichloromethane.

2.1. Crude oil samples and seawater

Two Brazilian crude oil samples (denominated A and D for simplicity) were studied. Both samples originated from the continental shelf of Rio de Janeiro State (Enchova (A) and Marlin (D)) and they were maintained under refrigeration (4 °C) prior to use. The seawater was filtrated in cellulose membrane (0.45 μm) before use.

2.2. Photocatalyst

Titanium dioxide (Degussa P-25, predominantly anatase, specific area of $50\,m^2\,g^{-1}$, non-porous), 70:30 anatase form, BET surface area $50\,m^2\,g^{-1}$, 30 nm average particle size was used as photocatalyst. All the experiments were carried out in an aqueous suspension of TiO_2 at a concentration of 0.1% (w/v). After each experiment, the suspension was filtered and the filtrate was subjected to analysis.

2.3. WSF

Pyrex flasks (2.0 l) with a Teflon tap at the bottom were filled with 1.5 l of seawater. Crude oil was added at the ratio 1:20 (v/v), and the solution was magnetically stirred for 30 min. The solutions were then kept in the dark at room temperature to reach equilibrium for up to 15 days. The Pyrex flasks remained stoppered for the entire period, except when water samples were drawn through the Teflon tap, without disturbing of the oil/seawater surface. This procedure has been described in details elsewhere [15] where the authors further pointed out numerous operational problems related to the preparation of seawater-soluble fraction (WSF) of crude oils.

2.4. Irradiation experiments

Samples (about 1200 ml) were exposed to artificial irradiation in a Pyrex® reactor (80 mm × 210 mm) in batch experiments. A 125 W high-pressure mercury lamp (Philips, HPL-N) was employed with major emission output at 366 nm for periods up to 7 days. Cooling water was circulated through the quartz tube to control the temperature. When TiO_2 was used as the photocatalyst, the suspension was kept in continuous stirring. The light intensity was measured at 366 nm by Cole–Parmer radiometer series 9811. Further details are given elsewhere [16].

2.5. Extraction, drying and concentration of samples

The samples (30 ml) were extracted by liquid–liquid simple extraction using dichloromethane (DCM) as solvent and they were dried using Pasteur pipettes containing cotton wool with anhydrous granular sodium sulfate (BDH Analar R).

To perform GC–MS analysis, extracted samples were rotary-evaporated at 30–40 °C close to dryness. The extract was transferred to a screw cap vial and kept in a freezer until required for analysis when the remaining solvent was removed using a gentle stream of nitrogen. Dried extracts were re-dissolved in 100 μl of pyrene-d_{10} standard solution in *n*-pentane and analyzed using GC–MS. A solvent blank and seawater blank were made according to this same procedure.

To examine the reproducibility of extraction of the WSF, a solution of WSF was tested using the addition of 100 μl of pyrene-d_{10}. In five extractions, the relative standard deviation (R.S.D.) of the pyrene peak was 4.4%.

Solid phase micro-extraction was also tested, but due to contamination problems, this procedure was abandoned.

2.6. GC–MS analysis

Gas chromatography–mass spectrometry analyses were performed using a Hewlett-Packard 5890 GC interfaced with a VG TS250 mass spectrometer and a VAX 2100 Workstation Data Processing System (VG). A GC-FID fitted with a 25 m × 0.2 mm (0.33 μm film thickness) DB-5 fused silica capillary column was also used. The temperature of the flame ionization detector (FID) was kept at 310 °C. The column temperature was programmed from 40 to 290 °C at a rate of $8\,°C\,min^{-1}$, and kept in this temperature for 10 min. Injection volume (1 μl) was made in the splitless mode. Helium was used as the carrier gas (flow rate $= 2\,ml\,min^{-1}$). Electron impact spectra were obtained at 70 eV in a mass range of 50–600 Da. The mass spectrometer was operated in total ion current mode and identification of compounds was made by comparison with mass spectra reported in the NIST library by a high probability match. Co-injection of authentic individual samples were not carried out since the aim was investigate the photochemical behavior of the mixture under conditions of photolysis and heterogeneous photocatalysis using TiO_2 and comparing to a less specific analytical method, UVF. Pyrene-d_{10} was added to dried and concentrated extracts as a quantitative standard. Quantitation of WSF by GC–MS was obtained by plotting the total area of the total ion current (TIC) as well by plotting the reconstructed total ion current (RIC) abundance to some pre-selected *m*/*z*. The concentrations of WSF compounds were calculated with reference to the deuterated quantitative standard. Calculations of concentration were made as follow:

$$C_a = A_a A_p^{-1} C_p \tag{1}$$

where C_a is the sample concentration, C_p the standard concentration added to sample (obtained by Eq. (2)), A_a the sample area (chromatogram) and A_p is the standard area (chromatogram).

$$C_p = C_{pi} v_{pi} v_a^{-1} \tag{2}$$

where C_{pi} is the added standard concentration, v_{pi} the standard volume added to sample and v_a the sample volume.

To examine the reproducibility of splitless injection for the determination of WSF, standard solutions of pirene-d_{10} in pentane were tested. This was performed by making ten 1.0 μl injections. Peak areas were obtained and relative standard deviations (RSD) calculated (5.2%) indicated a good agreement.

2.7. UVF analysis

Ultraviolet fluorescence spectrophotometry analyses were performed using a LS5 Perkin-Elmer spectrometer. Measurements were made on the DCM extract at excitation and emission wavelengths of 310 and 374 nm, respectively, using slitwidths of 5 and 10 nm. The spectrofluorimeter was calibrated with solutions of both crude oils as a reference for a quantification of the WSF. Samples were extracted as described above. Calibration solutions were freshly prepared in dichloromethane (DCM) in the day of the analysis. Solvent blanks were examined at the beginning of each sample analysis.

3. Results and discussion

Typical chromatograms obtained by GC–MS of both WSF of Brazilian crude oils, after 15 days of contact between the oil slick and the seawater are shown in Fig. 1. As expected, both chromatograms show the region relative to the unresolved complex mixture (UCM or "hump" after 20 min) characteristic of more heavily degraded oils. The UCM appears as an "envelope" or hump area between the lower baseline and the curve defining the base of resolved peaks. This envelope has often been attributed to degraded petroleum contamination made of branched and cyclic compounds that cannot be resolved by capillary columns. Gough and Rowland [17] have shown, using chemical degradation techniques, that UCM consists primarily of linear chains connected to branched points giving rise to "T-shaped" molecules. The authors concluded that the microbial recalcitrance of these compounds to microbial degradation

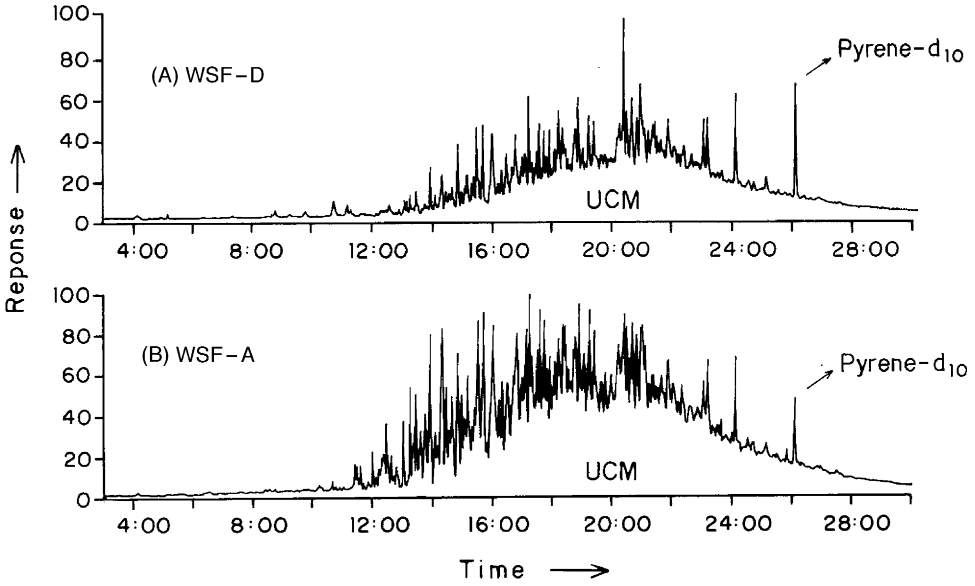

Fig. 1. Gas chromatograms (GC–TIC–MS) of the seawater-soluble fraction (WSF) from crude oil D (A) and crude oil A (B) (50 ml oil per liter of water (1:20)), after 15 days at room temperature in a dark room. UCM: unresolved complex mixture. RS: reference standard (pyrene-d_{10}).

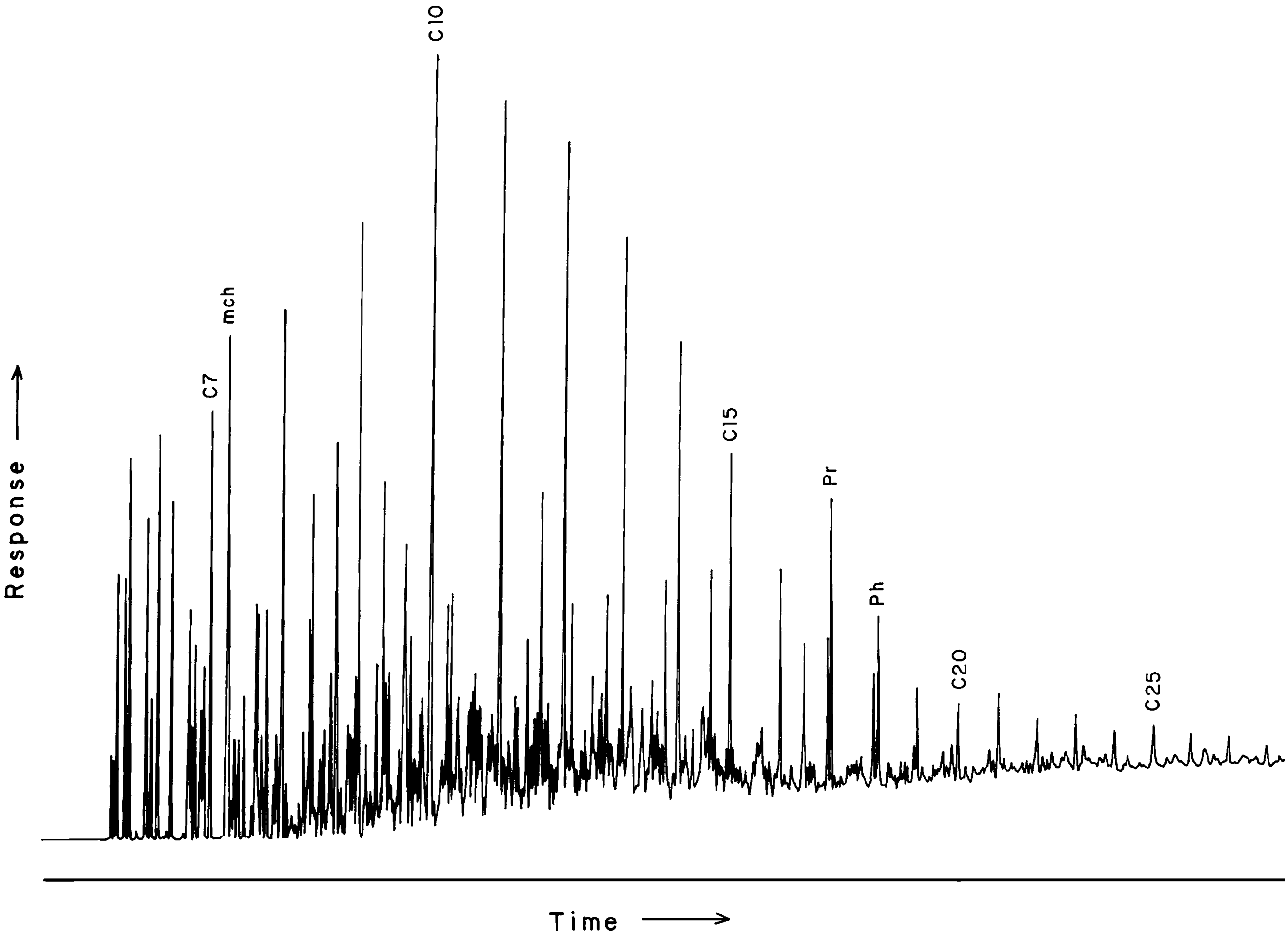

Fig. 2. Gas chromatogram (GC-FID) of the crude oil D.

arises partly from their structure. However, Burwood and Speers [18] characterized the UCM as a complex mixture of thiacyclane-I-oxides, suggesting a process of in situ formation through aerial oxidation of the corresponding thiacyclane during the course of prolonged equilibration. Le Dréau et al. [19] has showed that UCM shifts to higher carbon atom number zone when the alteration degree increases. In fact, relevant data on the UCM is limited, and still very little is known about it.

It is interesting to point out that for both WSF samples (Fig. 1) the UCM is much more pronounced than in the corresponding crude oil samples, as show the Fig. 2. The chromatograms presented in both figures (Figs. 1 and 2) clearly demonstrate the effects of weathering on the chemical composition of the crude oil D. Note that the *n*-alkanes most abundant peaks (Fig. 2) have been depleted on the WSF sample (Fig. 1), and the UCM dominates almost the total peak area. Although, *n*-alkanes pose very little toxicological concern, their degradation products, which appears concentrated in the WSF fraction, could be highly toxic to marine organisms.

The evolution of the UCM region in the WSF fraction as a function of contact time between the oily and the aqueous phase was further investigated with the help of GC–TIC–MS distribution chromatograms obtained for sample D (Fig. 3). Comparing the chromatogram obtained for the WSF after 3 days of contact (in the dark), with the one obtained after 9 days of contact, it is possible to detect the marked difference in the UCM region (and beyond retention time of 20 min). This clearly shows that the composition of the WFS is a function of the time in which the oil slick stays in contact with seawater. The major initial process appears to be the selective dissolution of some low-molecular-mass components. Burwood and Speers [18] also observed the formation of these envelopes that appeared to be time-dependent, very likely due to oxidation products of the crude rather than indigenous components.

A total of 97 main peaks could be detected in the WSF-A chromatogram, and 102 main peaks from chromatograms WSF-D. However, only few of them were identified using the NIST mass spectra library as reference. A list of these identified compounds and their retention time (RT) is given in Table 1 to WSF-A, and in Table 2 to WSF-D. It is interesting to note that no saturated hydrocarbons were identified. Such fact implies the virtual absence of suspended oil droplets in the aqueous phase, which often

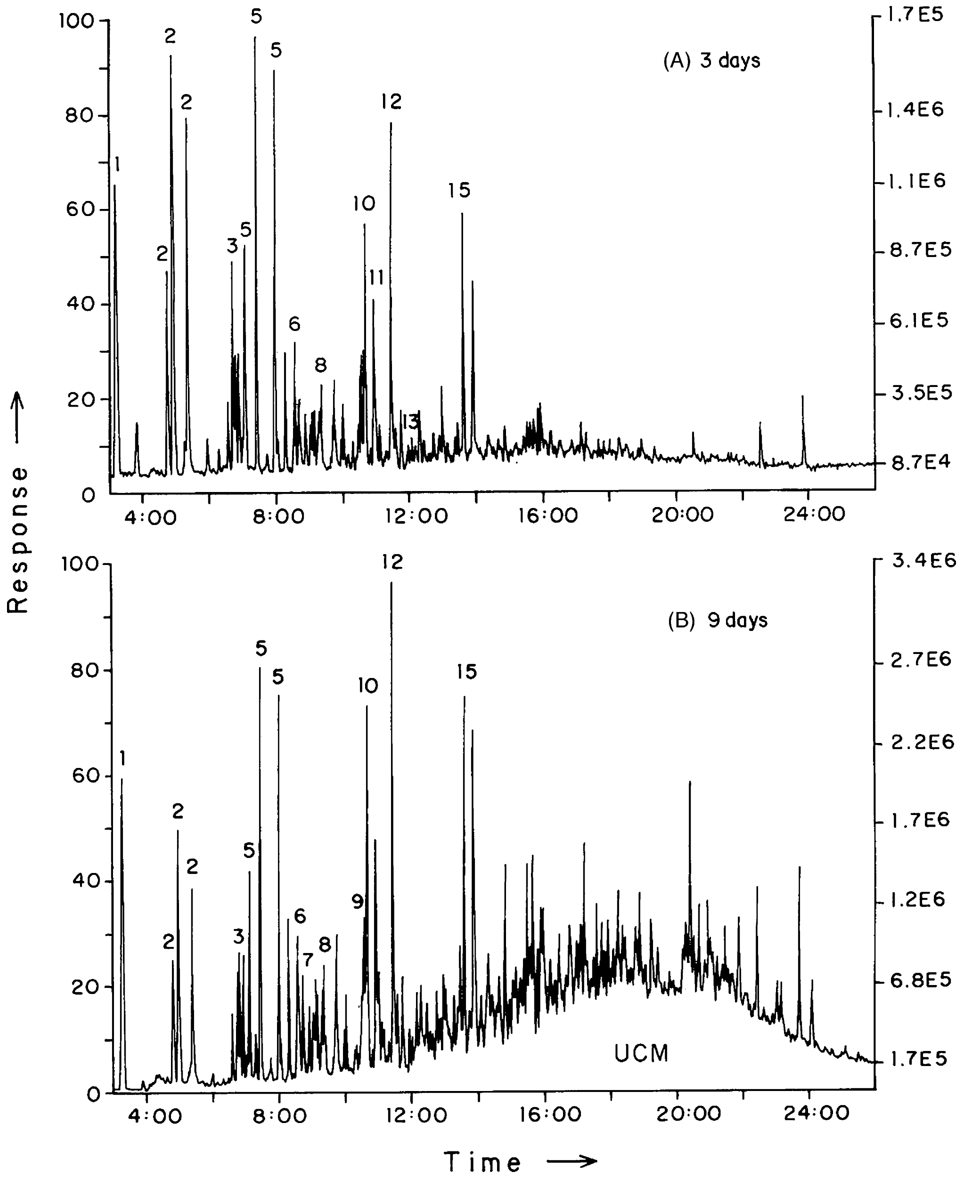

Fig. 3. Gas chromatograms (GC–TIC–MS) of the WSF-D after 3 days (A) and 9 days (B) of contact between the oil film on seawater. Number above the peaks correspond to listed compounds in the Table 2.

introduce large amounts of alkanes into the solution. The major feature is a series of resolved low molecular weight aromatic hydrocarbons comprising mainly methylbenzenes and naphthalenes, besides sulfur cyclic compounds. Alkylbenzenes and methylated naphthalenes are highly susceptible to bacterial attack, indicating that both WSF would not persist for long time in the marine ecosystem. For WSF-D (Table 3), only the first 15 more abundant peaks were identified, none of them in the UCM region. It is noted that after 15 days of contact (Fig. 1A) a significant decrease in the magnitude of these peaks is observed when compared with chromatograms obtained after 3 days of contact (Fig. 3B). This fact can be atributed to volatilization of the hydrocarbons. In the WSF samples, not only were the lighter BTEX (volatile benzene, toluene, ethylbenzene and xylene), and C$_3$-benzene fractions completely removed, but also the alkyl substituted C$_1$-naphthalene, C$_4$-benzene and methylphenol series were significantly reduced. Wang and Fingas [8] showed, using GC-SIM-MS distribution chromatograms of evaporated artificially weathered oils, that losses of alkylated benzenes and alkylated PAHs can reach up to 45%. However, this pattern is not so pronounced in crude oil A, which the input of the UCM was rapid and, apparently not time-dependent. It was observed that from first sample (1 day) until the last one (15 days) the same qualitative composition was found, although with changes on abundance of the peaks. Despite this time discrepancy, a difference between the D crude oil and A crude oil composition was

Table 1
Compounds identified in the WSF from the crude oil A

Peak number	Compound (WSF-A)	Retention time (min) (DB-5 column)
1	Dimethylphenol[a]	4.30
2	1-Hydroxy-3-methyl-2-butanone	5.09
3	1-Ethyl-1-hexyl-alcohol	5.10
4	4-Hydroxy-5-methyl-2-oxolanone	6.20
5	Methylcyclohexanol[a]	6.31
6	Trimethylbenzene[a]	8.01
7	Phenol	8.26
8	2,4-Undecadienyl-alcohol	8.35
9	Methylphenol[a]	9.41 and 10.14[b]
10	Dimethylcyclohexanol[a]	9.53
11	Tetramethylbenzene[a]	10.41
12	Naphthalene	11.27
13	Thiocyclohexanone	11.31
14	Dimethyl-thiocyclopentanone[a]	11.37, 12.02 and 12.30[b]
15	Trimethyl-thiocyclopentanone[a]	12.48, 13.03, 13.16 and 13.56[b]
16	5-H-benzo-(a)-cycloheptene	13.38
17	1,2,3,4-Tetrahydro-2-naphthalenol	15.43
18	Hexyl-methylbenzene[a]	17.37
19	2,6,10-Trimethyl-1-undecanol	21.16
20	1-(4,5,5-Trimethyl-1-cyclopentenil-methyl) benzene	21.54

[a] Indicates no position defined of alkyl group on the cyclic group.
[b] Indicates the retention times of the positional isomers.

Table 2
Compounds identified in the WSF from the crude oil D

Peak number	Compound (WSF-D)	Retention time (min) (DB-5 column)
1	Toluene	3.16
2	Dimethylbenzene[a]	4.48, 4.58 and 5.24[b]
3	Methylethylbenzene[a]	6.46
4	Phenol	7.24
5	Trimethylbenzene[a]	7.07, 7.27 and 8.01[b]
6	2-Methylphenol	8.36
7	3-Methylphenol	8.52
8	4-Methylphenol	9.23
9	Ethylphenol[a]	10.34
10	Dimethylphenol[a]	10.56
11	Tetramethylbenzene[a]	10.40
12	Naphtalene	11.26
13	Dimethyl-thiocyclopentanone[a]	12.02
14	Isopropyl-dimethylbenzene[a]	12.11
15	Methylnaphthalene[a]	13.35

[a] Indicates no position defined of alkyl group on the cyclic group.
[b] Indicates the retention times of the positional isomers.

suspected and it was attributed to nature, age and weathering conditions.

The chromatogram obtained for the WSF-D after 1 day of UV-Vis irradiation (Fig. 4B) shows numerous peaks with retention times ranging from 12.36 up to 25.30 min. It is

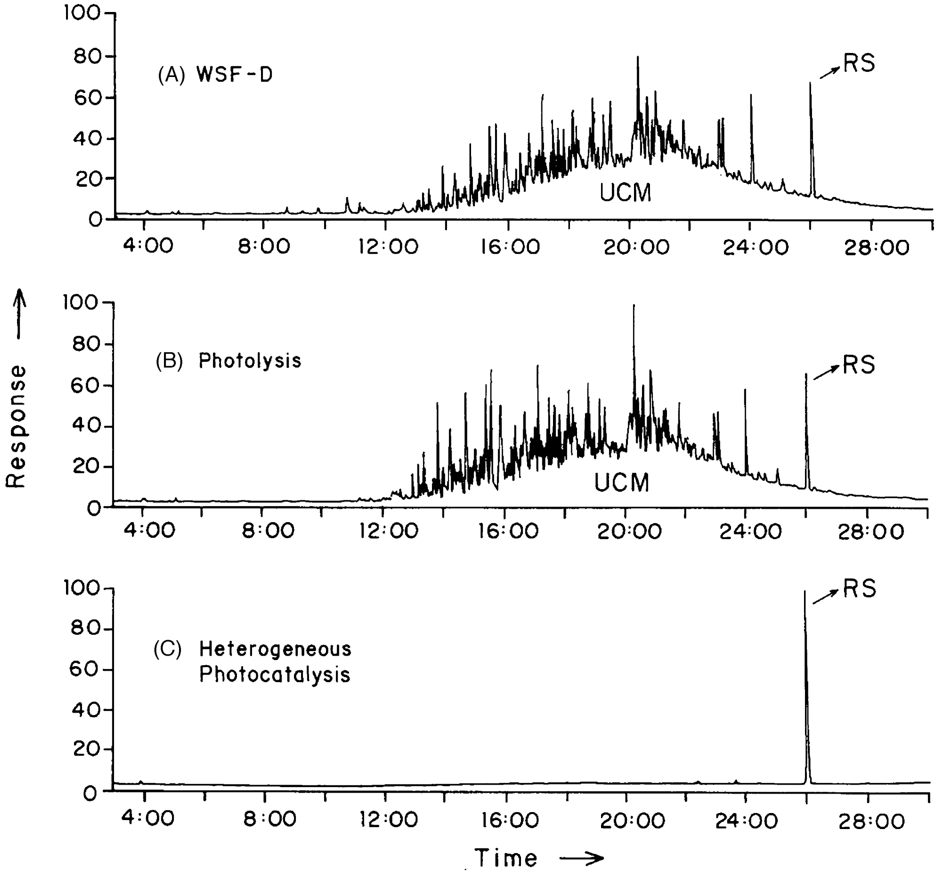

Fig. 4. Gas chromatograms (GC–TIC–MS): (A) only WSF-D before irradiation; (B) *photolysis*, irradiated WSF-D without photocatalyst for 1 day; (C) *heterogeneous photocatalysis*, irradiated WSF-D with photocatalyst, TiO_2, for 1 day. RS: reference standard (pyrene-d_{10}).

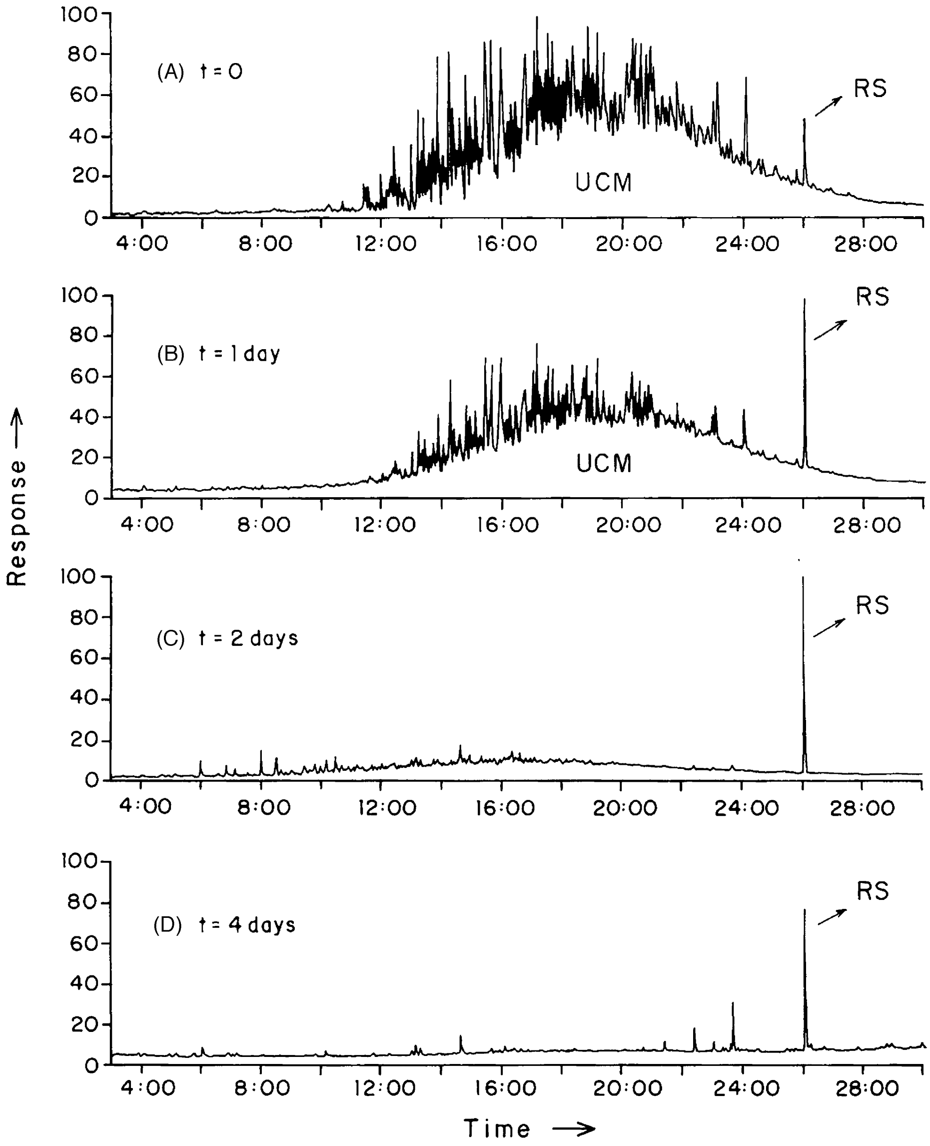

Fig. 5. Gas chromatograms (GC–TIC–MS) of the heterogeneous photocatalysis of the WSF-A: (A) $t = 0$; (B) $t = 1$ day; (C) $t = 2$ days; (D) $t = 4$ days of irradiation with catalyst (TiO_2). RS: reference standard (pyrene-d_{10}).

important to point out that only the peaks with retention time between 8.46 and 12.36 min disappeared after 24 h under photolysis. The possibility of losses to the atmosphere due to minor temperature changes and handling cannot be totally excluded. In a recent publication, Ziolli and Jardim [16] verified that no mineralization (e.g. complete oxidation throughout CO_2, H_2O and mineral salts) occurs during photolysis experiments of these crude oils, although some chemical transformation were observed using infrared analysis. Gas chromatograms obtained after 2–4 and 6 days of photolysis did not show further major differences, but the incorporation of oxygen during photodegradation might make the compounds more toxic to marine organisms. None of the photolysis products could be identified.

More interesting were the results obtained in the photodegradation in the presence of the semiconductor TiO_2. All compounds from D crude oil were completely oxidized within 24 h of irradiation, as shown in (Fig. 4C). Similarly, heterogeneous photocatalysis was able to degrade all WSF-A compounds initially present, although in this case longer irradiation time (4 days) was necessary (Fig. 5). The unresolved complex mixture “envelope” characteristic of the initial WSF-A chromatogram is significantly reduced during heterogeneous photocatalysis. Considering that organic compounds present in UCMs are well known for their resistance to biodegradation, heterogeneous photocatalysis may be an alternative way to degrade this type of compounds. On the other hand, chromatographic data obtained in the photolysis of the WSF-A (Fig. 6) show very little changes compared to the unexposed sample, although there was a gain of UCM abundance. This fact could be atributed to photo-initiated auto-oxidative processes as suggested for

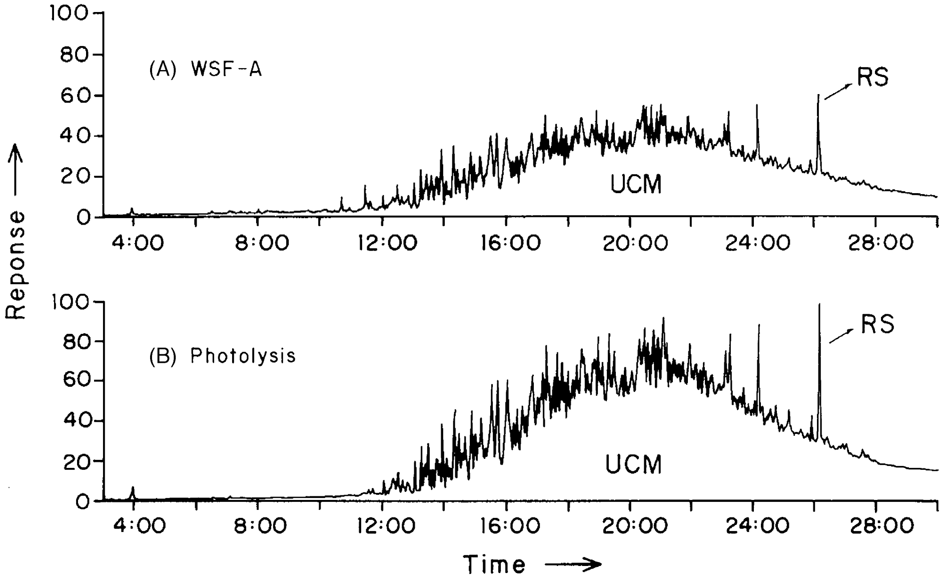

Fig. 6. Gas chromatograms (GC–TIC–MS) of the WSF-A samples: (A) before photolysis; (B) after 1 day of irradiation without photocatalyst. UCM: Unresolved complex mixture. RS: reference standard (pyrene-d_{10}).

Burwood and Speers [18]. Differently, in the heterogeneous photocatalysis process for crude oil A, some intermediary compounds were formed (a total of 63 new peaks) and a few of them were identified during irradiation time (Table 3). All the identified compounds contained oxygen atom and most of them lost the aromatic character during irradiation. This information was also indicated by UVF method, which relies on fluorescence of the more water-soluble aromatic components and, therefore, it is very dependent on oil composition (especially the content of polyaromatic hydrocarbons). The quantitative data obtained during preparation from the WSFs by slow stirring of the layer of Brazilian crude oils, A and D, on seawater for up to 15 days are presented in Fig. 7. A comparison between the crude oil A and D plots indicated that crude oil A contained about three time more aromatic hydrocarbons in the WSF than crude oil D. However, when WSF was irradiated in photolysis as well photocatalysis experiments, no aromatic hydrocarbons were detected by

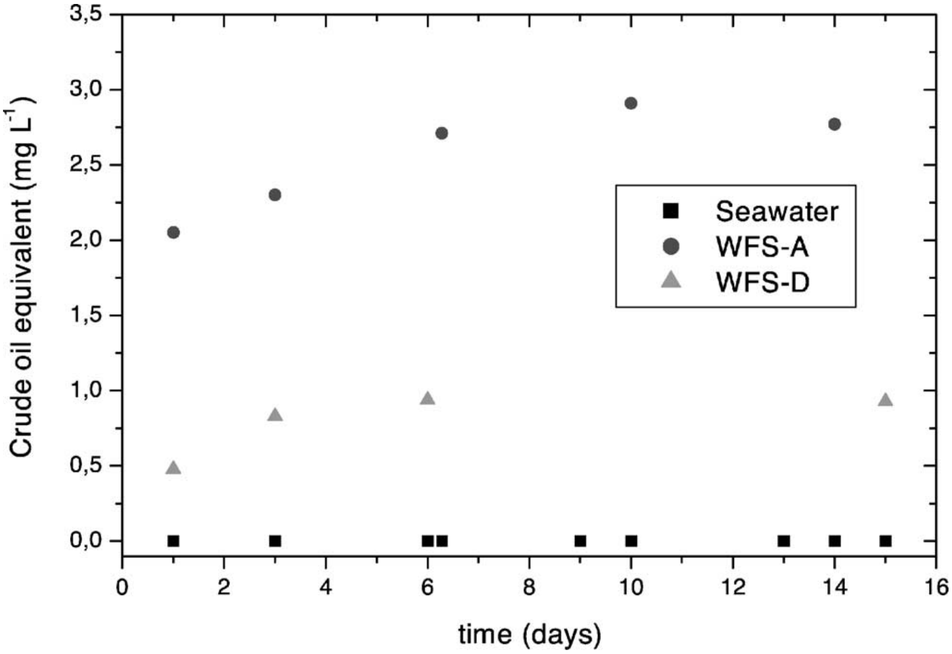

Fig. 7. UVF concentration of the WSF-A and WSF-D in DCM: (■) only seawater (control); (●) WSF-A before exposure to UV-Vis; (▲) WSF-D before exposure to UV-Vis irradiation.

Table 3
Compounds generated identified during heterogeneous photocatalysis

Irradiation time (days)	Compound (WSF-A)	Retention time (min) (HP DB-5 column)
1	4,4-Dimethyl-2-oxolanone	7.09
	2-Pentanone	8.31
	2,4-Dimethyl-1,3-cyclopentanedione	10.14
2	2-Hexanone	8.30
	1,4-Cyclohexanedione	9.25
	Methyl-1,3-cyclopentanedione[a]	11.24
	Alkyl-2-oxolanone	14.39 and 14.57[b]
	2,6,9-Undecanotrione	18.11
4	2-Methyl-1-pentanol	5.11
	Acetic anhydride	5.47
	Benzaldehyde	6.53
	Alquil-4,4-dimethyl-2-oxolanone	8.03
	2-Methyl-1,3-cyclopentanedione	9.27

[a] Indicates no position defined of alkyl group on the cyclic group.
[b] Indicates the retention times of the positional isomers.

UVF. This clearly shows that all the aromatic hydrocarbons initially present in the WSFs reacted under UV-irradiation to yield no-fluorescent compounds. This result is confirmed if we compare the presence of compounds containing functional groups able to fluoresce (listed in the Tables 1 and 2 with Table 3), before and after irradiation.

Regarding to quantitative behavior, the total concentration of all the initial compounds from WSFs presently at UCM as calculated from the total ion current (TIC) were 19.36 and 3.52 mg l^{-1}, respectively for crude oil A and crude oil D (mean values of triplicates). When the WSF were monitored by reconstructed total ion current (RIC) was not observed alterations in the concentrations of all selected *m/z* compounds of crude oil D. However, in crude oil A, the alkyl-benzene (*m/z* 91) and alkyl–methyl–benzene (*m/z* 105) increased their concentrations during photolysis experiments while the ions *m/z* 197 and 211 decreased their concentrations and only the ion *m/z* 105 C_7 maintained a constant concentration. The *m/z* 128 (naphthalene), *m/z* 142 (methyl-naphthalene) and *m/z* 156 (dimethyl-naphthalene) were also monitored by RIC but they do not appear in the chromatogram.

4. Conclusion

The dissolution of petroleum products is affected by weathering level of the crude oil, particularly for the aqueous extracts, the UCM dominates almost the total peak area from the chromatograms. Identification of the WSF composition changes due to irradiation is very important and it can yield compounds more toxic to marine organisms. However, photodegradation by heterogeneous photocatalysis using TiO_2 significantly enhances the photolytic degradation, indicating a high efficiency this process on photodegradation of organic compounds if compared to conventional photolysis. The UCM is completely degraded and oxygenated products can be tentatively identified in the samples. The high destruction of petroleum compounds in aquatic medium, at WSF concentrations of 45 and 15 mg C l^{-1}, showed that the TiO_2/UV-Vis process is a viable alternative for the elimination of these compounds in water (petrochemical wastewater, for example). Heterogeneous photocatalysis using TiO_2 has to be looked upon as an emerging technology attractive for photochemical transformations of water-soluble fraction (WSF) of crude oil in marine waters.

Acknowledgements

The authors are grateful to the Coordenação de Aperfeiçoamento de Pessoal e Ensino Superior (CAPES) for financial support. The authors also thanks Dr. R.Q. Aucelio for linguistic advice. R.L. Ziolli thanks Dr. George Wolff, Ms. Anu Thompson and Dr. Gareth Harriman for their help and valuable discussions during her stay period in the Environmental Organic Chemistry and Geochemistry Group, Oceanography Laboratory of the Department of Earth Sciences, University of Liverpool, UK, where the experimental part was development.

References

[1] H.F. Hemond, E.J. Fechner, Chemical Fate and Transport in the Environmental, Academic Press, San Diego, 1994.
[2] R.L. Ziolli, W.F. Jardim, Mecanismo de reação do TiO_2 na destruição fotocatalítica de compostos orgânicos potencialmente tóxicos, Química Nova, SP 21 (3) (1998) 319–325 (in Portuguese, with English Abstract).
[3] C.C. Lee, W.K. Craig, Water soluble hydrocarbons from crude oil, Bull. Environ. Contam. Toxicol. 12 (1974) 212–215.
[4] W.L. Lockhart, D.A.J. Murry, R.A. Danell, D.A. Metner, Aspects of the chemistry of the major soluble fractions of oils: analysis and effects, in: Proceedings of the 1984 Arctic Marine Oil Spill Conference API, Amer. Pet. Inst., 1984, pp. 75–81.
[5] D.A.J. Murray, W.L. Lockhart, G.R.B. Webster, Analysis of the Water-Soluble Fraction of Crude Oils and Petroleum Products by Gas Chromatography, OPP, vol. 2 (1), 1984, pp. 39–47.
[6] B. Dahl, G.C. Speers, A. Steen, N. Telnaes, J.E. Johansen, Quantification of steranes and triterpanes by gas chromatographic-mass spectrometric analysis, in: B.M. Thomas (Ed.), Proceedings of a Norwegian Petroleum Society Conference on Petroleum Geochemistry in Exploration of the Norwegian Shelf, Norwegian Petroleum Society, Norway, 1985, pp. 303–307.
[7] A.G. Requejo, Quantitative analysis of triterpane and sterane biomakers: methodology and application in molecular maturity studies, in: J.M. Moldowan, P. Albrecht, R.P. Philp (Eds.), Biological Markers in Sediments and Petroleum, Prentice-Hall, New Jersey, 1992, pp. 223–240.
[8] Z. Wang, M. Fingas, Developments in the analysis of petroleum hydrocarbons in oils, petroleum products and oil-spill-related environmental samples by gas chromatography, J. Chromatogr. A 774 (1997) 51–78.
[9] M. Ehrhardt, G. Petrick, The sensitized photo-oxidation of *n*-pentadecane as a model for abiotic decomposition of aliphatic hydrocarbons in seawater, Mar. Chem. 16 (1985) 227–238.
[10] M. Ehrhardt, K.A. Burns, M.C. Bicego, Sunlight-induced compositional alteration in the seawater-soluble fraction of a crude oil, Mar. Chem. 37 (1992) 53–64.

[11] K.A. Burns, Analytical methods used in oil spill studies, Mar. Poll. Bull. 26 (1993) 68–72.
[12] D.D. Riemer, P.J. Milne, R.G. Zika, W.H. Pos, Photoproduction of nonmethane hydrocarbons (NMHCs) in seawater, Mar. Chem. 71 (3–4) (2000) 177–198.
[13] M. Ehrhardt, G. Petrick, On the sensitized photo-oxidation of alkylbenzenes in seawater, Mar. Chem. 15 (1984) 47–58.
[14] M.D. Paine, W.C. Leggett, J.K. McRuer, K.T. Frank, Effects of hibernia crude oil on capelin (*Mallotus villosus*) embryos and larvae, Mar. Environ. Res. 33 (1992) 159–187.
[15] R.L. Ziolli, W.F. Jardim, Operational problems related to preparation seawater soluble fraction (WSF) of crude oil, J. Environ. Monitor. 4 (1) (2002) 138–141.
[16] R.L. Ziolli, W.F. Jardim, Photocatalytic decomposition of seawater-soluble crude oil fraction using high surface area colloid nanoparticles of TiO_2, J. Photochem. Photobiol. 147 (3) (2002) 205–212.
[17] M.A. Gough, S.J. Rowland, Characterization of unresolved complex mixtures of hydrocarbons in petroleum, Nature 344 (1990) 648–650.
[18] R. Burwood, G.C. Speers, Photo-oxidation as a factor in the environmental dispersal of crude oil, Est. Coast. Mar. Sci. 2 (1974) 117–135.
[19] Y. Le Dréau, F. Jacquot, P. Doumenq, M. Giuliano, J.C. Bertrand, G. Mille, Hydrocarbon balance of a site which had highly and chronically contaminated by petroleum wastes of a refinery (from 1956 to 1992), Mar. Poll. Bull. 32 (6) (1997) 456–468.