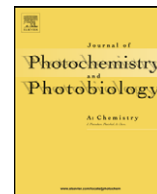


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## Synchronous fluorescence spectroscopy and gas chromatography to determine the effect of UV irradiation on crude oil

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### ABSTRACT

The fate of the crude oil under irradiation was studied. After the UV irradiation, the fraction present in the highest percentage shifted from C8–C9 fraction to C13 one, in GC–MS analysis. An increase of the relative amount of the C13–C25 fraction was observed, while a decrease in the relative amount of the C7–C12 fractions was present. The synchronous fluorescence spectrum showed a maximum at 396 nm. Two hours irradiation of the sample induced an increase of the fluorescence emission in the region 420–550 nm. After 20, 40, 60, and 100 h irradiation we observed a decrease of the fluorescence emission.

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### 1. Introduction

Oil extraction represents one of the most important extractive industries in the world. Basilicata is a region in Southern Italy where recently an extraction activity has been started by ENI Spa, the most important extraction firm in Italy. The extraction of crude oil present in Basilicata can cover 10% of Italian needs in the energy production. The oil extraction was performed mainly in Val d'Agri, a valley in Basilicata where both an extensive agricultural activity and some environmental constraints with the presence of National Park of Val d'Agri are present.

Crude oil can escape into the environment. Extraction techniques and transportation of crude oil can originate pollution phenomena due to dispersion of these compounds in the environment. Thus, terrestrial spills may soak into the ground, while spills at sea or on lake and rivers often disperse into the water column [1].

In this contest oil spill can represent an immediate damage to the tourist image of the region and for its economy. It is then important to have a rapid and efficient method able to determine the presence of oil accidental spills in the environment, in particular in the soil. Gas chromatography coupled with FID and with mass spectrometry has been used to determine and characterize crude oil [2–22].

Crude oil is subjected to some degradation processes. Biodegradation can be one of the most important processes in the environment. Photochemical degradation mediated by sunlight is an important pathway for the transformation of crude oil in tropical seawater, especially when the oil is rich in aromatics. Since chromophores are abundant in crude oils, many of the transformations are the result of direct photochemical processes due to the absorption of light in the UV region, or of photosensitized reactions due to the presence of compounds able to absorb light in the visible region.

All petroleum products have fluorescence. The use of fluorescence for the characterization of different crude oils has led to the development and commercial use of a new kind of fluorescence instruments. Of all of them, synchronous fluorescence spectroscopy is preferred because of its narrower spectral band, high selectivity and simplified spectrum [23]. John and Soutar [24] identified different types of crude oils obtained from different sources using this technique. They studied the effect of factors like wavelength increment, concentration, temperature and frequency bandpass on synchronous fluorescence spectra of different crude oils. They found little difference in the synchronous fluorescence spectra of different crude oils obtained from different sources, which indicates little variation in the relative amounts of aromatic components in each crude oil.

In different studies of oil dispersed in seawater, it was found that the synchronous fluorescence decreased with irradiation [25–28]. Photochemical weathering of Brazilian petroleum was evaluated by using EPR spectroscopy showing a partial destruction of the asphaltenic fraction of the oil [29].

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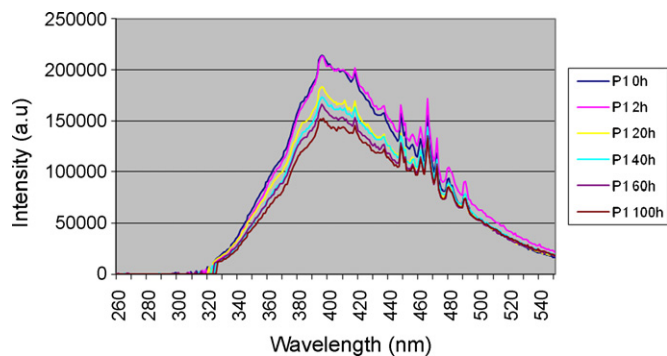


Fig. 1. Synchronous fluorescence spectra of crude oil before and after UV irradiation.

In this work we conducted photodegradation experiments on crude oil from Basilicata (Southern Italy) by using a high-pressure mercury lamp. The crude oil and the photodegradation mixture were analyzed by using GC–MS and synchronous fluorescence spectra.

## 2. Materials and methods

We used a sample of crude oil deriving from Centro Oli in Val d'Agri (Basilicata, Southern Italy). The sample showed the elemental analysis in the following composition: C, 85.13%; H, 12.31%; N, 0.00%; S, 2.74%. The elemental analysis was performed in duplicate by using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer.

Crude oil (10 ml) was irradiated in a sealed vial for SPME analysis with a 125-W high-pressure mercury arc (Helios Italquartz, Milan, Italy). In all the experiments the samples were irradiated for 100 h. The experiments were performed in triplicate.

Synchronous fluorescence scans were recorded in duplicate with petroleum in dichloromethane at a dilution of 1–1000 (v/v) using a quartz cell. The spectra at 90°-angle sample geometry were obtained from commercial fluorimeter, Jobin-Yvon FluoroLog-3 equipment. The wavelength interval,  $\Delta\lambda$ , between  $\lambda_{em}$  and  $\lambda_{ex}$ , was 20 nm with a 1.0-nm bandpass.

Crude oil solution in THF (tetrahydrofuran) (0.1 g/l) (Aldrich, Milan, Italy) was injected in a HP6890 (Agilent Technologies, Milan, Italy) plus gas-chromatograph equipped with a Phenomenex Zebtron ZB-5 MS capillary column (30 m  $\times$  0.25 mm ID  $\times$  0.25  $\mu$ m film thickness) (Supelco, Bellefonte, PA). As detector we used a

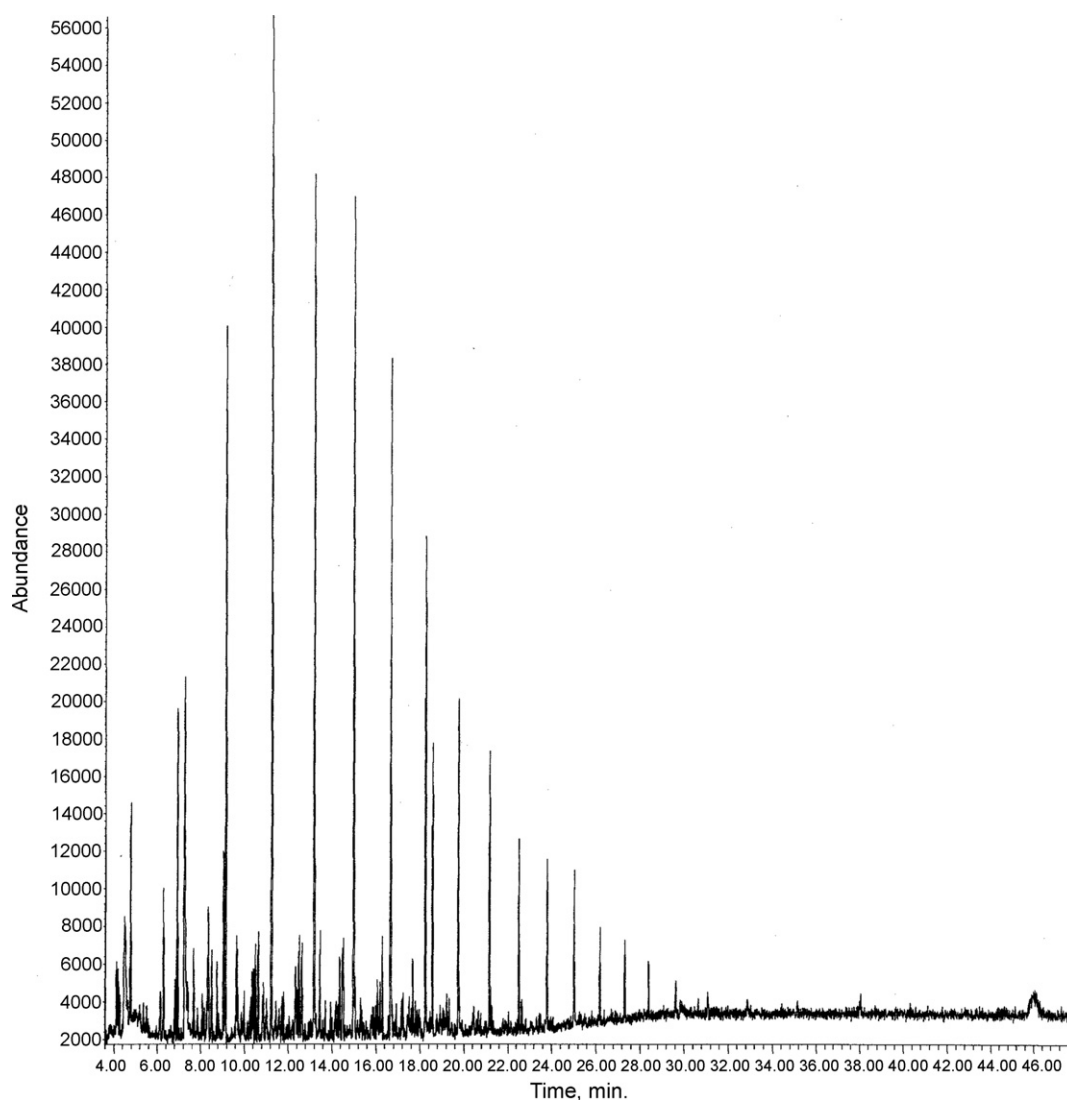


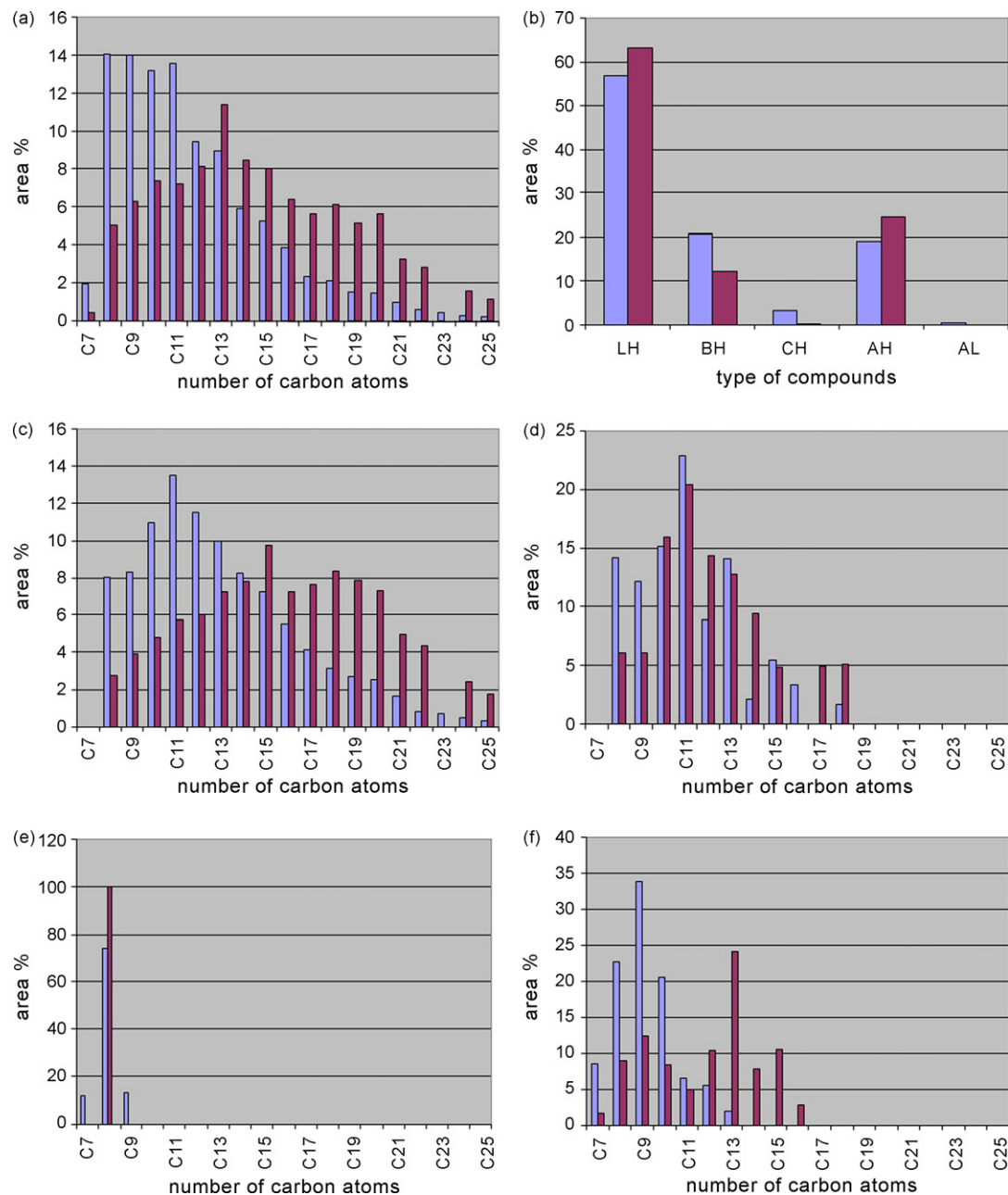
Fig. 2. Chromatogram of crude oil.

HP5973 mass selective detector (mass range: 15–800 amu; scan rate: 1.9 scans/s; EM voltage: 1435), helium at 0.8 ml/min was used as carrier gas. The injection port was split at 250 °C. The injection volume was 1  $\mu$ l. Detector was maintained at 230 °C. Oven was maintained at 60 °C for 2 min, then the temperature increased until 250 °C (10 °C/min); finally, this temperature was maintained for 20 min. All the analyses were performed in triplicate (R.S.D. 0.02%). The chromatograms obtained from the total ion current (TIC) were integrated without any correction for coelutions and the results were expressed in arbitrary surface units (asu). The peaks were tentatively identified from their mass spectra by comparison with spectra in Wiley6N and NIST98 libraries.

### 3. Results and discussion

In this study we used a sample of crude oil deriving from Centro Oli in Val d'Agri (Basilicata, Southern Italy). The sample showed the elemental analysis in the following composition: C, 85.13%; H, 12.31%; N, 0.00%; S, 2.74%.

The synchronous fluorescence spectrum of the crude oil is reported in Fig. 1 (dark blue line). The fluorescence spectrum showed a maximum at 396 nm. This type of emission is typical for anthracene-like structures. The emission in the ultraviolet zone in the region 310–350 nm, typical for the presence of naphthalene structures was not very high. The emission in the



**Fig. 3.** GC-MS analysis of crude oil in solution. (a) Composition of crude oil (blue column), UV irradiated crude oil (red column), as a function of the number of carbon atoms; (b) composition of crude oil as a function of the type of compounds. LH: linear aliphatic hydrocarbons; BH: branched aliphatic hydrocarbons; CH: cyclic aliphatic hydrocarbons; AH: aromatic hydrocarbons; AL: alkenes; (c) composition of the linear aliphatic hydrocarbons fraction as a function of the number of carbon atoms; (d) composition of the branched aliphatic hydrocarbons fraction as a function of the number of carbon atoms; (e) composition of the cyclic aliphatic hydrocarbons fraction as a function of the number of carbon atoms; (f) composition of the aromatic hydrocarbons fraction as a function of the number of carbon atoms.

**Table 1**  
GC–MS analysis of crude oil from Basilicata

Entry	t <sub>R</sub> (min)	Compound	Area (%)	Photodegraded area (%)
1	4.03	2,3-Dimethylhexane	0.28	
2	4.11	2-Methylheptane	1.04	0.21
3	4.19	Toluene	1.08	0.19
4	4.26	3-Methylheptane	0.64	0.13
5	4.38	1,2-Dimethylcyclohexane	0.23	
6	4.62	Cis-1-ethyl-3-methylcyclopentane	0.85	
7	4.76	Octane	3.09	0.82
8	5.35	2,6-Dimethylheptane	0.47	
9	5.50	Ethylcyclohexane	0.45	0.16
10	6.11	2,4-Dimethylheptane		0.34
11	6.13	2,3,4-Trimethylhexane	1.07	
12	6.28	1,3-Dimethylbenzene	2.06	0.70
13	6.63	Cycloheptane	0.25	
14	6.81	1,4-Dimethylbenzene	0.81	0.30
15	6.92	Nonane	3.19	1.17
16	7.62	Propylcyclohexane	0.28	
17	7.69	2,6-Dimethyloctane	0.92	0.30
18	7.88	3-Ethyl-2-methylheptane		0.16
19	8.18	Propylbenzene	0.38	
20	8.27	3-Ethyl-2,4-dimethylpentane	0.13	
21	8.32	4-Methylnonane	0.42	0.18
22	8.37	1-Ethyl-4-methylbenzene	1.39	0.51
23	8.51	3-Methylnonane	0.74	0.26
24	8.77	1-Ethyl-2-methylbenzene	0.58	0.47
25	9.06	1,2,4-Trimethylbenzene	1.30	
26	9.15	Decane	4.21	1.43
27	9.65	2,6-Dimethylnonane	0.61	0.21
28	9.70	1,2,3-Trimethylbenzene	0.63	0.21
29	9.99	3-Methyldecane	0.50	
30	10.30	1-Methyl-3-propylbenzene	0.23	0.08
31	10.37	5-Methyldecane	0.47	0.17
32	10.44	1-Methyl-2-(1-methylethyl)benzene	0.49	0.16
33	10.51	2-Methyldecane		0.18
34	10.64	3,7-Dimethylnonane	0.77	0.25
35	10.84	1-Ethyl-2,3-dimethylbenzene	0.32	0.08
36	10.88	1-Ethyl-1,3-dimethylbenzene	0.43	0.15
37	11.01	1-Ethyl-3,5-dimethylbenzene	0.56	0.11
38	11.25	Undecane	5.19	1.72
39	11.45	4-Ethyl-1,2-dimethylbenzene	0.25	0.08
40	11.59	4,5-Dimethylnonane	0.33	0.19
41	11.72	1,2,4,5-Tetramethylbenzene	0.33	0.12
42	11.79	4-Methyldecane	0.24	
43	12.50	4-Methylundecane	0.70	0.23
44	13.19	Dodecane	4.43	1.79
45	13.25	(1-Methyl-1-butenyl)benzene	0.22	
46	13.44	2,6-Dimethylundecane	0.67	0.31
47	13.70	4,5-Dimethyl-2-undecene	0.30	
48	14.17	5-Methyldodecane	0.24	
49	14.26	4,8-Dimethylundecane	0.25	0.14
50	14.34	3,8-Dimethyldecane	0.52	0.29
51	14.47	2,9-Dimethylundecane	0.49	0.27
52	14.98	Tridecane	3.82	2.16
53	15.04	1-Methylnaphthalene	0.37	0.28
54	15.30	2-Methyldecane	0.23	0.15
55	15.35	2-Methylnaphthalene	0.21	0.15
56	16.06	2-Methyltridecane		0.29
57	16.18	3-Methyltridecane	0.29	0.24

Table 1 (Continued)

Entry	t <sub>R</sub> (min)	Compound	Area (%)	Photodegraded area (%)
58	16.29	2,6,10-Trimethyldodecane	0.50	
59	16.66	Tetradecane	3.18	2.34
60	16.92	2,3-Dimethylnaphthalene	0.23	0.28
61	17.22	1,5-Dimethylnaphthalene	0.39	0.27
62	17.24	1,8-Dimethylnaphthalene		0.49
63	17.32	Dimethylbenzo[b]thiophene		0.15
64	17.54	1,3-Dimethylnaphthalene	0.09	0.12
65	17.79	3-Methyltetradecane	0.25	0.27
66	18.24	Pentadecane	2.77	2.92
67	18.51	1,3,6-Trimethylnaphthalene	0.07	0.16
68	18.83	1,6,7-Trimethylnaphthalene	0.19	0.16
69	18.91	2,3,6-Trimethylnaphthalene		0.48
70	19.21	Trimethylnaphthalene		0.70
71	19.47	Trimethylnaphthalene		0.39
72	19.74	Hexadecane	2.12	2.15
73	19.81	2,4,6-Trimerhylazulene		0.52
74	20.78	3-Methylhexadecane		0.28
75	20.99	7-Ethyl-1,4-dimethylazulene		0.38
76	21.16	Heptadecane	1.58	2.28
77	22.02	7,9-Dimethylhexadecane	0.23	
78	22.39	Phenanthrene		0.36
79	22.51	Octadecane	1.20	2.51
80	22.64	2-Methylpentadecane	0.46	
81	23.13	9,10-Dihydro-1-methylphenanthrene		0.10
82	23.79	Nonadecane	1.04	2.36
83	24.08	4-Methylnaphtho[2,1-b]thiophene		0.38
84	24.35	2-Methylanthracene		0.39
85	25.02	Eicosane	0.97	2.18
86	25.50	3,4-Dimethyldibenzothiophene		0.51
87	25.72	3,6-Dimethylphenanthrene		0.35
88	25.88	2,7-Dimethylphenanthrene		0.42
89	26.13	2-Ethyl-1,3,4,5,8-pentamethylnaphthalene		0.31
90	26.18	Heneicosane	0.64	1.48
91	26.91	Benzo[ghi]fluoroanthrene		0.40
92	27.30	Docosane	0.32	1.30
93	28.40	Tricosane	0.28	
94	29.61	Tetracosane	0.18	0.73
95	31.07	Pentacosane	0.13	0.53

region 250–310 nm, typical of benzenoid structures, was very low.

In GC–MS analyses we used a non-polar capillary column (Phenomenex Zebron ZB-5 MS). All the experiments were performed using the same column. The tentative identification of some of the recovered compounds is reported in Table 1.

The analysis was performed on a solution of crude oil in THF. This solvent was used in order to have a solvent unable to superimpose itself to a lot of signals. In this analysis we could determine the presence of peaks from C7 until C25 (Fig. 2). As reported in Table 1 we identified the presence of 74 compounds.

In Fig. 3(a, blue columns) we report the composition of the identified peaks in function of the number of carbon atoms. The main fractions in our samples were those from C8 until C11. In Fig. 3(b) we reported the composition of crude oil as a function of the type of

compounds found. We selected linear aliphatic hydrocarbons (LH), branched aliphatic hydrocarbons (BH), cyclic aliphatic hydrocarbons (CH), aromatic hydrocarbons (AH), and alkenes (AL). The main components in our sample of crude oil were the linear aliphatic hydrocarbons, followed by branched and aromatic hydrocarbons. The presence of alkenes was very low.

Fig. 3(c) shows the composition of the linear aliphatic fraction in function of the number of carbon atoms. We found linear hydrocarbons from octane to pentacosane. The main fraction was represented by undecane. The fraction decane–tridecane represents almost 50% of the linear aliphatic fraction of the sample.

The composition in function of the number of carbon atoms of the branched aliphatic hydrocarbons fraction is reported in Fig. 3(d). This fraction showed components in the range C8–C18, and the main components are in the range C8–C13. Fig. 3(e) refers to the presence of cyclic hydrocarbons: we observed only cyclic aliphatic hydrocarbons with seven to nine carbon atoms and the main components showed eight carbon atoms. Fig. 3(f) shows the composition of the aromatic hydrocarbon fraction. It contained compounds in the range C7–C13 and the main fraction was represented by C9 one.

We performed our experiments irradiating the crude oil in a SPME vial with a 125-W high-pressure mercury arc (Helios Italquartz, Milan, Italy) until 100 h.

Two hours irradiation of the sample induced a slight increase of the fluorescence emission in the region 420–550 nm (Fig. 1, pink line). This region is typical for polycondensed aromatic structures. After 20, 40, 60, and 100 h irradiation we observed a decrease of the fluorescence emission. In particular, the maximum at 396 nm remained but with a lower intensity after 100 h irradiation. Also the shape of the curve remained the same after this irradiation period. This behaviour can be understood admitting both the formation during the irradiation of compounds able to quench the fluorescence emission of condensed aromatic structures and the selective degradation of these compounds.

The chromatogram obtained after irradiation is reported in Fig. 4. The results of the GC–MS analysis are reported in Fig. 3 (red columns). In Fig. 3(a) we collected the distribution in function of the number of carbon atoms. We observed that, in the UV irradiation, the fraction present in the highest percentage shifted from C8–C9 fraction to C13 one. In this condition, we observed an increase of the relative amount of the C13–C25 frac-

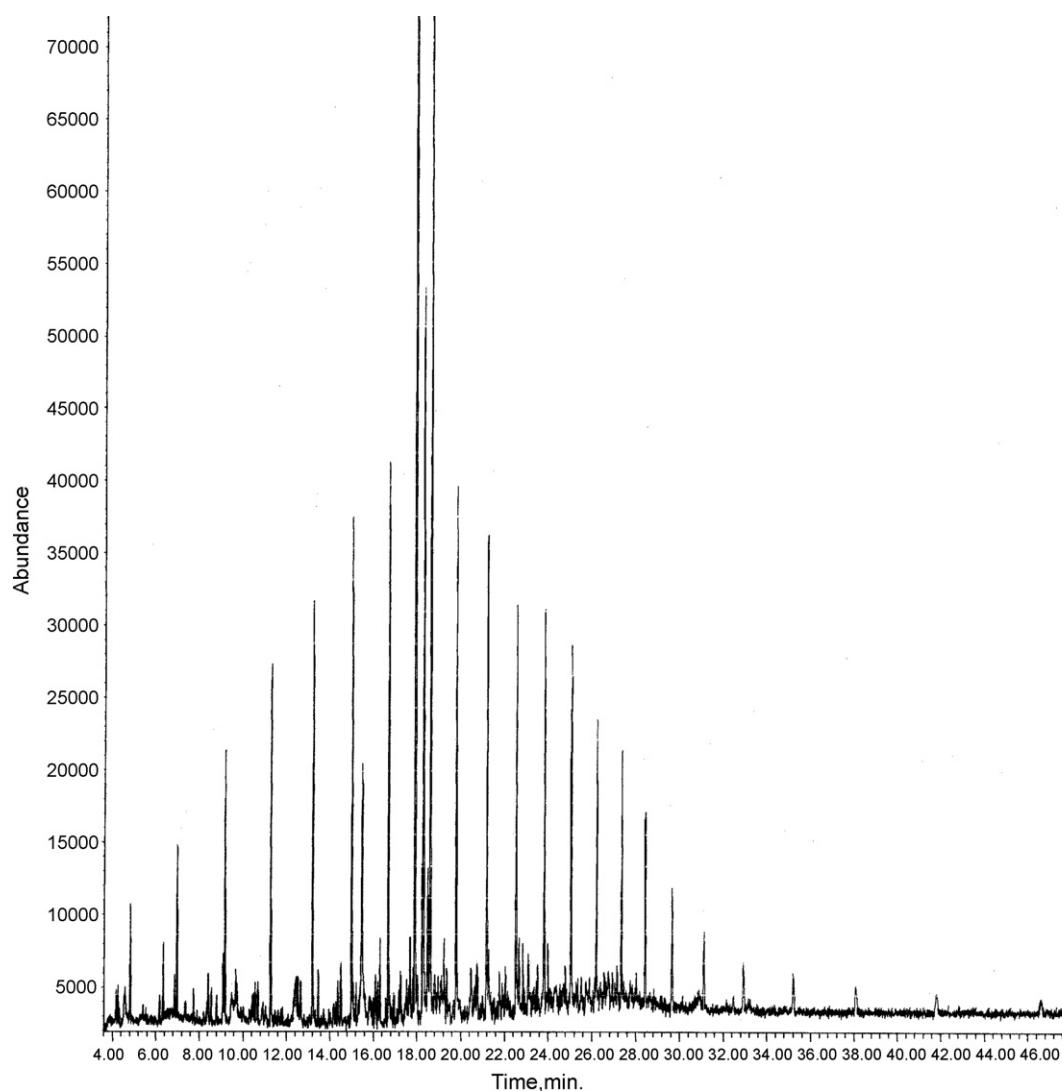


Fig. 4. Chromatogram of irradiated crude oil.

tion, while we noted a decrease in the relative amount of the C7–C12 fractions.

In Fig. 3(b) we collected the distribution of the compounds in function of chemical type of the compounds as reported above. The GC–MS in solution analysis of the mixture deriving from UV irradiation showed an increase of the relative amounts of both linear alkanes and aromatic compounds, while we observed a sharp decrease of the relative amounts of branched and cyclic alkanes. After irradiation we did not find alkenes.

On the basis of the above reported results we can suppose that linear alkanes did not participate to the photochemical reaction. In fact the observed increase of the relative amounts could be due to the decrease of the other components (i.e. branched and cyclic alkanes) in the mixture. Our results do not confirm this hypothesis. In fact, the analysis of the composition of linear alkanes fraction after the irradiation showed several changes in the composition of this fraction. The results are reported in Fig. 3(c). While in crude oil the hydrocarbon present in the highest percentage was undecane, in the irradiated crude oil pentadecane was the alkane present with highest percentage area. We observed a decrease of the C8–C14 fraction and an increase of C15–C25 fractions. All our analytical determinations are in agreement with a decrease of the amount of branched alkanes in crude oil after irradiation. The modifications of the composition of this fraction are showed in Fig. 3(d). The GC–MS analysis showed that the most abundant fraction did not change after irradiation. In UV irradiation, we observed an increase in C14, C17, and C18 fraction. GC–MS analysis identified very few cyclic alkanes in crude oil, all in the range C7–C9 (Fig. 3(e)). Only C8 components were found after UV irradiation. The percentage area of the aromatic compounds in GC–MS analysis increased (Fig. 3(b)). However, we observed a sharp decrease of benzene-like structures and an increment in naphthalenic structures (Fig. 3(f)). The increasing of aromatic compounds could be due to the fragmentation of larger aromatic structures during photodegradation.

In conclusion, GC–MS analysis and fluorescence spectroscopy gave complementary information about the fate of the enormous number of compounds present in crude oil when it is irradiated. Gas chromatographic analysis showed the modifications occurred in non-fluorescent compounds such as alkanes. It showed also that the amount of benzenoid structures decreased while the number of naphthalenic structures increased. These compounds are fluorescent, and we did not observe this behaviour in the fluorescence spectra. We observed a decrease both in region 270–300 nm (benzene) and in region 310–370 nm (naphthalene). This behaviour can be explained assuming the formation of degradation products able to act as fluorescence quenchers. Furthermore, the

fluorescence spectroscopy gave information on the photochemical behaviour of polycondensed aromatic compounds we cannot determine in the gas chromatographic analysis. Also in this case we observed a decrease of the fluorescence. On the basis of the results collected in this work we are not able to explain this behaviour: in particular, we do not know whether polycondensed aromatic compounds are destroyed during irradiation or whether the fluorescence is quenched. In the future, the use of more complex analytical instruments (such as FTICR, Fourier transform ion cyclotron resonance) will give useful data able to explain this behaviour.

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