A Comparison of Results Obtained Using Liquid Injection and Headspace Solid-Phase Microextraction for Crude Oil Analysis by GC with Mass Spectrometer Detection

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Abstract

Gas chromatographic (GC) analysis in solution and head space solid-phaes microextraction (SPME)–GC analysis of a sample of crude oil gave different results. The SPME technique allowed the identification of a larger number of components than by using usual GC–mass spectrometry (MS). The method failed within the range of C14–C25 where GC–MS in solution allowed to obtain more representative results; on the contrary, SPME allowed to obtain data on the presence of volatile compounds that can not be identified in GC–MS analysis in solution. Furthermore, in the range C8–C12, SPME allowed to identify approximately 30 compounds not shown in the GC–MS analysis in solution. SPME analysis showed the presence of some alkenes not identified in GC–MS analysis in solution. SPME–GC–MS can be used in the analysis of crude oil in contaminated soil.

Introduction

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

Oil spills can represent an immediate damage to the image of the region and damage its tourist economy. It is then important to have a rapid and efficient method able to determine the presence of oil from accidental spills in the environment, in particular in the soil. This interest is due to the possible adverse effects of the presence of oil in the soil for both agricultural activity (soil productivity and quality of the products) and the preservation of the integrity of the park.

Gas chromatography (GC) coupled with flame ionization detector (FID) and with mass spectrometry (MS) has been used to determine and characterize crude oil. This method has been used in order to determine the composition of crude oil (1–3), to

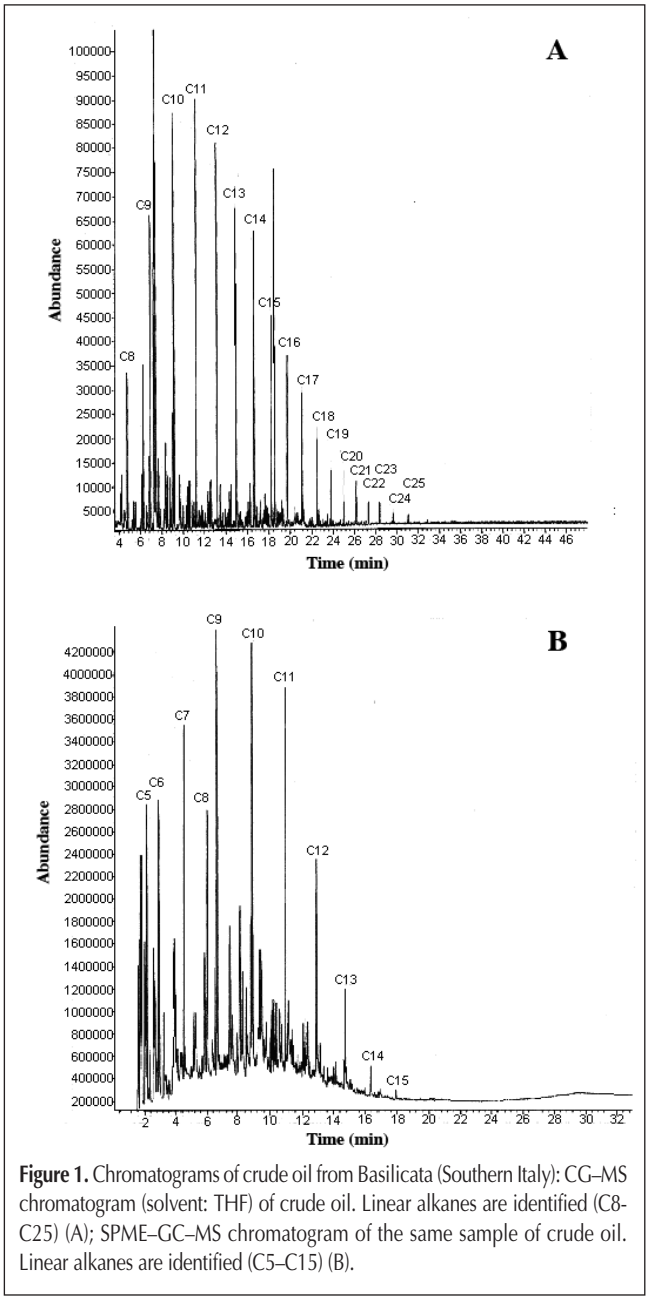

Figure 1. Chromatograms of crude oil from Basilicata (Southern Italy): CG–MS chromatogram (solvent: THF) of crude oil. Linear alkanes are identified (C8-C25) (A); SPME–GC–MS chromatogram of the same sample of crude oil. Linear alkanes are identified (C5–C15) (B).

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Table IA. GC–MS and SPME–GC–MS Analysis of Crude Oil From Basilicata

	GC–MS			SPME–GC–MS		
Entry	t_R (min)	Compound	Area %	t_R (min)	Compound	Area %
1				1.58	propane	0.09
2				1.64	butane	0.72
3				1.74	2-methylbutane	0.57
4				1.78	pentane	1.97
5				1.98	2-methylpentane	0.73
6				2.04	3-methylpentane	0.90
7				2.12	hexane	1.30
8				2.31	methylcyclopentane	0.77
9				2.53	2-methylhexane	1.00
10				2.65	3-methylhexane	1.22
11				2.80	*cis*-1,2-dimethylcyclopentane	0.80
12				2.91	heptane	3.23
13				3.25	methylcyclohexane	1.14
14				3.30	2,4-dimethylpentane	0.24
15				3.39	ethylcyclopentane	0.32
16				3.61	1,2,4-trimethylcyclopentane	0.44
17	4.03	2,3-dimethylhexane	0.28	3.80	2,3-dimethylhexane	0.41
18	4.11	2-methylheptane	1.04	3.87	2-methylheptane	1.42
19	4.19	toluene	1.08	3.97	toluene	1.55
20	4.26	3-methylheptane	0.64	4.01	3-methylheptane	1.26
21	4.38	1,2-dimethylcyclohexane	0.23	4.13	1,2-dimethylcyclohexane	0.96
22				4.30	1-hexene	0.48
23	4.62	*cis*-1-ethyl-3-methylcyclopentane	0.85	4.37	*cis*-1-ethyl-3-methylcyclopentane	0.77
24	4.76	octane	3.09	4.51	octane	3.75
25				4.96	2,4-dimethylhexane	0.66
26	5.35	2,6-dimethylheptane	0.47	5.08	2,6-dimethylheptane	1.06
27	5.50	ethylcyclohexane	0.45	5.22	ethylcyclohexane	1.13
28				5.28	1,1,3-trimethylcyclohexane	0.92
29				5.53	1-octene	0.68
30	6.13	2,3,4-trimethylhexane	1.07	5.68	2,3,4-trimethylhexane	0.58
31				5.85	2-methyloctane	2.30
32	6.28	1,3-dimethylbenzene	2.06	6.01	1,3-dimethylbenzene	3.69
33	6.63	cycloheptane	0.25			
34				6.27	1-nonene	0.30
35				6.34	1-methyl-2-propylcyclopentane	1.21
36	6.81	1,4-dimethylbenzene	0.81	6.53	1,4-dimethylbenzene	1.40
37	6.92	nonane	3.19	6.66	nonane	3.90
38				6.82	3,4,4-trimethyl-1-hexene	0.48
39				6.90	2-methyloctane	0.48
40				7.01	1-heptene	0.79
41				7.09	4-methyloctane	0.48
42				7.21	3,5-dimethyloctane	0.74
43				7.33	1-ethyl-3-methylcyclopentane	0.66
44	7.62	propylcyclohexane	0.28			
45	7.69	2,6-dimethyloctane	0.92	7.41	2,6-dimethyloctane	1.80
46	8.18	propylbenzene	0.38			
47	8.27	3-ethyl-2,4-dimethylpentane	0.13			
48				7.58	3-ethylheptane	1.32
49				7.89	4-ethyloctane	0.90
50	8.32	4-methylnonane	0.42	8.09	4-methylnonane	2.74
51				8.16	3,4,5-trimethyl-1-hexene	0.29
52	8.37	1-ethyl-4-methylbenzene	1.39			
53	8.51	3-methylnonane	0.74	8.23	3-methylnonane	1.27
54	8.77	1-ethyl-2-methylbenzene	0.58	8.47	1-ethyl-2-methylbenzene	0.83
55				8.54	1-decene	1.11

Table IB. (Continued) GC–MS and SPME–GC–MS Analysis of Crude Oil From Basilicata

	GC–MS			SPME–GC–MS		
Entry	t_R (min)	Compound	Area %	t_R (min)	Compound	Area %
56	9.06	1,2,4-timethylbenzene	1.30	8.77	1,2,4-trimethylbenzene	1.70
57	9.15	decane	4.21	8.89	decane	4.00
58					3-ethyloctane	1.03
59	9.65	2,6-dimethylnonane	0.61	9.36		
60	9.70	1,2,3-trimethylbenzene	0.63	9.40	1,2,3-trimethylbenzene	1.54
61				9.58	1-methylprolylcyclohexane	0.81
62	9.99	3-methyldecane	0.50		3-methyldecane	1.24
63	10.30	1-methyl-3-propylbenzene	0.23	9.69		
64				9.84	1-ethyl-2,2,6-trimethylcyclohexane	0.45
65				10.01	1-methyl-3-propylbenzene	0.85
66	10.37	5-methyldecane	0.47	10.08	5-methyldecane	0.67
67	10.44	1-methyl-2-(1-methylethyl)benzene	0.49	10.15	1-methyl-2-(1-methylethyl)benzene	0.64
68	10.64	3,7-dimethylnonane	0.77	10.22	3,7-dimethylnonane	0.69
69				10.36	3-methyldecane	0.25
70	10.84	1-ethyl-2,3-dimethylbenzene	0.32	10.54	1-ethyl-2,3-dimethylbenzene	0.50
71	10.88	1-ethyl-1,3-dimethylbenzene	0.43	10.59	1-ethyl-1,3-dimethylbenzene	0.83
72	11.01	1-ethyl-3,5-dimethylbenzene	0.56	10.72	1-ethyl-3,5-dimethylbenzene	1.01
73	11.25	undecane	5.19	10.97	undecane	2.98
74				11.31	5-methylundecane	0.87
75	11.45	4-ethyl-1,2-dimethylbenzene	0.25	11.42	4-ethyl-1,2-dimethylbenzene	0.54
76				11.50	5-(1-methylpropyl)nonane	0.36
77	11.59	4,5-dimethylnonane	0.33	11.61	4,5-dimethylnonane	0.30
78				11.62	2-undecene	0.23
79				11.75	1-undecene	0.37
80	11.72	1,2,4,5-tetramethylbenzene	0.33	12.06	1,2,4,5-tetramethylbenzene	0.81
81	11.79	4-methyldecane	0.24			
82	12.50	4-methylundecane	0.70	12.12	4-methylundecane	0.37
83				12.20	2-methylundecane	0.50
84				12.25	1,3-diethyl-5-methylbenzene	0.21
85				12.33	3-methylundecane	0.85
86	13.19	dodecane	4.43	12.89	dodecane	1.53
87	13.25	(1-methyl-1-butenyl)benzene	0.22			
88	13.44	2,6-dimethylundecane	0.67	13.15	2,6-dimethylundecane	0.37
89				13.69	1-dodecene	0.11
90	13.70	4,5-dimethyl-2-undecene	0.30			
91				14.04	3-methylundecane	0.21
92	14.17	5-methyldodecane	0.24			
93	14.26	4,8-dimethylundecane	0.25			
94	14.34	3,8-dimethyldecane	0.52			
95				14.20	4,6-dimethyldodecane	0.17
96	14.47	2,9-dimethylundecane	0.49			
97	14.98	tridecane	3.82	14.68	tridecane	0.54
98	15.04	1-methylnaphthalene	0.37	14.73	1-methylnaphthalene	0.26
99	15.30	2-methyldecane	0.23			
100	15.35	2-methylnaphthalene	0.21	15.03	2-methylnaphthalene	0.05
101	16.18	3-methyltridecane	0.29			
102	16.29	2,6,10-trimethyldodecane	0.50			
103	16.66	tetradecane	3.18	16.35	tetradecane	0.19
104	16.92	2,3-dimethylnaphthalene	0.23	16.90	2,3-dimethylnaphthalene	0.08
105	17.22	1,5-dimethylnaphthalene	0.39			

identify the presence of biomarkers (4–7), to identify the presence of particular components (8–10), to determine the presence of oil from spill (11–13), or the presence of crude oil in soil and sediments (14,15). The possible effects of sample preparation procedures on the results of the analysis has been studied (16). GC–MS–MS studies have been performed (17). Integrated chromatographic techniques have been used (18–21). Solid-phase microextraction (SPME) has not been used in this type of analysis.

SPME is a sample preparation technique based on sorption, which is useful for extraction and concentration of analytes either by submersion in a liquid phase (L-SPME) or exposure to a gaseous phase (SHS-SPME). Following exposure of the fiber to the sample, sorbed analytes can be thermally desorbed in a conventional GC injection port.

The methodology has been developed by Pawliszyn and coworkers at the University of Waterloo, in Ontario, Canada. SPME provides many advantages over conventional sample preparation techniques (22). The SPME technique is simple to use, takes less than 1 h to complete, is less expensive, does not require solvent extraction, and allows characterization of headspace in contact with the sample. In the last 10 years this non-invasive methodology was adopted to perform the analysis of volatile organic compounds (23–26).

In this paper, we report the results of our experiments on the analysis of a sample of crude oil from Val d'Agri by using GC–MS and SHS-SPME–GC–MS techniques. Our efforts were devoted to identify the most efficient method for the analysis and characterization of crude oil in environmental samples. In our project we want: (*i*) to characterize the crude oil extracted in Basilicata by using both GC–MS and SHS-SPME–GC–MS. However, GC–MS analysis can not consider a volatile fraction. To consider this fraction, we performed an SPME analysis of crude oil; (*ii*) identify the methodology able to give the best characterization of crude oil; (*iii*) to study the possible use of SPME in the determination of petroleum hydrocarbons environmental pollution. In particular, we are interested in identifing analytical methods able to characterize the modifications of crude oil after exposure to sunlight. In particular, our future work will be devoted to the study of the modifications that UV irradiation can induce on the nature of crude oil. The photochemical degradation of crude oil is evident after spills in sea water.

Materials and Methods

We used a sample of crude oil from Centro Oli in Val d'Agri (Basilicata, Southern Italy). Crude oil solution in THF (0.1M) was injected in a HP6890 plus GC (Agilent Technologies, Milan, Italy) equipped with a Phenomenex Zebron ZB-5 MS capillary column (30 m × 0.25 mm i.d. × 0.25 µm film thickness) (Supelco, Bellefonte, PA). The detector used was an 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 detector was maintained at 230°C. The oven was maintained at 60°C for 2 min, and 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. 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). All the peaks were identified from their mass spectra by comparison with spectra in Wiley6N and NIST98 libraries.

An SPME fiber coated with 100 µm of nongrafted poly(dimethylsiloxane) (PDMS) phase (Supelco 57300-U, mounted on a Supelco 57330 support) (Supelco, Bellefonte, PA) was conditioned for 1 h at 250°C in a stream of helium. A single fiber was used for the complete study. A blank run was performed

Table IC. (Continued) GC–MS and SPME–GC–MS Analysis of Crude Oil From Basilicata

	GC–MS			SPME–GC–MS		
Entry	t_R (min)	Compound	Area %	t_R (min)	Compound	Area %
106	17.54	1,3-dimethylnaphthalene	0.09			
107	17.79	3-methyltetradecane	0.25			
108	18.24	pentadecane	2.77	17.94	pentadecane	0.05
109	18.83	1,3,6-trimethylnaphthalene	0.07			
110	18.91	1,6,7-trimethylnaphthalene	0.19			
111	19.74	hexadecane	2.12			
112	21.16	heptadecane	1.58			
113	22.02	7,9-dimethylhexadecane	0.23			
114	22.51	octadecane	1.20			
115	22.64	2-methylpentadecane	0.46			
116	23.79	nonadecane	1.04			
117	25.02	eicosane	0.97			
118	26.18	heneicosane	0.64			
119	27.30	docosane	0.32			
120	28.40	tricosane	0.28			
121	29.61	tetracosane	0.18			
122	31.07	pentacosane	0.13			

after the analysis in order to confirm that no residual compound was polluting the fiber or the column. The headspace was generated from 10 mL samples placed in a 20-mL flask. The flask was sealed and heated for 20 min in an aluminium block maintained at 45°C (40°C in the flask). During this time, the fiber was maintained over the sample. The fiber was then introduced into the injection port of the GC. The injection port, equipped with glass insert (internal diameter 0.75 mm) was splitless at 250°C. The desorption time of 1.0 min was used. Detector was maintained at 230°C. Oven was maintained at 40°C for 2 min, then the temperature increased until 250°C (8°C/min); finally, this temperature was maintained for 10 min. All the analyses were performed in triplicate. The chromatograms obtained from the total ion current (TIC) were integrated without any correction for coelutions, and the results were expressed in arbitrary surface unites (asu). All the peaks were identified from their mass spectra by comparison with spectra in Wiley6N and NIST98 libraries.

Results and Discussion

In this study we used a sample of crude oil from Centro Oli in Val D'Agri (Basilicata, Southern Italy). The sample showed in the elemental analysis the following composition: C, 85.13%; H, 12.31%; N, 0.00%; S, 2.74%. In Figure 1A we report the chromatogram of a sample of crude oil obtained by using GC coupled with an MS detector. In all our analyses, we used a non-polar capillary column. All the experiments were performed using the same column. The identification of the recovered compounds is reported in Table I.

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 over a lot of signals. In this analysis, we could determine the presence of peaks from C7 to C25. As reported in Table I, we identified the presence of 74 compounds. In Figure 1B, we reported the chromatogram obtained for our sample in SPME analysis. In our study we identify the presence of 88 compounds (Table I). In this sample we identified the presence of compounds with different mass until pentadecane. In Figure 1B, the most important components were linear alkanes; the peaks corresponding to linear alkanes starting from pentane until pentadecane are identified in the chromatogram.

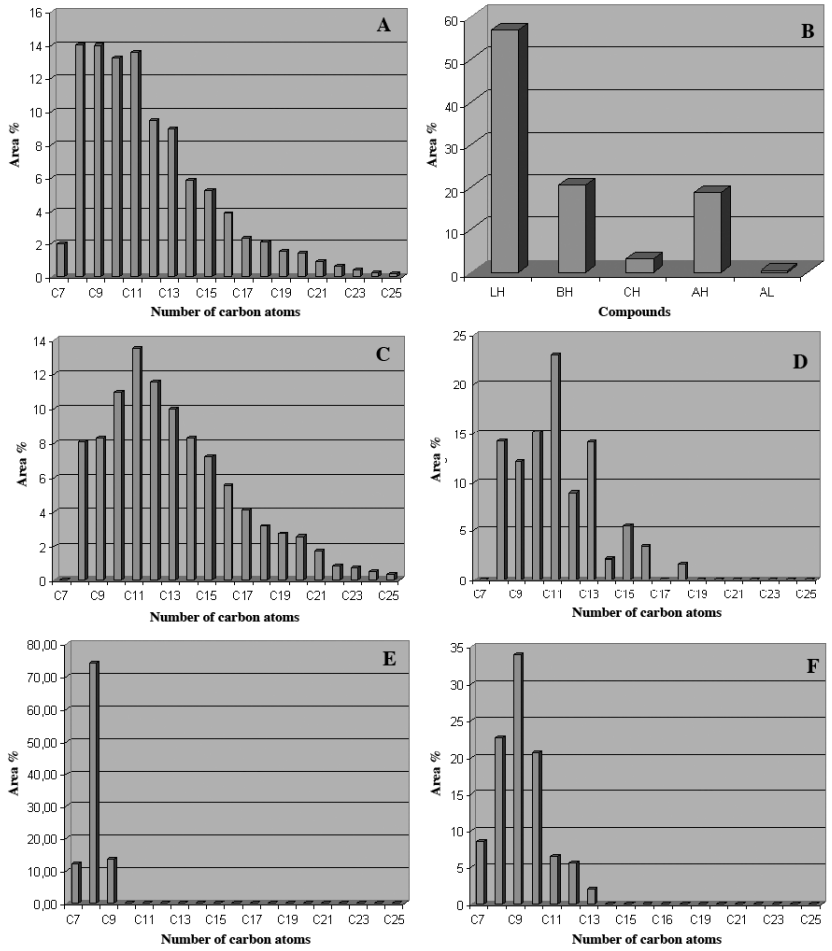

Figure 2. GC–MS analysis of crude oil from Basilicata (Southern Italy) in solution (solvent: THF): composition of crude oil as a function of the number of carbon atoms (A); composition of crude oil as a function of the type of compounds (LH, linear aliphatic hydrocarbons; BH, branched aliphatic hydrocarbons; CH, cyclic aliphatic hydrocarbons; AH, aromatic hydrocarbons; AL, alkenes) (B); composition of the linear aliphatic hydrocarbons fraction as a function of the number of carbon atoms (C); composition of the branched aliphatic hydrocarbons fraction as a function of the number of carbon atoms (D); composition of the cyclic hydrocarbons fraction as a function of the number of carbon atoms (E); composition of the aromatic hydrocarbons fraction as a function of the number of carbon atoms (F).

Table I shows that the SPME technique allowed the identification of a larger number of components than by using standard GC–MS. The method failed within the range C14–C25, where GC–MS in solution allowed more representative results to be obtained; on the contrary, SPME allowed to obtain data on the presence of volatile compounds that can not be identified in GC–MS analysis in solution. Furthermore, in the range C8–C12, SPME allowed the identification of approximately 30 compounds not shown in the GC–MS analysis in solution. Finally, SPME analysis showed the presence of some alkenes not identified in GC–MS analysis in solution.

In Figure 2A, 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 C9 to C11.

In the case of SPME analysis (Figure 3A), we observed that C8–C10 fractions represented 50% of all the compounds detected. The main fractions contained eight-ten carbon atoms while in the analysis in solution the main fractions were in the range C8–C11.

In Figure 2B 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.

In the case of SPME analysis (Figure 3B) linear alkenes represented 28%, branched alkanes 35%, while cyclic alkanes were 12% of the TIC. Aromatic hydrocarbons represented 19% of the total area and alkenes were only 5.6% of the TIC.

In comparison with the analysis in solution, SPME allowed the identification a larger amount of branched and cyclic hydrocarbons. The presence of aromatic compounds does not change, while we observed the presence of an important amount of alkenes, never identified in the analysis in solution.

Figure 2C 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 represent almost 50% of the sample.

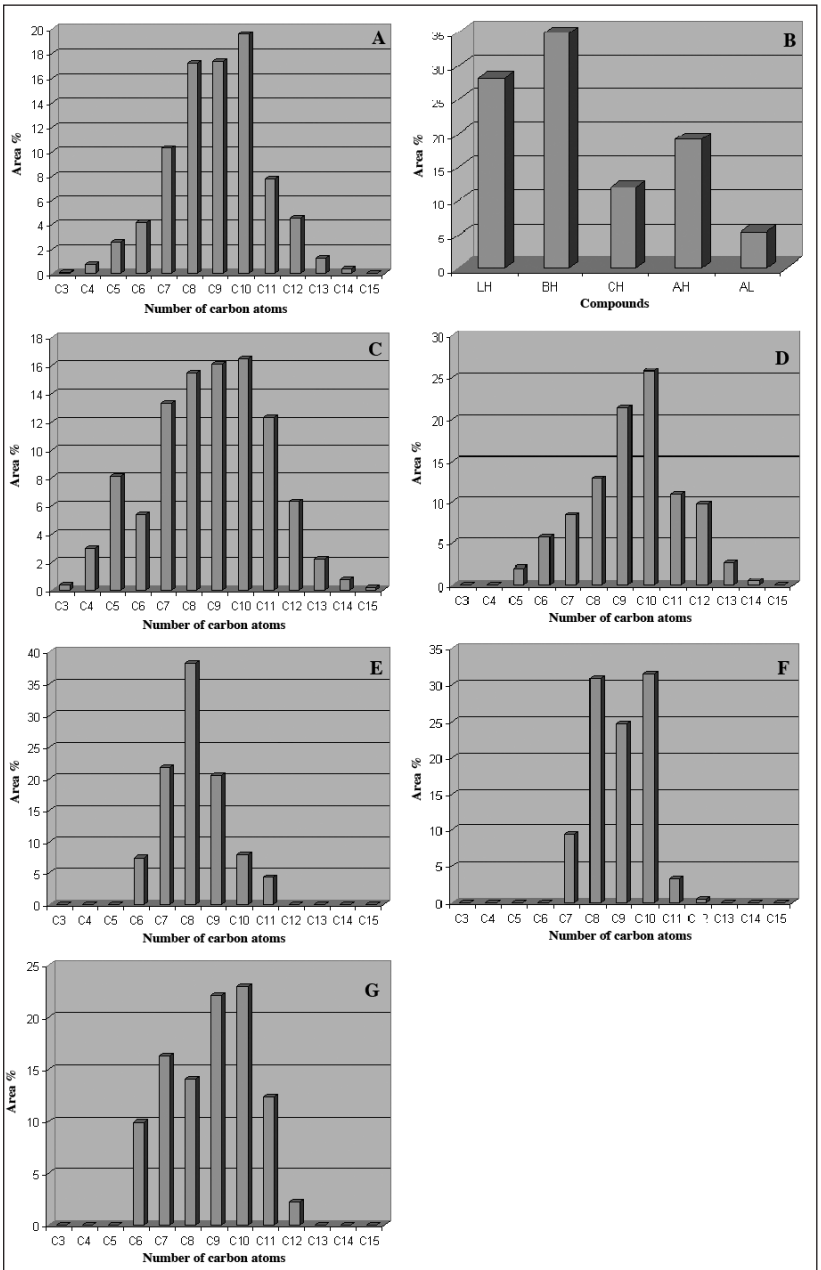

Figure 3. SPME–GC–MS analysis of crude oil from Basilicata (Southern Italy): composition of crude oil as a function of the number of carbon atoms (A); composition of crude oil as a function of the type of compounds (B). (LH, linear aliphatic hydrocarbons; BH, branched aliphatic hydrocarbons; CH, cyclic aliphatic hydrocarbons; AH, aromatic hydrocarbons; AL, alkenes); composition of the linear aliphatic hydrocarbons fraction as a function of the number of carbon atoms (C); composition of the branched aliphatic hydrocarbons fraction as a function of the number of carbon atoms (D); composition of the cyclic hydrocarbons fraction as a function of the number of carbon atoms (E); composition of the aromatic hydrocarbons fraction as a function of the number of carbon atoms (F); composition of the alkenes fraction as a function of the number of carbon atoms (G).

In Figure 3C we collected the distribution of linear alkanes in a function of the number of carbon atoms in the SPME analysis. The main fractions were obtained for C8–C10 fractions, while the main fraction in the analysis in solution was that with eleven carbon atoms.

The composition in function of the number of carbon atoms of the branched aliphatic hydrocarbons fraction is reported in Figure 2D. This fraction showed components in the range C8–C18, and the main components are in the range C8–C13.

SPME analysis (Figure 3D) showed that the main fraction was that containing 10 carbon atoms, while, in the analysis in solution, the main fraction contained 11 carbon atoms.

Figure 2E refers to the presence of cyclic hydrocarbons. We observed only cyclic aliphatic hydrocarbons with 7–9 carbon atoms and the main components showed 8 carbon atoms.

In SPME analysis (Figure 3E), we observed that all the compounds were in the range of C6–C11, and the main component was that having 8 carbon atoms, as reported in the analysis in solution.

Figure 2F shows the composition of the aromatic hydrocarbon fraction. It contained compounds in the range C7–C13, and the main fraction was represented by the C9 one.

Figure 3F represents the distribution of the aromatic fraction in function of the number of carbon atoms in the SPME analysis: clearly, in spite of the almost similar percent area in both the anlyses, the distribution was completely different. When the analysis was performed in solution, the main component showed 9 carbon atoms. Using SPME, the main components were those containing 8 and 10 carbon atoms.

Finally, Figure 3G shows the distribution of the alkenes fractions in SPME analysis. This distribution could not be obtained with the results of the analysis in solution considering the very low presence of alkenes detected by using this procedure.

In conclusion, we showed that GC analysis in solution and headspace SPME–GC analysis of a sample of crude oil gave different results. SHS-SPME technique seems to be more sensible for low molecular mass molecules and alkenes, while traditional GC analysis gave a more accurate description of high mass molecules.

To test the utility of SPME in the determination

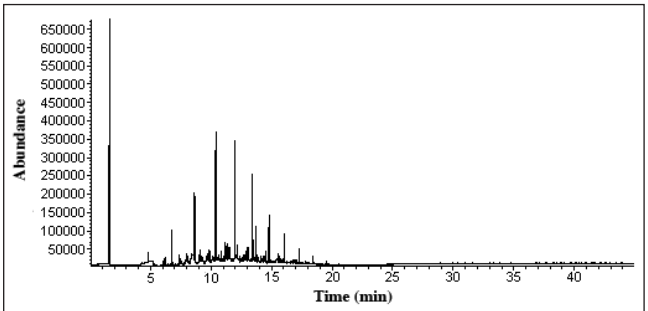

Figure 4. SHS-SPME–GC–MS analysis of a contaminated soil after an accidental spill of crude oil from a tank truck. The sample was analyzed two years after the accident.

of environmental pollution due to crude oil spill, we used this methodology in the analysis of contaminated soil. This soil was contaminated in a car accident involving a tank truck bearing crude oil. The sample was collected and analyzed two years after the accident. The result is reported in Figure 4, and the presence of hydrocarbons is clearly detectable without chemical treatment of the sample. It is simple to distinguish between crude oil, gasoline, gasohol, and kerosene by using the presence of additives (in the case of gasoline) or by using specific markers (27).

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