

# Fast solid-phase extraction–gas chromatography–mass spectrometry procedure for oil fingerprinting Application to the Prestige oil spill

Roberto Alzaga\*, Paolo Montuori, Laura Ortiz, Josep M. Bayona, Joan Albaigés

*Environmental Chemistry Department, IIQAB-CSIC, Jordi Girona 18–26, E-08034 Barcelona, Spain*

## Abstract

A rapid and simple fractionation procedure using solid-phase extraction (SPE) cartridges was developed for an accurate determination of aliphatic and polycyclic aromatic hydrocarbons in petroleum residues and further application in chemical fingerprinting of oil spills by gas chromatography–mass spectrometry (GC–MS). Among the adsorbents evaluated, SiO<sub>2</sub>/C<sub>3</sub>–CN exhibited the best selectivity, providing, by elution with *n*-hexane (4 ml) and *n*-hexane–CH<sub>2</sub>Cl<sub>2</sub> (1:1) (5 ml), two well-resolved aliphatic and aromatic hydrocarbon fractions, with recoveries of 97 ± 7.2 and 99.7 ± 13.9%, respectively. The SPE fractionation procedure was compared with the conventional silica–alumina adsorption chromatography showing similar results but practical advantages in terms of reproducibility, analysis time, solvent reduction and cost. Moreover, is particularly suitable for routine analysis with a high sample throughput. The developed methodology was tested in the characterization of fuel–oil samples collected along the Spanish north–west coast, after the Prestige oil spill accident.

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## 1. Introduction

Modern oil spill identification systems are largely based on the determination of series of petroleum chemical markers, which display unique profiles, characteristic of the source or the weathering stage of the pollutant. The determination of these compounds is carried out by gas chromatography–flame ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS) of the aliphatic and aromatic fractions, therefore involving a chemical class fractionation step [1–3]. The isolation of these fractions in a large number of samples, usually to be analysed after an accidental oil spill or in a monitoring network, may be hampered by the lack of reproducibility originated by the differences in adsorbent activities [4–8]. In the case of marine oil spills, stable oil–water emulsions up to 50% of water or samples containing a variety of impurities (i.e. sand, algae, plankton, etc.) may even require a previous clean-up step.

Numerous procedures for the fractionation of petroleum hydrocarbons have been reported in the literature [5,8–10]. These procedures include liquid–liquid extraction with solvents that allow charge transfer complex, column liquid chromatography on various stationary phases (i.e. silica, alumina, and silica–alumina combination), TLC and normal-phase HPLC [4,7,10–15]. Solid-phase extraction (SPE) has been used as an alternative technique for its selectivity, a faster elution profile and minimization of solvent consumption [5,8,16,17]. By choosing a selective adsorbent and eluents of increasing polarity (i.e. pentane, hexane, dichloromethane, etc.), it is possible to achieve fractions enriched in specific chemical classes [18]. However, fractionation of petroleum samples and related products by SPE owns some drawbacks. Due to the small amount of adsorbent, only few mg of oil sample can be fractionated in order to avoid column overloading. On the other hand, although a broad spectrum of sorbents are commercially available for SPE, silica is the preferred stationary phase, despite its limited selectivity for the lower aromatic hydrocarbons (e.g. alkylnaphthalenes) [2,5,7,8].

In order to respond to the identification of accidental oil spills in the marine environment, it is worth to have a fast

\* Corresponding author. Tel.: +34-93-4006100; fax: +34-93-2045904.  
E-mail address: [ramqam@iiqab.csic.es](mailto:ramqam@iiqab.csic.es) (R. Alzaga).

and reliable analytical method for the separation and characterization of the different classes of chemical markers. The aim of this study was the evaluation of different commercially available adsorbents for the fractionation of oil spill samples using SPE cartridges. Special attention was paid to method simplicity, reproducibility, recovery and speed to ensure its applicability to routine analysis with a high sample throughput. Fractionation selectivity for a variety of chemical markers was evaluated, and the quantitative data obtained for aliphatic and aromatic hydrocarbons was compared with that of a conventional silica–alumina column chromatography fractionation. The method has been implemented for the monitoring of the Prestige oil spill in the Galician coast (north-west Spain).

## 2. Experimental

### 2.1. Reagents, materials and standards

Trace analysis (SupraSolv) dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and *n*-hexane ( $\text{C}_6\text{H}_{14}$ ) were obtained from Merck (Darmstadt, Germany). Solid-phase cartridges of silica ( $\text{SiO}_2$ , 500 mg, 3 ml) and silica/cyanopropyl ( $\text{SiO}_2/\text{C}_3\text{-CN}$ , 1.0/0.5 g, 6 ml) were obtained from Interchim (Montluçon, France). Cyanopropyl cartridge ( $\text{C}_3\text{-CN}$ , 500 mg, 3 ml) was from Applied Separation (Allentown, PA, USA). All the solid-phase cartridges were of polypropylene. Alumina ( $\text{Al}_2\text{O}_3$  neutral, 70–230 mesh, Merck) and silica ( $\text{SiO}_2$ , 70–230 mesh, Merck) were activated overnight at 400 °C and then deactivated with 5% (w/w) of water.

Aliphatic hydrocarbon standards (*n*- $\text{C}_{15}$ , *n*- $\text{C}_{16}$ , pristane, *n*- $\text{C}_{19}$ , *n*- $\text{C}_{22}$ , *n*- $\text{C}_{23}$ , *n*- $\text{C}_{28}$ , *n*- $\text{C}_{32}$ , *n*- $\text{C}_{36}$ ) were obtained from Fluka (Buchs, Switzerland) and a polycyclic aromatic hydrocarbons (PAHs) standard solution (10 ng/ $\mu\text{l}$  in cyclohexane), containing acenaphthene, acenaphthylene, anthracene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*a*]pyrene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*c,d*]pyrene, naphthalene, phenanthrene and pyrene, was purchased to Dr. Ehrenstorfer-Schäfers (Augsburg, Germany). Cholestane from Aldrich (Steinheim, Germany) and perdeuterated PAHs [ $^2\text{H}_{10}$ ]anthracene (anthracene- $\text{d}_{10}$ ), [ $^2\text{H}_{10}$ ]pyrene (pyrene- $\text{d}_{10}$ ) and [ $^2\text{H}_{12}$ ]perylene (perylene- $\text{d}_{12}$ ) were used as surrogates. Triphenylamine from Merck was used as internal standard (IS).

### 2.2. Procedure and sample preparation of spilled oil

The determination of oil-contaminated samples collected in the marine environment, involves first the water content in order to refer the PAH concentration to the oil content in the sample. Therefore, fuel-oil-contaminated samples (i.e. 1.0 g) were dissolved in 5 ml of  $\text{CH}_2\text{Cl}_2$ , phase separated,

and percolated through 2 g of anhydrous  $\text{Na}_2\text{SO}_4$  column. The fuel-oil content in the sample was determined by gravimetry in 1.0 ml of the eluate, which was carefully evaporated until dryness. The hydrocarbon determination was carried out in another anhydrous  $\text{CH}_2\text{Cl}_2$  aliquot corresponding to 5–10 mg of extract. Dichloromethane was exchanged to hexane (1.0 ml) by a gentle solvent evaporation under a nitrogen flow and the surrogates were added at concentrations of 1.0  $\mu\text{g}/\text{ml}$ . The solution was transferred onto the  $\text{SiO}_2/\text{C}_3\text{-CN}$  SPE cartridge and eluted, under a positive pressure, with 4 ml of *n*-hexane (FI) and 5 ml of *n*-hexane– $\text{CH}_2\text{Cl}_2$  (1:1) (FII). These fractions, containing, respectively, the aliphatic and aromatic hydrocarbons, were concentrated to a volume of 1.0 ml under a gentle stream of nitrogen. Fifty microlitres of each fraction were added to 425  $\mu\text{l}$  of hexane, spiked with 25  $\mu\text{l}$  of a solution of triphenylamine in hexane (8.0  $\mu\text{g}/\text{g}$ ) as IS for GC–MS analysis. In case of fuel-oil samples, before the SPE fractionation, cartridges were conditioned with 4.0 ml of hexane. SPE procedural blanks were evaluated, showing the presence of a predominant peak of butylated hydroxytoluene (base peak  $m/z$  205) at the beginning of the chromatogram ( $t_R = 8.86$  min), which does not interfere with any of the target analytes.

Adsorption chromatography was performed in a glass column (45 cm  $\times$  1.2 cm) packed with  $\text{Al}_2\text{O}_3$  (top) and  $\text{SiO}_2$  (bottom) (6 g of each adsorbent, 5% (w/w), water deactivated) in hexane. About 50–100 mg of the oil sample dissolved in hexane with the surrogates were absorbed on top of the column and further eluted using the following solvents: (1) 20 ml hexane; and (2) 45 ml hexane– $\text{CH}_2\text{Cl}_2$  (80:20). Recovered fractions were concentrated by rotary evaporation until 3 ml and under nitrogen stream until 1.0 ml. A dilution with isooctane (i.e. 1:100) was necessary prior to the GC–MS analysis. In the Prestige fuel-oil samples, the aliphatic and aromatic fractions represented  $21.6 \pm 2.0$  and  $50.7 \pm 3.1\%$  ( $n = 4$ ), respectively, of the total oil. The rest of the sample ( $27.7 \pm 5.0\%$ ) remained in the column.

### 2.3. Apparatus

The analysis was accomplished with a TRACE-MS Thermo Finnigan TRACE-GC 2000 gas chromatograph equipped with a split/splitless injector (splitless time: 0.80 min; flow: 50 ml/min). The carrier gas was helium at a constant flow of 1.2 ml/min. A capillary column (J&W Scientific, Folsom, CA, USA) HP-5 MS 30 m  $\times$  0.25 mm i.d., 0.25  $\mu\text{m}$  film was used as analytical column. Initial column temperature was held for 1 min at 70 °C, programmed at 15 °C/min to 150 °C min (ramp 1) and then at 6 °C/min (ramp 2) to a final temperature of 320 °C which was held for 10 min. The injector temperature was 310 °C. Finally, data were acquired in the full scan mode from 50 to 490 units (2.4 scans/s) with 5 min of solvent delay and processed by the X-calibur software.

Table 1  
Characteristics of the SPE columns

Sorbent type	Amount (mg)	Particle size distribution ( $\mu\text{m}$ )	Mean pore size ( $\text{\AA}$ )	Characteristics
Silica ( $\text{SiO}_2$ )	500	40–63	60	Spheric, non-endcapped
Cyanopropyl ( $\text{C}_3\text{-CN}$ )	500	40–120	60	Irregular, acid washed silica, non-endcapped
$\text{SiO}_2/\text{C}_3\text{-CN}$	1000/500	40–63	60	Spheric, non-endcapped

### 3. Results and discussion

Adsorption chromatography is a well-established methodology for the separation of alkanes and PAHs [19]. It offers a high selectivity, combining different adsorbents such as florisil, silica gel, alumina, etc. with the eluent polarity, and a high capacity. The adsorbent activity is a crucial parameter that affects reproducibility [20]. Water adsorbent deactivation has usually been performed in order to improve the recovery of the high-molecular-mass PAHs. As major drawbacks, adsorption chromatography is time consuming (procedural blank, glassware cleaning, adsorbent activation–deactivation, etc.), the column packing procedure is labour-intensive and difficult to standardize, and involves the use of large solvent volumes that have to be pre-concentrated prior to GC analysis.

In order to develop a more convenient procedure for an accurate determination of aliphatic and PAHs in petroleum residues and further application in chemical fingerprinting of oil spills by GC–MS, the use of SPE cartridges was explored. Three different SPE columns ( $\text{SiO}_2$ ,  $\text{C}_3\text{-CN}$  and  $\text{SiO}_2/\text{C}_3\text{-CN}$ ) were evaluated. The characteristics of the columns are shown in Table 1. Different eluents of increasing polarity and their elution volumes were tested for the determination of the best fractionation conditions of the standard mixture of alkanes and PAHs indicated in Section 2.1. The results are shown in Table 2.

Using the  $\text{SiO}_2$  column, alkanes were quantitatively recovered (80% of the total spiked amount) with only 1.5 ml of hexane (FI, 0–1.5 ml) and only a small fraction (12%) was recovered with the subsequent 1.5 ml. Alkane recoveries were in the range of 82% for  $n\text{-C}_{36}$  to 105% for  $n\text{-C}_{15}$  with a mean total recovery value of  $95 \pm 8.0\%$ . However, some PAHs also eluted in FI. Sixty-five and twenty-six percent of the total spiked naphthalene and acenaphthene, respectively, were eluted within the 1.5–3.0 ml. Moreover, within the 3.0–4.5 ml, a fraction of the three- to four-ring PAHs, such as anthracene (68%), phenanthrene (56%) and pyrene (53%) were also eluted. The rest of the PAHs were eluted when the eluent polarity increased. Fraction II (20%  $\text{CH}_2\text{Cl}_2$  in hexane) contained the higher-molecular-mass PAHs (i.e. fluoranthene (85%), benzo[*g,h,i*]perylene (86%) and benzo[*a*]pyrene (96%)) in the first 1.5 ml, representing the 55% of the total PAHs. The following elution (1.5–3.0 ml), representing the 12% of total PAHs, was enriched in dibenzo[*a,h*]anthracene (i.e. 60% of the total spiked). PAH recoveries were in the range of 76% for

dibenzo[*a,h*]anthracene to 107% for benzo[*a*]pyrene with a mean total recovery value of  $97 \pm 7.0\%$  ( $n = 5$ ). Although it is possible to achieve a reasonable separation among alkanes and PAHs, the selectivity exhibited by the  $\text{SiO}_2$  column is rather limited, especially for low-molecular-mass PAHs such as naphthalene and its alkylated derivatives, which are target analytes in oil spill fingerprinting because they are indicators of early weathering processes as a result of their high volatility and solubility.

These results are in accordance with previous works [5,7], although a selective separation of alkanes and PAHs using  $\text{SiO}_2$  columns in diesel fuel has been reported [8]. In order to increase the selectivity, silver nitrate impregnated silica SPE columns have been successfully applied for the separation of aliphatic and aromatic hydrocarbons [17]. However, these columns are not commercially available and the adsorbent preparation is mandatory prior to analysis.

The cyanopropyl column ( $\text{C}_3\text{-CN}$ ) exhibited the worst performance in terms of selectivity between alkanes and

Table 2  
Evaluation of spiked aliphatic and polycyclic aromatic hydrocarbons (PAHs) fractionation with  $\text{SiO}_2$ , cyanopropyl ( $\text{C}_3\text{-CN}$ ) and  $\text{SiO}_2/\text{C}_3\text{-CN}$  solid-phase columns with different volume and eluent polarities

Column	Elution volume (ml)	Recovery (%)		
		Alkanes	PAHs	
$\text{SiO}_2$	FI: 100% hexane	0–1.5	80	
		1.5–3.0	12	7
		3.0–4.5	3	23
	FII: $\text{CH}_2\text{Cl}_2$ –hexane (20:80, v/v)	0–1.5		55
		1.5–3.0		12
		3.0–4.5		
$\text{C}_3\text{-CN}$	FI: 100% hexane	0–1.5	81	18
		1.5–3.0	9	79
		3.0–4.5	1	2
	FII: $\text{CH}_2\text{Cl}_2$ –hexane (20:80, v/v)	0–1.5		1
		1.5–3.0		
		3.0–4.5		
$\text{SiO}_2/\text{C}_3\text{-CN}$	FI: 100% hexane	0–1.5		
		1.5–3.0	92	
		3.0–4.5		
	FII: $\text{CH}_2\text{Cl}_2$ –hexane (50:50, v/v)	0–1.5		2
		1.5–3.0		80
		3.0–4.5		17

Table 3

Comparison of adsorption column chromatography (CC) and solid-phase extraction (SPE) for aliphatic hydrocarbon determination ( $\mu\text{g/g}$ ) in Prestige fuel-oil sample

Compound	CC		SPE		Recovery (%)
	Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>		Si/CN		
	Average ( $\mu\text{g/g}$ )	R.S.D. <sup>a</sup> (%)	Average ( $\mu\text{g/g}$ )	R.S.D. <sup>b</sup> (%)	
<i>n</i> -C <sub>12</sub>	357	9.4	365	13.0	102.1
<i>n</i> -C <sub>13</sub>	523	8.7	550	8.0	105.2
<i>n</i> -C <sub>14</sub>	691	8.7	657	12.0	95.1
<i>n</i> -C <sub>15</sub>	689	7.3	665	7.5	96.5
<i>n</i> -C <sub>16</sub>	627	8.3	623	8.1	99.3
<i>n</i> -C <sub>17</sub>	593	7.4	562	3.5	94.7
Pristane	314	9.4	289	8.4	92.1
<i>n</i> -C <sub>18</sub>	573	9.0	487	10.9	84.9
Phytane	352	7.6	382	4.8	108.6
<i>n</i> -C <sub>19</sub>	640	7.4	656	6.7	102.4
<i>n</i> -C <sub>20</sub>	749	6.6	681	4.5	90.9
<i>n</i> -C <sub>21</sub>	754	9.9	676	7.9	89.6
<i>n</i> -C <sub>22</sub>	812	9.8	594	6.8	73.2
<i>n</i> -C <sub>23</sub>	807	10.6	720	10.1	89.2
<i>n</i> -C <sub>24</sub>	819	6.4	795	16.8	97.0
<i>n</i> -C <sub>25</sub>	830	6.1	804	13.2	96.9
<i>n</i> -C <sub>26</sub>	946	9.8	827	11.4	87.5
<i>n</i> -C <sub>27</sub>	668	13.5	653	14.1	97.7
<i>n</i> -C <sub>28</sub>	554	9.0	538	2.8	97.2
<i>n</i> -C <sub>29</sub>	528	4.0	484	2.1	91.8
<i>n</i> -C <sub>30</sub>	699	4.9	661	12.0	94.6
<i>n</i> -C <sub>31</sub>	542	3.1	564	4.0	104.1
<i>n</i> -C <sub>32</sub>	427	5.0	400	3.6	93.6
<i>n</i> -C <sub>33</sub>	395	3.2	377	9.0	95.4
<i>n</i> -C <sub>34</sub>	397	10.1	351	13.9	88.4
<i>n</i> -C <sub>35</sub>	467	7.0	459	15.5	98.4
<i>n</i> -C <sub>36</sub>	357	9.4	365	13.0	102.1
<i>n</i> -C <sub>37</sub>	523	8.7	550	8.0	105.2
<i>n</i> -C <sub>38</sub>	691	8.7	657	12.0	95.1
<i>n</i> -C <sub>39</sub>	689	7.3	665	7.5	96.5
<i>n</i> -C <sub>40</sub>	627	8.3	623	8.1	99.3
<i>n</i> -C <sub>41</sub>	593	7.4	562	3.5	94.7

<sup>a</sup>  $n = 5$ .

<sup>b</sup>  $n = 3$ .

PAHs (Table 2). Indeed, PAHs eluted with hexane as well as alkanes, showing that this column present low  $k'$  values and it is not suitable to separate these analytes.

The SiO<sub>2</sub>/C<sub>3</sub>-CN column exhibited the best results for the separation of alkanes and PAHs (Table 2). Alkanes were quantitatively recovered when 3.0 ml of hexane were percolated ( $92 \pm 6.8\%$  of total amount). In order to increase the PAHs recovery, as well as to reduce the solvent volume, the eluent polarity was increased for FII (CH<sub>2</sub>Cl<sub>2</sub>-hexane, 1:1). PAHs recoveries were  $95 \pm 5.3\%$  ( $n = 5$ ). It is important to remark that the recovery values are acceptable taking into account the low analyte mass used (300 ng). Although an even higher solvent polarity of the eluent could be used (i.e. 100% CH<sub>2</sub>Cl<sub>2</sub>) this was disregarded because PAH recoveries were not improved and more polar compounds co-eluted when oil spill samples were analysed, worsening the achieved selectivity. The optimum conditions established for the fractionation step were FI 4.0 ml of hexane (aliphatic hydrocarbons) and FII 5.0 ml of hexane-CH<sub>2</sub>Cl<sub>2</sub> (1:1) (PAHs).

In order to evaluate the developed analytical procedure with real samples, a comparison of the SPE cartridge fractionation versus adsorption chromatography was carried out with the fuel-oil spilled in the Prestige accident. These results are shown in Table 3 for alkanes and Table 4 for PAHs. Good agreement in concentrations was obtained for the determined analytes. Using SPE, relative recoveries of alkanes and PAHs were of  $97 \pm 7.2$  and  $99.7 \pm 13.9\%$ , respectively, compared to adsorption chromatography. These results show that both fractionation methodologies are comparable, although due to the small amount of sample analysed in SPE (5–10 mg), to avoid the column capacity overloading, analytes below 50  $\mu\text{g/g}$  could not be determined. However, SPE shows clear advantages compared to adsorption chromatography in terms of analysis time (i.e. 5 min versus 1 h per sample), solvent volume employed (i.e. 10 ml versus 100 ml) and analysis cost. Moreover, the time employed for solvent pre-concentration is highly reduced as only a gentle stream of nitrogen is required instead of a rotary evaporation.

Table 4  
Comparison of adsorption chromatography (LC) and solid-phase extraction (SPE) for PAH determination ( $\mu\text{g/g}$ ) in Prestige fuel-oil sample

PAHs	Acronym	LC		SPE		Recovery (%)
		$\text{Al}_2\text{O}_3/\text{SiO}_2$		Si/CN		
		Average ( $\mu\text{g/g}$ )	R.S.D. <sup>a</sup> (%)	Average ( $\mu\text{g/g}$ )	R.S.D. <sup>b</sup> (%)	
Fluorene	F	86.5	5.5	97.7	2.0	112.9
Acenaphthene	ANA	65.9	6.6	61.5	4.5	93.3
Acenaphthylene	ANY	ND <sup>c</sup>		ND		
Naphthalene	N	345	4.8	375	3.2	108.5
Methylnaphthalene	N1	1149	7.5	1076	1.6	93.7
Dimethylnaphthalene	N2	1576	3.3	1232	0.7	78.2
Trimethylnaphthalene	N3	1144	6.7	1017	3.6	88.9
Phenanthrene	Ph	337	4.7	339	0.6	100.5
Methylphenanthrene	Ph1	847	5.9	892	1.7	105.4
Dimethylphenanthrene	Ph2	942	8.0	886	1.1	94.1
Trimethylphenanthrene	Ph3	551	4.5	592	7.6	107.4
Anthracene	A	44.9	4.6	NQ <sup>d</sup>		
Fluoranthene	FL	24.8	11.4	NQ		
Methylfluoranthene	FL1	348	10.8	321	1.1	92.0
Dimethylfluoranthene	FL2	419	6.8	400	3.2	95.5
Trimethylfluoranthene	FL3	317	9.5	304	1.3	96.1
Pyrene	Py	96.8	6.6	117	3.4	120.9
Dibenzothiophene	D	84.9	8.2	107	2.9	126.2
Methyldibenzothiophenes	D1	296	6.1	345	5.3	116.8
Dimethyldibenzothiophenes	D2	456	11.7	477	2.4	104.6
Trimethyldibenzothiophenes	D3	416	9.4	402	2.3	96.7
Chrysene + triphenylene	C	96.6	5.2	110	3.9	113.6
Methylchrysene	C1	319	5.9	261	6.3	81.7
Dimethylchrysene	C2	314	11.4	306	1.2	97.7
Trimethylchrysene	C3	364	11.8	252	6.4	69.3
Benzo[ <i>b</i> ]fluoranthene + benzo[ <i>k</i> ]fluoranthene	B(b+k)F	13.6	19.6	NQ		
Benzo[ <i>e</i> ]pyrene	BeP	39.6	10.9	NQ		
Benzo[ <i>a</i> ]pyrene	BaP	25.9	14.6	NQ		
Perylene	PE	9.7	16.4	ND		
Benzo[ <i>a</i> ]anthracene	BaA	49.1	4.5	NQ		
Dibenzo[ <i>a,h</i> ]anthracene	DBA	4.7	21.6	ND		
Indeno[1,2,3- <i>c,d</i> ]pyrene	IN	5.1	18.4	ND		
Benzo[ <i>g,h,i</i> ]perylene	BPE	14.8	21.8	ND		

<sup>a</sup>  $n = 5$ .

<sup>b</sup>  $n = 3$ .

<sup>c</sup> ND: not detected.

<sup>d</sup> NQ: not quantified (below LOQ).

As a summary, Table 5 shows the fractionation of chemical markers used for oil fingerprinting when  $\text{SiO}_2/\text{C}_3\text{-CN}$  SPE columns were used. The high selectivity allows a quantitative elution in two resolved fractions. As example, steranes and diasteranes were quantitatively isolated in FI and triaromatic steroids in FII allowing an accurate determination of different geochemical indices based on these molecular markers.

A final aspect to be taken into account when analysing marine oil samples is the presence of water, that for a heavy residue may account for 50–60% of its mass. This may affect, not only the quantitation analysis, but also the fractionation process itself. In addition, a variety of impurities (i.e. sand, algae, plankton, etc.) are commonly present in marine samples and they have to be separated prior to analysis. The filtration of the sample, dissolved in  $\text{CH}_2\text{Cl}_2$ , through a bed

Table 5  
Fractionation of chemical markers for oil fingerprinting using the  $\text{SiO}_2/\text{C}_3\text{-CN}$  SPE procedure

Compound class	Diagnostic ions ( $m/z$ )	FI	FII
Aliphatic hydrocarbons	57, 71, 85		
<i>n</i> -Alkanes		XXX	
Isoprenoids		XXX	
Alkylcyclohexanes	82, 83	XXX	
Hopanes	191	XXX	
Steranes and diasteranes	217, 218	XXX	
Long-chain alkylbenzenes	91, 105, 119	XX	X
Polycyclic aromatic hydrocarbons			
Two to six aromatic rings	Variable		XXX
Alkyldibenzothiophenes	134, 148, 162, 176		XXX
Triaromatic steroids	231		XXX

of anhydrous  $\text{Na}_2\text{SO}_4$  was used as a preliminary work-up of the samples. Finally, a special care should be taken in the evaporation of extracts to prevent any loss of volatile compounds (i.e. naphthalene) in the oil residues.

#### 4. Conclusions

Among the commercially available SPE adsorbents evaluated,  $\text{SiO}_2/\text{C}_3\text{-CN}$  exhibited the best selectivity for aliphatic and aromatic hydrocarbons separation in two well-resolved fractions. Special attention was paid to the determination of the lower PAHs (i.e. naphthalene and alkylated derivatives), which are quantitatively recovered in FII, improving previous SPE methodologies involving only  $\text{SiO}_2$  as adsorbent. The  $\text{SiO}_2/\text{C}_3\text{-CN}$  SPE method was evaluated against the conventional adsorption chromatography being both methods highly comparable. However, the SPE methodology shows practical advantages in terms of analysis time, consumables, solvent reduction and cost and is particularly suitable for routine applications requiring a high sample throughput, like in oil fingerprinting studies. The separation of hydrocarbons into aliphatic and aromatic components was demonstrated with the fuel-oil spilled by the Prestige tanker in the Spanish north-west Atlantic coast, in November 2002.

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