Extraction of Polycyclic Aromatic Hydrocarbons (PAHs), Polycyclic Aromatic Sulfur Heterocycles (PASHs) and Alkylated Derivatives from Seawater using Solid-Phase Microextraction (SPME)-Gas Chromatography-Mass Spectrometry (GC-MS)

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Abstract

Polycyclic aromatic compounds (PACs) represent a category of compounds known as highly toxic and can cause both short-and long-term effects. Therefore, it is of major interest to be able to characterize any contamination of the water column by this family of chemical compounds, both quantitatively and qualitatively. Many analytical developments have been applied to the determination of 14, 16 or 24 polycyclic aromatic hydrocarbons (PAHs) in aqueous samples but no work which focuses on the analysis of a large number of dissolved PACs has been published to our knowledge. In this context, a solid-phase microextraction (SPME) coupled to gas chromatography-mass spectrometry (GC-MS) method has been applied to the extraction of polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic sulfur heterocycles (PASHs) and alkylated derivatives from seawater. With an 8 mL sample volume the present method showed good linearity for concentrations ranging from 1 to 100 ng/L with correlation coefficients between 0.971 and 0.997. The limits of detection (LOD) are below 0.2 ng/L and ranged from 0.01 ng/L for 3-methylphenanthrene to 0.1 ng/L for naphthalene. The SPME-GC-MS procedure was applied to the analysis of PAHs, PASHs and alkylated derivatives in the Water Accommodated Fraction (WAF) of seawater samples prepared in the la laboratory from a crude oil.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) form a large group of environmental contaminants and some of them exhibit a carcinogenic or mutagenic potential. Some analogues of these compounds, such as polycyclic aromatic sulfur heterocycles (PASHs), are also potentially mutagenic and carcinogenic (Andersson and Schmid, 1995; MacFall et al., 1984, Mössner and Wise, 1999). They were detected in several environmental samples: urban dust (Mostafa et al., 2009), sediments (Brack and Schirmer, 2003), coal flue gas (Thuß et al., 2000). They were also analyzed in fossil materials (Moustafa and Andersson, 2011). Moreover, PASHs can be potential indicators of the origin and maturity of crude oils (Budzinski et al., 1993; Hegazi et al., 2003). In view of their importance in environmental chemistry, toxicology and organic geochemistry etc., there is increasing interest in the isolation, identification and quantification of these compounds (Becker et al., 1998; Hegazi and Andersson, 2007; Liang et al., 2006; Schade and Andersson, 2006).

The detection of polycyclic aromatic compounds PACs in aqueous samples requires very selective and sensitive methods. The classical methods for the extraction of analytes from aqueous samples are liquid-liquid extraction (LLE) and solid-phase extraction (SPE) techniques. Although these conventional extraction methods offer precise results, they are generally time-consuming and require large amounts of organic solvents.

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In recent years, the introduction of solid-phase microextraction (SPME) as a rapid extraction technique by Arthur and Pawliszyn in 1990, has gained increasing acceptance for a wide range of applications. It is a fast, simple, inexpensive, and solvent-free extraction technique (Pawliszyn, 1997). SPME has been successfully used for the analysis of PACs in water (Cortazar et al., 2002; Doong et al., 2000; González et al., 2007; King et al., 2004; Rainawati and Balasubramanian, 2009; Popp et al., 2000) but in these works only PAHs were analyzed. Thus, in this paper we propose a totally automated extraction procedure that uses SPME followed by GC-MS to determine PAHs, PASHs and alkylated derivatives in the water accommodated fraction (WAF) of seawater samples prepared in the laboratory from a crude oil.

2 Experimental Set-up

2.1 Analytical Standards

Reference PAHs (eighteen compounds) and deuterated internal standards were obtained from Cambridge Isotope Laboratories, Inc. A solution containing eighteen alkylated PAHs (SRM 1491a) at concentrations in the range 1-2 µg/mL in toluene was purchased from NIST (Gaithersburg, MD, USA). In addition, eight PASHs and eight alkylated derivatives were synthesized in one of our laboratories (Institute of Inorganic and Analytical Chemistry, 2012) and a solution at a concentration of 100 µg/mL in methanol was prepared. A list of the investigated chemicals and relative internal standards and abbreviations for each compound is reported in Table 1.

2.2 Preparation of Water Accommodated Fraction (WAF)

The water accommodated fraction (WAF) was prepared according to guidelines established by CROSSERF (Singer et al., 2000). This experiment was conducted in order to transfer compounds from the oil to the water phase only by solubilization. The principle of this experiment was to introduce oil at the water surface of a closed flask. To avoid significant transfer to the air phase, the headspace had to be lower than 25% of the whole volume of the flask. The oil/water ratio was set at 1:100 000 (10 mg of oil for 1 L of seawater), and agitation was ensured by using a magnetic stirrer. The experimental device was set in an air-conditioned room at 21 °C for 24 h to reach the equilibrium (Figure 1). The oil used was Erika oil. Finally, samples were collected through a tap located approximately at the bottom of the flask.

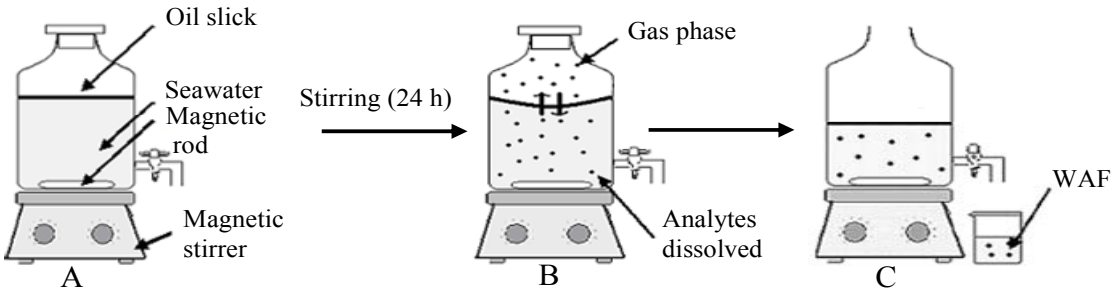

Figure 1 Preparation of water accommodated fraction (A: Oil was poured onto the water surface, B: Agitation during 24 h, C: Sampling of the WAF).

2.3 Solid-Phase Microextraction Procedure

The SPME polydimethylsiloxane fibers (100 µm film thickness) were obtained from Supelco (Sigma-Aldrich, South Africa). Prior to the extraction, fibers were conditioned in the injection port of the gas chromatograph for 3 h at 270 °C. The entirely automated extractions were performed by a commercial auto-sampler Multipurpose Sampler (GERSTEL®) mounted on the GC-MS system. The SPME procedure was performed by placing 8 mL of seawater sample in 10 mL vials capped with PTFE-coated septa. The fibers were immersed into the seawater with agitation at 250 rpm during 60 min. After extraction, the fiber was thermally desorbed for 10 min into the GC-MS injector port in the splitless mode at 270 °C. Blank desorptions of the fiber were carried to ensure that no contamination was present both before and during use.

2.4 Apparatus and Analytical Conditions

The analysis of compounds was achieved using a 7890A Agilent GC (Agilent Technologies, Santa Clara, California). Chromatographic separations were performed using a fused-silica HP-5MS capillary column (length 30 m, i.d. 0.25 mm, film thickness 0.25 µm; J&W Scientific, Agilent, Folsom, CA, USA). Helium was used as carrier gas at a flow of 1 mL/min. The oven program of temperature was: from 50 ºC (1 min) to 150 ºC at 10 ºC /min, and then to 320 ºC (5 min) at 5 ºC /min. The temperatures of the transfer line and the ion source were 300, 280 ºC, respectively. Electron ionization (EI) was operated at 70 eV Compounds were quantified in the selected ion monitoring (SIM) mode.

3 Results and Discussion

3.1 Identification of Compounds

The analysis in Scan and SIM modes of milli-Q water spiked by different solutions of PAHs, PASHs and their corresponding alkylated compounds allowed the identification of each compound and confirmation of their retention time (Table 1).

Table 1 Identification of compounds.

Number	Cas number	Compound name	Abbreviation	Rt (min)
1	[1146-65-2]	*Naphthalene-d_8*	*N-d_8*	8.68
2	[91-20-3]	Naphthalene	N	8.72
3	[91-57-6]	2-Methylnaphthalene	2-MN	10.32
4	[90-12-0]	1-Methylnaphthalene	1-MN	10.54
5	[95-15-8]	Benzo[*b*]thiophene	BT	8.85
6	[1195-14-8]	2-Methylbenzothiophene	2-MBT	10.34
7	[14315-14-1]	5-Methylbenzothiophene	5-MBT	10.43
8	[2404-87-7]	3-Phenylthiophene	3-PhenylT	11.95
9	[581-42-0]	2,6-Dimethylnaphthalene	2,6-DMN	11.84
10	[575-43-9]	1,6-Dimethylnaphthalene	1,6-DMN	12.10
11	[573-98-8]	1,2-Dimethylnaphthalene	1,2-DMN	12.57
12	[93951-97-4]	*Acenaphthylene-d_8*	*Acy-d_8*	12.47
13	[208-96-8]	Acenaphthylene	Acy	12.51
14	[15067-26-2]	*Acenaphthene-d_{10}*	*Ace-d_{10}*	12.94
15	[83-32-9]	Acenaphthene	Ace	13.04
16	[81103-79-9]	*Fluorene-d_{10}*	*F-d_{10}*	14.40
17	[86-73-7]	Fluorene	F	14.58
18	[33262-29-2]	*Dibenzothiophene-d_8*	*DBT-d_8*	17.40
19	[132-65-0]	Dibenzothiophene	DBT	17.47
20	[268-77-9]	Naphtho[2,3-*b*]thiophene	N[2,3-*b*]T	18.41
21	[31317-07-4]	4-Methyldibenzothiophene	4-MDBT	19.24
22	[20928--02-3]	2-Methyldibenzothiophene	2-MDBT	19.60
23	[1207-12-1]	4,6-Dimethyldibenzothiophene	4,6-DMDBT	21.01

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24	[31317-19-8]	2,7-Dimethyldibenzothiophene	2,7-DMDBT	21.73
25	[132034-91-4]	4,6-Diethyldibenzothiophene	4,6-DEDBT	24.08
26	[31317-09-6]	2,4,6,8-Tetramethyldibenzothiophene	2,4,6,8-TMDBT	24.98
27	[1517-22-2]	*Phenanthrene-d_{10}*	*Phe-d_{10}*	17.86
28	[85-01-8]	Phenanthrene	Phe	17.95
29	[832-71-3]	3-Methylphenanthrene	3-MPhe	19.96
30	[2531-84-2]	2-Methylphenanthrene	2-MPhe	20.07
31	[883-20-5]	9-Methylphenanthrene	9-MPhe	20.41
32	[832-69-9]	1-Methylphenanthrene	1-MPhe	20.50
33	[483-87-4]	1,7-Dimethylphenanthrene	1,7-DMPhe	22.62
34	[483-65-8]	Retene	R	25.49
35	[1719-06-8]	*Anthracene-d_{10}*	*Ant-d_{10}*	18.05
36	[120-12-7]	Anthracene	Ant	18.12
37	[613-12-7]	2-Methylanthracene	2-MAnt	20.22
38	[93951-69-0]	*Fluoranthene-d_{10}*	*Fluo-d_{10}*	22.79
39	[206-44-0]	Fluoranthene	Fluo	22.86
42	[25889-60-5]/[1706-01-0]	1/3-Methylfluoranthene	1/3-MFluo	25.44
40	[1718-52-1]	*Pyrene-d_{10}*	*Pyr-d_{10}*	23.69
41	[129-00-0]	Pyrene	Pyrene	23.76
43	[3353-12-6]	4-Methylpyrene	4-MPyr	26.22
44	[2381-21-7]	1-Methylpyrene	1-MPyr	26.35
45	[1718-53-2]	*Benzo[a]anthracene-d_{12}*	*B[a]Ant-d_{12}*	29.17
46	[56-55-3]	Benzo[*a*]anthracene	B[*a*]Ant	29.25
47	[1719-03-5]	*Chrysene-d_{12}*	*Chry-d_{12}*	29.32
48	[218-01-9]	Chrysene	Chry	29.42
49	[3351-31-3]	3-Methylchrysene	3-MChry	31.21
50	[1705-85-7]	6-Methylchrysene	6-MChry	31.57
51	[239-35-0]	Benzo[*b*]naphtho[2,1-*d*]thiophene	B[*b*]N[2,1-*d*]T	28.15
52	[205-43-6]	Benzo[*b*]naphtho[1,2-*d*]thiophene	B[*b*]N[1,2-*d*]T	28.57
53	[17164-77-1]	2-(2-Naphthyl)benzothiophene	2-(2-Naphthyl)BT	32.39
54	[93951-98-5]	*Benzo[b]fluoranthene-d_{12}*	*B[b]Fluo-d_{12}*	33.80
55	[205-99-2]	Benzo[*b*]fluoranthene	B[*b*]Fluo	33.83
56	[93952-01-3]	*Benzo[k]fluoranthene-d_{12}*	*B[k]Fluo-d_{12}*	33.90
57	[207-08-9]	Benzo[*k*]fluoranthene	B[*k*]Fluo	33.92
58	[205440-82-0]	*Benzo[e]pyrene-d_{12}*	*B[e]P-d_{12}*	34.83
59	[192-97-2]	Benzo[*e*]pyrene	B[*e*]P	34.93
60	[63466-71-7]	*Benzo[a]pyrene-d_{12}*	*B[a]P-d_{12}*	35.03
61	[50-32-8]	Benzo[*a*]pyrene	B[*a*]P	35.10
62	[1520-96-3]	*Perylene-d_{12}*	*P-d_{12}*	35.35
63	[198-55-0]	Perylene	P	35.44
64	[201-96-4]	Benzo[*b*]phenanthro[9,10-*d*]thiophene	B[*b*]ph[9,10-*d*]T	38.46
65	[203578-33-0]	*Indeno[1,2,3-cd]pyrene-d_{12}*	*I[1,2,3-cd]Pyr-d_{12}*	39.11
66	[193-39-5]	Indeno[1,2,3-*cd*]pyrene	I[1,2,3-*cd*]Pyr	39.13
67	[93951-66-7]	*Benzo[ghi]perylene-d_{12}*	*B[ghi]P-d_{12}*	39.90
68	[191-24-2]	Benzo[*ghi*]perylene	B[*ghi*]P	39.94
69	[13250-98-1]	*Dibenzo[a,h]anthracene-d_{14}*	*DB[a,h]Ant-d_{14}*	39.26
70	[53-70-3]	Dibenzo[*a,h*]anthracene	DB[*a,h*]Ant	39.36

Surrogates used for quantification in *italic*, corresponding quantified compounds below.
CAS: chemical abstract service registry number.
Rt: Retention time.

3.2 Calibration and SPME Method Validation

3.2.1 Calibration Curves and Linearity

An internal calibration procedure was carried out for the quantification of the targets compounds. The objective was to establish the calibration curve and calculate the limits of detection and quantification of each compound studied. The linearity of the method was evaluated at five levels of concentration (1, 5, 10, 50 and 100 ng/L), by extracting spiked milli-Q water samples, and k = 3 replicates per level were performed. The concentration of internal standard was constant and equal to 80 ng/L for each level of concentration. Fifteen pairs (x_i, y_i) of observations of two quantitative variables X and Y for each compound were obtained, where: X = area of compound/area of internal standard (A/A_d) and Y = concentration of compounds/concentration of internal standard (C/C_d). Thus, the chromatograms obtained from five levels of calibration are quantified to plot the calibration curves using the following equation:

$$A/A_d = f\,(C/C_d) \qquad (1)$$

The naphtho[2,3-*b*]thiophene was taken as an example to illustrate this study. The area ratio for this compound is calculated with respect to its internal standard, phenanthrene-d_{10}. A linear model, with good linearity, was obtained for all calibration curves as shown in the calibration curve of naphtho[2,3-*b*]thiophene (Figure 2) ($R^2 > 0.99$). The regression coefficients are between 0.971 and 0.997 for all the compounds studied (Table 2).

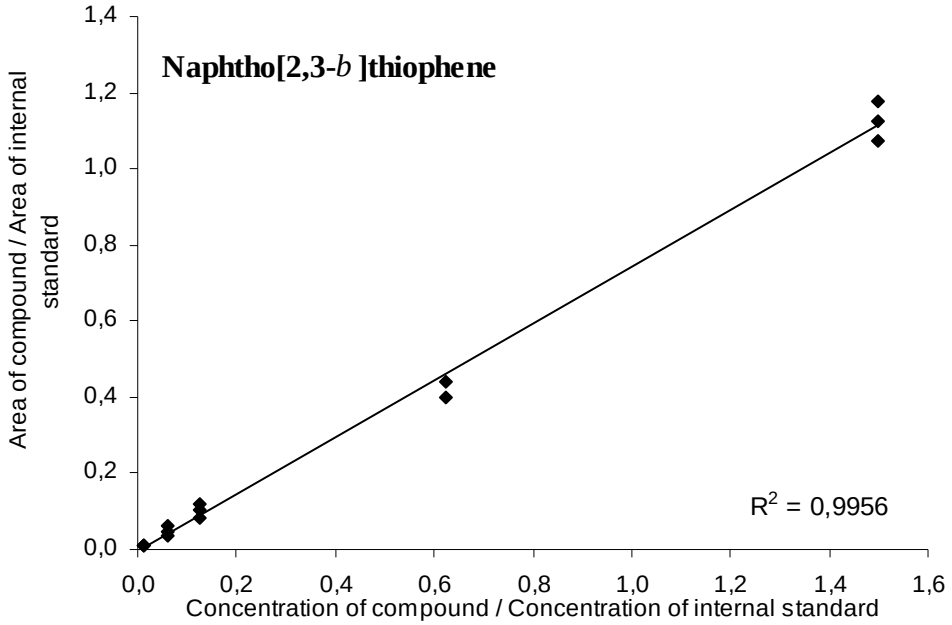

Figure 2. Calibration curve of naphtho[2,3-*b*]thiophene.

3.2.2 Limits of Detection and Quantification

The limit of quantification (LOQ) is the lowest amount of analyte in a sample that can be quantitatively determined with suitable precision and accuracy. The following value is commonly used:

$$LOQ = 3.33\ LOD \qquad (2)$$

The limit of detection (LOD) is the analyte concentration that results in a significantly higher measured signal than that obtained when the concentration is nil.

The limits of detection (LOD) were calculated according to the calibration curve method Calculation of the LOD by this method takes into account not only the values a_0 and a_1 of the calibration straight line ($Y = a_0 + a_1 X$), but also the quality of the adjustment characterised by the residual standard deviation SD_r.

In this case, the formula used is:

$$LOD = t_\nu \frac{SD_r}{a_1} \sqrt{\frac{1}{k}} \qquad (3)$$

where t_υ is Student's t at (n-2) degrees of freedom, υ is equal to (n-1) or (nk-1) degrees of freedom according to the validity of the model, k is the number of repetitions of the signal for each measurement.

As the linear model was validated in the case of naphtho[2,3-*b*]thiophene, the calibration curve method was applied to this compound as an example. As the model proposed has no constant, the limit of detection is determined using the formula (3), with a number of degrees of freedom υ equal to four:

LOD = 0.02 ng/L

The limit of quantification can then be deduced from this using the formula (2):

LOQ = 0.1 ng/L

The limits of quantification and detection were calculated for all the other components studied using the same method. Table 2 shows the results for the PACs investigated. The detection limits for all compounds are below 0.2 ng/L. A comparison with some papers for the determination of PAHs in water shows that the detection limits for a 8 mL sample are particularly low (between 0.02 and 0.1 ng/L). Popp et al., 2000, used the SPME coupled to liquid chromatography- fluorescence detection (LC-FD) and a water sample of 5 mL to obtain LOD between 1 and 6 ng/L. King et al., 2004 used the SPME with a 100 µm PDMS fiber in combination with GC-MS and calculated an LOD between 1 and 29 ng/L for 16 PAHs for a 30 mL water sample.

Table 2 Limits of detection and quantification (LOD and LOQ, in ng/L), selected ions for quantification (m/z) and correlation coefficients (R^2) of the calibration curves (from 1 to 100 ng/L) for the investigated compounds.

Compounds	Selected ions (m/z)	(R^2)	LOD (ng/L)	LOQ (ng/L)
N	128-127-102	0.985	0.1	0.3
2-MN	142-141	0.986	0.1	0.3
1-MN	142-141	0.985	0.1	0.3
BT	134-89	0.978	0.1	0.3
2-MBT	147-148-115	0.992	0.1	0.2
5-MBT	147-148-115	0.987	0.1	0.3
3-PhenylT	160-115	0.993	0.02	0.1
2,6-DMN	156-141	0.971	0.1	0.5
1,6-DMN	156-141	0.977	0.1	0.4
1,2-DMN	156-141	0.971	0.1	0.4
Acy	152-151-76	0.993	0.1	0.2
Ace	154-153-152-76	0.992	0.03	0.1
F	166-165	0.989	0.1	0.3
DBT	184-139-152	0.992	0.03	0.1
N[2,3-*b*]T	184-139-152	0.995	0.03	0.1
4-MDBT	198-194	0.994	0.05	0.2
2-MDBT	198-194	0.996	0.02	0.1
4,6-DMDBT	212-211	0.992	0.04	0.1

2,7-DMDBT	212-211	0.991	0.04	0.1
4,6-DEDBT	225-240	0.978	0.1	0.4
2,4,6,8-TMDBT	240-225	0.977	0.1	0.4
Phe	178-176-152	0.990	0.05	0.2
Ant	178-176-152	0.987	0.05	0.2
3-MPhe	192-191	0.996	0.01	0.03
2-MPhe	192-191	0.997	0.01	0.05
2-MAnt	192-191	0.989	0.05	0.2
9-MPhe	192-191	0.992	0.01	0.03
1-MPhe	192-191	0.996	0.02	0.1
1,7-DMPhe	206	0.995	0.03	0.1
R	234	0.990	0.1	0.3
Fluo	202-200-201	0.990	0.04	0.1
Pyr	202-200-201	0.995	0.04	0.1
1/3-MFluo	216	0.997	0.02	0.05
4-MPyr	216	0.993	0.04	0.1
1-MPyr	216	0.994	0.04	0.1
B[*a*]Ant	228-227	0.996	0.02	0.1
Chry	228-227	0.995	0.04	0.1
3-MChry	242	0.993	0.05	0.2
6-MChry	242	0.991	0.05	0.2
B[*b*]N[2,1-*d*]T	234-232	0.995	0.02	0.05
B[*b*]N[1,2-*d*]T	234-232	0.995	0.02	0.06
2-(2-Naphthyl)BT	260	0.988	0.1	0.3
B[*b*]Fluo	252-250-126	0.995	0.05	0.2
B[*k*]Fluo	252-250-126	0.993	0.04	0.1
B[*e*]Pyr	252-250-126	0.994	0.06	0.2
B[*a*]Pyr	252-250-126	0.979	0.04	0.1
P	252-250-126	0.993	0.1	0.2
B[*b*]ph[9,10-*d*]T	284-282-252	0.989	0.1	0.3
I[1,2,3-*cd*]Pyr	276-138	0.995	0.1	0.3
B[*ghi*]P	276-138	0.995	0.1	0.2
DB[*a,h*]Ant	278-276-139	0.997	0.1	0.2

3.3 Quantification of PACs and Alkylated PACs in the WAF

The PACs were quantified by SPME-GC-MS in the water accommodated fraction (WAF) prepared with an oil/water ratio of 1:100 000. Nearly all the target compounds were detected and could also be quantified (Table 3). Alkylated PACs, for which we do not have all alkylated PACs isomer available as standards, were quantified as groups, as it shown in Figure 3.

Table 3. Concentration of PACs in the WAF of an Erika oil.

Compounds	[PACs] ng/L	R.S.D. (%) *n = 2*	Compounds	[PACs] ng/L	R.S.D. (%) *n = 2*
N	6215	121	3-MPhe	468	9
2-MN	9004	30	2-MPhe	470	9
1-MN	7690	8	2-MAnt	162	13
2,6-DMN	3022	26	9-Mphe	348	9
1,6-DMN	2153	5	1-Mphe	333	7
1,2-DMN	1060	23	1,7-DMPhe	55	9
C_2-N	14318	9	C_2-Phe/Ant	823	5
C_3-N	7627	9	C_3-Phe/Ant	208	7
C_4-N	1335	10	R	nd	-

BT	1505	38	C_4-Phe/Ant	127	8
2-MBT	2008	6	Fluo	53	10
5-MBT	1570	50	Pyr	161	8
C_1-BT	7723	29	1/3-MFluo	42	6
C_2-BT	8470	6	4-MPyr	93	8
C_3-BT	5414	16	1-Mpyr	89	3
C_4-BT	1425	21	C_1-Fluo/Pyr	263	7
3-PhenylT	1051	130	C_2-Fluo/Pyr	98	0
Acy	18	7	C_3-Fluo/Pyr	39	1
Ace	1145	3	B[*b*]N[2,1-*d*]T	33	11
F	865	1	B[*b*]N[1,2-*d*]T	11	17
C_1-F	1342	5	B[*a*]Ant	30	14
C_2-F	969	8	Chry	82	10
C_3-F	510	10	C_1-Chry	69	13
DBT	601	10	C_2-Chry	31	3
2-MDBT	449	8	C_3-Chry	13	6
4-MDBT	349	11	2-(2-Naphtyl)BT	0	47
4,6-DMDBT	35	12	3-MChry	26	2
2,7-DMDBT	52	9	6-Mchry	6	2
4,6-DEDBT	1	20	B[*b*]Fluo	3	2
2,4,6,8-TMDBT	2	16	B[*k*]Fluo	1	26
C_1-DBT	1192	12	B[*e*]P	4	7
C_2-DBT	576	8	B[*a*]P	2	13
C_3-DBT	161	6	P	1	29
C_4-DBT	46	2	B[*b*]Ph[9,10-*d*]T	1	27
Phe	2290	10	In[1,2-*cd*]Pyr	1	48
Ant	228	13	DB[*a,h*]Ant	2	49
N[2,3-*b*]T	16	8	B[*ghi*]P	1	25

Kanan, R., S. LeFloch, J.T. Andersson, K. LeMenach, and H. Budzinski, Extraction of Polycyclic Aromatic Hydrocarbons (PAHs), Polycyclic Aromatic Sulfur Heterocycles (PASHs) and Alkylated Derivatives from Seawater using Solid-phase Microextraction (SPME)-Gas Chromatography/Mass Spectrometry (GC/MS), Proceedings of the Thirty-fifth AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada, Ottawa, ON, pp. 928-940, 2012.

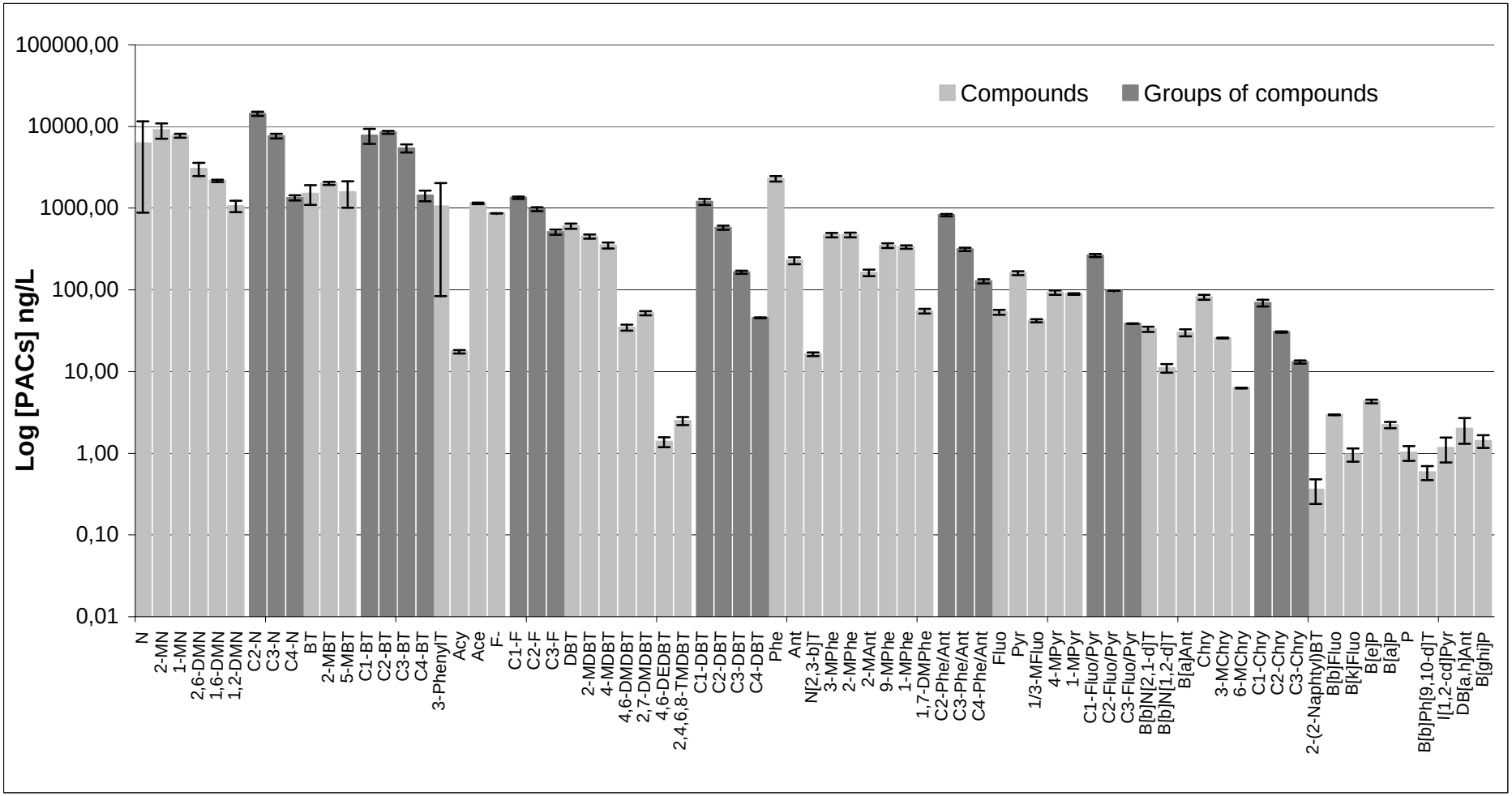

Figure 3 **Analysis of PACs and alkylated derivatives in the WAF of Erika oil by SPME-GC-MS.**

Kanan, R., S. LeFloch, J.T. Andersson, K. LeMenach, and H. Budzinski, Extraction of Polycyclic Aromatic Hydrocarbons (PAHs), Polycyclic Aromatic Sulfur Heterocycles (PASHs) and Alkylated Derivatives from Seawater using Solid-phase Microextraction (SPME)-Gas Chromatography/Mass Spectrometry (GC/MS), Proceedings of the Thirty-fifth AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada, Ottawa, ON, pp. 928-940, 2012.

Because standards are not commercially available for every alkylated PAC, the quantification of alkylated PAC homologues was generally performed with the approximation that the response factors for alkylated homologues are equal to the response factor of the respective unsubstituted (parent) compound (Burkhardt et al., 2005). The study of the response factors of individual compounds showed that no significant differences were observed between the response factors of isomers within the same homologue group (Figure 4). For theses reasons, and in accordance with the literature (Planas et al., 2006; Wang et al., 1994), in this study, average response factors were used to quantify all the isomers of each group. As an example, average response factors of dimethylnaphthalenes was used to quantify the whole profile of C_2-naphthalenes.

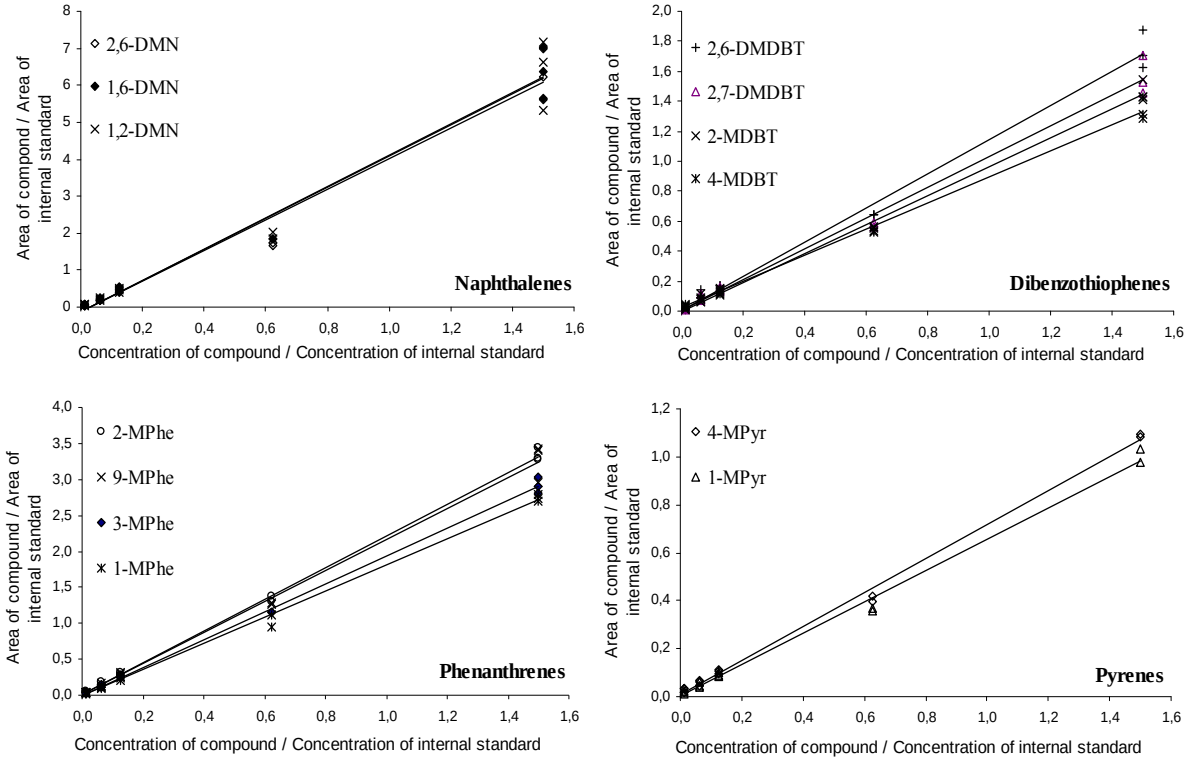

Figure 4 Calibration curves of alkylated derivatives.

The other groups, for which we do not have any alkylated PACs isomer (C_2-, C_3- and C_4-benzothiophenes, C_3-, C_4-naphthalenes, C_2-, C_3-fluoranthenes/pyrenes and C_2-, C_3-chrysenes), were quantified using average response factors obtained from methylbenzothiophenes, dimethylnaphthalenes, methylpyrenes and methylchrysenes, respectively (Kanan et al., 2012). The average response factors of dimethydibenzothiophenes (C_2-DBT) and tetramethyldibenzothiophene (C_4-DBT) were used for quantification of C_3-DBT. The average response factors of 1,7-dimethylphenanthrene (C_2-phe/Ant) and retene (C_4-phe/Ant) were used for quantification of C_3-Phe/Ant (Kanan et al., 2012). In the case of fluorene, no alkylated compounds were available in standard solutions, the whole profiles of C_1-, C_2-and C_3-fluorenes were quantified using the response factor of the appropriate parent (Burkhardt et al., 2005).

4 Conclusions

The SPME-GC-MS method was applied successfully to determine polycyclic aromatic compounds and alkylated derivatives in the water accommodated fraction (WAF) of seawater samples prepared in the laboratory from a crude oil. With a sample volume of only 8 mL of

seawater, the proposed method is sensitive, simple and shows good linearity and detection limits lower than 0.2 ng/L. SPME has practical advantages such as not requiring any preliminary sample preparation step, since it combines sampling and preconcentration in one step, and avoiding the use of expensive and toxic solvents. Because standards are not commercially available for every alkylated PAC isomer, the concentration of the alkylated groups is reported as generally semiquantitative.

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