Quantification of Polycyclic Aromatic Compounds (PACs), and Alkylated Derivatives by Gas Chromatography-Tandem Mass Spectrometry (GC/MS/MS) to Qualify a Reference Oil

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds listed as priority pollutants by international environmental protection agencies due to their carcinogenic, mutagenic, and toxic effects. Several studies have indicated that some polycyclic aromatic sulfur heterocycles (PASHs) are also carcinogenic and/or mutagenic. Gas chromatography-tandem-mass spectrometry (GC-MS-MS) has been used in the analysis of PAHs in complex matrices. However, no GC-MS-MS studies have focused on the determination of PAHs and PASHs. Moreover, previous MS-MS studies were not targeted toward alkylated derivatives, which are significant contributors in the composition of crude oils. In the present work, a simple methodology has been developed for the analysis of PAHs, PASHs and alkylated derivatives in the Erika fuel oil using solid-phase extraction (SPE) coupled to gas chromatography-tandem mass spectrometry (GC-MS-MS). The LOD and LOQ of the method range between 0.01 and 0.1 ng/mL and between 0.1 and 0.5 ng/mL, respectively. The calibration curves showed a good linearity for most of the compounds.

1 Introduction

Each case of spill entails a series of questions as regards the potential toxicity of the oil, and generally preliminary information is provided by the quantification of the 16 PAHs of the US EPA list. Like PAHs, some of their analogues, such as polycyclic aromatic sulfur heterocycles (PASHs), are also mutagenic and carcinogenic (Andersson and Schmid, 1995; Mössner and Wise, 1999). However, when dealing with petrogenic products, the parents (PAHs and PASHs) are less abundant than their alkylated analogues, whereas their effect on the environment is liable to be similar. Moreover, oils remaining at the sea or water surface are affected by weathering process such as emulsification, natural dispersion, evaporation, and especially dissolution. Even if solubility decreases as the number of alkyl substituent carbons increases, the resulting water soluble fractions are strongly dominated by alkylated compounds. Finally, contamination of the fauna, either due to dispersed oil droplets or dissolved contaminants, is also liable to predominantly come from these compounds.

The quantification of alkylated homologous groups in GC-MS has generally been performed using the response factor of the respective unsubstituted compounds (Burkhardt et al., 2005). However, new techniques such as GC-MS-MS, useful to get a more reliable chromatogram of these complex groups of peaks, can deal with very different transitions from one compound to the other, and this kind of approximation can no longer be used. On the other hand, only few alkylated analogues can be obtained from commercial solutions (Burkhardt et al., 2005), hence the necessity of using a petroleum product containing the whole profiles of alkylated homologous groups and their corresponding parents (PAHs and PASHs), and completely characterized in order to represent a reliable reference. Thus, this

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paper describes a method for the determination of PAHs, PASHs and alkylated homologous groups in the Erika oil, using purification with solid-phase extraction (SPE) and GC-MS-MS detection.

2 Experimental Set-up

2.1 Standards and Reagents

The solutions were prepared from certified reference materials purchased from LGC Standards (Molsheim, France): CUS 9305, which contains nineteen PAHs and two PASHs at a concentration of 100 µg/mL in methanol, and CUS 9207, which contains the corresponding internal standards: naphthalene-d_8, biphenyl-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and benzo[*a*]pyrene-d_{12} at a concentration of 1 µg/mL in acetone. 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, six PASHs and eight alkylated derivatives were synthesized in one of our laboratories (Institute of Inorganic and Analytical Chemistry, 2012) and prepared at a concentration of 100 µg/mL in methanol. A mixture of standard solutions containing all analytes was prepared in dichlorometane. Compound names and abbreviations mentioned in this study are summarized in Table 1. A batch of the oil that was loaded inside the tanker Erika was sent to Cedre by the refinery and received on the 12th of December 1999. Pentane (95%), dichloromethane and acetonitrile (HPLC quality) were purchased from SDS (Peypin, France).

2.2 Purification of the Oil Sample

The purification of the oil sample is performed by solid phase extraction (SPE). The cartridges used are polar columns Si/CN-S-1.5G/9 Upti-clean SPE® manufactured by the company Interchim (Montlucon, France). The cartridge was conditioned with a mixture of pentane/dichloromethane (80/20, v/v) and compounds were eluted using 5 mL of pentane/dichloromethane (80/20, v/v) as mobile phase. The elution is accelerated through a vacuum pump. The extract obtained is then concentrated using an evaporator Büchi Syncore (Lille, France).

2.3 Instrumentation and GC-MS-MS Conditions

The analysis of compounds was achieved using a 7890A Agilent GC system coupled to an Agilent 7000A Triple quadrupole (Agilent Technologies, Santa Clara, California). Splitless injections of 1 µL of the sample were carried out. The injector temperature was kept at 300 °C. 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 °C (1 min) to 150 °C at 10 °C/min, and then to 320 °C (5 min) at 5 °C/min. The temperatures of the transfer line and ion source were 300 and 280 °C, respectively. Electron ionization (EI) was operated at 70 eV. Compounds were detected and quantified by monitoring two specific transitions. Table 2 gives the monitored transitions for each compound.

3 Resultats and Discussion

3.1 Identification of Compounds

The analysis in Scan and SIM (Selected Ion Monitoring) modes of different solutions of PAHs and PASHs and their corresponding alkylated, coupled with a literature research (Wang et al., 2007), 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*	9.17
2	[91-20-3]	Naphthalene	N	9.22
3	[95-15-8]	Benzo[*b*]thiophene	B[*b*]T	9.34
4	[91-57-6]	2-Methylnaphthalene	2-MN	10.8
5	[1195-14-8]	2-Methylbenzothiophene	2-MBT	10.82
6	[14315-14-1]	5-Methylbenzothiophene	5-MBT	10.93
7	[90-12-0]	1-Methylnaphthalene	1-MN	11.05
8	[1486-01-7]	*Biphenyl-d_{10}*	*B-d_{10}*	11.92
9	[92-52-4]	Biphenyl	B	11.98
10	[581-42-0]	2,6-Dimethylnaphthalene	2,6-DMN	12.36
11	[2404-87-7]	3-Phenylthiophene	3-PhenylT	12.48
12	[575-43-9]	1,6-Dimethylnaphthalene	1,6-DMN	12.65
13	[208-96-8]	Acenaphthylene	Acy	13.09
14	[573-98-8]	1,2-Dimethylnaphthalene	1,2-DMN	13.15
15	[83-32-9]	Acenaphthene	Ace	13.63
16	[86-73-7]	Fluorene	F	15.26
17	[1517-22-2]	*Phenanthrene-d_{10}*	*Phe-d_{10}*	18.66
18	[132-65-0]	Dibenzo[*b,d*]thiophene	DB[*b,d*]T	18.25
19	[85-01-8]	Phenanthrene	Phe	18.74
20	[120-12-7]	Anthracene	Ant	18.92
21	[268-77-9]	Naphtho[2,3-*b*]thiophene	N[2,3-*b*]T	19.23
22	[31317-07-4]	4-Methyldibenzothiophene	4-MDBT	20.07
23	[20928--02-3]	2-Methyldibenzothiophene	2-MDBT	20.41
24	[832-71-3]	3-Methylphenanthrene	3-MPhe	20.8
25	[2531-84-2]	2-Methylphenanthrene	2-MPhe	20.91
26	[613-12-7]	2-Methylanthracene	2-MAnt	21.07
27	[883-20-5]	9-Methylphenanthrene	9-MPhe	21.25
28	[832-69-9]	1-Methylphenanthrene	1-MPhe	21.36
29	[1207-12-1]	4,6-Dimethyldibenzothiophene	4,6-DMDBT	21.89
30	[31317-19-8]	2,7-Dimethyldibenzothiophene	2,7-DMDBT	22.60
31	[483-87-4]	1,7-Dimethylphenanthrene	1,7-DMPhe	23.51
32	[206-44-0]	Fluoranthene	Fluo	23.76
33	[129-00-0]	Pyrene	Pyr	24.68
34	[132034-91-4]	4,6-Diethyldibenzothiophene	4,6-DEDBT	24.95
35	[31317-09-6]	2,4,6,8-Tetramethyldibenzothiophene	2,4,6,8-TMDBT	25.87
36-37	[25889-60-5]/[1706-01-0]	1/3-Methylfluoranthene	1/3-MFluo	26.32
38	[483-65-8]	Retene	R	26.44
39	[3353-12-6]	4-Methylpyrene	4-MPyr	27.15
40	[2381-21-7]	1-Methylpyrene	1-MPyr	27.28
41	[239-35-0]	Benzo[*b*]naphtho[2,1-*d*]thiophene	B[*b*]N[2,1-*d*]T	29.12
42	[205-43-6]	Benzo[*b*]naphtho[1,2-*d*]thiophene	B[*b*]N[1,2-*d*]T	29.52
43	[1719-03-5]	*Chrysene-d_{12}*	*Chry-d_{12}*	30.22
44	[56-55-3]	Benzo[*a*]anthracene	B[*a*]Ant	30.27
45	[218-01-9]	Chrysene	Chry	30.39
46	[3351-31-3]	3-Methylchrysene	3-MChry	32.20
47	[1705-85-7]	6-Methylchrysene	6-MChry	32.53
48	[17164-77-1]	2-(2-Naphthyl)benzothiophene	2-(2-Naphtyl)BT	33.35
49	[63466-71-7]	*Benzo[a]pyrene-d_{12}*	*B[a]Pyr-d_{12}*	36.03
50-51	[205-99-2]+[207-08-9]	Benzo[*b+k*]fluoranthene	B[*b+k*]Fluo	34.94
52	[192-97-2]	Benzo[*e*]pyrene	B[*e*]Pyr	35.93

53	[50-32-8]	Benzo[*a*]pyrene	B[*a*]Pyr	36.11
54	[198-55-0]	Perylene	P	36.45
55	[201-96-4]	Benzo[*b*]phenanthro[9,10-*d*]thiophene	B[*b*]ph[9,10-*d*]T	39.44
56	[193-39-5]	Indeno[1,2,3-*cd*]pyrene	I[1,2,3-*cd*]Pyr	40.22
57	[53-70-3]	Dibenzo[*a,h*]anthracene	DB[*a,h*]Ant	40.38
58	[191-24-2]	Benzo[*ghi*]perylene	B[*ghi*]P	41.02

Internal standards used as surrogates in *italic*. CAS: chemical abstracts service registry number.

As regards alkylated compounds, not available in the standards solutions, the analysis of an oil Erika in SCAN and SIM mode allowed the identification of characteristic profiles for each alkylated homologue group.

3.2 Selection of MS-MS Transitions

Full scan mass spectra for all of the compounds showed basically the molecular ion, with little fragmentation. Thus, the molecular ions were selected as the precursor ions for the development of the multiple reaction monitoring (MRM) method. Then, product ion spectra were acquired by collision induced dissociation (CID) with helium gas. Collision energies (CEs) from 5 to 50 eV were applied and the most intense product ions were selected for each precursor. In general the collision energy (CE) that gave the most intense response was chosen for each MRM transition. For example, the transitions *m*/*z* 184-152 and 184-139 at CE 20 eV for the DB[*b,d*]T were selected (Figure. 1). In most cases, the losses from the molecular ion of one, two or three hydrogen atoms were chosen as the quantitative and /or confirmative transitions for the determination of compounds with improved selectivity and sensitivity.

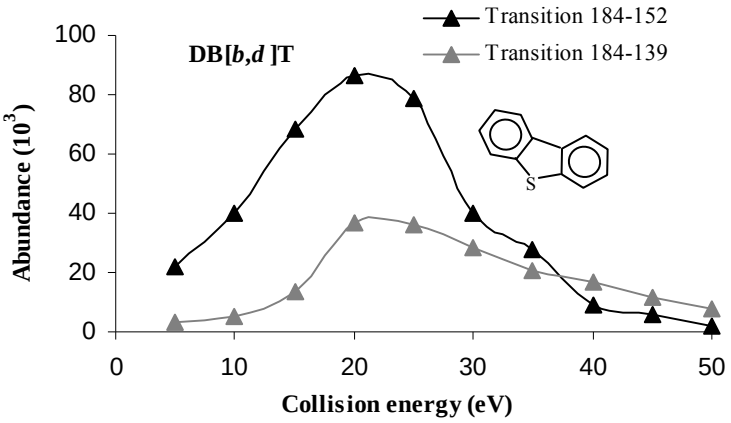

Figure 1 Abundance of quantitative and qualitative transitions according to the collision energies (eV) for the dibenzo[*b,d*]thiophene.

In some cases, for example, 4-methylpyrene and 1-methylpyrene, the molecular ion was selected as the quantitative transition due to the lack of other suitable ions. For the deuterated internal standards, the chosen transitions are parent ion-parent ion, at collision energy 0 eV. These conditions have been verified experimentally in the case of matrices loaded by injection of extracts of biological tissues spiked with deuterated internal standards which were not affected by the presence of interfering compounds. The MS-MS parameters for determination of the target compounds are summarised in Table 2.

Table 2 Selection of the main parameters for the GC-MS-MS analysis of PACs.

Compounds	Precursor ion (m/z)	Product ion-quantifier (Q) (m/z)	Product ion-qualifier (q) (m/z)	Collision energy Q/q (ev)
N	128	102	127	20/20
2-MN	142	141	115	20/20
1-MN	142	141	115	20/20
B [*b*]T	134	89	108	25/25
2-MBT	148	147	115	40/40
5-MBT	148	147	115	40/40
3-PhenylT	160	115	128	30/30
2,6-DMN	156	141	115	25/25
1,6-DMN	156	141	115	25/25
1,2-DMN	156	141	115	25/25
B	154	152	153	35/35
Acy	152	151	150	25/25
Ace	154	152	153	35/35
F	166	165	164	40/40
DB[*b*,*d*]T	184	152	139	20/20
N [2,3-*b*]T	184	152	139	20/20
4-MDBT	198	197	165	30/25
2-MDBT	198	197	165	30/25
4,6-DMDBT	212	211	197	30/25
2,7-DMDBT	212	211	197	30/25
4,6-DEBT	240	239	225	35/35
2,4,6,8-TMDBT	240	239	225	35/35
Phe	178	176	152	40/15
Ant	178	176	152	40/15
3-MPhe	192	191	189	30/30
2-MPhe	192	191	189	30/30
2-MAnt	192	191	189	30/30
9-MPhe	192	191	189	30/30
1-MPhe	192	191	189	30/30
1,7-DMPhe	206	191	205	20/20
R	234	219	205	15/15
Fluo	202	201	200	20/20
Pyr	202	201	200	20/20
1/3-MFluo	216	216	215	0/20
4-MPyr	216	216	215	0/20
1-MPyr	216	216	215	0/20
B[*a*]Ant	228	226	227	30/30
Chry	228	226	227	30/30
3-MChry	242	241	239	30/30
6-MChry	242	241	239	30/30
B[*b*]N[2,1-*d*]T	234	202	189	25/25
B[*b*]N[1,2-*d*]T	234	202	189	25/25
2-(2-Naphthyl)BT	260	258	215	20/20
B[*b*]Fluo	252	250	251	25/25
B[*k*]Fluo	252	250	251	25/25
B[*e*]Pyr	252	250	251	25/25
B[*a*]Pyr	252	250	251	25/25
P	252	250	251	25/25
B[*b*]ph[9,10-*d*]T	284	282	252	20/20
I[1,2,3-*cd*]Pyr	276	274	275	35/35

DB[*a*,*h*]Ant	278	276	277	25/25
B[*ghi*]P	276	274	275	35/35

3.3 Limits of Detection, Limits of Quantification and Linearity

Calibration curves were calculated using linear regression on seven concentrations (1, 5, 10, 50, 100, 500 and 1000 ng/mL). Good correlation coefficients were obtained for the most of the target compounds, however calibration curves for some of compounds were not linear ($R^2 < 0.960$). The limits of detection and quantification were calculated according to the calibration curve method (Kanan et al., 2012) and values for each compound examined are shown in Table 3.

Table 3 Correlation coefficients (R^2), limits of detection and quantification (LOD and LOQ) obtained for the compounds studied.

Compounds	(R^2)	LOD (ng/mL)	LOQ (ng/mL)
N	0.972	0.003	0.01
2-MN	0.977	0.004	0.01
1-MN	0.977	0.004	0.01
BT	0.973	0.004	0.01
2-MBT	0.979	0.01	0.02
5-MBT	0.968	0.01	0.02
3-PhenylT	0.990	0.01	0.02
2,6-DMN	0.977	0.01	0.02
1,6-DMN	0.976	0.01	0.02
1,2-DMN	0.976	0.01	0.02
B	0.994	0.003	0.01
Acy	0.987	0.01	0.02
Ace	0.993	0.004	0.01
F	0.984	0.01	0.02
DBT	0.985	0.003	0.01
N[2,3-*b*]T	0.983	0.004	0.01
4-MDBT	0.980	0.004	0.01
2-MDBT	0.974	0.01	0.02
4,6-DMDBT	0.971	0.01	0.02
2,7-DMDBT	0.965	0.01	0.02
4,6-DEDBT	0.942	0.01	0.02
2,4,6,8-TMDBT	0.967	0.01	0.02
Phe	0.977	0.003	0.01
Ant	0.955	0.01	0.02
3-MPhe	0.962	0.01	0.02
2-MPhe	0.977	0.01	0.02
2-MAnt	0.965	0.01	0.02
9-MPhe	0.972	0.01	0.02
1-MPhe	0.985	0.004	0.01
1,7-DMPhe	0.970	0.01	0.02
R	0.970	0.01	0.02
Fluo	0.972	0.01	0.02
Pyr	0.967	0.01	0.02
1/3-MFluo	0.976	0.01	0.02
4-MPyr	0.970	0.01	0.02
1-MPyr	0.979	0.01	0.02
B[*a*]Ant	0.986	0.01	0.04

Chry	0.989	0.01	0.04
3-MChry	0.974	0.01	0.04
6-MChry	0.981	0.01	0.03
B[*b*]N[2,1-*d*]T	0.990	0.003	0.01
B[*b*]N[1,2-*d*]T	0.992	0.01	0.02
2-(2-Naphthyl)BT	0.967	0.01	0.04
B[*b*]Fluo	0.950	0.03	0.10
B[*k*]Fluo	0.953	0.03	0.09
B[*e*]Pyr	0.956	0.03	0.10
B[*a*]Pyr	0.980	0.01	0.05
P	0.957	0.03	0.09
B[*b*]ph[9,10-*d*]T	0.950	0.03	0.09
I[1,2,3-*cd*]Pyr	0.930	0.04	0.12
DB[*a,h*]Ant	0.945	0.03	0.11
B[*ghi*]P	0.954	0.02	0.08

From the calibration curves, quantification of all individual compounds was performed on Erika oil with five repetitions. This first characterization of the oil was used to check the variability of quantitative analysis for compounds well identified, and thus confirm the possibility of using this oil as reference product.

3.4 Analysis of Response Factors and Definition of the Method

For the use of a reference oil, it should determine the concentration of alkylated derivatives. However, these alkylated compounds are difficult to quantify. Indeed, only a few of alkylated isomers are present in the standards solutions (Burkhardt et al., 2005).

The quantification of alkylated derivatives in GC-MS has generally been performed with the approximation that response factors for alkylated compounds are equal to the response factor of the respective unsubstituted (parent) compound (Burkhardt et al., 2005). However, if this approximation might seem reasonable when considering only the molecular ion after a simple fragmentation, this estimate seemed more uncertain in case of the analysis by GC-MS-MS. To assess the reliability of the analysis by GC-MS and the applicability to the MS-MS, a comparison of response factors was conducted.

The study of the response factors of individual compounds in MRM mode showed that the response factors of the alkylated compounds are very different from those of parent compounds (Figure 2). Therefore, it is not possible to quantify the alkylated homologous groups using the response factors of their appropriate parents.

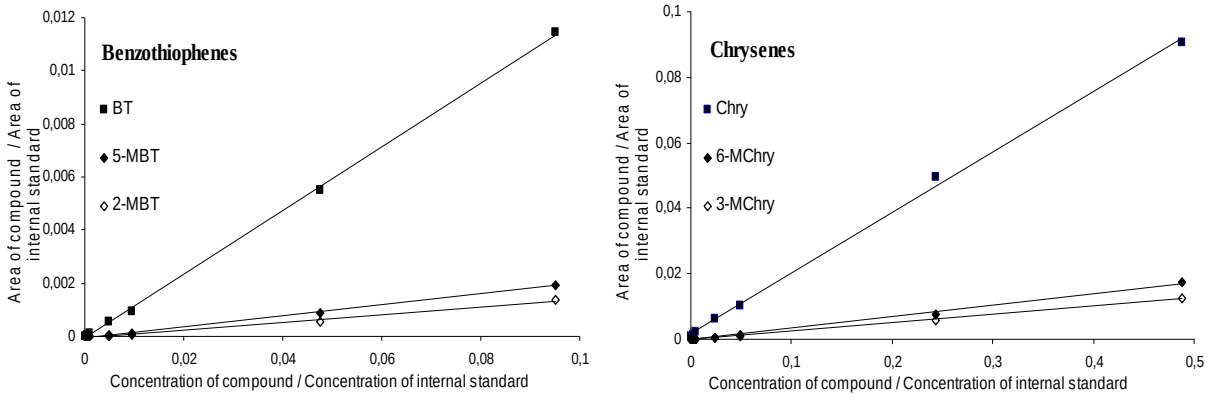

Figure 2 Calibration curves of benzothiophenes and chrysenes in MRM mode.

A comparison of response factors of the isomers within the same homologue group was conducted, and generally no significant differences were observed between the response factors of isomers belonging to the same group (Figure 3). Thus, in the case of groups for which some alkylated isomers are available in standard solutions, the hypothesis to apply the average response factors to quantify all the isomers of each group of alkylated compounds is possible (Palanas et al., 2006). As an example, for C_1-benzothiophenes, the average response factors of two calibrated isomers (2-MBT and 5-MBT) were used to quantify the whole profile of C_1-benzothiophenes.

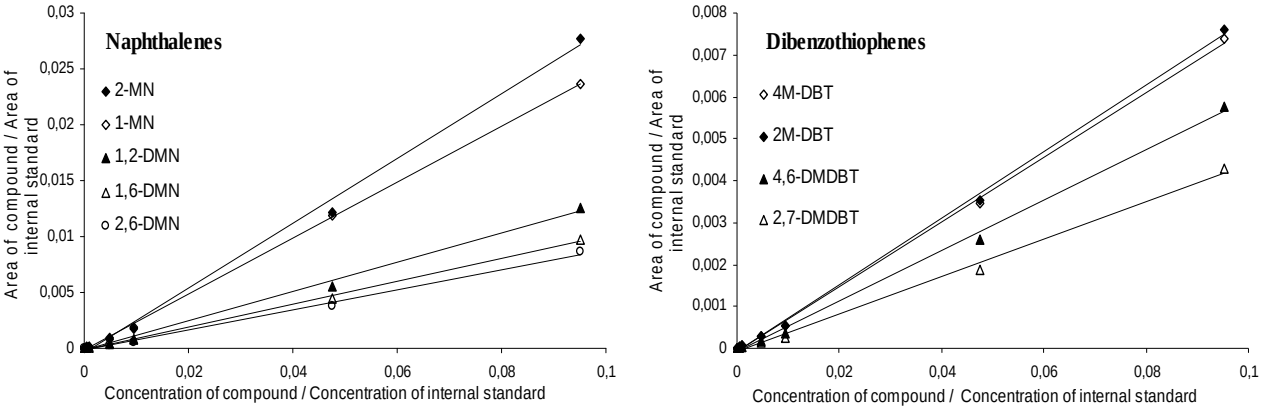

Figure 3 Calibration curves of naphthalenes and dibenzothiophenes in MRM mode.

An additional study was conducted to better understand the possibilities to quantify the other groups for which we do not have any alkylated isomer (for example, this is the case of C_3-phe/Ant, C_3- and C_4-naphthalenes). Figure 4 shows the response factors of the alkylated derivatives obtained in MRM and SIM modes.

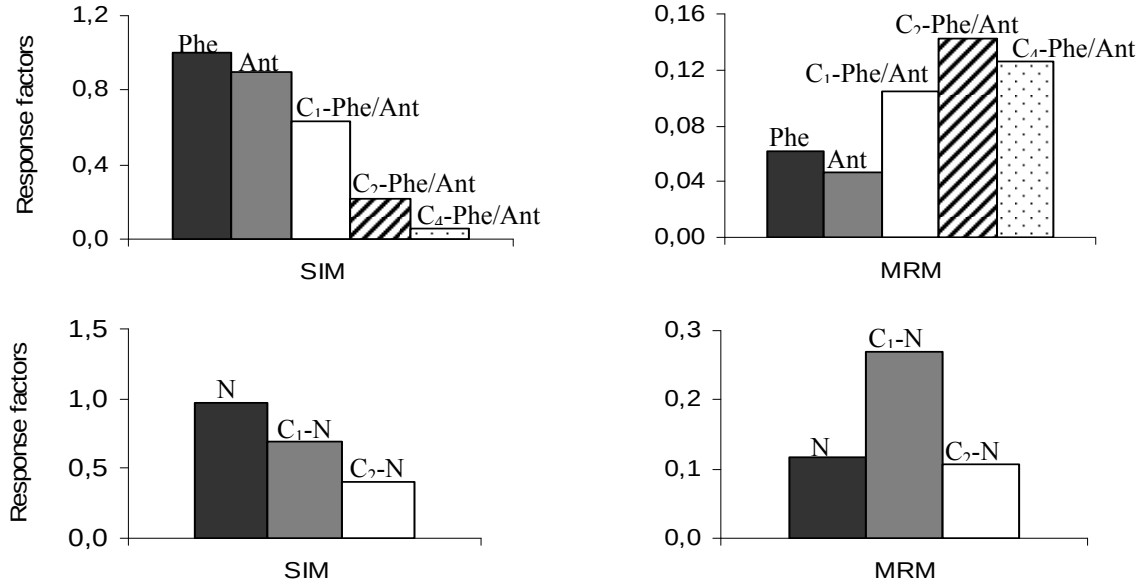

Figure 4 Comparison of the response factors of the groups of phenanthrenes/anthracenes and naphthalenes in SIM and MRM modes.

In MRM mode, the selected transitions for each compound are not all based on the same mass loss. For example, for the C_1-Phe/Ant, the transition is 192-191 (molecular mass-1) while for the C_4-Phe/Ant, the transition 234-219 (molecular mass-15) was chosen. Thus, unlike the SIM mode, where we consider only the molecular ions, the MRM analysis showed no changes in the response factors related to the number of alkyl substituent carbons, especially when the mass loss of transitions were different.

Thus, the groups, for which alkylated isomers are not available in standard solutions, were quantified in SIM mode. The groups (C_2-, C_3- and C_4-benzothiophenes, C_3-, C_4-naphthalenes, C_2-, C_3-fluoranthenes/pyrenes, C_2- and C_3-chrysenes), were quantified using the average response factors obtained from methylbenzothiophenes, dimethynaphthalenes, methylpyrenes and methylchrysenes, respectively. 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.

In the case of fluorene, no alkylated compounds were available in the standards solutions. An estimation of response factor was carried out by considering the ratios between the response factors of the parents and their C_1 alkylated homologues for each PACs group. This study showed that this ratio lies between 0.4 and 0.6 (Figure 5). So the response factor of C_1-fluorenes is estimated at the half of the response factor of the appropriate parent. The higher alkylated derivatives (C_2- and C_3-fluorenes) were quantified using the same response factor.

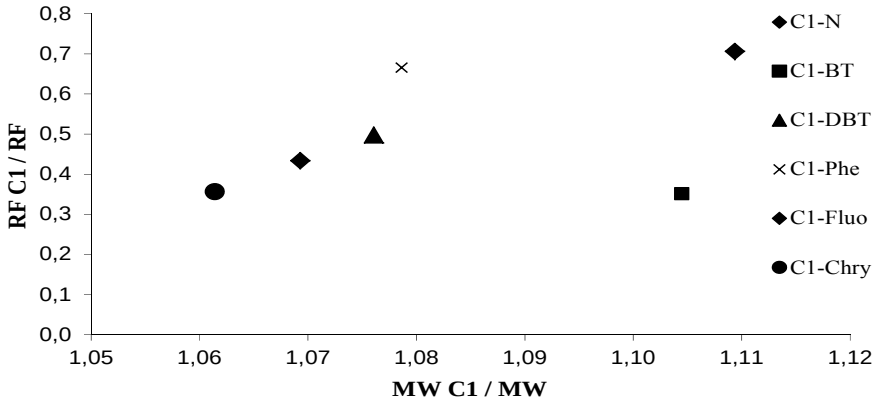

Figure 5 Estimation of the response factor of C_1-fluorenes. (RF C_1/RF: response factors of C_1 alkylated homologues/response factors of the appropriate parents. MW C_1/MW: Molecular weight of C_1 alkylated homologues/molecular weight of the appropriate parents).

3. 5 Validation of the Erika Oil

The analysis of the response factors made it possible to define, for each group of alkylated compounds, a quantification method adapted to the number of compounds present in the calibration solutions. The proposed method (SPE-GC-MS-MS) was then applied to analysis the Erika fuel oil, which provides a reference product containing all the compounds that can be quantified in any sample of oil or contaminated with a petroleum product. To verify the relevance of this reference in routine analysis, 5 repetitions, with five sample preparations, were performed during this characterization to estimate the variability of the measurements (Figure 6). Table 4 presents the quantifications of all families analyzed, and the associated relative standard deviations, which range from 5 to 10% in almost all cases.

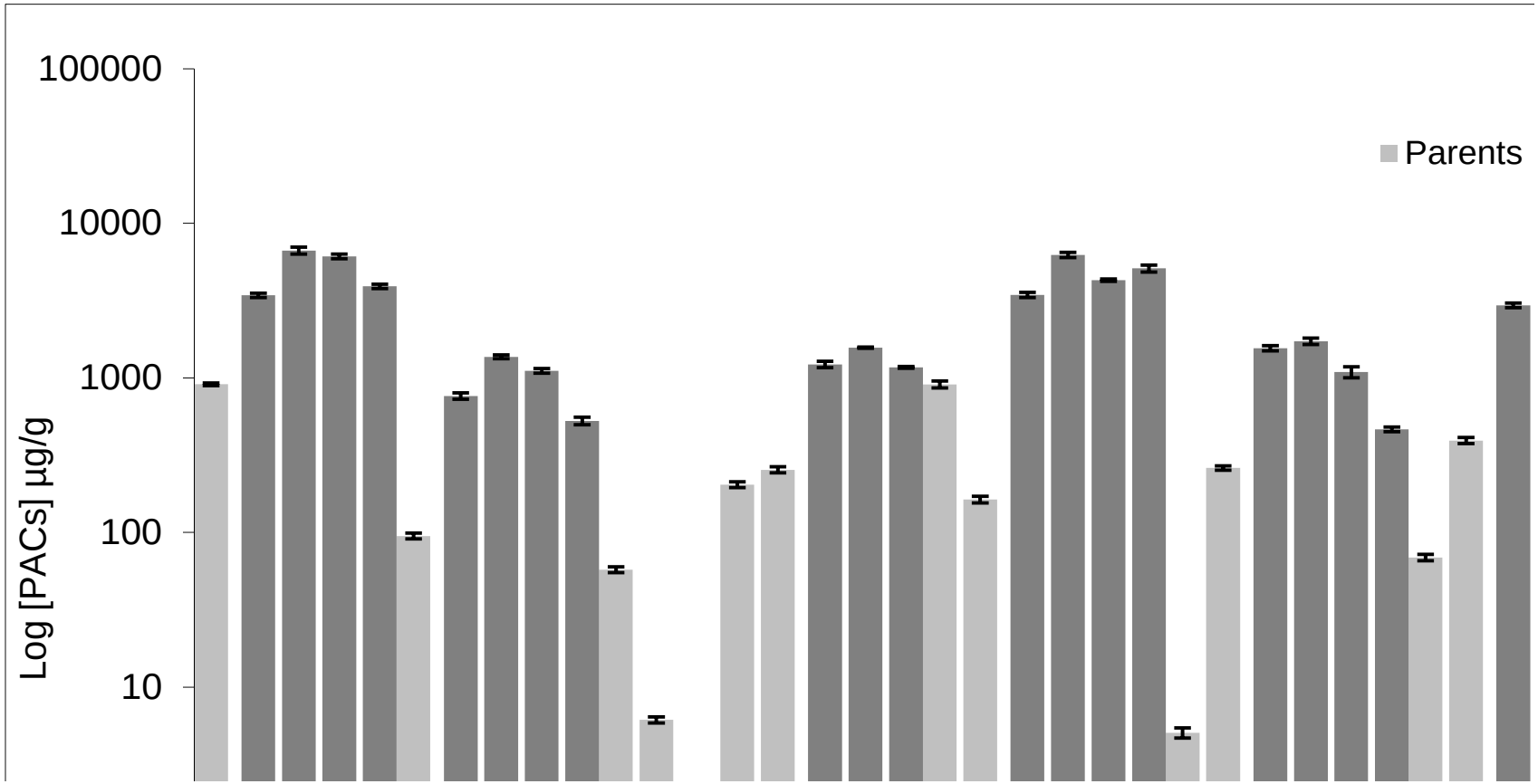

Figure 6 **Distribution of compounds in the Erika oil (µg/g).**

Kanan, R., J.T. Andersson, J. Receveur, J. Guyomarch, S. LeFloch, and H. Budzinski, Quantification of Polycyclic Aromatic Compounds (PACs) and Alkylated Derivatives by Gas Chromatography/Tandem Mass Spectrometry (GC/MS/MS) to Qualify a Reference Oil, Proceedings of the Thirty-fifth AMOP Technical Seminar on Environmental Contamination and Response, Environment Canada, Ottawa, ON, pp. 916-927, 2012.

Table 4 Concentration of PACs and alkylated derivatives in the Erika oil.

Compounds	[PACs] (µg/g)	R.S.D. (%) *n = 5*	Compounds	[PACs] (µg/g)	R.S.D. (%) *n = 5*
N	908.15	9.9	C_1-DBT	1552.98	8.5
C_1-N	3416.27	7.5	C_2-DBT	1725.95	10.3
C_2-N	6664.10	11.5	C_3-DBT	1090.29	8.3
C_3-N	6109.93	7.6	C_4-DBT	464.36	7.9
C_4-N	3906.80	6.9	Fluo	68.94	10.9
BT	94.86	9.9	Pyr	392.94	10.0
C_1-BT	762.77	10.5	C_1-Fluo/Pyr	2943.53	7.7
C_2-BT	1367.60	6.4	C_2-Fluo/Pyr	4344.33	8.4
C_3-BT	1111.68	5.9	C_3-Fluo/Pyr	4387.36	7.5
C_4-BT	526.45	8.2	B[*b*]N[2,1-*d*]T	143.36	9.8
B	57.40	9.7	B[*b*]N[1,2-*d*]T	28.21	10.5
3-PhenylT	6.14	10.1	B[*a*]Ant	259.70	10.2
Acy	1.98	14.3	Chry	467.83	12.2
Ace	203.59	9.3	C_1-Chry	4745.13	8.8
F	254.02	9.9	C_2-Chry	6367.30	6.4
C_1-F	1221.29	10.9	C_3-Chry	4825.38	9.1
C_2-F	1567.87	2.0	2-(2-Naphtyl)BT	12.85	12.5
C_3-F	1169.08	2.8	B[*b*+*k*]Fluo	106.46	8.8
Phe	907.48	11.9	B[*e*]Pyr	133.73	16.4
Ant	163.37	11.2	B[*a*]Pyr	118.44	10.1
C_1-Phe/Ant	3444.52	8.7	P	48.89	8.3
C_2-Phe/Ant	6239.04	8.7	B[*b*]ph[9,10-*d*]T	5.65	14.2
C_3-Phe/Ant	4279.82	4.0	I[1,2,3-*cd*]Pyr	13.74	16.4
C_4-Phe/Ant	5105.50	11.5	DB[*a*,*h*]Ant	37.42	8.6
N[2,3-*b*]T	5.06	16.9	B[*ghi*]P	38.63	15.7
DB[*b*,*d*]T	261.15	7.5			

R.S.D.: Relative standard deviation.

4 Conclusions

The results of this study showed that it was reasonable to quantify in MRM mode the alkylated PACs homologues group for which we have some of alkylated isomers. Thus, the analysis of 53 individual compounds made it possible to quantify 10 of the 25 groups of alkylated compounds. For the other groups of alkylated compounds, approximations were made in SIM mode in view of the comparative analysis of the response factors in MRM and SIM modes. Finally, the proposed method permitted the characterization of the Erika fuel oil with a low variability of results. So this product will be used as reference in routine for the quantitative analysis of the whole groups of compounds identified in this study. Moreover, the data obtained during the various tests developed have shown the inadequacy of approximations in SIM mode. If the MS-MS now offers an attractive alternative, it remains to improve the methods of quantification in simple MS, particularly in the context of automated sample preparation such as the SBSE (Stir bar sorptive extraction) or the SPME (solid-phase microextraction) in the case of water samples (Kanan et al., 2012).

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