

Chemical Characterization of Oil-Water Systems Using Stir Bar Sorptive Extraction (SBSE)-Thermal Desorption (TD)-Gas Chromatography-Mass Spectrometry (GC-MS)

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Abstract

The latest oil spills have shown an increasing demand for detailed assessments of the chemical contamination introduced into the water column. This is particularly true for the Deepwater Horizon incident, for which chemical dispersion of the oil was largely used as an emergency response. Even at low concentrations resulting from dilution processes, hydrocarbons are known to generate impacts, and health questions can be raised.

When spilled at sea, a crude oil is subjected to weathering processes such as evaporation, emulsification, photo-oxidation and dispersion in the water column under natural conditions. Many oil compounds are dissolved in seawater, such as the polycyclic aromatic compounds (PACs) which represent a category of compounds known as highly toxic and that 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. Several methods have been applied to the determination of PACs (from 16 to 21 compounds) in aqueous sample but no work which focuses on the analysis of a large number of dissolved PACs has been published to our knowledge. In this context, we present a new method of analysis by stir bar sorptive extraction technique and thermal desorption coupled to capillary gas chromatography-mass spectrometry (SBSE-TD-GC-MS) fully dedicated to the analysis of 52 compounds or groups of compounds. This protocol was successfully applied to the analysis of PACs in the Water Accommodated Fraction (WAF) and the Water Soluble Fraction (WSF) of seawater samples prepared in the laboratory from a crude oil.

1 Introduction

The presence of semi-volatile contaminants in aqueous samples has been routinely determined by liquid-liquid extraction (LLE), solid phase extraction (SPE) or solid-phase microextraction (SPME). A novel approach using sorptive extraction was introduced by Baltussen et al., 1999. This technique uses a stir bar coated with polydimethylsiloxane (PDMS) and was named stir bar sorptive extraction (SBSE). Like the SPME method, SBSE is a solventless enrichment technique. It is based on the sorption of analytes onto a thick film of polydimethylsiloxane (PDMS) coated on a stir bar. After extraction, the analytes are generally thermally desorbed from the stir bar and immediately transferred to a capillary column of a gas chromatograph. SBSE methods have been successfully applied to the determination of polycyclic aromatic hydrocarbons (PAHs) in aqueous samples (Garc ia-Falc on et al., 2004; Kollahgar et al., 2002; Popp et al., 2001), but no application of SBSE for the analysis of PAHs, PASHs (polycyclic aromatic sulfur heterocycles) and alkylated derivatives in seawater has been reported. Thus, this article proposes an extraction method using stir bar sorptive extraction (SBSE) coupled to GC-MS to determine polycyclic aromatic compounds (PACs) in

the Water Accommodated Fraction (WAF) and Water Soluble Fraction (WSF) of seawater samples prepared in the laboratory from a crude oil.

2 Experimental Set-up

2.1 Standard Solutions

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-d₈, biphenyl-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and benzo[*a*]pyrene-d₁₂ at a concentration of 1 µg/mL in acetone. 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.

2.2 Preparation of WAF and WSF

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 molecules 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 less 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 using a magnetic stirrer. This agitation was set at a minimum level to prevent oil from being dispersed in the water column. The experimental device was set up in an air-conditioned room at 21 °C for 24 h to reach equilibrium. The oil used was an Arabian Light crude oil. Finally, samples were collected through a tap located approximately 3 cm above the bottom of the flask. The water soluble fraction (WSF) was prepared according to the same procedure but in an open flask. Evaporation thus took place in conditions closer to those encountered in the event of an oil spill at sea.

2.3 Stir Bar Sorptive Extraction Procedure

Compounds were extracted by introducing the polymethylsiloxane coated stir bar (0.5 mm film thickness, 20 mm length, Twister, Gerstel, Mülheim an der Ruhr, Germany) into 100 mL of seawater sample, to which 10 mL of methanol containing the five perdeuterated internal standards at a concentration of 1 ng/mL was added. Samples were stirred at 700 rpm at room temperature for 6 h. After extraction, the stir bar was removed with clean tweezers, dried with lint-free tissue and placed in the automatic sampler in order to thermally desorb the compounds. Prior to use, the stir bars were conditioned in an empty thermal desorption tube at 300 °C for 4 h with helium flow at a flow desorption rate of 50 mL/min.

2.4 Thermal Desorption and GC-MS Conditions

The PAHs and PASHs were identified and quantified using a Thermal Desorption Unit (TDU) combined with a Cooled Injection System (CIS) from Gerstel (Mülheim an der Ruhr, Germany) mounted on a 7890 Agilent GC system coupled to an Agilent 5975 mass spectrometer (Agilent Technologies, Little Falls, DE, USA). The analytical system was equipped with an automated sampler MPS2 (Gerstel). Desorption was achieved at 280 °C for 10 min under a helium flow of 50 mL/min in the splitless mode and with a transfer line maintained at 300 °C. The desorbed compounds were cryofocused in the cooled injection system (CIS-4, Gerstel) at 10 °C and then transferred to the HP-5 MS column (30 m x 0.25 mm i.d. x 0.25 µm film thickness, constant helium flow of 1 mL/min) by a rapid increase of the CIS temperature (from 10 °C to 300 °C at 12 °C/s). The oven temperature program was: from 50 °C (1 min) to 150 °C at 10 °C/min, and then to 320 °C (5 min) at 5 °C/min. A

Selected Ion Monitoring (SIM) mode acquisition method, with two, three or four characteristic ions, was chosen for the detection of the analytes. The target compounds, the selected SIM ions and the retention times under the given experimental conditions are listed in Table 1.

Table 1 Abbreviation, retention times and selected SIM ions for the investigated compounds.

Compound name	Abbreviation	Rt (min)	Selected ions (m/z)
<i>Naphthalene-d₈</i>	<i>N-d₈</i>	9.10	136-135
Naphthalene*	N	9.13	128-127-102
Benzo[<i>b</i>]thiophene	B[<i>b</i>]T	9.26	134-89
2-Methylbenzothiophene	2-MBT	10.72	147-148-115
5-Methylbenzothiophene	5-MBT	10.84	147-148-115
<i>Biphenyl-d₁₀</i>	<i>B-d₁₀</i>	11.81	154-153-152-76
Biphenyl	B	11.87	164-162
3-Phenylthiophene	3-PhenylT	12.36	160-115
Acenaphthylene*	Acy	12.96	152-151-76
Acenaphthene*	Ace	13.51	154-153-152-76
Fluorene*	F	15.11	166-165
<i>Phenanthrene-d₁₀</i>	<i>Phe-d₁₀</i>	18.49	188-187
Dibenzo[<i>b,d</i>]thiophene	DB[<i>b,d</i>]T	18.08	184-139-152
Phenanthrene*	Phe	18.56	178-176-152
Anthracene*	Ant	18.74	178-176-152
Naphtho[2,3- <i>b</i>]thiophene	N[2,3- <i>b</i>]T	19.04	184-139-152
2-Methyldibenzothiophene	2-MDBT	20.23	198-194
4-Methyldibenzothiophene	4-MDBT	19.88	198-194
4,6-Dimethyldibenzothiophene	4,6-DMDBT	21.69	212-211
2,7-Dimethyldibenzothiophene	2,7-DMDBT	22.46	212-211
4,6-Diethyldibenzothiophene	4,6-DEDBT	24.78	225-240
2,4,6,8-Tetramethyldibenzothiophene	2,4,6,8-TMDBT	25.67	240-225
Fluoranthene*	Fluo	23.55	202-200-201
Pyrene*	Pyr	24.46	202-200-201
<i>Chrysene-d₁₂</i>	<i>Chry-d₁₂</i>	30.06	240-239
Benzo[<i>b</i>]naphtho[2,1- <i>d</i>]thiophene	B[<i>b</i>]N[2,1- <i>d</i>]T	28.88	234-117-232
Benzo[<i>b</i>]naphtho[1,2- <i>d</i>]thiophene	B[<i>b</i>]N[1,2- <i>d</i>]T	29.30	234-117-232
Benzo[<i>a</i>]anthracene*	B[<i>a</i>]Ant	29.99	228-206-227
Chrysene*	Chry	30.16	228-206-227
2-(2-Naphthyl)benzothiophene	2-(2-Naphthyl)BT	33.15	260-258-130
<i>Benzo[<i>a</i>]pyrene-d₁₂</i>	<i>B[<i>a</i>]Pyr-d₁₂</i>	35.80	264-263
Benzo[<i>b+k</i>]fluoranthene*	B[<i>b+k</i>]Fluo	34.65	252-250-126
Benzo[<i>e</i>]pyrene	B[<i>e</i>]Pyr	35.70	252-250-126
Benzo[<i>a</i>]pyrene*	B[<i>a</i>]Pyr	35.89	252-250-126
Perylene	P	36.22	252-250-126
Benzo[<i>b</i>]phenanthro[9,10- <i>d</i>]thiophene	B[<i>b</i>]ph[9,10- <i>d</i>]T	39.29	284-282-252
Indeno[1,2,3- <i>cd</i>]pyrene*	I[1,2,3- <i>cd</i>]Pyr	39.99	276-138
Dibenzo[<i>a,h</i>]anthracene*	DB[<i>a,h</i>]Ant	40.17	278-276-139
Benzo[<i>ghi</i>]perylene*	B[<i>ghi</i>]P	40.80	276-138

Surrogates used for quantification in *italics*, corresponding to quantified compounds below.

* Priority contaminants selected by the US Environmental Protection Agency (EPA).

3 Results and Discussion

3.1 Calibration Curves and Linearity

The linearity of the method was determined from 7 levels of concentration (0.1, 0.5, 1, 5, 10, 50 and 100 ng/L) with three repetitions per level. Correlation coefficients (R^2) were higher than 0.99 for the majority of compounds studied (Table 2).

3.2 Limits of Detection, Limits of Quantification and Recovery

The limits of detection and quantification were calculated according to the calibration curve method. As shown in Table 2, detection limits were in the range from 0.01 to 0.04 ng/L and quantification limits from 0.03 to 0.1 ng/L.

Table 2 Limits of detection and quantification (LOD and LOQ, in ng/L), correlation coefficients (R^2) of the calibration curves (from 0.1 to 100 ng/L) for the investigated compounds.

Compounds	(R^2)	LOD (ng/L)	LOQ (ng/L)
N	0.995	0.03	0.1
B[b]T	0.994	0.03	0.1
2-MBT	0.996	0.03	0.1
5-MBT	0.996	0.03	0.1
B	0.997	0.02	0.1
3-PhenylT	0.995	0.03	0.1
Acy	0.996	0.03	0.1
Ace	0.997	0.03	0.1
F	0.996	0.02	0.1
DB[b,d]T	0.997	0.02	0.1
Phe	0.997	0.03	0.1
Ant	0.998	0.01	0.04
N[2,3-b]T	0.996	0.02	0.1
2-MBT	0.998	0.01	0.05
4-MBT	0.998	0.02	0.1
4,6-DMDBT	0.998	0.01	0.04
2,7-DMDBT	0.998	0.01	0.04
4,6-DEDBT	0.984	0.04	0.1
2,4,6,8-TMDBT	0.997	0.01	0.03
Fluo	0.998	0.01	0.04
Pyr	0.998	0.01	0.04
B[b]N[2,1-d]T	0.998	0.01	0.04
B[b]N[1,2-d]T	0.998	0.01	0.04
B[a]Ant	0.999	0.01	0.03
Chry	0.998	0.01	0.05
2-(2-Naphthyl)BT	0.997	0.01	0.04
B[b+k]Fluo	0.996	0.02	0.1
B[e]Pyr	0.997	0.02	0.1
B[a]Pyr	0.995	0.03	0.1
P	0.996	0.02	0.1
B[b]ph[9,10-d]T	0.992	0.02	0.1
I[1,2,3-cd]Pyr	0.988	0.01	0.04
DB[a,h]Ant	0.988	0.01	0.03
B[ghi]P	0.993	0.01	0.04

The absolute recovery of the internal standards using the SBSE-TD-GC-MS method was calculated by analysing pre-spiked stir bars (Table 3). Internal standards were directly added onto the stir bar, in the same quantity as with the regular protocol. The recovery of internal standards, considered as representative of the whole method, was calculated by comparing the response (area) of the equipment using the regular protocol relatively to the

spiked bar, which represented 100% of the internal standards introduced at the beginning of the sample preparation.

Table 3 Recovery (%) of internal standards at 100 ng/L ($n = 3$).

Internal standards	100 ng/L	
	Recovery (%)	R.S.D. (%)
N-d ₈	66	20
B-d ₁₀	69	5
Phe-d ₁₀	70	2
Chry-d ₁₂	72	13
B[a]Pyr-d ₁₂	58	23

R.S.D.: Relative standard deviation.

3.3 Analysis of PACs in the WAF and WSF

The SBSE procedure was applied for determining the polycyclic aromatic compounds (PACs) in the water accommodated fraction and water soluble fraction of seawater samples.

Alkylated derivatives, which are not available in the standard solutions, were quantified as groups (Figure 1). This quantification was performed with the approximation that the response factors for alkylated homologue are equal to the response factor of the appropriate parent (Burkhardt et al., 2005).

SBSE-TD-GC-MS analyses of PACs in the WAF and WSF have shown that naphthalenes and alkylated benzothiophenes are the dominant semi-volatile compounds because of their relatively high solubility in water. Higher PACs (4 rings and more) make up only a very small proportion of the WAF or WSF (Faksness et al., 2008) (Figure 1).

These results illustrate the flexibility of the method that enables the quantification of compounds from the ng/L level, characteristic of high molecular weight PACs, to around 80 000 ng/L as typical for the most abundant and soluble PACs contained in petroleum products. This linearity of the method over a very wide range of concentrations was previously demonstrated (Balcon et al., 2011). The fields of applications are consequently large, from the monitoring of baseline levels to significant levels of contamination as generally observed during oil spills.

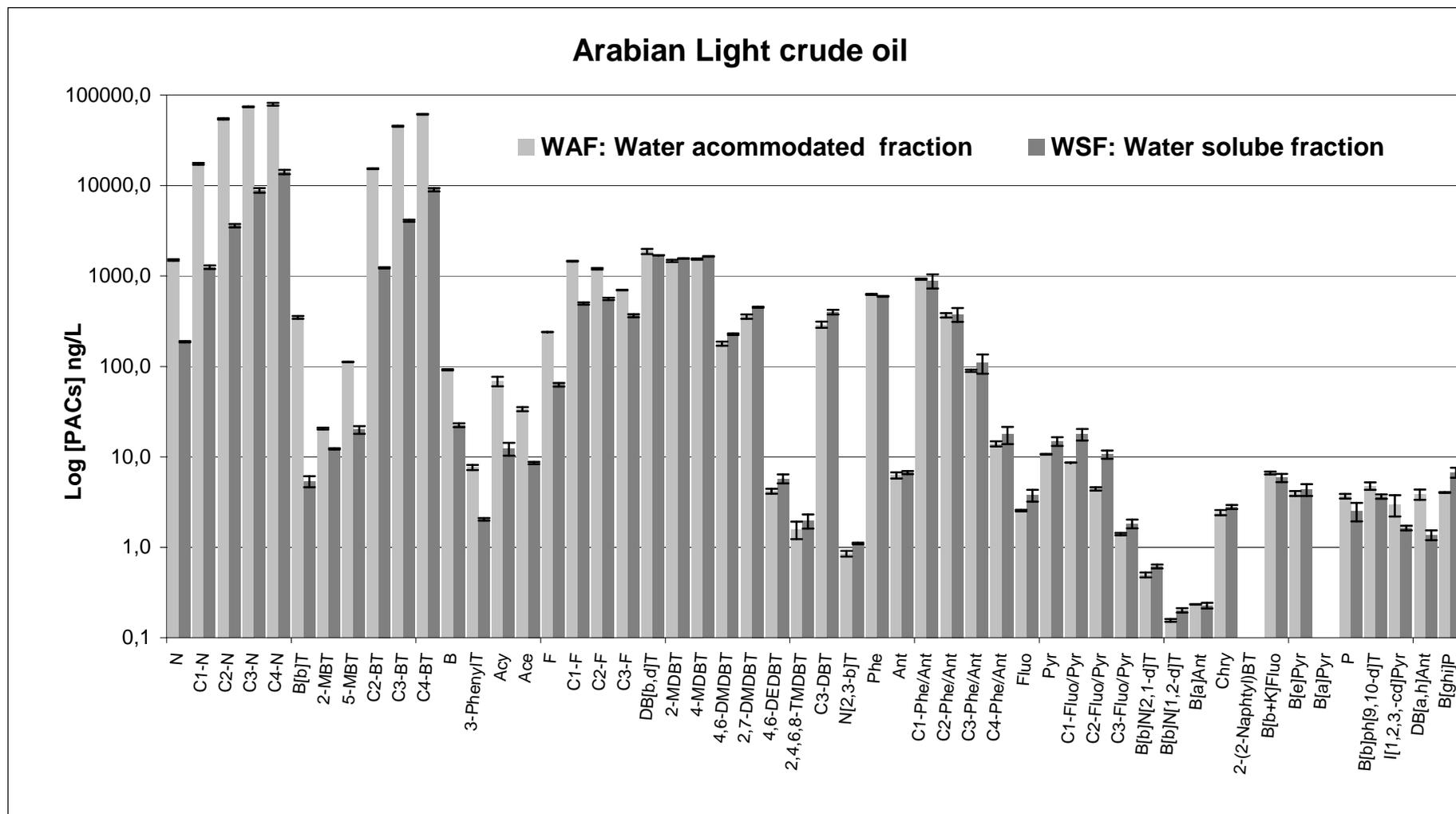


Figure 1 Analysis of PACs and alkylated PACs in the WAF and WSF of an Arabian Light crude oil.

4 Conclusions

The proposed SBSE-TD-GC-MS method for the determination of polycyclic aromatic compounds (PACs) has been validated for the water accommodated fraction (WAF) and the water soluble fraction (WSF) of seawater samples prepared in the laboratory from a crude oil. Moreover, in addition to the PAHs commonly quantified, PASHs and alkylated compounds were investigated in this study. The good LOD, quantification (on the sub-ng level), linearity, the simplicity and automation make this technique the right tool for the analysis of these compounds in seawater.

5 Acknowledgements

This research was supported by a PhD grant from the Syrian government. Gilbert Le Lann, director of Cedre, is acknowledged for financial support.

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