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On-site determination of polynuclear aromatic hydrocarbons in seawater by stir bar sorptive extraction (SBSE) and thermal desorption GC–MS

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Abstract

The identification and quantification of semi-volatile contaminants dissolved in water is currently done in laboratory after a sampling step. This procedure is not satisfactory first because risks of samples contamination and analytes losses remain, in particular when these are present in ultra-trace concentrations, and secondly because procedures are time-consuming. The coupling of the stir bar sorptive extraction (SBSE), a new device of extraction technique, and a new generation of gas chromatography mass spectrometry (GC–MS), the field apparatus EM 640 S from Bruker, could be an answer to the challenge of on-site analysis. This analytical system was used to analyze 24 PAHs, among them 15 EPA priority pollutants. It was shown that this coupling led to encouraging results with LODs around the sub-ppt level for most of the compounds and R.S.D. included between 1 and 48%. The existence of competition phenomena between the various analytes inside the absorbent phase was demonstrated with the release (up to 80%) of light compounds. This result shows the necessity to work on the kinetic domain rather than on the thermodynamic equilibrium that is influenced by nature and concentration of other compounds. The matrix effects were also studied through the comparative analysis of ultrapure water, artificial and natural seawaters spiked with PAHs and the influence of ionic strength and particulate organic matter was investigated.

Keywords: PAH; GC–MS; Thermal desorption (TD); Stir bar sorptive extraction (SBSE); Polydimethylsiloxane (PDMS); In situ; Seawater; Environmental analyses

1. Introduction

The analysis of dissolved organic contaminants in seawater by gas chromatography is complicated for several reasons, among them the very low concentration levels at which these compounds are present [1] and the fact that water can damage the column and the mass spectrometer if introduced directly in the analytical system. To overcome these limitations, several sample preparation methods were developed as liquid–liquid extraction procedure (LLE) on the basis of the common Soxhlet extraction. LLE has been largely replaced in the past few years by solid-phase extraction (SPE) using a variety of adsorbents to increase selectivity and reduce bleeding phenomena. Indeed, SPE avoids several drawbacks of LLE such as the high volume of organic solvent that is required and the impossibility to couple it on-line with gas or liquid chromatography. However, SPE is a multi-step process (washing, conditioning and eluting steps) that is prone to loss of analytes if not fully automated and still needs toxic solvents. Furthermore, SPE is limited to semi-volatile compounds as the boiling points of the analytes must be substantially above that of the solvents. Polar compounds are also difficult to extract by using SPE due to their great affinity for water matrix. Finally, breakthrough volumes and cartridge capacities are often too low to achieve sufficient detection limits.

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Recently, several new techniques have been developed to overcome these limitations, in particular the solvent-less procedures that are more environmentally-friendly and less laborious as solid-phase microextraction (SPME) [2], supported liquid membrane extraction (SLM) [3], automated purge and trap system [4], supercritical fluid extraction (SFE) [5], on-line capillary microextraction [6] or membrane extraction with sorbent interface (MESI) [7]. A novel technique, namely stir bar sorptive extraction (SBSE), appears as one of the most promising for the analysis of semi-volatile compounds due to its simplicity and its analytical potentialities. Indeed, this technique enables a 500-fold increase in enrichment and thus sensitivity compared to SPME [8]. Whatever, only very few applications were published on the SBSE technique as analyses of dicarboximide fungicides [8], organochlorine pesticides [9] and polychlorobiphenyls [10].

The principle of the SBSE is based on the sorptive extraction of dissolved molecules in a polymer, the PolyDiMethylSiloxane (PDMS). This polymer is packed under the shape of a thin layer (500 μm) deposited on a 2 cm length glass-coated magnet. Without any preliminary conditioning nor preconcentration step, this stir bar named twister is directly plunged for a fixed time into the solution to be analyzed. Developed initially within the framework of pharmaceutical applications (blood analyses), the SBSE came into the agribusiness domain with the oenological analysis [8], and then in the environmental field with the water analysis.

In this contribution, the goal was to develop a new powerful on-site analytical method for the determination of contaminants in complex matrices such as seawater. Then, two novel techniques, the SBSE on the one hand and a special mobile gas chromatography mass spectrometer (GC–MS) especially designed for use in rough environment on the other hand, were coupled to obtain a new analytical system. Then, performances of this original system were studied through the analysis of polynuclear aromatic hydrocarbons (PAHs) dissolved in water. These analytes have never been analyzed by SBSE to our knowledge although they represent a serious environmental issue, particularly in case of accidental oil pollution affecting the shoreline during months (examples of the heavy fuel oil spills in 1999 and 2002 due to tankers ERIKA and PRESTIGE). In addition, the mechanisms that rule the extraction were studied and the influence of matrix effects on these phenomena was discussed.

2. Experimental

2.1. Analytes and samples preparation

The solutions were prepared with the standard reference material 1491, delivered by Promochem (London, UK) that contains 24 PAHs in hexane/toluene mixture. Complementary experiments were performed with the PAH mix from Quebec Ministry of Environment supplied by Supelco and with deuterated compounds. Milli-Q water (18.2 MΩ cm) was spiked with calibration mix in presence of 5% ultrapure methanol (Aldrich) to avoid adsorption on glass walls. Artificial seawater was prepared by dissolving 32 g NaCl, 14 g $MgSO_4{\cdot}7H_2O$ and 0.2 g $NaHCO_3$ in 1 L of milli-Q water [11]. Natural seawater was sampled at Saint-Anne du Portzic and at the beach of Moulin Blanc (Brest, France) in summer by middle tide. Seawater was analyzed just after its sampling to avoid any further evolution.

2.2. Extraction procedures

Sample extraction was performed by introducing a suitable amount of water (200 mL) in an amber-colored closed 200 mL vial (supplied by Supelco) to reduce headspace volume and prevent any photosensitization. Cleaning of vials was achieved by a classical procedure including several acetone washings, water rinsing and finally a 4-h pyrolysis at 400 °C. Twisters, purchased from Gerstel Company (Belgium), have a length of 2 cm and a polymer thickness of 0.5 mm. Their cleaning was achieved by thermodesorption and checked with a blank analysis. To increase sensitivity two twisters from two extractions were introduced simultaneously and desorbed in the GC–MS chamber. Extractions were conducted at room temperature (results not presented here indicate that extraction temperature does not play any significant role between 15 and 30 °C); extractions lasted 1 h (cf. kinetics effect section) with an extraction speed of 900 rpm.

2.3. Desorption procedures

Thermodesorptions (TD) were realized at a temperature of 280 °C (tested from 260 to 280 °C, maximum possible value), a pressure of 100 h Pa (tested from 15 to 150 h Pa) during 60 s (tested from 20 to 120 s). The shape of the empty glass tube where twisters are introduced was also optimized (use of different shoulder shapes).

Chemical desorptions (CD) were also performed for complementary experiments. Then, an ultrasonic device (model 88155 from DVE GS working at 35 kHz) at controlled temperature was used with an elution phase composed of 5 mL methylene chloride added with 100 μL toluene. Internal deuterated standards were added at the beginning of the elution to allow recovery calculations. After 30 min elution, the enriched solvent was preconcentrated in a rotavapor at 800 h Pa and 40 °C to evaporate the methylene chloride.

2.4. GC–MS analyses

The Bruker EM 640 S is a transportable, compact and rugged GC–MS especially designed for fast and reliable on-site analyses. The instrument's dimensions are only 75 cm × 45 cm × 35 cm ($h \times w \times d$), no external pump is necessary, external temperature can vary from 0 to 40 °C and the system is ready for use within 30 min after arrival on-site. The apparatus is controlled by a ruggedized portative computer with a multi-task operating system, allowing simultaneous data acquisition and identification. Moreover, its specifications are quite interesting with a high sensitivity since 1 ng methyl stearate in full scan mode gives a signal at *m*/*z* 298 with *S*/*N* 10:1 and a large dynamic range (from 1 to 640 amu) allowing detection of most organic compounds. The GC–MS was equipped with a 30 mm × 0.3 mm fused silica column with 0.25 μm DB5 stationary phase. The carrier gas was helium 6.0 quality from the Air Liquid company (France) at 4 mL/min (tested from 2 to 15 mL/min). The temperature program was 40 °C hold for 5 min, 10 °C/min till 280 °C and 280 °C for 16 min.

For complementary experiments, aromatic compounds were analyzed by gas chromatography coupled to mass spectrometry. The GC was an HP 6890 N (Hewlett-Packard, Palo Alto, CA, USA) equipped with a split/splitless injector (Pulsed Splitless mode, time: 1 min, flow 50 mL/min). The injector temperature was maintained at 270 °C. The interface temperature was 300 °C. The GC temperature gradient was: from 50 °C (1 min) to 300 °C (20 min) at 5 °C/min and to 320 °C (2 min) at 2 °C/min. The carrier gas was Helium at a constant flow of 1 mL/min. The capillary column used was an HP 5 MS (Hewlett-Packard, Palo Alto, CA, USA): 60 m × 0.25 mm i.d. × 0.25 μm film thickness. The GC was coupled to an HP 5973 Mass Selective Detector (MSD) (electronic impact: 70 eV, voltage: 2000 V). PAHs quantification was done using single ion monitoring mode with the molecular ion of each compound at a minimum of 2.0 cycles/s.

PAHs were quantified relatively to the perdeuterated PAHs introduced at the beginning of the sample preparation procedure.

3. Results and discussion

3.1. SBSE–TD–GC–MS analyses of spiked water

The quality of the chromatogram presented in Fig. 1 demonstrates the possibility of coupling the EM 640 S with the SBSE extraction technique. Baseline is horizontal, compounds are correctly separated and none of the contaminants sometimes met in SPE (phthalate, ether, dodecane or 2-undecanone as usually reported) was observed. This absence of contamination can be explained by the simplicity of the protocol.

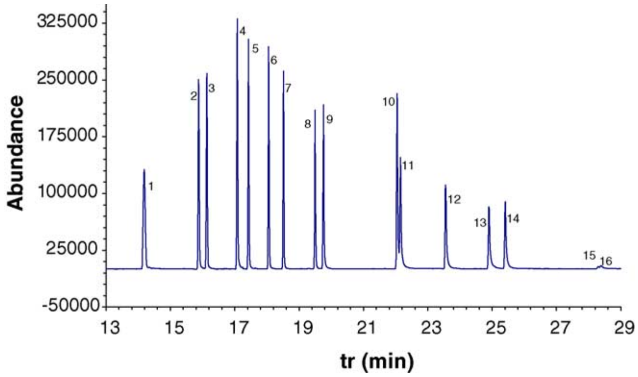

Fig. 1. GC–MS chromatogram from the standard sample at 0.3 ppb in milli-Q water (experimental conditions: SIM mode, $q_{\mathrm{He}} = 4$ mL/min, $P_{\mathrm{He}} = 75$ h Pa). For peak identities, see Table 1.

Table 1
Identification of compounds

Numbers	Compounds	t_r (min)	Fit/reverse fit/purity
1	Naphthalene	14.15	955/987/955
2	2-Methylnaphthalene	15.87	881/932/923
3	1-Methylnaphthalene	16.12	919/959/922
4	Biphenyl	17.07	946/984/950
5	2,6-Dimethylnaphthalene	17.42	932/985/934
6	Acenaphthylene	18.05	899/953/934
7	Acenaphthene	18.51	957/991/959
8	2,3,5-Trimethylnaphthalene	19.49	937/968/948
9	Fluorene	19.74	949/976/962
10	Phenanthrene	22.02	911/966/927
11	Anthracene	22.13	851/964/867
12	1-Methylphenanthrene	23.54	836/973/846
13	Fluoranthene	24.87	842/981/850
14	Pyrene	25.37	821/954/851
15	Chrysene	28.22	929/975/950
16	Benz[*a*]anthracene	28.31	973/994/973
17	Benzo[*b*]fluoranthene	30.80	906/981/906
18	Benzo[*k*]fluoranthene	31.70	973/994/973
19	Indeno[1,2,3-*cd*]pyrene	36.30	974/978/988
20	Dibenz[*a*,H]anthracene	36.53	856/928/917
21	Benzo[*g*,*h*,*i*]perylene	37.61	994/994/994

However, the gaussian shape of the chromatogram reveals a problem in the analytes injection. This deficiency could also explain why only 21 out of the 24 compounds (Table 1) are detected. The problem is observed for the last injected compounds, which correspond to the heaviest ones. The system, based on compensations of stream of helium flow, could be improved by using a cold trap to focus them.

3.2. Determination of limits of detection

The performances of the SBSE–TD–GC–MS, i.e. linearity (determined from four points), reproducibility (calculated on triplicates) and sensitivity are presented in Table 2. R.S.D. determinations were based on triplicate stir bar sorptive extractions and conventional GC–MS analyses (with TD). The limits of detection were determined on the basis of a signal-to-noise ratio (S/N) of four rather than three as often found in the literature. These limits, in the range of sub-ng/L, are particularly low and correspond to the concentrations frequently met in coastal seawater [1]. Table 2 summarizes the results obtained for the different compounds (some doubts are remaining concerning the injection of the heaviest ones, see Section 3.1).

3.3. Influence of the matrix effects

The limits of sensitivity being satisfactory, the influence of the matrix effects was then studied. For that purpose milli-

Table 2
Quantification ions, calibration and limit of detection of main compounds. LOD[a] was determined with a S/N of 4 and R.S.D. were obtained at the indicated LODs

Compounds	Quantification ions	Calibration R^2	LOD[a] (ng/L)	R.S.D. (%), $n = 3$
Naphthalene	128	0.80	0.32	8
2-Methylnaphthalene	142	0.88	0.19	4
1-Methylnaphthalene	142	0.91	0.18	1
Biphenyl	154	0.95	0.14	5
2,6-Dimethylnaphthalene	156	0.96	0.14	16
Acenaphthylene	152	0.98	0.18	14
Acenaphthene	154	0.96	0.17	10
2,3,5-Trimethylnaphthalene	166, 170	0.98	0.22	3
Fluorene	166, 170	0.98	0.23	11
Phenanthrene	178, 192	0.96	0.23	40
Anthracene	178, 192	0.94	0.43	48
1-Methylphenanthrene	178, 192	0.86	0.47	15
Fluoranthene	202, 228, 252	0.83	1.15	3
Pyrene	202, 228, 252	0.86	0.95	18
Chrysene	228	nd	14.6	nd
Benz[*a*]anthracene	228	nd	10.7	nd
Benzo[*b*]fluoranthene	252	nd	37.5	nd
Benzo[*k*]fluoranthene	252	nd	70.6	nd
Indeno(1,2,3-*cd*)pyrene	276	nd	1200	nd
Dibenz(*a*,*h*)anthracene	278	nd	600	nd
Benzo(*g*,*h*,*i*)perylene	276	nd	667	nd

nd: Not determined.

Q water (18.2 MΩ cm), artificial seawater (1000 g H_2O/32 g NaCl/14 g $MgSO_4 \cdot 7H_2O$/0.4 g $NaHCO_3$) and natural seawater (sampled at Saint Anne du Portzic and Le Moulin Blanc beaches) were analyzed in the same conditions (Fig. 2).

Fig. 2 shows that the chromatogram shapes corresponding to measurements obtained on various matrices are comparable. This result confirms the possibility of using the SBSE for the analysis of a complex environments such as seawater. A finer observation of chromatogram reveals that the intensities of the lightest compounds (MW < 160 or $t_r < 19$ min) are higher (20%) for the Milli-Q water than for the artificial seawater. The opposite phenomenon was observed for the compounds of higher molecular weight (MW > 160 or $t_r > 19$ min). Salts thus have an influence, which depends on compounds. We can explain this observation by the decrease of the compounds solubility in the aqueous phase, which would favor the sorption of these compounds by moving their partition coefficient $K_{\mathrm{PDMS/Water}}$ in favor of the polymeric phase [12]. The heaviest compounds would be then more pre-concentrated and could expel the lightest compounds, which present a lesser affinity for the polymer. This assumption thus supposes the existence of competition phenomena between molecules (cf. kinetics effects section).

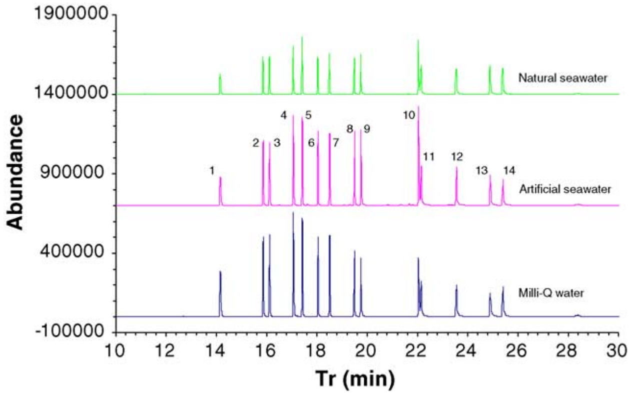

Fig. 2. Comparison of chromatograms recorded for different samples: milli-Q water, artificial seawater and natural seawater.

On the other hand, the intensities obtained with natural seawater are lower than those obtained on artificial seawater (Fig. 2). As seawater samples were analyzed without any filtration PAHs were liable to be adsorbed on natural organic complexants in suspension, thus lowering their available concentrations and consequently, their peak intensities [13,14].

As phenomena are governed by sorptive extraction, bulk diffusion plays an essential role, which was studied through the extraction time.

3.4. Kinetics effects

Several experiments were conducted with different extraction times from 15 min up to 40 h (Fig. 3). The first observation concerns the variability of the molecules behavior: all the compounds do not converge asymptotically towards a maximum adsorptive limit as expected [5]. Indeed, the theory predicts a one compartment first-order kinetic model [15] that should lead to a maximum intensity given by Eq. (1) [13]:

$$I_{\max} \sim \frac{RC_0 K V_s V_w}{K V_s + V_w} \qquad (1)$$

where $I_{\max}$ is the MS peak intensity, R the recovery, C_0 the initial concentration, K the partition coefficient PDMS/water

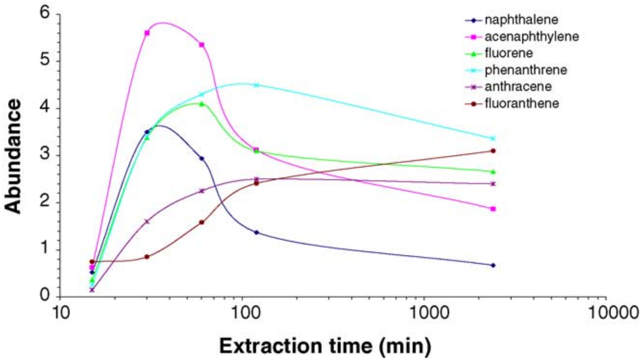

Fig. 3. Evolution of MS intensities vs. the stir bar sorptive extraction time for representative compounds $C_0 = 300$ ppt.

relative to the equilibrium, V_s and V_w the volumes of PDMS and water phases, respectively.

On the contrary, certain molecules such as naphthalene lose up to 80% of their intensity between 1 and 40 h extraction times. This result could indicate the existence of competition phenomena and supports the hypothesis presented previously in the study on salt influence. Purely kinetic phenomena (diffusion from the bulk into the polymer) would then coexist with thermodynamics phenomena (competition between molecules inside of the polymer) [16].

Another observation is the existing corroboration between the molecular mass of compounds and the optimal times of extraction: the lighter the compounds, the shorter the optimal durations of extraction (Fig. 3). This result can be explained by the differences in the molecules diffusivity.

An assumption to explain the release of light compounds would be their volatilization during the extraction. Indeed, extraction during 40 h allows a partition PDMS/water but also water/gas of the headspace via the Henry's law and finally gas/teflon cap. As the PDMS/water is a dynamic equilibrium, a progressive elimination of light compounds could then result in their adsorption on the teflon cap of the vial, depleting the PDMS/water partition. To elucidate this assumption two complementary experiments were performed in the same conditions (40 h): one with a current teflon cap and the other one with an aluminium cap (Fig. 4). To quantify the target PAHs and to determine the recovery yields, three deuterated PAHs (Naphthalene-d_8, Phenanthrene-d_{10} and Chrysene-d_{12}) were spiked prior to extraction with liquid solvent (methylene chloride). Calibration curves of the target PAHs were established previously relatively to these internal standards by liquid injection.

This experiment demonstrates firstly that light compounds are not particularly adsorbed on the teflon cap (superposition of black and white circles in Fig. 4) and secondly that they are not completely sorbed in the twister. Indeed, yield recoveries are around 20% for naphthalene (MW = 128), 60% for fluorene (MW = 166), and reach 100% only for compounds heavier than 200 g mol^{-1} approximately. Therefore, two domains can be distinguished: above around 200 g mol^{-1} competitive effects are negligible and under this threshold value, release can be observed. The slope of the curve decreases for most volatile compounds suggesting that even very light compounds can be detected, which was checked for molecules such as benzene (results not presented here).

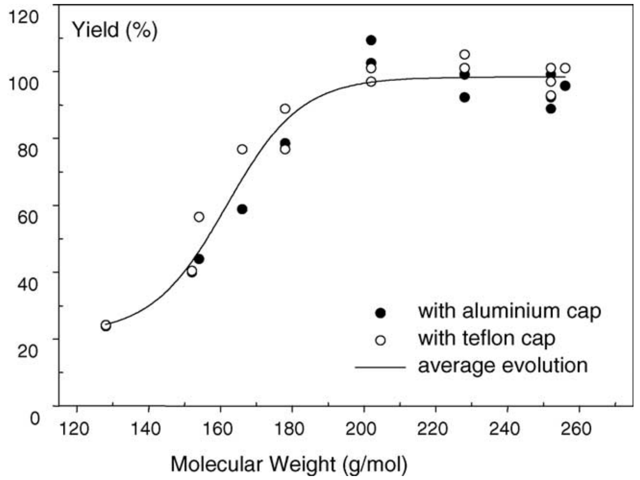

Fig. 4. Comparison of extraction yields vs. molecular weights obtained after extractions realized in vials covered with aluminium and teflon caps.

Furthermore, as molecular masses are connected with polarity, and thus with hydrophobicity, there should exist a relation between molecular weights and report of the intensities obtained after 1 and 40 h. This relation is revealed by the graph presented in Fig. 5.

A linear relation between MW and the logarithm of the ratio I_{40}/I_1 is clearly demonstrated ($R^2 = 0.962$). This confirms the trends observed in Figs. 3 and 5; molecules with MW greater than 180–200 g mol^{-1} are preferably sorbed in the twister since no release was observed ($I_{40}/I_1 > 1$ and $\log[I_{40}/I_1] > 0$ for MW > 180 g mol^{-1}). In summary, competition effects and diffusion phenomena have an opposite effect for most of compounds that leads to the existence of an

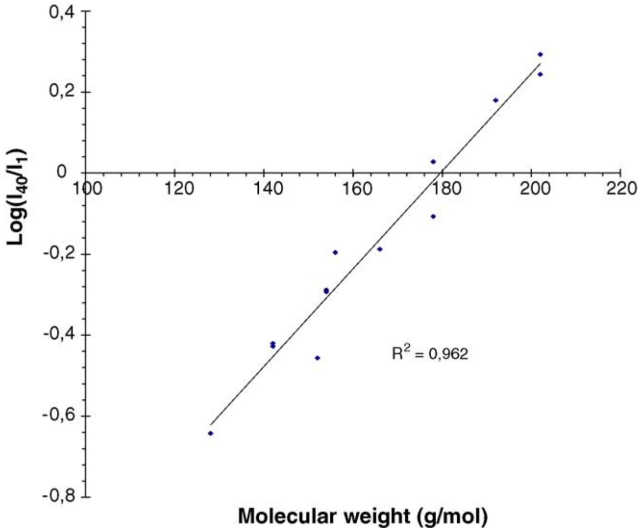

Fig. 5. Evolution of the logarithm of the MS intensities after 40 and 1 h ratio vs. the molecular weight of compounds.

Table 3
Identification and estimation of PAHs in natural seawater sampled at Saint-Anne and Moulin Blanc

Numbers	Compounds	Saint-Anne		Moulin Blanc		LOD (ng/L)
		S/N	C^* (ng/L)	S/N	C^* (ng/L)	
1	Naphthalene	13.5	1.10	5.7	0.46	0.32
2	2-Methylnaphthalene	5.5	0.26	7.1	0.34	0.19
3	1-Methylnaphthalene	3.5	0.16	5	0.23	0.18
4	Biphenyl	3.6	0.12	1.5	0.05	0.14
5	2,6-Dimethylnaphthalene	1.5	0.05	2.5	0.09	0.14
6	Acenaphthylene	2.2	0.10	2.0	0.09	0.18
7	Acenaphthene	2	0.08	1	ND	0.17
8	2,3,5-Trimethylnaphthalene	1	ND	1	ND	0.22
9	Fluorene	1.5	0.08	1	ND	0.23
10	Phenanthrene	4.2	0.24	1.8	0.10	0.23
11	Anthracene	2.8	0.29	1	ND	0.43
12	1-Methylphenanthrene	2.6	0.30	1	ND	0.47
13	Fluoranthene	2.8	0.80	1	ND	1.15
14	Pyrene	3.2	0.75	2	0.47	0.95
15	Chrysene	1	ND	1	ND	14.6
16	Benz[*a*]anthracene	2.3	8.70	1	ND	10.7

ND correspond to the non-detected compounds.

optimized extraction time estimated at 1 h (good extraction yield for a reasonable extraction time). We can imagine that this maximum should be shifted towards higher values with lower concentrations as in natural seawaters.

3.5. SBSE–TD–GC–MS analyses of natural seawater

To check the performances of the technique on natural seawater not spiked with PAHs, two samples were taken from Saint-Anne du Portzic and from the beach of the Moulin Blanc (Brest, Finistère, France) and were analyzed. Samples were taken in coastal environment at high tide at the distance of 1 m from the shore at 50 cm depth, directly in the extraction jar and analyzed consecutively (Fig. 6). A blank was done before each extraction, with the same twisters to make sure that there was no residual contamination.

These chromatograms show that the PAHs naturally present in the environment in lack of any reported contamination can be detected, even if the concentrations are below the limit of detection of the technique for most compounds.

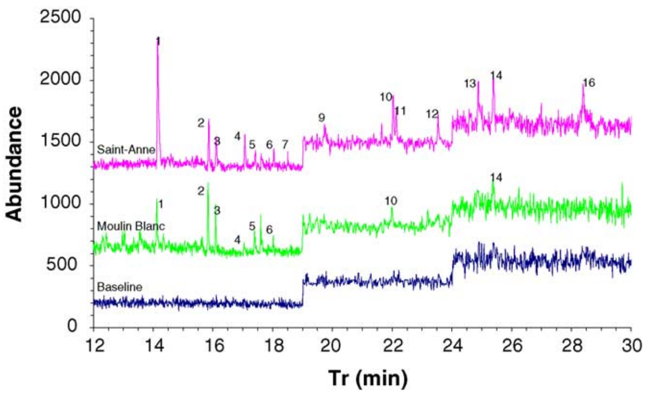

Fig. 6. GC–MS chromatograms from two coastal seawater samples in SIM mode. For figures, see Table 3.

In Table 3, calculated concentrations are noted C^* to remind S/N < 4 in major cases.

However, these results open numerous perspectives as the monitoring of river and estuarian waters ($C \sim 0.1$–50 ng/L according to [1,14,17]) and drinking water ($HAP_{flu+bbf+bgp+bap+bkf+ind} < 200$ ng/L and [benzo (a) pyrene] < 10 ng/L according to the decree no. 89-3 of January 3rd, 1989). The survey of the water quality in shellfish, oyster and fish-farming environment could also be investigated for chronic pollutions.

4. Conclusions

This study demonstrates the possibility of coupling two new technologies, the SBSE and the transportable GC–MS EM 640S. It leads to an on-site procedure able to separate, identify and quantify PAHs in water samples at concentrations around the sub-ppt level after 1 h of extraction with no manipulation nor solvent. However, these concentrations still remain a little too high for monitoring seawater quality. Therefore, the development of specific twisters and the use of a cold trap focusing system are worth being studied to decrease LODs and improve reproducibility. Elsewhere, the analysis of the signal intensities versus the extraction times showed an evolution of the relative molecular distribution inside of the absorbent phase, and more precisely a decrease of the lighter compounds. A linear relationship was obtained between the molecular weight and the logarithm of the 1 h versus 40 h signal intensity ratio. This result demonstrates the coexistence of both thermodynamic and kinetic effects even with these low concentrations of contaminants. Then, this study shows the necessity to work in the kinetic domain and questions the principle of the long way extraction procedures, as the semi-permeable membrane devices. The long- and short-extraction procedures could then be considered as complementary, first giving information about bioaccumulation, and simulating the integrated concentrations inside benthic organisms, then secondly informing about the bioavailable concentrations of analytes in the water column.

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