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Simultaneous determination of polycyclic aromatic hydrocarbons and benzene, toluene, ethylbenzene and xylene in water samples using a new sampling strategy combining different extraction modes and temperatures in a single extraction solid-phase microextraction-gas chromatography–mass spectrometry procedure

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ABSTRACT

This study proposes a new optimization approach for the simultaneous determination of polycyclic aromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene and xylene isomers (BTEX) from water samples using the solid-phase microextraction technique followed by gas chromatography–mass spectrometry (GC–MS) separation and detection. The objective of the study was to achieve compromise extraction conditions, suitable for all semi-volatile and volatile compounds, under which the amount extracted is maximized for all analytes. This was achieved by careful optimization of the fiber coating, salting-out effect, extraction time and temperature and extraction mode (headspace or direct immersion). With the optimized fiber coating – PDMS/DVB 65 μm – the other selected factors were optimized using a response surface methodology through central composite designs. As expected, the optimized results for each class of analytes varied significantly, probably due to the differences in their volatility and the equilibrium constants for the analyte/fiber coating. In order to overcome this issue, a new optimization approach was proposed based on a combination of extraction modes and extraction temperatures in a single extraction procedure. The final optimized procedure was: 48 min of extraction in direct immersion mode with the sample maintained at 80 °C followed by a further 32 min of headspace extraction with the sample temperature kept at 10 °C. The proposed procedure was compared with conventional methods based on the use of a single extraction mode and temperature (80 min of headspace extraction at 60 °C or 80 min of direct immersion extraction at 50 °C). The newly proposed method was shown to be more attractive as it extracted higher amounts of both semi-volatile and volatile compounds in a single extraction procedure compared to the conventional approaches. The optimized method was validated and excellent results were obtained.

1. Introduction

The compounds known as PAHs (polycyclic aromatic hydrocarbons) and BTEX (benzene, toluene, ethylbenzene and xylene) are among the most carcinogenic, mutagenic and toxic found in aquatic systems. There are several sources of these compounds in the environment, the main one being associated with spills involving the release of petroleum products like gasoline, diesel fuel, and lubricants, among others [1,2]. BTEX and PAH compounds are toxic to both the environment and to human health, since they can act as central nervous system depressants and even exhibit chronic toxicity. Thus, any contamination from these sources deserves attention, not only by direct contact (such as inhalation of vapors) but also from the presence of these compounds in water bodies used for human consumption [3]. In addition, PAH compounds also can be find in several other matrices, such as alcohol drinks [4], instant coffee [5], wood [6,7], food [8–10], peats [11], canned bivalves [12] and soil [13]. In this context, in order to protect groundwater, environmental agencies require the evaluation of environmental liabilities for gas stations, in which these aromatic hydrocarbons should be

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monitored and quantified [14]. There are several sample preparation techniques described in the literature for the determination of these contaminants in water, but in all cases each class of analytes is analyzed separately. These techniques include liquid–liquid extraction [15], stir bar sorptive extraction [16,17], solid phase microextraction (SPME) [18–20], and hollow fiber–liquid phase microextraction [21]. The SPME technique is extremely attractive and easy to operate. It combines the sampling and preconcentration of analytes in a single process, and enables direct desorption into the chromatographic system for analysis. The advantages of SPME compared to traditional methods of sample preparation are ease of operation, re-use of the fiber, portable system, minimal contamination and loss of the sample during transport and storage and, finally, the literature proposes numerous extraction phases [22]. Ideally, in an SPME method for trace analysis the analyte uptake by the fiber coating should be maximized while simultaneously minimizing the extraction time. However, fully achieving these two goals represents an analytical challenge, as the optimized value for a certain variable usually maximizes the analyte uptake but leads to poor sample throughput, or vice versa. Several variables need to be studied and optimized so that compromise conditions for both the thermodynamics and kinetics of the extraction process can be found. The sample temperature is a very important variable in extraction by SPME, since a high temperature increases the volatility of the analytes and facilitates their diffusion toward the fiber coating, thus shortening the equilibration time. Therefore, carrying out the extraction at a high temperature initially appears to be an excellent choice. However, the equilibrium sorption of analytes by the fiber is an exothermic process. Thus, an increase in the extraction temperature has an antagonistic effect on the thermodynamics (negative) and on the kinetics (positive) of an SPME process [23]. Another important variable is the extraction mode, which is dependent on the analyte volatility and/or on the complexity of the sample. The use of headspace extraction (HS-SPME) is the preferred mode when it is applied to volatile compounds, or when the sample is very complex and can damage the fiber coating. The extraction mode involving the direct immersion (DI-SPME) of the fiber coating in the sample is the preferred choice for samples containing analytes of low volatility, i.e., compounds for which headspace extraction takes a long time to reach equilibrium. Based on these factors it can be assumed that if a single extraction temperature and a single extraction mode are used for the extraction of a set of target analytes with very different properties, the extraction efficiency for a certain class of compounds will be improved to the detriment of others. This scenario can be observed in the literature, where BTEX [24,25] and PAH [19] are not analyzed in the same extraction procedure by SPME. Our research group has been successfully employing new optimization strategies for use in SPME in order to simultaneously maximize the extraction efficiency for analytes with different volatilities in a single extraction procedure. The application of two extraction temperatures in a single HS-SPME procedure has been demonstrated to be significantly better than the conventional procedure based on a single extraction temperature for the screening of volatiles from plant matrices, as a higher number of compounds can be reliably indentified [26]. Cold-fiber SPME (CF-SPME) was applied to extract PAHs and phthalate esters (PEs) from gaseous samples. In this case, two coating temperatures were used [27]. The extraction began with a high coating temperature to extract the semi-volatiles and finished lowering the coating temperature to extract the more volatile compounds. CF-SPME was also applied to develop a method for the simultaneous determination of PAHs and PEs from soil samples [23]. It was verified that the combination of a high temperature for the coating of the CF-SPME device applied in direct immersion mode with a further headspace extraction with the coating at a low temperature leads to much better results than traditional procedures. As a continuation of these studies, this paper proposes a new optimization strategy employing SPME based on the use of two extraction modes employing a different temperature for each, aiming at achieving the highest possible extraction efficiency for two classes of compounds with quite different volatilities (BTEX and PAHs) from water samples in a single assay. To the best of our knowledge, there are no reports in the literature on the simultaneous determination of BTEX and PAHs from water samples by SPME.

2. Experimental

2.1. Instrumentation

A Shimadzu gas chromatograph (GCMS-QP2010 Plus) equipped with an Rtx-5MS column (30 m × 0.25 mm ID × 0.25 μm thickness) manufactured by Restek (Benner Circle, Bellefonte, PA, USA) and split/splitless injector was used throughout the study. Ultrapure helium at 1 mL min^{-1} was used as the carrier gas. The column oven program was as follows: 35 °C (10 min), 20 °C min^{-1} up to 80 °C, 6 °C min^{-1} to 300 °C (10 min). Injection and ion source temperatures were both maintained at 260 °C. Desorption of the SPME fiber was fixed at 10 min. The injection was carried out in splitless mode for 2 min. After this time, the split ratio was fixed at 1:20. No carryover effect was observed. Two water baths (Microquímica, Florianópolis, Brazil), each set at a different temperature, were used in this study. SPME fibers were obtained from Supelco.

2.2. Reagents and solutions

A stock solution of BTEX containing benzene, toluene, and xylene ethybenzene each at 2000 mg mL^{-1} in methanol was obtained from Sigma–Aldrich (Milwaukee, WI, USA). The PAH stock solution containing acenaphythylene, fluorene, anthracene, phenanthrene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, indeno-1-2-3-pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene, each at 1000 mg mL^{-1} in acetone, was purchased from Supelco (Bellefonte, PA, USA). A stock solution containing the two classes of compounds was prepared at a concentration of 66.66 mg mL^{-1} using acetone as the solvent. Sodium chloride was obtained from Nuclear (Diadema, São Paulo, Brazil). All extractions were performed in 40-mL SPME vials (Supelco) containing 25 mL of aqueous sample under constant magnetic stirring.

2.3. Method optimization

Method optimization was carried out by the multivariate methodology. Central composite designs for three variables were employed to generate response surfaces. Five levels of each variable were studied, totalizing 18 experiments (including a triplicate center point). All response surfaces were mathematically best described by a quadratic model consisting of 10 coefficients rather than linear models. All of the quadratic equations generated had at least 6 degrees of freedom, determination coefficients (R^2) better than 0.9, no significant lack-of-fit and a random distribution of the model residuals. However, in order to avoid unnecessary extension of the manuscript this information is not considered in the results and discussion sections. The Statistica® 6.0 computer program was used throughout the study to process the data obtained. Method optimization consisted of four steps: (i) optimization of fiber coating; (ii) simultaneous optimization of salting-out effect and extraction time and temperature for the headspace mode; (iii) simultaneous optimization of salting-out effect and extraction time and temperature for the direct immersion mode; and (iv) simultaneous optimization of salting-out effect, total extraction time and

the fraction of the total extraction time in which the extraction will be performed in headspace mode.

2.3.1. Fiber coating optimization

Three different fibers were tested (PDMS 100 μm, PDMS/DVB 65 μm and DVB/CAR/PDMS 50/30 μm). Assays were performed using 25 mL of the aqueous solution containing the analytes at 8 μg L^{-1} with the addition of 2.0 g of NaCl. As the differences in analyte properties were previously known, a combined extraction procedure was adopted, consisting of extracting at 70 °C for 45 min in the direct mode, followed by a further 15 min of headspace extraction with the sample temperature lowered to 1 °C, totalizing 60 min of extraction.

2.3.2. HS-SPME mode optimization

The variables extraction temperature (10–80 °C), extraction time (30–120 min) and sodium chloride mass (0–9 g) were simultaneously optimized through a central composite design, totalizing 18 experiments.

2.3.3. DI-SPME mode optimization

The variables extraction temperature (10–80 °C), extraction time (30–120 min) and sodium chloride mass (0–9 g) were simultaneously optimized.

2.3.4. Combination of direct immersion and headspace modes - DI-HS-SPME

The variable percentage of extraction time in the headspace (0–100%), total extraction time (10–120 min) and sodium chloride mass (0–9 g) were simultaneously optimized. The extraction temperatures used in each mode in this part of the experiment were selected based on the optimized values obtained in steps (ii) and (iii), that is, 80 °C for direct immersion mode and 10 °C for the headspace mode. In this step, the extraction began with the DI-SPME mode. After the period determined by the experimental design, the fiber was inserted in the sample headspace and the vial was immediately transferred from the bath at 80 °C to the bath at 10 °C, in which the total extraction time of the design was completed.

2.4. Method comparison

In order to compare the three methods developed, the following sets of optimized conditions were carried out: (i) DI-SPME: 80 min in direct immersion mode at 50 °C and 6 g NaCl; (ii) HS-SPME: 80 min in the headspace at 60 °C and 4 g NaCl; (iii) DI-HS-SPME: 48 min at 80 °C in direct immersion mode, followed by a further 32 min at 10 °C in the headspace with 6 g NaCl.

2.5. Method validation and application

Validation of the method was carried out by obtaining the main figures of merit, that is, the linear range, linear correlation coefficient, detection and quantification limits, evaluated as three and ten times the signal-to-noise ratio, respectively, precision, evaluated as relative standard deviation, and accuracy, evaluated as % recovered in recovery tests. The new optimization method proposed in this study was applied to two river water samples (Tubarão River, Tubarão, Santa Catarina, Brazil and Araranguá River, Araranguá, Santa Catarina, Brazil), bottled mineral water purchased in a local market and tap water collected in Florianópolis, Santa Catarina, Brazil.

3. Results and discussion

3.1. Method optimization

3.1.1. Fiber coating optimization

Fiber optimization is an important part of SPME method development, as a proper choice can improve both the sensitivity and selectivity of the extraction. Three different commercially available SPME fibers were tested: PDMS 100 μm, PDMS/DVB 65 μm and DVB/CAR/PDMS 50/30 μm. The conditions used in these experiments are described in Section 2. Fig. 1 shows the results obtained.

As can be seen in Fig. 1, a greater number of volatile compounds (from 1 to 5 in Fig. 1) were best extracted by the DVB/CAR/PDMS fiber. This was probably due to the presence of carboxen (activated carbon), which is suitable for the sorption of light (volatile) molecules. For the heavier (semi-volatile) compounds (11–16), the PDMS 100 μm fiber showed excellent extraction ability. As these are also the most hydrophobic compounds of the analytes evaluated, this result was to be expected, since PDMS is a non-polar coating. The PDMS/DVB fiber presented an intermediate behavior compared to the other fibers evaluated and was therefore chosen as the optimal fiber coating to continue the study. This result can be explained by the fact that, for the analytes evaluated, this fiber contains a more suitable combination of liquid (PDMS) and solid (DVB) sorbent materials compared to the other fibers evaluated, leading to an equilibrated sorption of both volatile and semi-volatile compounds.

3.1.2. Multivariate optimization of DI-SPME extraction conditions

The variables extraction time (10–120 min) and temperature (10–80 °C) and the effect of salting-out through the NaCl mass (0–9 g) were simultaneously optimized by means of a central composite design. The response used as the input data was obtained by calculating the geometric mean of the set of 19 normalized peak areas corresponding to the target analytes. Thus, this response obtained represents a compromise response for all the analytes. Fig. 2 shows the response surfaces obtained. One can observe that the surface reaches a maximum after around 80 min of extraction, and the optimum conditions of NaCl mass and extraction temperature are 6 g and 50 °C, respectively.

However, as the response surfaces represent compromise conditions for all analytes, it should be noted that they were plotted for each analyte separately. In the case of the analytes for which the optimal conditions were similar, the peak areas were transformed into a single response by calculating the geometric mean and new response surfaces were plotted. These results are shown in Fig. 3. In Fig. 3A the set of analytes which presented similar optimal conditions were the more volatile BTEX compounds, and Fig. 3B represents the behavior for the remaining PAH compounds. It can be observed that the effect of both extraction time and temperature varied significantly for the two groups, as expected. For the BTEX compounds (Fig. 3A), lower extraction temperatures (10 °C) improved analyte uptake. Conversely, for the PAH compounds (Fig. 3B) their responses increased at higher temperatures (80 °C).

In general, it can be observed that on comparing the groups the optimal extraction conditions are significantly different (especially extraction temperature) and that any compromise condition will reduce the extraction efficiency of one group to the detriment of the other.

Based on these results, it is clear that a new sampling strategy is required to improve the extraction of all target analytes.

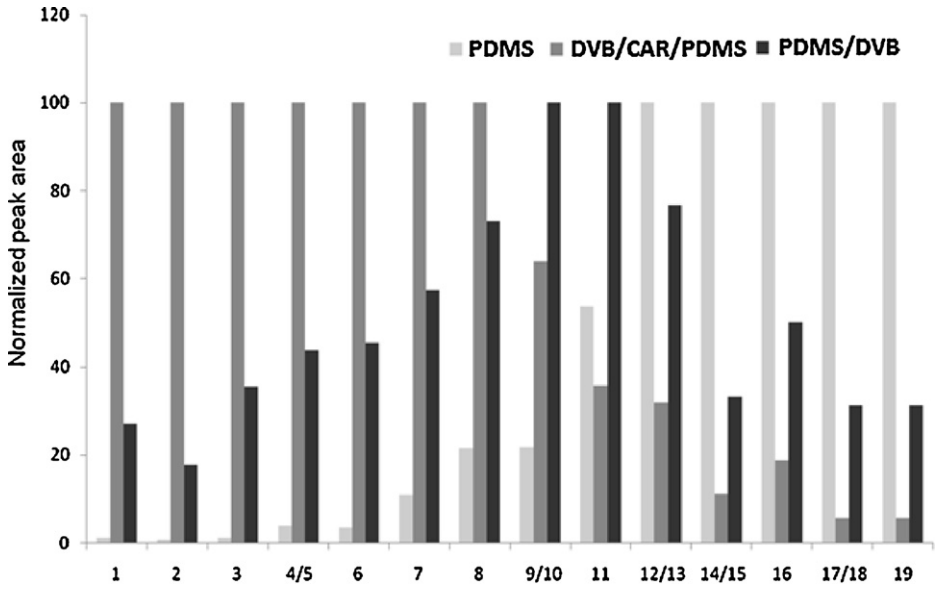

Fig. 1. Comparison of the responses obtained in the optimization of the fibers: PDMS, DVB/CAR/PDMS, PDMS/DVB for analysis of BTEX and PAH by DI-HS-SPME. Analytes: 1 – benzene, 2 – toluene, 3 – ethylbenzene, 4 – p-xylene, 5 – m-xylene, 6 – o-xylene, 7 – acenaphythylene, 8 – fluorene, 9 – anthracene, 10 – phenanthrene, 11 – pyrene, 12 – benzo(a)anthracene, 13 – chrysene, 14 – benzo(k)fluoranthene, 15 – benzo(a)pyrene, 16 – benzo(b)fluoranthene, 17 – indeno-1-2-3-pyrene, 18 – dibenzo(a,h)anthracene, 19 – benzo(g,h,i)perylene.

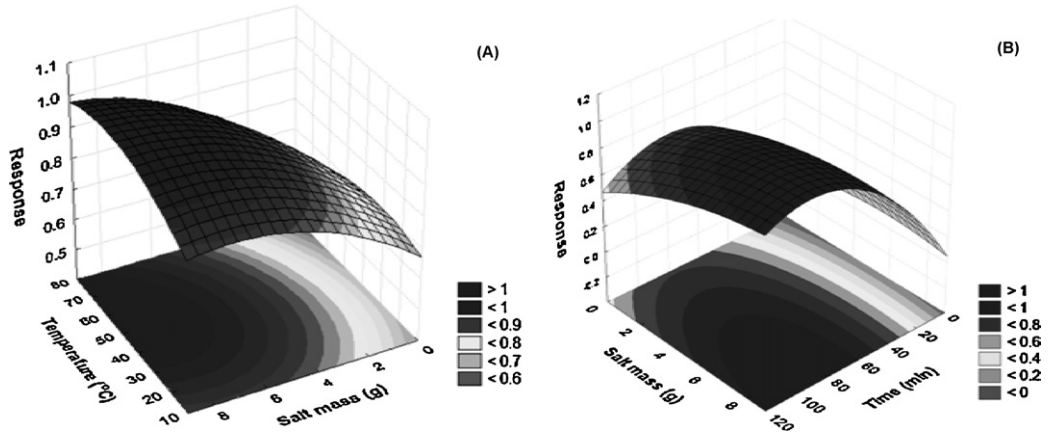

Fig. 2. Response surface (A) temperature versus salt mass and (B) time versus salt mass obtained in the extraction of analytes by DI-SPME.

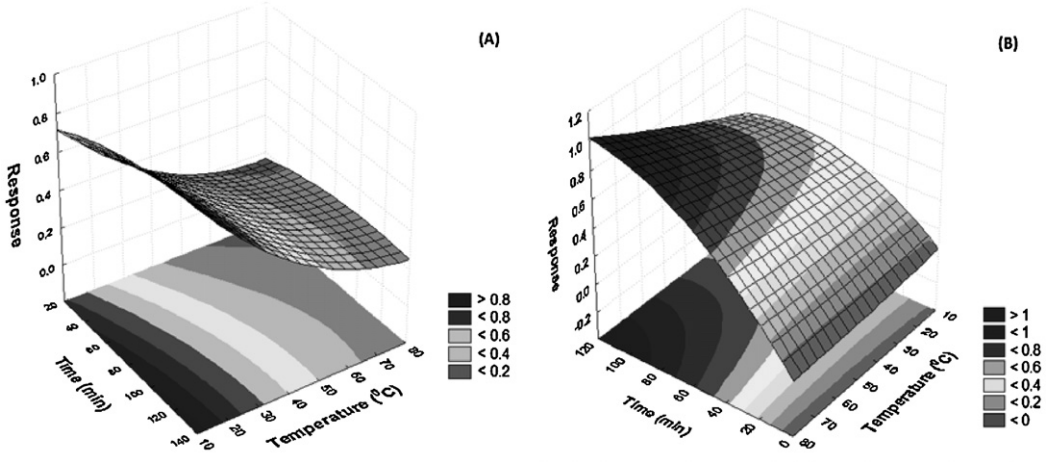

Fig. 3. Response surface of temperature versus time for (A) Group 1 – benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene. (B) Group 2 – acenaphythylene, fluorene, anthracene, phenanthrene, pyrene, benzo(a)anthracene, chrysene, benzo(K)fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, indeno-1-2-3-pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene (Mode DI-SPME).

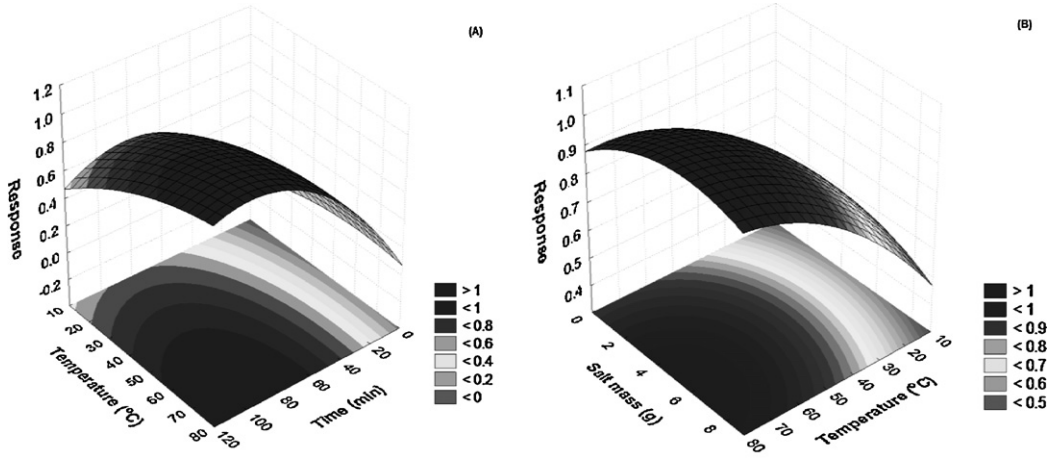

Fig. 4. Response surface (A) time versus temperature and (B) salt mass versus temperature obtained in the extraction of all the target analytes by HS-SPME.

3.1.3. Multivariate optimization of HS-SPME extraction conditions

Extraction time (30–120 min) and temperature (10–80 °C) and the effect of salting-out through the NaCl mass (0–9 g) were simultaneously evaluated by means of a central composite design. Fig. 4 shows the main results obtained. As can be observed, the compromise headspace extraction conditions for all the analytes are 5 g NaCl and extraction time and temperature of 60 °C and 80 min, respectively.

In order to highlight the differences in the behavior of the analytes in relation to the extraction conditions (especially temperature) in headspace mode, the analytes which presented similar optimized extraction conditions were plotted in a single response surface, as shown in Fig. 5.

As expected, the responses were again divided into two groups of analytes: BTEX (Fig. 5A) and PAHs (Fig. 5B). For BTEX, the extraction time representing the lower level (30 min) was sufficient to reach equilibrium, and 10 °C was the optimal extraction temperature. Conversely, 80 °C was the optimized extraction temperature for the semi-volatile PAHs, with an equilibration time of over 80 min.

Both the DI-SPME and HS-SPME optimum conditions revealed that it is not possible to reach a satisfactory compromise extraction condition for all of the analytes as their volatilities/equilibrium constants with the fiber coating are significantly different.

It should be mentioned that the use of higher temperatures in the DI-SPME mode was more suitable for the semi-volatile compounds, and lower extraction temperatures in the HS-SPME mode led to better responses for the volatile compounds. Based on these findings the new optimization strategy proposed in this study consisted of using both extraction modes in the same procedure, each employing the previously determined optimized value for the extraction temperature.

3.1.4. Multivariate optimization of the combination of direct immersion and headspace modes: DI-HS-SPME

The optimization of the salting-out effect, total extraction time and the fraction of this time in which the SPME fiber is exposed to the sample headspace was multivariately evaluated by means of a central composite design. The salting-out effect was evaluated by varying the NaCl mass from 0 to 9 g. The total extraction time (defined as the sum of the extraction times in the DI-SPME and HS-SPME modes) was varied from 10 to 120 min. The percentage of time in HS-SPME mode was studied from 0 (total extraction time performed in DI-SPME) to 100% (total extraction time in HS-SPME). During the period in the DI-SPME mode the sample was submitted to 80 °C, and for the HS-SPME mode the sample temperature was

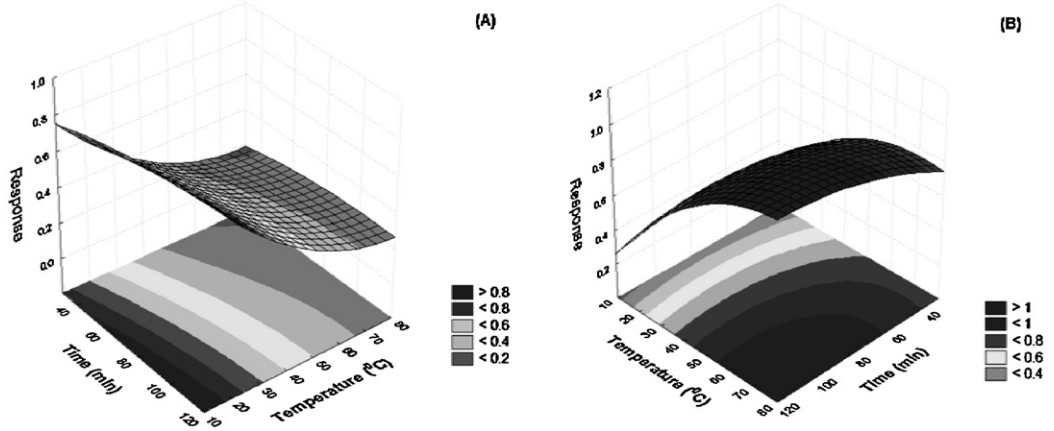

Fig. 5. Response surface of temperature versus extraction time for (A) Group 1 – benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene. (B) Group 2 – acenaphythylene, fluorene, anthracene, phenanthrene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, indeno-1-2-3-pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene (Mode HS-SPME).

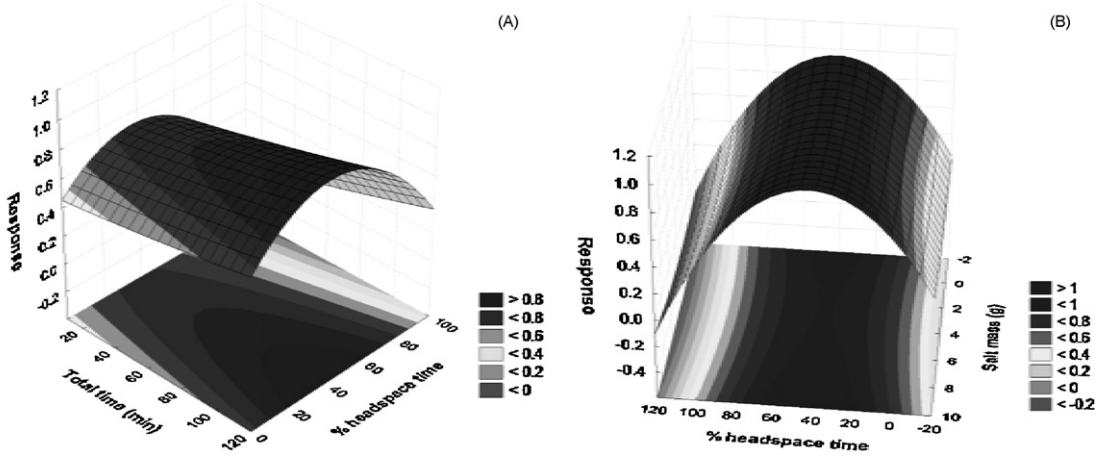

Fig. 6. Response surfaces (A) for total time versus %headspace time and (B) for salt mass versus % headspace time obtained in the extraction of analytes by DI-HS-SPME.

kept at 10 °C. This was achieved with the aid of two water baths. The response surfaces can be visualized in Fig. 6.

Fig. 6A shows that applying more than 80 min of extraction does not increase the response significantly. Thus, taking into account the sensitivity and sample throughput, 80 min was chosen as the total extraction time. Applying 80 min as the total extraction time, around 60% (48 min) should be applied in DI-SPME and 40% (32 min) in HS-SPME mode. In relation to the NaCl mass (Fig. 6B) an intermediate value was adopted as the optimum, that is, 6 g NaCl/25 mL sample.

A possible explanation for the need for the higher extraction time in the DI-SPME mode compared with the HS-SPME mode can be given in terms of the determining step of mass transfer of the analytes from the sample to the fiber coating. For a better extraction of the analytes from the sample headspace the equilibrium should be reached faster, since the rate determining step in this case is the evaporation of the compounds from the aqueous sample or their diffusion through the coating. The rate determining step for the semi-volatiles could be their diffusion through the boundary layer around the fiber in aqueous solution or the analyte diffusion through the fiber coating, which are slower steps and are favored in direct immersion mode.

3.2. Method comparison

In order to better visualize the differences between the method proposed in this study based on the use of two extraction modes and two extraction temperatures in a single procedure and the conventional methods based on the use of a single extraction mode and temperature, three extraction conditions were applied. The results can be seen in Fig. 7.

For the DI-HS-SPME method, the conditions were: 6 g NaCl, 48 min in DI-SPME mode at 80 °C followed by 32 min in HS-SPME mode at 10 °C. The conditions for the HS-SPME method were: 4 g NaCl and 80 min of extraction at 60 °C. DI-SPME was conducted with 6 g NaCl and 80 min of extraction at 50 °C.

In a general way, one can observe from Fig. 7 that neither DI-SPME nor HS-SPME extraction modes alone satisfactorily extracted all of the analytes simultaneously. However, the DI-HS-SPME extraction method proposed in this study was shown to be the most suitable method for most of the analytes evaluated, as it integrates in a single extraction process two extraction modes, each with its optimized extraction temperature. Thus, the optimum extraction conditions are reached for analytes with very different volatilities/equilibrium constants with the coating in a single extraction

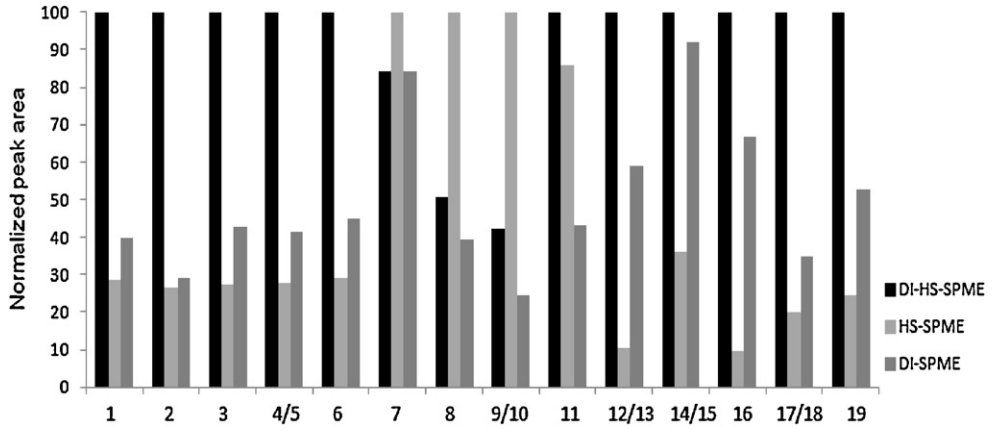

Fig. 7. Responses obtained in the comparison of the methodologies: HS-DI-SPME, HS-SPME and DI-SPME. Analytes: 1 – benzene, 2 – toluene, 3 – ethylbenzene, 4 – p-xylene, 5 – m-xylene, 6 – o-xylene, 7 – acenaphythylene, 8 – fluorene, 9 – anthracene, 10 – phenanthrene, 11 – pyrene, 12 – benzo(a)anthracene, 13 – chrysene, 14 – benzo(k)fluoranthene, 15 – benzo(a)pyrene, 16 – benzo(b)fluoranthene, 17 – indeno-1-2-3-pyrene, 18 – dibenzo(a,h)anthracene, 19 – benzo(g,h,i)perylene.

Table 1
Analytical figures of merit for the DI-HS-SPME method developed in this study for the determination of BTEX and PAH compounds from aqueous samples.

Analytes	LOD ($\mu g L^{-1}$)	Linear range ($\mu g L^{-1}$)	R	RSD[a]%	RSD[b]%
Benzene	0.15	0.6–10	0.99975	1.7	6.5
Toluene	0.10	0.3–10	0.99986	1.9	10.3
Ethylbenzene	0.07	0.3–10	0.99987	16.1	11.3
p-Xylene/m-xylene	0.08	0.3–10	0.99988	16.2	11.5
o-Xylene	0.30	1–10	0.99961	11.6	3.2
Acenaphythylene	0.27	1–10	0.99886	1.5	3.8
Fluorene	0.20	0.6–10	0.99909	12.9	2.5
Anthracene/phenanthrene	0.28	1–10	0.99862	18.8	1.6
Pyrene	0.27	1–10	0.99958	24.9	3.2
Benzo(a)anthracene/chrysene	0.17	0.6–10	0.99972	17.2	11.2
Benzo(k)fluoranthene/benzo(a)pyrene	0.32	1–10	0.99030	14.9	10.1
Benzo(b)fluoranthene	0.24	0.9–10	0.99613	15.1	11.1
indeno-1-2-3-Pyrene/dibenzo(a,h)anthracene	0.31	1–10	0.99914	0.6	4.7
benzo(g,h,i)perylene	0.30	1–10	0.99904	6.8	12.6

[a] RSD – 1 $\mu g L^{-1}$; $n = 5$.
[b] RSD – 10 $\mu g L^{-1}$; $n = 5$.

Table 2
Spiked concentrations and recoveries determined for the application of the newly developed method with separation/detection by GC–MS. ND (not detected), DE (detected). Detected means concentration between detection and quantification limits.

Araranguá river				Tubarão river			Tap water			Mineral bottled water		
Analytes[c]	Sample ($\mu g L^{-1}$)	Rec[a] (%)	Rec[b] (%)	Sample ($\mu g L^{-1}$)	Rec[a] (%)	Rec[b] (%)	Sample ($\mu g L^{-1}$)	Rec[a] (%)	Rec[b] (%)	Sample ($\mu g L^{-1}$)	Rec[a] (%)	Rec[b] (%)
1	ND	81	63	DE	77	60	ND	110	120	ND	103	110
2	DE	115	98	ND	108	85	ND	94	98	ND	89	93
3	DE	70	85	DE	66	60	ND	110	74	ND	120	99
4/5	DE	71	83	DE	65	61	ND	111	73	ND	113	100
6	ND	90	60	ND	102	70	ND	99	101	ND	111	74
7	ND	88	61	ND	68	60	ND	96	97	ND	81	82
8	ND	78	60	ND	78	83	ND	65	69	ND	60	71
9/10	ND	81	61	ND	99	101	ND	98	99	ND	60	66
11	DE	60	99	DE	110	120	ND	61	78	ND	72	90
12/13	ND	83	104	ND	99	104	ND	109	108	ND	90	93
14/15	ND	75	83	ND	84	68	ND	85	68	ND	89	111
16	DE	70	120	DE	91	101	ND	92	101	ND	97	106
17/18	DE	110	115	DE	120	116	ND	76	84	ND	68	77
19	DE	109	115	DE	117	117	ND	77	83	ND	68	78

[a] 1 $\mu g L^{-1}$.
[b] 5 $\mu g L^{-1}$.
[c] *Analytes*: 1 – benzene, 2 – toluene, 3 – ethylbenzene, 4 – p-xylene, 5 – m-xylene, 6 – o-xylene, 7 – acenaphythylene, 8 – fluorene, 9 – anthracene, 10 – phenanthrene, 11 – pyrene, 12 – benzo(a)anthracene, 13 – chrysene, 14 – benzo(k)fluoranthene, 15 – benzo(a)pyrene, 16 – benzo(b)fluoranthene, 17 – indeno-1-2-3-pyrene, 18 – dibenzo(a,h)anthracene, 19 – benzo(g,h,i)perylene.

procedure, allowing the analyte uptake to be simultaneously maximized.

3.3. Method validation and application

The DI-HS-SPME proposed in this study was validated by obtaining the main analytical figures of merit. The results can be visualized in Table 1.

Satisfactory detection and quantification limits (3 and 10 times the signal-to-noise ratio, respectively) were determined – 0.07–0.32 $\mu g L^{-1}$. Precision was evaluated in two concentrations through the relative standard deviation. Satisfactory values of between 1% and 25% were obtained.

The proposed method was applied in the determination of BTEX and PAHs in river, tap and bottled mineral water samples. Since the concentrations of the analytes of the samples were all below the quantification limits, the samples were spiked with the analytes to evaluate the method accuracy.

The results can be visualized in Table 2. All of the compounds presented satisfactory recoveries at the two concentration levels studied. This demonstrates the good reliability and potential of the newly developed method.

4. Conclusions

The new optimization approach proposed in this study, which was based on the use of two extraction modes and two extraction temperatures in a single assay, was demonstrated to be an excellent alternative to the conventional SPME extraction protocols, as it was able to extract compounds with quite different volatilities in the same procedure by the SPME technique. This study was also able to show that to use all of the potential of the SPME technique it is necessary to apply new optimization strategies rather than the conventional ones. By doing this, it was shown that classes of compounds with significantly different extraction conditions can be extracted in a single assay, increasing the sample throughput. This approach can be easily extended to other combinations of compounds and matrices.

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