



# A new approach based on a combination of direct and headspace cold-fiber solid-phase microextraction modes in the same procedure for the determination of polycyclic aromatic hydrocarbons and phthalate esters in soil samples

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## ABSTRACT

This study describes a new approach to cold-fiber solid-phase microextraction (CF-SPME) based on a combination of different extraction modes in the same extraction procedure. Also, the high quantity of water required to facilitate both the desorption of analytes from the matrix and their transport to the fiber coating is reported. The extraction mode was changed from the direct to the headspace mode in a single extraction while manipulating the extraction times and coating temperature to improve the extraction of compounds with different volatilities. Compounds with low volatility were better extracted in the direct mode, while the headspace mode was more appropriate for volatile compounds. Polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PEs) in sand or soil samples were used as model compounds and matrices in this study. The optimized conditions were: sample pH in the range of 4–7, addition of 12 mL of 194 g L<sup>-1</sup> aqueous NaCl solution in a 15 mL vial, and 80 min total extraction time with a sample temperature of 90 °C (50 min in direct mode with coating at 90 °C followed by 30 min in headspace mode with coating at 30 °C). The proposed procedure was compared with conventional CF-SPME (with and without addition of water) and was found to be more effective for all the analytes, since it is capable of extracting both heavier and lighter compounds from soil samples in a single extraction procedure. The use of an excess of water and a combination of extraction modes in the same CF-SPME procedure are the main factors responsible for this enhancement. The proposed method was applied to the extraction of PAHs and PEs in spiked soil samples and excellent results were obtained for most of the compounds evaluated.

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## 1. Introduction

The solid-phase microextraction (SPME) technique [1] is based on the partitioning of the analytes between the diverse phases of the system and the fiber coating. Considering a tightly closed extraction vial containing an aqueous sample of volume  $V_m$ , a headspace volume ( $V_{hs}$ ) and the fiber with a coating volume  $V_f$ , the amount extracted by the coating  $n_f$  under equilibrium conditions is given by [2,3]:

$$n_f = \frac{K_{hsf}K_{mhs}V_fV_mC_0}{V_m + K_{mhs}V_{hs} + K_{mhs}K_{hsf}V_f} \quad (1)$$

In Eq. (1),  $K_{mhs}$  is the partition coefficient representing the analyte distribution between the aqueous matrix and the headspace,  $K_{hsf}$  is the partition coefficient representing the analyte distribution between the headspace and the fiber coating and  $C_0$  is the initial concentration of the analyte in the sample. According to Eq. (1), the amount of analyte extracted by the fiber coating  $n_f$  at equilibrium is directly proportional to the analyte concentration in the sample, which makes quantitative analysis by SPME feasible. It is also clear from Eq. (1) that regardless of the location of the fiber coating (in the condensed phase or in the sample headspace), the amount extracted by the coating  $n_f$  is the same under equilibrium conditions, considering that all the other terms remain constant [4].

Thus, the choice of extraction mode will be dependent on the analyte volatility and/or sample complexity. The use of HS-SPME is the preferred mode when volatile compounds (high  $K_{mhs}$ ) are the target analytes and/or for low-volatility compounds when the sample may contain substances that can damage the fiber coating. Alternatively, the direct extraction mode can be used for liquid

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samples with low-volatility analytes, that is, compounds for which headspace extractions would take a long time to reach equilibrium.

Although SPME has been successfully used in the determination of several analytes in solid samples [5–9], this task represents a challenge due to the high adsorptive capacity of these matrices [10]. In this case, the extraction must be carried out in the sample headspace mode, otherwise irreversible damage to and/or breakage of the fiber may occur. Other factors which influence the efficiency of analyte extraction from a solid matrix, and should thus be evaluated, include sample mass, water addition, pH of the suspension formed, ionic strength and extraction time and temperature. Among these factors, the sample temperature is one of the most important, since a high temperature will influence not only the rate but also the extent of desorption of the analytes from the solid sample [11]. However, it is well known that the sorption of the analytes by the coating is an exothermic process and thus this variable has a dual effect on the extraction efficiency. The extraction temperature must therefore be carefully evaluated empirically. The combination of the aforementioned points led to the conclusion that, particularly for heavier analytes, a method using regular SPME fibers can suffer considerable lack of sensitivity when dealing with complex solid samples, since the extraction temperature required to release the analytes from the matrix may be too high for the sorption of the analytes by the fiber coating to prevail over desorption.

In this context, a cold-fiber solid-phase microextraction (CF-SPME) technique was developed to minimize the exothermic effect of SPME [12]. In the CF-SPME device the sample can be heated to a high temperature and the coating can be simultaneously cooled, with a significant increase in the matrix-to-coating partition coefficients of the analytes. The CF-SPME device was miniaturized and automated in 2006 [13].

Zhang and Pawliszyn [12] used CF-SPME to extract BTEX compounds from clay soil and sand samples. They reported a significant increase in the amount extracted by the coating as the amount of water in the clay matrix increased from zero (recoveries of 6–27% with sample and coating temperatures of 250 °C and 30 °C, respectively) to five (recoveries of 80–98% with sample and coating temperatures of 170 °C and 30 °C, respectively) percent. In conclusion, for the compounds of relatively high volatility evaluated, a combination of high temperature and low sample humidity was required to achieve good quantitative results.

Ghiasvand et al. [14] developed a method to quantify seven PAHs in sand and sediment samples by CF-SPME. According to the authors, a combination of 40 min of extraction at 150 °C with the coating at 5 °C led to reasonable results for the first five target analytes without water addition. However, for the two heaviest compounds, even the addition of 50  $\mu\text{L}$  of water to 50 mg of sample led to an increase in the recovery from 40% to 52%. In addition, the authors reported a very high pressure in the extraction vial due to water evaporation at 150 °C, which clearly represents a high source of inaccuracy in the results due to leaking. The authors solved this problem by increasing the extraction time to 180 min, thus obtaining a quantitative extraction without water addition for these two heavier compounds.

From the results of the aforementioned papers it can be concluded that the use of a high temperature difference between the sample and the coating does not ensure the successful application of CF-SPME. The analytes must be released from the matrix in order to be available for extraction by the coating. Therefore, a careful evaluation of sample temperature, extraction time and water addition are necessary to obtain the highest performance of the CF-SPME device. These variables, along with sample pH, salting-out effect and coating temperature, can interact strongly with each other, and it seems clear that a simple univariate optimization approach is not suitable to evaluate these factors. Instead,

a response surface optimization methodology, i.e., a multivariate tool, could be used to study these variables, such as those used for CF-SPME optimization [15,16].

The need to develop a reliable method for a high number of compounds in a single extraction procedure within a reasonable time and the challenge of dealing with complex samples such as soil, together with the need to increase the applicability and show the potential of the CF-SPME device, were the main reasons for carrying out this study. Thus, a series of novelties are presented in terms of the CF-SPME technique in order to solve the problems related to vial leakage due to water addition: (1) the use of a high amount of water to aid the desorption of analytes from the matrix without encountering vial leakage problems; (2) the use of the direct extraction mode of CF-SPME, which was feasible due to the use of an unbreakable stainless steel support and relatively inexpensive PDMS membrane used as the coating material; and, most importantly, (3) the use of a combination of extraction modes in a single extraction procedure, initially in direct mode for the sorption of the heavier compounds followed by headspace extraction of the lighter analytes.

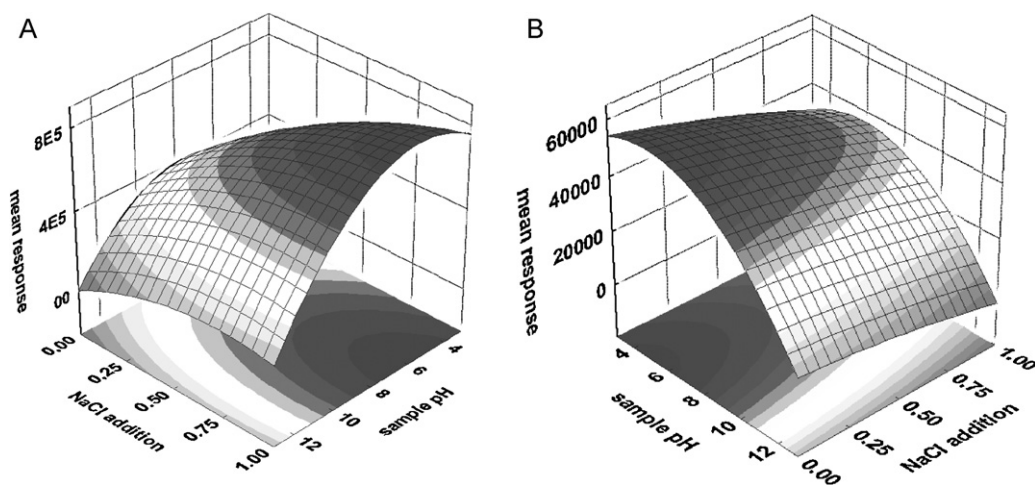
## 2. Experimental

### 2.1. Instrumental

Chromatographic analysis was carried out in a Shimadzu GC-14B gas chromatograph (Kyoto, Japan) equipped with a split-splitless injector and flame ionization detector (FID). Ultra pure  $\text{N}_2$  was used as the carrier and make-up gas at 1.8 and 40  $\text{mL min}^{-1}$ , respectively. Ultra pure  $\text{H}_2$  and synthetic air were used for FID detection. In all runs, the injector and detector temperatures were set at 300 and 320 °C, respectively. The oven temperature program for the separation of the analytes was: 50 °C (1 min), increasing at 6 °C  $\text{min}^{-1}$  up to 300 °C (10 min). The separation of analytes was carried out in an OV-5 capillary column (OV Specialty Chemical, 30 m length, 0.25 mm internal diameter and 0.25  $\mu\text{m}$  film thickness).

### 2.2. Reagents and materials

A stock solution of eighteen PAHs including 1-methylnaphthalene, anthracene, fluoranthene, naphthalene, acenaphthene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, acenaphthylene, pyrene, benzo(ghi)perylene, fluorene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, 2-methylnaphthalene and phenanthrene in benzene: dichloromethane (50:50) was obtained from Supelco (Bellefonte, PA, USA) at a concentration of 2000  $\mu\text{g mL}^{-1}$ . Dimethylphthalate (DMP), diethylphthalate (DEP), dibutylphthalate (DnBP), bis(2-ethylhexyl)phthalate (DEHP), bis(2-ethylhexyl)adipate (DEHA), and benzyl butyl phthalate (BBP) were obtained from Supelco at 500  $\mu\text{g mL}^{-1}$  in methanol. A stock solution containing the two classes of compounds was prepared at 100  $\mu\text{g mL}^{-1}$  in methanol. Sodium chloride was obtained from Nuclear (Diadema, São Paulo, Brazil), which was left in the muffle at 350 °C (with occasional opening of the door) for at least 48 h to remove any impurities before used. The CF-SPME device, temperature controller and solenoid valve used in this study were the same as those described in previous papers [13–16]. The extractor phase used was a PDMS membrane with 178  $\mu\text{m}$  wall thickness and 1 cm length. Liquid carbon dioxide was used to cool the fiber coating. The elution peaks followed the order: (1) naphthalene, (2) 1-methylnaphthalene, (3) 2-methylnaphthalene, (4) acenaphthene, (5) dimethylphthalate, (6) acenaphthylene, (7) fluorene, (8) diethylphthalate,



**Fig. 1.** Response surfaces obtained through optimization of NaCl addition and buffer pH. On the NaCl axis 0 indicates no salt addition and 1 indicates NaCl saturation. (A) Response surface for the three lightest PEs and (B) response surface for the three heaviest PEs. Extraction time: 60 min. Fiber temperature:  $35 \pm 5^\circ\text{C}$ . Sample temperature:  $90^\circ\text{C}$ . Aqueous solution volume: 2 mL.

(9) phenanthrene, (10) anthracene, (11) dibutylphthalate, (12) fluoranthene, (13) pyrene, (14) benzylbutylphthalate, (15) di(2-ethylhexyl)adipate, (16) benzo(a)anthracene, (17) chrysene, (18) di(2-ethylhexyl)phthalate, (19) benzo(b)fluoranthene, (20) benzo(k)fluoranthene, (21) benzo(a)pyrene, (22) indeno(1,2,3-cd)pyrene, (23) dibenz(a,h)anthracene, and (24) benzo(ghi)perylene. Peaks 8 and 9, 15 and 16, 18–20, and 22 and 23 were co-eluted and were therefore analyzed considering the sum of their peak areas.

### 2.3. Experimental procedure and optimization strategy

All optimization steps were carried out by weighing 50 mg of silica or soil into 15 mL SPME vials with screw tops and PTFE silicone septa. An appropriate volume of the stock solution ( $5\ \mu\text{l}$  of the stock solution at  $100\ \mu\text{g mL}^{-1}$  in the case of the optimization steps and repeatability study) was added to the silica or soil samples. The vial was rapidly closed and kept in a freezer at  $-20^\circ\text{C}$  for at least 48 h for stabilization. For the analysis, the vial was removed from the freezer and the required volume of aqueous phosphate buffer at a final concentration of  $5\ \text{mmol L}^{-1}$  or aqueous sodium chloride solution at the desired pH was transferred to it by means of a micropipette. A magnetic stir bar was placed in the vial, which was tightly closed and submitted to the extraction procedure. For all experiments constant magnetic stirring was used and a sample temperature of  $90^\circ\text{C}$  was employed to minimize leaking of the analytes.

Three procedures were optimized through central composite designs where more than one variable was simultaneously evaluated for later comparison.

#### 2.3.1. CF-SPME headspace mode

The simultaneous effect of sample pH and salt addition on the extraction efficiency was studied. In this case, aqueous buffer (sodium phosphate at a final concentration of  $5\ \text{mmol L}^{-1}$ ) solutions were prepared at pH values of 3, 8 and 14 with NaCl concentrations ranging from no addition to saturation. The objective of this study was to check whether any combination of sample pH and NaCl concentration could hydrolyze the PEs. Also, the simultaneous optimization of the water volume (0–12 mL) and NaCl concentration (zero to saturation) was evaluated. Finally, the effect of extraction time (15–60 min) and coating temperature ( $15$ – $75^\circ\text{C}$ ) on the extraction efficiency was studied.

#### 2.3.2. CF-SPME direct mode

The effect of extraction time and coating temperatures on the extraction efficiency was evaluated. Coating temperatures of  $90^\circ\text{C}$  (no cooling) and  $60^\circ\text{C}$  were selected to carry out this study. Several combinations of extraction times (from 30 to 160 min) were evaluated with the coating temperature kept initially at  $90^\circ\text{C}$  for a predetermined period. The total extraction time was then varied with the coating at  $60^\circ\text{C}$ . Also, the effect of NaCl concentration (no addition to saturation) on the extraction efficiency was studied.

#### 2.3.3. Combination of direct and headspace CF-SPME

Simultaneous optimization of the NaCl concentration, total extraction time and the fraction of the total extraction time for which the coating is exposed to the headspace was carried out. These factors were simultaneously optimized varying the NaCl concentration from zero to saturation, total extraction time from 30 to 120 min, and the fraction of total extraction time in headspace mode from 0 (all the time in direct mode) to 100% (all the time in headspace mode).

## 3. Results and discussion

The main focus of this proposal is to maximize the amount of all target analytes extracted from a complex sample within a reasonable time without encountering problems with leakage due to the use of an excess of water. Throughout the study, response surfaces were plotted for each of the target analytes, and the optimal conditions were compared. For some compounds the best extraction conditions were similar, and the set of responses (peak area) for this group of analytes was transformed into a single response by calculating the geometric mean (mean response). Thus, the influence of the extraction conditions for each group of analytes was better understood, also facilitating the presentation of the results and their discussion.

### 3.1. Optimization CF-SPME headspace mode

The main objective of studying the sample pH and ionic strength together was to evaluate whether the PEs could be hydrolyzed, since a high extraction temperature is employed ( $90^\circ\text{C}$ ) throughout the study. Thus, only PEs were considered.

Fig. 1 clearly shows that sample pH must be controlled, since the analytical signal is greatly influenced by this variable. It can also be seen that, for all of the six PEs, a pH higher than 8 produces



a strong decrease in the amount extracted, probably due to hydrolysis of the PEs. Thus, in further experiments a sample pH range of 4–7 was adopted. Sodium chloride addition led to different effects depending on the volatility of the PEs, as can be seen in Fig. 1. Saturation with NaCl provided the best extraction conditions for the three lightest PEs, while for the three heaviest PEs salt should not be used. The behavior for the heaviest PEs can be explained by the increase in sample viscosity as the NaCl concentration increases. In addition, the peak areas for the three heaviest PEs were considerably lower than those for the three lightest, indicating that direct extraction of the heavier PE compounds may be the most suitable mode.

The effect of water volume and NaCl concentration was considered for both PEs and PAHs. The target compounds were clearly separated into two groups based on their peak intensities. In the first group are the compounds eluting prior to 213 °C, for which analytical response was satisfactory. The second group contains the compounds with peaks eluting between 213 and 300 °C, for which the response was very low. This behavior can be explained by the fact that even at 90 °C there is a low evaporation rate for the heavier compounds from the condensed phase to the sample headspace, and this becomes the rate determining step of the analyte transfer from the sample to the fiber coating. This result indicates that for these compounds the direct extraction mode would produce faster extractions. For this reason, Fig. 2 shows only the combined responses for the first group of “lighter” analytes.

In Fig. 2 the strong effect of water (or NaCl aqueous solution) on the amount extracted can be noted. This result can be attributed to the fact that water molecules deactivate silica particles, causing them to bind with less intensity to the analytes. Furthermore, an increase in the water (or NaCl solution) volume promotes a reduction in the headspace volume with a consequent increase in the analyte concentration in the sample headspace, this effect being more pronounced when water is saturated with NaCl. When an aqueous solution saturated with NaCl is used, the response remains constant and at its maximum value in the range of 9–12 mL. However, when water without NaCl is used, the profile reaches a maximum (but with lower responses compared to NaCl saturation) at 8 mL and decreases after this point. In other words, the high ionic strength can compensate for dilution of the analytes in the liquid phase as the water volume is increased. Thus, for headspace extraction of the compounds belonging to the first group, 12 mL of saturated NaCl aqueous solution is recommended. Fortunately, this volume is also adequate for direct extraction. Thus, this variable was not evaluated for this extraction mode.

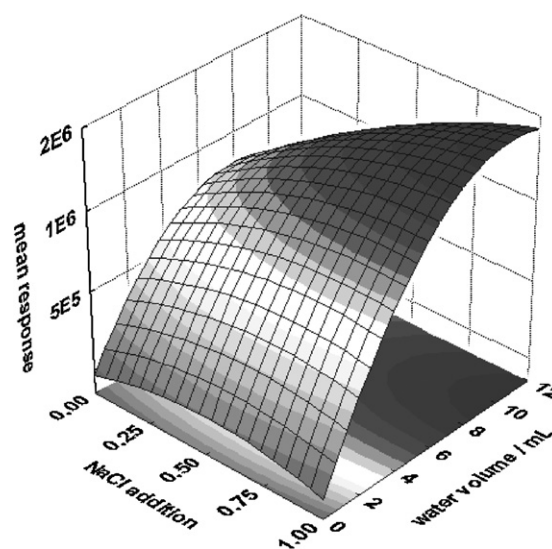


Fig. 2. Response surface obtained for the optimization of NaCl addition and water volume. On the NaCl axis, 0 indicates no NaCl addition, and 1 indicates that the water volume added is saturated with NaCl. Sample temperature: 90 °C. Extraction time: 60 min. Coating temperature:  $35 \pm 5$  °C. Extraction mode: headspace. 15 mL-vials were used throughout.

Extraction time and coating temperatures were simultaneously optimized. Fig. 3A represents the mean response for the compounds eluting prior 213 °C (the first 12 compounds), and Fig. 3B the combined response for two compounds (13th and 14th) eluting in the range of 230–238 °C. The other analytes had a very low response, probably due to their very low concentration in the headspace. It can be seen that the optimal condition for the “lighter” analytes (Fig. 3A) is reached after approximately 40 min of extraction with coating temperature in the range of 15–30 °C. However, Fig. 3B shows that equilibrium for these compounds is far from being reached, which is also the tendency for the heavier compounds. It should also be mentioned that an enhancement in the extraction yield is promoted by the heating–cooling environment of the CF-SPME device. On comparing the response surfaces for each analyte eluting prior to 213 °C (data not shown), the increase in the amount extracted was in the range of 1.5–3.5-fold, depending on the analyte volatility. However, Fig. 3B shows that for these analytes the coating temperature exerts little influence on the analyte uptake. In fact, low coating temperatures slightly decreased the amount

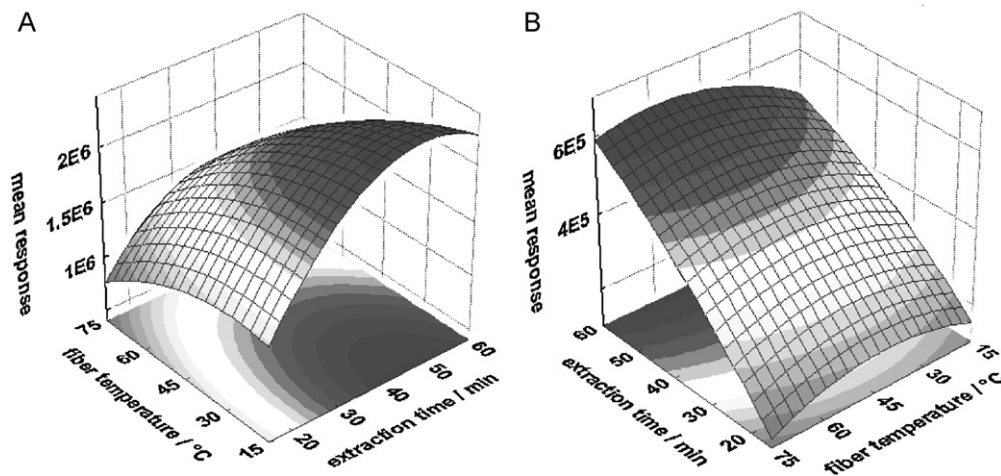
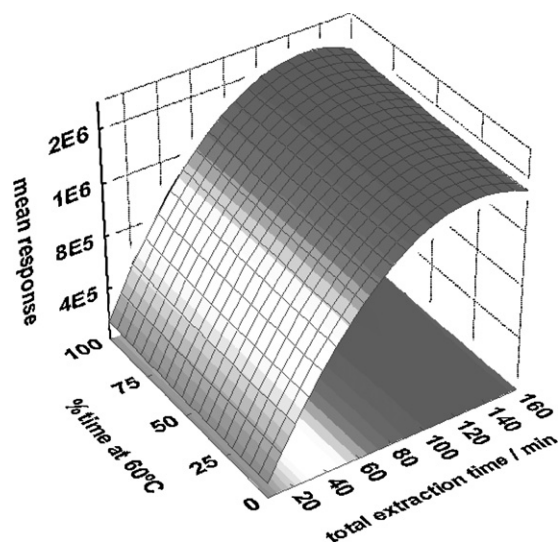


Fig. 3. Response surfaces for evaluation of extraction time and coating temperature. (A) Combined response for compounds eluting prior 213 °C. (B) Combined response for two compounds eluting in the range of 230–238 °C. Sample temperature: 90 °C. Saturated aqueous NaCl solution volume: 12 mL. Extraction mode: headspace.



**Fig. 4.** Response surface obtained for the optimization of total extraction time with the coating at different temperatures: 90 °C (no cooling) and 60 °C. Water volume: 12 mL without NaCl. Sample temperature: 90 °C. Mean response for compounds eluting in the range of 214–300 °C.

extracted for these compounds, the optimal value being in the range of 45–65 °C. The differences in the behavior of the coating temperature in relation to the amount extracted by the coating as the size of the analyte changes may be attributed to a combination of factors: (i) the water/coating or headspace/coating partition coefficient for the compounds increases as their molar masses increase (or their volatility decreases). Thus, even at high temperatures, low volatility analytes can be extracted using a PDMS coating; and (ii) the extraction process is dependent on the diffusion of the analytes through the coating. Thus, as the diffusion coefficient is related to the temperature and viscosity of the diffusion media and on the molecular volume of the diffusing substance, it is expected that the extraction rate will be negatively affected as the coating temperature decreases, this effect being more pronounced as the molar mass of the analyte increases. The main goals in trace analysis are to maximize the analyte uptake (which requires a large temperature difference between the sample and the coating in the case of CF-SPME), and to minimize the sample preparation time (which requires a low or null temperature difference between the sample and the coating). Therefore, the best coating temperature should be evaluated empirically, especially when compounds with quite different molecular sizes are the target analytes. In conclusion, for compounds eluting from 214 °C onward the direct extraction mode is recommended, and for the headspace mode the optimized conditions are 40 min of extraction with a coating temperature in the range of 15–30 °C.

### 3.2. Optimization CF-SPME direct mode

The extraction time and coating temperature were simultaneously optimized. The coating temperatures studied were 90 °C (without cooling the coating) and 60 °C. Compared to headspace extractions, the situation for the direct mode of extraction was inverted, since the extraction yield for heavier analytes (eluting in the range of 214–300 °C) was more efficient than for lighter analytes. Fig. 4 shows the response surface for this step of the optimization using as the response the geometric mean of the peak area for heavier compounds.

The response surface obtained for the lighter compounds was also plotted (data not shown), and the profile was very similar to that of Fig. 4. However, peak intensities were very low and a trend

of increasing recovery as the molar mass of the analytes increased was observed. Fig. 4 also shows that the coating temperature did not change the amount extracted in the range evaluated, and equilibrium was reached after about 100 min of extraction. The negligible effect of coating temperature on the extraction efficiency can be thermodynamically explained in terms of the high PDMS/water partition coefficients of the compounds. Therefore, PDMS can efficiently extract the analytes from water with the coating at either 90 °C or 60 °C. In order to check how lower coating temperatures could affect the extraction capability of PDMS and, more importantly, increase the recovery of lighter compounds, an 80 min extraction was performed in direct mode with 14 mL of water (to minimize the partitioning of lighter compounds toward the sample headspace) with the coating at 30 °C. The amount extracted for all compounds (including the volatiles) diminished compared to the use of coating temperatures in the range of 60 and 90 °C for direct extraction. This finding may be due to the decrease in the extraction rate of the analytes, either through lowering their diffusivity in the coating or increasing the diffusion path in the static layer surrounding the fiber coating. Thus, for the direct extraction mode, 80 min of extraction with a coating temperature in the range of 60–90 °C are the optimized values for these variables.

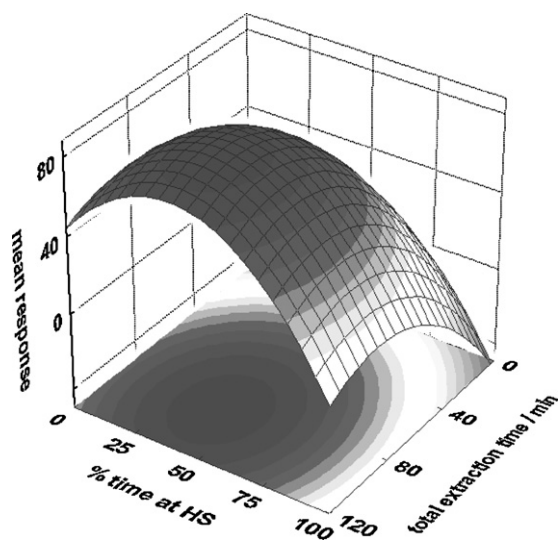
For the evaluation of the ionic strength effect, the sodium chloride concentration was varied from no addition to saturation. Two groups were clearly separated based on the similarity of the effect of the variable on the response: compounds eluting before and after 213 °C. The best condition for compounds eluting up to 213 °C is NaCl saturation. Conversely, for heavier compounds, no salt addition should be used. The decrease in extraction efficiency for heavier compounds as NaCl concentration increases may be related to the increase in sample viscosity. As a compromise condition for both groups, 40% of NaCl saturation could be successfully adopted when the direct extraction mode was used to extract all of the target analytes.

### 3.3. Optimization of the combination of direct and headspace CF-SPME

As clearly observed in the above optimization procedures, neither the headspace nor direct extraction modes alone was sufficient to extract all of the target analytes. Thus, in this proposal, the factors NaCl concentration, total extraction time and the fraction of the total extraction time in which the fiber is located in the sample headspace were simultaneously evaluated through a three-variable central composite design. In this approach, the extraction always begins with the direct extraction mode and, after the designated time, the coating is located in the sample headspace until the total extraction period is completed. Figs. 5–7 show the response surfaces obtained.

It should be emphasized that the response used to plot Figs. 5–7 was the geometric mean for all of the compounds, thus representing a compromise response for all of the analytes. As can be seen in Figs. 5 and 7, the optimal NaCl concentration was 54% of NaCl saturation (194 g L<sup>-1</sup>). Considering all compounds, this is an intermediate value between no addition (the best condition for heavier compounds) and saturation (the optimal value for the lighter group). This is in agreement with the previous optimization results. Thus, the NaCl concentration of 194 g L<sup>-1</sup> was adopted as the optimized condition.

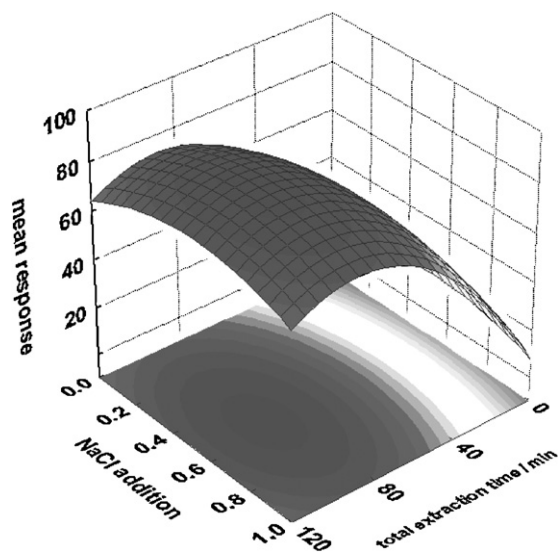
As can be observed from Figs. 5 and 6 the equilibrium is reached in around 80 min. Although 80 min seems to be a long extraction time, it should be considered that 24 compounds with different volatilities are being extracted from a complex sample. In Figs. 5 and 7 it can be seen that the procedure proposed herein leads to better results compared to the use of only direct or headspace modes. The optimal values obtained for the extraction



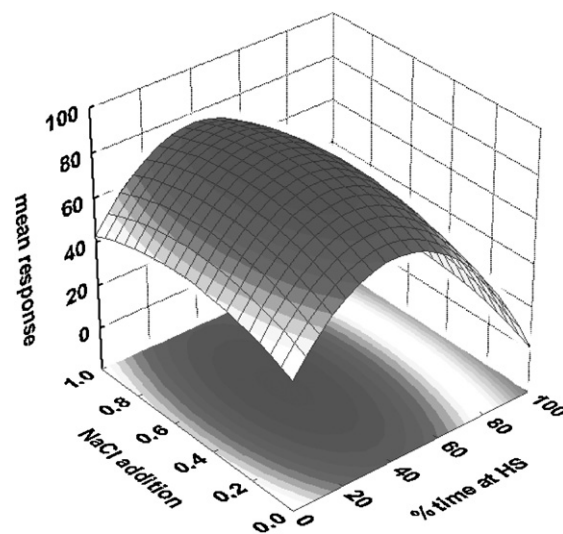
**Fig. 5.** Response surface obtained for the simultaneous optimization of NaCl concentration, total extraction time and % of extraction time with the coating in the sample headspace. Coating temperatures: 90 °C (direct mode) and 30 °C (HS mode). Water or NaCl aqueous solution volume: 12 mL. Salt concentration: 54% of NaCl saturation. Mean response was calculated as the geometric mean of peak area for all compounds.

time were 50 min in direct mode followed by 30 min of extraction in headspace mode, which corresponds to approximately 40% of the total extraction time (80 min) in headspace mode.

The use of the direct extraction mode leads to much faster extraction of the heavier compounds compared to the headspace mode, since analyte diffusion through the boundary layer or through the coating is a faster step than the evaporation of analytes from the aqueous sample, which is the mass transfer rate-determining step for the heavier compounds in a headspace extraction. Thus, while the extraction in direct mode occurs, volatile compounds tend to be concentrated in the sample headspace. At the end of the extraction period in the direct mode the coating is located in the sample headspace and its temperature has changed to



**Fig. 6.** Response surface obtained for the simultaneous optimization of NaCl concentration, total extraction time and % of extraction time with the coating in the sample headspace. Coating temperatures: 90 °C (direct mode) and 30 °C (HS mode). Water or NaCl aqueous solution volume: 12 mL. % time at HS: 40% of total extraction time. Mean response was calculated as geometric mean of peak area for all compounds.

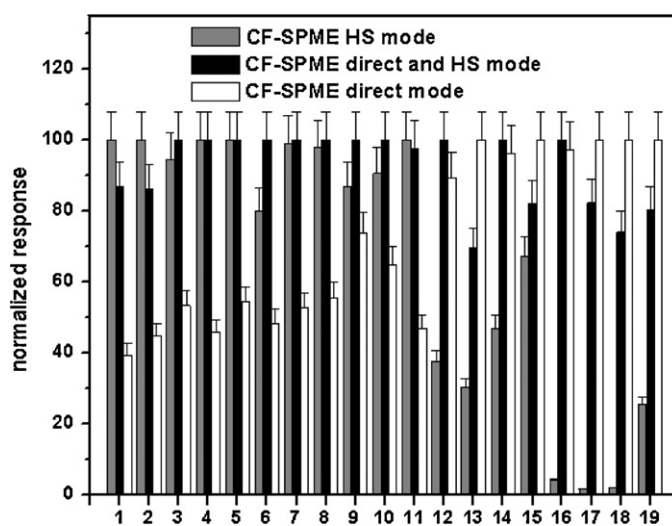


**Fig. 7.** Response surface obtained for the simultaneous optimization of NaCl concentration, total extraction time and % of extraction time with the coating in the sample headspace. Coating temperatures: 90 °C (direct mode) and 30 °C (HS mode). Water or NaCl aqueous solution volume: 12 mL. Total extraction time: 80 min. Mean response was calculated as the geometric mean of peak area for all compounds.

30 °C, the volatiles can be efficiently extracted and the compounds already sorbed by the coating in the direct extraction are not subsequently lost, since they remain trapped in the cooled coating.

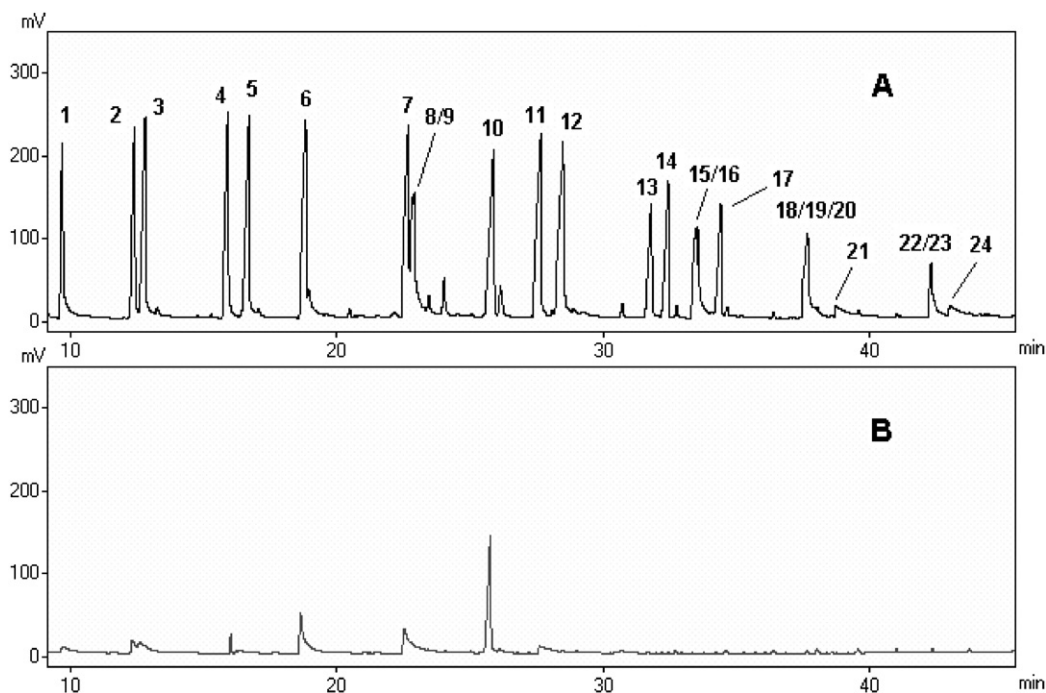
#### 3.4. Comparison between the different procedures

In order to better visualize the differences between the proposed method, based on the use of direct and headspace extraction modes in the same procedure, and the use of only direct or headspace extractions some comparisons were made. It can be observed from the results in Fig. 8 that the headspace mode led, in general, to better responses for the lighter analytes, decreasing the extraction yield as the volatility decreased. The opposite behavior is observed for the direct mode. Therefore, when the aim is to extract both groups of analytes, neither of the extraction modes applied alone will be



**Fig. 8.** Comparison between different extraction conditions ( $n = 3$ ). Numbers on the x-axis represent analytes in the elution order. Peak co-elution can be found in Section 2. CF-SPME in HS mode: 80 min of extraction with coating at 30 °C. CF-SPME in direct mode: 80 min of extraction with CF-SPME without cooling the coating. CF-SPME in direct and HS modes: 50 min of extraction in direct mode without cooling the coating followed by 30 min in HS with coating at 30 °C.





**Fig. 9.** Comparison between different extraction methods using CF-SPME and 50 mg of silica spiked at  $10 \mu\text{g g}^{-1}$ . (A) Optimized condition proposed in this study: sample temperature:  $90^\circ\text{C}$ , 12 mL of NaCl aqueous solution at  $194 \text{ g L}^{-1}$  and pH 4–7 in 15-mL vial, 80 min of extraction, the first 50 min being in direct mode with coating at  $90^\circ\text{C}$  followed by 30 min of headspace extraction with coating at  $30^\circ\text{C}$ . (B) Conventional CF-SPME approach: no water addition, sample temperature:  $160^\circ\text{C}$ , incubation time: 15 min at  $160^\circ\text{C}$ , coating temperature:  $5^\circ\text{C}$ , and extraction time: 80 min. Peak identification can be found in Section 2.

suitable. However, the proposed condition did lead to a satisfactory extraction for all the analytes, as it integrates both extraction modes in the same extraction procedure.

Another important factor that should be considered is related to the use of water as a sample modifier. Throughout this study, a high amount of water was used to deactivate the matrix. For this reason, we had to restrict the sample temperature to a value at which analyte losses due to leaking were minimized, that is,  $90^\circ\text{C}$ . The approaches generally described in the literature for the development of a CF-SPME method involve the reverse procedure, i.e., the sample temperature is optimized first and then the sample water content. Thus, water addition is usually initially avoided since it is evaluated later using the optimized sample temperature (a high value), which leads to a very high internal pressure in the extraction vial. In this context, it is necessary to test which of these approaches leads to better results. The proposed method was compared to the result for the extraction of the analytes spiked in silica without water, with a sample temperature of  $160^\circ\text{C}$ , 15 min of incubation time at  $160^\circ\text{C}$  and 80 min of extraction with the coating at  $5^\circ\text{C}$ . The results are shown in Fig. 9.

Fig. 9 shows that the approach based on the use of high water content and intermediate sample temperature along with the use of a combination of extraction modes in the same procedure was much more efficient compared to the use of high sample temperature and no water addition. This result indicates again that the use of a large temperature difference between the sample and coating alone is no guarantee of the successful application of CF-SPME. This result also shows that the effect of water addition is much more important than the use of high sample temperature alone in terms of releasing the analytes from the solid matrix.

### 3.5. Analytical parameters and method application

The main analytical parameters of merit were determined for the newly proposed extraction approach. The analytical curve was

constructed with 50 mg of spiked silica samples under the optimized conditions.

As can be observed from the results in Table 1, satisfactory analytical data were obtained for all compounds, especially considering the difficulties associated with treating the solid samples for gas chromatographic determination. It should be emphasized that the detection limits could be much improved by using a more sensitive instrument, such as a gas chromatograph coupled to a mass spectrometer (GC–MS) operating in selected ion monitoring (SIM) mode. Also, by using a GC–MS instrument it is possible to quantify

**Table 1**

Analytical figures for the optimized new approach of CF-SPME using 50 mg of silica sample.

Analytes <sup>a</sup>	$R^b$	LOD <sup>c</sup> ( $\mu\text{g g}^{-1}$ )	Linear range ( $\mu\text{g g}^{-1}$ )	RSD (%) <sup>d</sup>
1	0.9999	0.2	0.7–40	5
2	0.9993	0.4	1.3–40	12
3	0.9976	0.7	2.0–40	16
4	0.9970	0.7	2.0–40	16
5	0.9999	0.2	0.6–40	4
6	0.9966	0.7	2.0–40	17
7	0.9989	0.5	1.2–40	12
8/9	0.9950	0.9	3.0–40	16
10	0.9974	0.7	2.0–40	15
11	0.9986	0.5	1.5–40	11
12	0.9998	0.4	1.2–40	6
13	0.9965	0.8	3.0–40	19
14	0.9942	0.9	3.0–40	16
15/16	0.9936	0.8	2.8–40	16
17	0.9983	0.7	2.4–40	15
18–20	0.9946	0.8	2.5–40	19
21	0.9999	1.0	3.3–40	4
22/23	0.9921	2.0	6.7–40	19
24	0.9967	2.3	7.7–40	18

<sup>a</sup> Analyte identification can be found in Section 2.

<sup>b</sup> Correlation coefficient.

<sup>c</sup> Limit of detection estimated as three times the signal-to-noise ratio.

<sup>d</sup> Relative standard deviation for  $n=5$  and  $10 \mu\text{g g}^{-1}$ .

**Table 2**

Relative recoveries obtained for some target compounds spiked in soil samples with different clay and organic matter contents through the optimized method proposed in this study.

	Organic matter/clay content (%)					
	8.4/32	2.5/58	1.5/24	0.8/14	2.9/65	0/0 <sup>a</sup>
Naphthalene	99.0	91.3	100.6	97.6	95.7	100.0
1-Methylnaphthalene	98.7	111.8	112.2	113.8	110.6	100.0
2-Methylnaphthalene	94.9	106.6	108.3	109.7	107.7	100.0
Acenaphthene	85.3	103.4	103.2	105.1	104.7	100.0
Dimethylphthalate	90.3	106.4	109.4	111.3	110.0	100.0
Acenaphthylene	96.0	103.6	101.9	103.9	94.2	100.0
Fluorene	76.6	105.8	103.3	104.7	104.7	100.0
Anthracene	65.7	90.0	84.1	86.1	85.3	100.0
Dibutylphthalate	58.9	86.0	88.8	89.4	81.2	100.0
Fluoranthene	73.2	84.0	104.9	99.5	92.5	100.0
Pyrene	53.7	50.1	61.3	46.1	63.6	100.0
Benzylbutylphthalate	84.3	94.5	45.5	26.1	49.9	100.0
Chrysene	71.7	50.6	48.0	21.7	15.5	100.0

<sup>a</sup> Silica sample.

individually co-eluting peaks by selecting the characteristic  $m/z$  for each compound. In order to test the method, recovery tests were carried out on five spiked soil samples ( $50 \text{ mg at } 20 \mu\text{g g}^{-1}$ ) with different clay and organic matter contents. The results for the recovery tests were presented relative to the results of the calibration curve for the silica sample and can be found in Table 2. As can be seen, a very good result was obtained for the target analytes. The conventional approach of CF-SPME ( $160^\circ\text{C}$  as sample temperature, 15 min of incubation time at  $160^\circ\text{C}$ , 80 min of extraction with the coating at  $5^\circ\text{C}$  and no water addition) was also applied to the same spiked samples but none of the analytes was detected, demonstrating that the proposed method is much better compared to the conventional approach.

## 4. Conclusions

The use of a high amount of water and an intermediate sample temperature was shown to be significantly more efficient in both releasing the analytes from the solid matrix and minimizing leaking compared to the conventional CF-SPME procedures. The use of a combination of extraction modes in the same extraction procedure improved the speed and efficiency of extraction for both heavy and light analytes. This procedure can be easily automated, simply by programming any available SPME autosampler.

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