# A new optimization strategy for gaseous phase sampling by an internally cooled solid-phase microextraction technique

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## ARTICLE INFO

## ABSTRACT

This study describes a new optimization strategy for internally cooled solid-phase microextraction based on a multivariate approach. The coating temperature was changed in an extraction while manipulating the extraction times to improve the extraction of compounds with different volatilities. Polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PEs) and adipate were used as model compounds in this study. The optimization strategy was in two steps: (1) multivariate optimization of extraction time and initial coating temperature and (2) multivariate optimization of total extraction time and the time required to cool the coating to a lower temperature as determined in step 1. The observed analytical response in relation to the coating temperature was found to be dependent on the analyte volatility and size. The optimized extraction condition for PEs was 23 min extraction while maintaining the coating at 140 °C, followed by 7 min of cooling the coating at 10 °C. For the PAHs the coating temperature was maintained at 60 °C for the first 20 min and at 5 °C in the last 20 min of extraction. Comparisons have been made between the proposed optimized conditions with the conventional internally cooled fiber approach and the results thoroughly discussed. The proposed optimization strategy was found to be more effective for all the analytes, especially for the semi-volatiles, compared to the conventional method.

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## 1. Introduction

Solid-phase microextraction (SPME), first introduced by the research group of Pawliszyn [1], is widely accepted and is the subject of an ever increasing number of publications. This technique is simple, relatively fast, solvent-free, inexpensive, easily automated, and safe. It has been successfully applied in both headspace sampling and directly in aqueous samples, with good selectivity [2]. SPME offered an important advancement in the extraction efficiency of several organic pollutants at trace levels from different matrices, such as foodstuff [3–5], environmental [6–8] and biological samples [9–11].

Later, with the objective of overcoming the exothermic characteristic of analyte sorption by an extraction phase, new configurations for SPME were proposed. In this case, the method involved the use of elevated sample temperatures during extractions while simultaneously cooling the extraction phase. By this approach a significant increase in the analyte matrix-to-coating partition coefficients can be observed which lead to exhaustive extractions of most analytes. Based on this proposal, Chia et al. [12] developed a simple device to determine polychlorodibenzo-p-dioxins and polychlorodibenzofurans in contaminated soil samples. The authors cooled the PDMS fiber using chilled alcohol during the extraction procedure. Refrigeration of the SPME fiber to cool the fiber was also used by Achten et al. [13] to detect methyl tert-butyl ether in water. The authors cooled the CAR/PDMS fiber at 0 °C using a cryostat.

However, the internally cooled or cold-fiber solid-phase microextraction (CF-SPME) device proposed in 1995 by Zhang and Pawliszyn [14] proved to be more attractive and efficient approach to minimize the SPME exothermic effect. In the cited reference, the authors proposed a hypothesis based on extraction of an analyte in the gas phase at high temperature with a liquid polymer at low temperature. In this proposal, authors assumed that the entropy change which, was dependent only on its initial and final values in the system, was the driving force for mass transfer processes to occur. Based on this assumption, evaluation of the system was carried out by considering the following steps: (a) a gaseous mixture of the analytes; (b) cooling of the analyte vapor from the sample temperature to the coating temperature; and (c) absorption of the analyte vapor by the coating at the coating temperature. After some algebraic work and further considerations which were demonstrated

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by Zhang and Pawliszyn [14], authors established the following equation:

$$K_T = K_0 \frac{T_s}{T_f} \exp\left[ \frac{C_p}{R} \left( \frac{\Delta T}{T_f} + \ln \frac{T_f}{T_s} \right) \right] \quad (1)$$

where $T_s$ and $T_f$ are the sample and fiber coating temperatures, respectively, $C_p$ is the heat capacity of the analyte, $R$ is the gas constant, $\Delta T$ is the difference in temperature between the headspace sample and the fiber coating, $K_0$ is the partition coefficient of the analyte between the gas and the coating when both are at the same temperature $T_s$, and $K_T$ is the partition coefficient of the analyte between coating at $T_f$ and the gas phase at $T_s$.

From Eq. (1), it can be observed that $\Delta T$ and $K_T$ are exponentially related [14–16]. This implies that very high analyte recoveries suitable for reliable quantitative analysis can be attained with a high sample and low extraction phase or coating temperature.

Considering the potential of the device as a sample preparation technique, it was miniaturized and automated in 2006 [15]. Subsequently, the technique has been applied to the extraction of PAHs from soil and sediment samples [16] and the analysis of fragrances from Iranian rice samples [17]. Carasek and Pawliszyn analyzed the aroma profile of tropical fruits [18] and determined off-flavor compounds in cork stopper samples [19] using the same CF-SPME technique. Last but not the least, the technique was applied as a tool to extract perfume and flavor compounds from shampoo samples [20]. Physico-chemical applications of the device was performed by Haddadi, through studies on the desorption kinetics of PAHs from solid samples [21] while Sanchez-Prado studied photodegradation products of hexachlorobenzene [22].

However, it is worth mentioning that in all these studies the interaction between coating and sample temperatures was not evaluated except for Carasek et al. who used a multivariate approach to study the effect of this interaction. Although Carasek et al. achieved optimal extraction efficiency with low coating temperature in both cases [19], this condition may not be same for all the target compounds. This is because the diffusion coefficient is affected by changes in both temperature and the molecular radius of the analyte. The relationship between the diffusion coefficient $D$ of a substance and the molecular radius $r$ in a medium with viscosity $\mu$ at absolute temperature $T$ is given by the Einstein–Stokes equation:

$$D = \frac{kT}{r\mu\pi} \quad (2)$$

where $k$ is the Boltzmann constant. From Eq. (2), a general decrease in viscosity with increasing temperature will lead to increased diffusion of compounds through a medium. This implies that a careful manipulation of the temperature as molecular radius is constant could maximize the thermodynamic gain and thus improve the diffusion of most analytes through the coating.

In view of this, a heterogeneous mixture of compounds in terms of their volatilities and partition coefficients with PDMS was studied. Five phthalic acid esters and adipate and eighteen polycyclic aromatic hydrocarbons were selected as target compounds. The main objective of this study was to improve the extraction efficiency for all studied compounds in a minimal extraction time while changing the coating temperature. To achieve this goal, authors optimized extraction time, coating temperature and the time needed to cool the coating to a lower temperature so as to maximize the amount extracted for all compounds. The new proposed optimization strategy to CF-SPME method was performed with a mixture of gaseous samples.

## 2. Experimental

### 2.1. 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, fluorine, 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). This solution was diluted to 1000 µg mL$^{-1}$ with a mixture of benzene:dichloromethane (50:50). 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 µg mL$^{-1}$ in methanol. The cold fiber device, temperature controller and solenoid valve used in this study were the same as those used in previous papers [15–22]. A PDMS membrane with 178 µm wall thickness and 1 cm length was used as the extractor phase. Liquid $CO_2$ was used to cool the fiber coating. All commercial SPME fibers were purchased from Supelco.

### 2.2. Experimental procedure and optimization strategy

For both PAHs and PEs the optimization was carried out by transferring 400 ng of each compound into empty 15 mL vials for the SPME. In all cases, sample temperature was controlled by means of a heating block (operational range from room temperature to 200 °C) specially designed for this purpose (Dist, Florianópolis, Brazil). Sample temperature during stabilization and incubation was kept constant for 10 min for all compounds studied. Desorption of the analytes was carried out in the injector port of the chromatograph at 300 °C for 7 min in splitless mode. No carry-over effect was observed.

The Central Composite multivariate method was used for the optimization process by considering the following two steps. (1) Optimization of the extraction time and coating temperature. (2) Optimization of the total extraction time and the time required to cool the coating to a lower temperature based on the results from the previously optimized coating temperature in the first step. This implies that the optimized method would comprise an initial higher temperature extraction of analytes and subsequently lower the coating temperature for an optimized period for further extraction. Thus, the total extraction time was the overall time for extraction at both coating temperatures. All experiments were conducted manually.

### 2.3. Instrumental

Chromatographic analysis was carried out in a GC-14B Shimadzu gas chromatograph (Kyoto, Japan) equipped with a split-splitless injector and flame ionization detector (FID). Ultra pure $N_2$ was used as the carrier and make-up gas at 1.2 and 40 mL min$^{-1}$, respectively. Ultra pure $H_2$ and synthetic air were used for FID detection. In all cases, injector and detector temperatures were set at 300 °C and 320 °C, respectively. The oven temperature program for the separation of PEs was: 80 °C (1 min), increasing at 10 °C min$^{-1}$ up to 300 °C (1 min). For PAHs, the oven was initially held at 80 °C for 1 min, followed by ramping at 8 °C min$^{-1}$ to 320 °C for 10 min. The separation of PAHs and PEs was carried out in an OV-5 capillary column (OV Specialty chemical, 30 m × 0.25 mm × 0.25 µm).
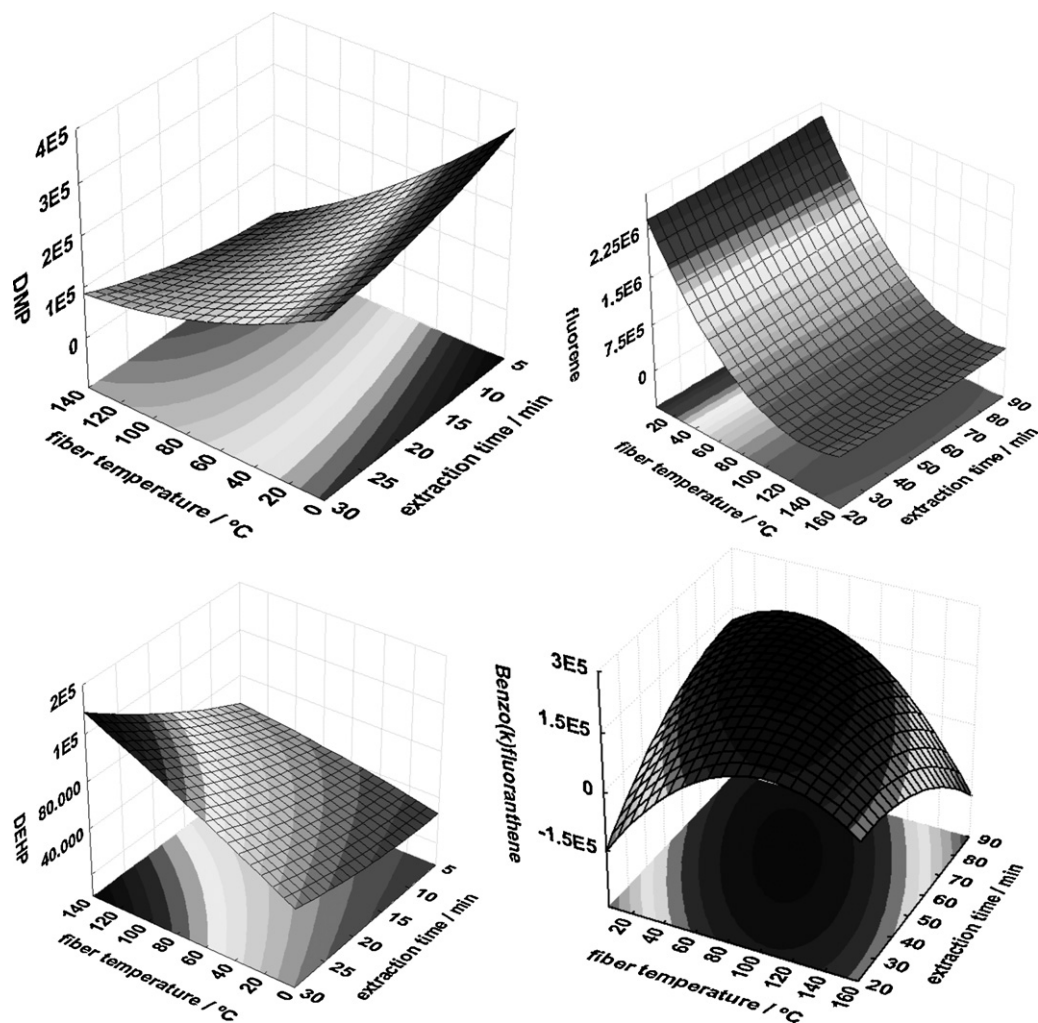
**Fig. 1.** Response surfaces obtained through simultaneous optimization of extraction time and fiber temperature. Sample temperature was 160 °C for PAHs and 140 °C for PEs. Response used on *z*-axis was peak area.

## 3. Results and discussion

### 3.1. Sample temperature

The sample temperature is a key parameter which influences the analyte desorption from the matrix into the headspace especially in the case of heavier compounds/semi-volatiles, and also influences the analyte diffusion through the extraction phase/coating. For this particular study, the sample temperature was chosen from a univariate optimization strategy. The optimized extraction temperature profile (60–160 °C) for a 30 min extraction obtained for PEs using 100 μm PDMS showed a rapid decrease in the amount extracted for compounds which can be easily volatized, DMP, DEP and DnBP as the sample temperature increases. On the other hand, for the heavier semi-volatiles (BBP, DEHA and DEHP), the extraction temperature profile reached a maximum extracted amount before decreasing. This observation indicates that even at elevated coating temperatures, the heavier compounds could be extracted due to their elevated partition coefficient within PDMS. The same study of extraction temperature profile (50–180 °C) for a 50 min extraction was applied for the PAHs. In view of this, a sample temperature of 140 °C and 160 °C was chosen for PEs and PAHs, respectively.

### 3.2. Multivariate optimization of extraction time and coating temperature

The importance of optimizing the extraction time and the coating temperature is due to the fact that the amount of analyte extracted at any given time is dependent on strongly the coating temperature which in turn affects the analyte partition coefficient with the system, as suggested by Eq. (1). Fig. 1 shows the response surfaces obtained for DMP and DEHP representing PEs and fluorene and benzo(k)fluoranthene as representative PAH compounds.

For very volatile compounds such as DMP and fluorene, the response was improved by lowering the coating temperature, which is in agreement with Eq. (1), i.e., a lower coating temperature increases analyte partition coefficient in the extraction phase for volatile compounds. Equilibrium was attained at 5 min for PEs and 20 min for PAHs with a coating temperature of 10 °C for PEs and 5 °C for PAHs, respectively. However, response surface for DEHP (semi-volatile) (Fig. 1) with respect to coating temperature was different compared to DMP. This was due to the fact that a higher fiber coating temperature (140 °C) favoured extraction of semi-volatiles. In addition to the higher temperature favouring semi-volatiles, the rate of extraction was also improved at higher coating temperature of 140 °C compared to 10 °C. Similar response was observed

**Table 1**
Optimum fiber temperature range for each analyte studied with extraction temperature at 140 °C for PEs and 160 °C for PAHs.

| Analytes[a] | Optimum fiber temperature (°C) |
| --- | --- |
| Naphthalene | <5 |
| 1-Methylnaphthalene | <5 |
| 2-Methylnaphthalene | <5 |
| Acenaphthene | <5 |
| Acenaphthylene | <5 |
| Fluorene | <5 |
| Phenanthrene | <5 |
| Anthracene | <5 |
| Fluoranthene | 25–35 |
| Pyrene | 30–40 |
| Benzo(a)anthracene/crysene[b] | 55–65 |
| Benzo(b)fluoranthene/benzo(k)fluoranthene[b] | 75–85 |
| Benzo(a)pyrene | 65–75 |
| Indeno(1,2,3-cd)pyrene/dibenz(a,h)anthracene[b] | 70–90 |
| Benzo(ghi)perylene | 80–100 |
| Dimethylphthalate | 10–15 |
| Diethylphthalate | 10–20 |
| Dibutylphthalate | 45–65 |
| Benzylbutylphthalate | 100–120 |
| Bis(2-ethylhexyl)adipate | 80–100 |
| Bis(2-ethylhexyl)phthalate | 135–140 |

[a] The order of compounds in the table is the elution order in the chromatographic system, respecting each class.
[b] These compounds have a high degree of co-elution, and were analyzed as the sum of their peak areas.

for benzo(k)fluoranthene where a relatively higher temperature yielded higher extracted amounts with shorter equilibration time. The results for the optimum coating temperature for each analyte studied are given in Table 1.

The contrasting behavior of these compounds within the coating at different temperatures suggests that there could be a possible kinetic parameter involved, which becomes more pronounced as the volatility of the analyte and the coating temperature decrease. This behavior can be attributed to the difficulty of diffusion of heavier analytes through the coating at very low temperatures and therefore the heavier analytes could be extracted by condensation on the PDMS surface rather than absorption process by the PDMS coating. To prove this assertion, experiments were performed to verify whether, especially for heavier analytes, the coating might act otherwise, as an absorbent at low temperatures. PEs were used as model compounds and extractions were performed with and without the PDMS coating (in the latter case using only the stainless steel plunger). All experiments were performed at a general lower coating temperature of 10 °C for these studies. In addition, experiments using the same set of compounds with CF device and the PDMS coating were performed but under optimized coating temperature for each specific compound. The experiments were done to demonstrate the importance of use higher coating temperature needed for efficient extraction of the semi-volatile compounds. Results are shown in Table 2.

**Table 2**
Comparison of CF-SPME at low temperature with or without PDMS coating. Extraction time and coating temperature were fixed at 30 min and 10 °C, respectively. Peak area was set as 100 for CF with PDMS coating at 10 °C. All RSD values ($n = 6$) were below 10%.

| Compounds | CF with PDMS coating at 10 °C | CF without PDMS coating at 10 °C | CF with PDMS at optimal $T_f$ |
| --- | --- | --- | --- |
| DMP | 100.00 | 18.85 | 100.00 ($T_f = 10$–15 °C) |
| DEP | 100.00 | 32.14 | 100.00 ($T_f = 10$–20 °C) |
| DnBP | 100.00 | 43.68 | 120.00 ($T_f = 45$–65 °C) |
| BBP | 100.00 | 58.75 | 175.13 ($T_f = 100$–120 °C) |
| DEHA | 100.00 | 81.34 | 266.52 ($T_f = 80$–100 °C) |
| DEHP | 100.00 | 99.92 | 384.32 ($T_f = 135$–140 °C) |

It can be observed from Table 2 that the CF-SPME with PDMS coating at 10 °C yielded better results for all compounds compared to the CF without PDMS coating (stainless steel only) also at 10 °C. However, in the case of the stainless steel material where extraction was obviously not due to an absorption process, the extraction efficiency increases with increasing molecular mass. For example, the extraction efficiency for DEHP (highest molecular mass compound) with and without the PDMS coating was statistically not different at the lower coating temperature of 10 °C. This observation suggests that the coating extraction properties were similar for both PDMS and the stainless steel at very low temperatures. Therefore, in a conventional univariate CF-SPME method where the coating temperature is constantly kept low throughout the extraction process, it is possible that the PDMS fiber may be acting as a rigid rubber-like material. This change the property of the PDMS coating will lead increasing polymer viscosity which will in turn affect the diffusion of analytes through the PDMS fiber. The final result is that the extraction efficiency of the PDMS coating will be lowered for semi-volatiles despite the improvement in extraction as the temperature was lowered (Table 2). To minimize this effect, it is appropriate to use higher coating temperature for the extraction of heavier analytes (semi-volatiles) which improves their diffusion through the coating.

This implies that to improve the extraction efficiency for all analytes, it is important to determine the initial appropriate coating temperature required for all analytes, especially for heavier compounds so as to improve their diffusion through the PDMS coating during extraction rather than maintaining a constant lower temperature. By selecting an appropriate initial coating temperature, losses likely to occur at lower temperatures due to the poor diffusion of the analytes could be minimized or prevented for most semi-volatiles.

### 3.3. Multivariate optimization of total extraction time and the required time for coating cooling

From Table 1, it can be observed that generally the optimized temperatures for effective extraction for volatiles were lower while that for semi-volatiles were higher as expected. Therefore for the selected compounds in this study, an initial higher coating temperature of 140 °C and 60 °C was maintained for PEs and PAHs, respectively. Due to the varying coating temperatures required for the different analytes, in addition to the initial higher temperature, a lower coating temperature was also chosen to enhance extraction efficiency. In the case of PEs the lower temperature was set at 10 °C while that for PAHs was 5 °C as the optimized lower coating temperature conditions.

To improve the extraction efficiency further, the time required to cool the coating was investigated. Details of the results are shown in Fig. 2 in which the response surface of the total extraction time and time required to cool the coating were monitored. In this study, a compromise between the compounds was obtained using the mean response calculated as the geometric mean for all peak areas. This optimization step consisted of determination the total extraction time and the fraction of this time required to cool the coating to the lower coating temperature selected.

As a result, longer extraction time (23 min) was obtained for PEs at a relatively higher temperature due to their lower volatilities. This was followed by a shorter extraction time of 7 min at a lower temperature of 10 °C. The time used for the second part of the extraction was maintained at 7 min as longer extraction times at very low coating temperatures do not improve the extraction efficiency of the heavier compounds because the coating becomes more rigid. The final optimized time was therefore 30 min. On the contrary, for PAHs relatively shorter extraction time of 20 min was maintained with a coating temperature of 5 °C. This is because
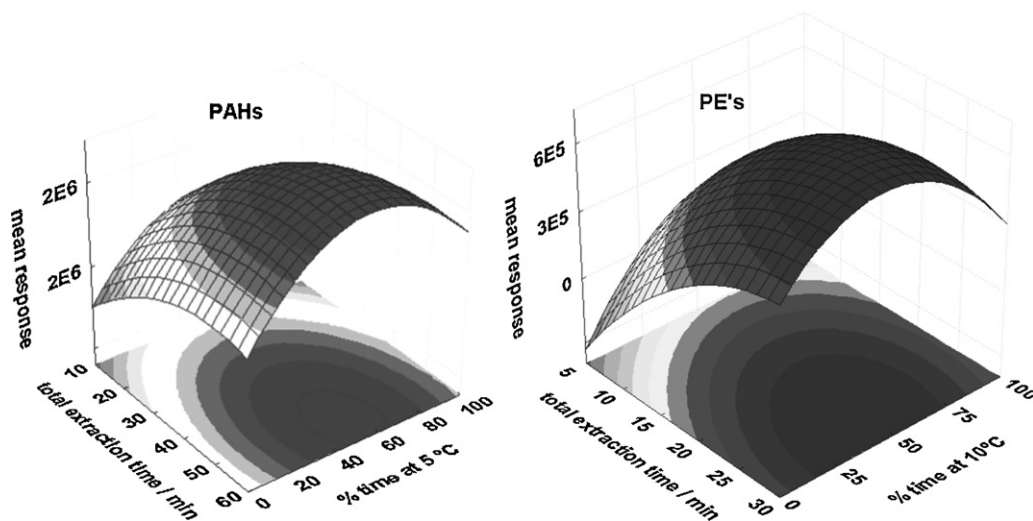
**Fig. 2.** Optimization of total extraction time and % time with the coating at low temperature. High and low coating temperatures were 140 and 10 °C for PEs, and 60 °C and 5 °C for PAHs, respectively. Mean response was calculated as the geometric mean for all peak areas.

the PAHs are relatively lighter molecules and therefore could diffuse easily through the coating at lower temperatures due to their improved partition coefficient.

### 3.4. Comparative study between the new CF-SPME multivariate and the conventional univariate CF-SPME optimization

In order to demonstrate the advantage of the new multivariate CF-SPME optimization strategy as an alternative potential analytical method over the conventional univariate method, results for their extraction efficiencies obtained from a thorough comparative study were evaluated. Fig. 3A shows the extraction efficiencies for PEs using the proposed multivariate optimization strategy, the conventional univariate method and a regular SPME method. Generally, the proposed multivariate approach led to higher extraction efficiency for all the studied analytes compared to the other two methods. It was distinctively obvious that at higher temperatures, the regular SPME method (a 23 min extraction at 140 °C) and the proposed multivariate method (a 23 min extraction at 140 °C followed by a 7 min extraction at 10 °C) effectively extracted higher amounts of the semi-volatiles. It is worth to notice that the further decrease in the temperature to 10 °C with the new multivariate method did not result in any loss of analytes. This is because the further decrease in temperature only results in the trapping of the extracted analytes in the PDMS phase. However, the volatiles were poorly extracted under these conditions due to the decrease in their partition coefficients in the PDMS at elevated temperatures. On the other hand, at lower temperatures all the volatiles were effectively extracted. Again the proposed multivariate approach demonstrated a significant advantage because by lowering the temperature of the PDMS coating, the partition coefficients of the volatiles are improved and therefore resulting in higher extracted amounts.

A similar extraction pattern is observed for the PAHs as indicated in Fig. 3B where comparison of the extraction efficiency of the proposed multivariate method is established with that of the conventional univariate approach. The conventional univariate method (maintaining coating temperature at 5 °C throughout the extraction) showed relatively poor extraction efficiency for the semi-volatiles due to the possible change in the coating extraction characteristics. This is because at lower temperatures the coating acts as a rigid material and thus prevents effective extraction of the semi-volatiles due to their larger molecular sizes. However, with the new proposed method, the relatively higher temperature of

60 °C allowed effective extraction of the semi-volatiles prior to the further decrease in the coating temperature.

A chromatogram obtained for extraction of the PAH's and PEs using the optimized CF-SPME procedure is presented in Fig. 4.
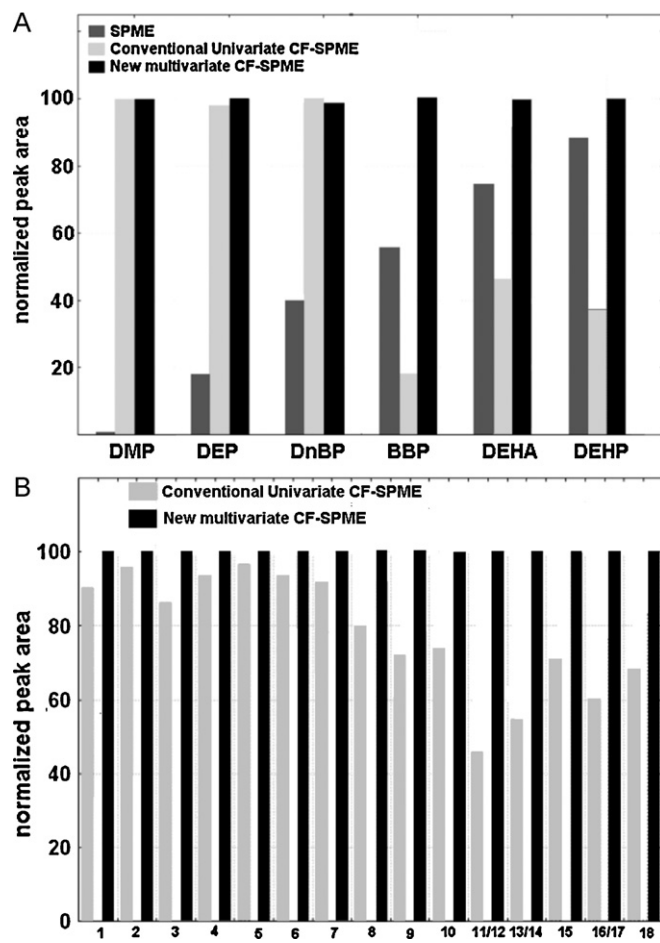


**Fig. 3.** (A) Comparison of the extraction efficiency of SPME, conventional univariate CF-SPME and proposed multivariate CF-SPME methods for the extraction of PEs and (B) comparison of the extraction efficiency of the conventional univariate CF-SPME and the new multivariate CF-SPME methods for the extraction of PAHs. Numbers on the x-axis correspond to the PAHs in their elution order as shown in Table 1.
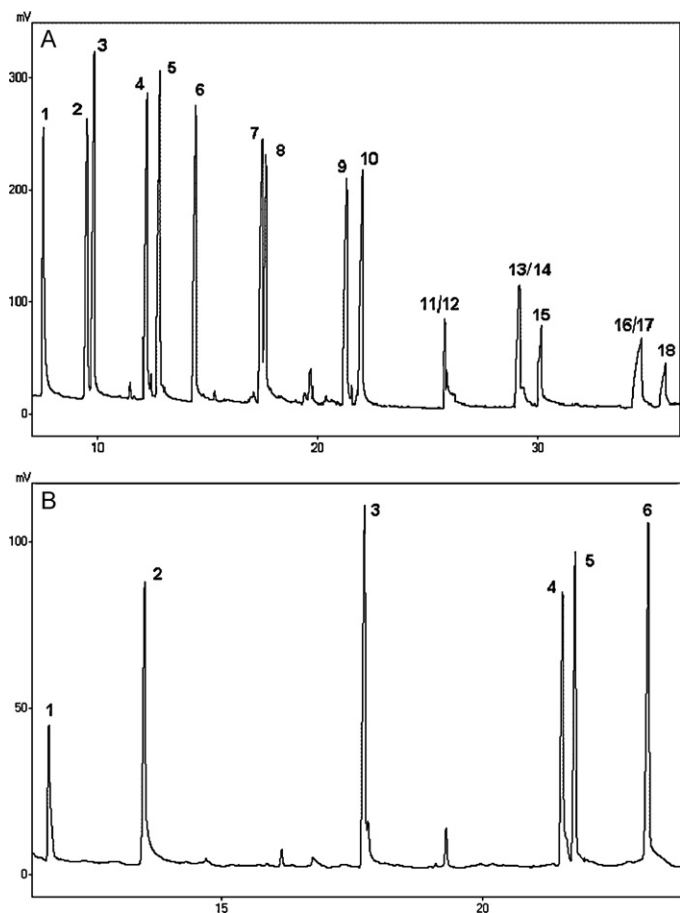
**Fig. 4.** GC-FID chromatogram of extracted (A) 300 ng of PHAs and (B) 200 ng of PEs using optimized CF-SPME procedure. PAHs: (1) naphthalene, (2) 1-methylnaphthalene, (3) 2-methylnaphthalene, (4) acenaphthene, (5) acenaphthylene, (6) fluorene, (7) phenanthrene, (8) anthracene, (9) fluoranthene, (10) pyrene, (11) benzo(a)anthracene, (12) crysene, (13) benzo(b)fluoranthene, (14) benzo(k)fluoranthene, (15) benzo(a)pyrene, (16) indo(1,2,3-cd)pyrene, (17) dibenzo(a,h)anthracene, and (18) benzo(ghi)perylene. PEs: (1) DMP, (2) DEP, (3) DnBP, (4) BBP, (5)DEHA, and (6) DEHP.

## 4. Conclusion

The results of this study showed that in order to obtain the best performance of any CF-SPME device, careful optimization of the sample temperature, extraction time and, especially, initial coating temperature are needed. Authors were able demonstrate that the optimum coating temperature differed according to the volatility and size of the analyte and therefore offered an alternative approach for CF-SPME method development. The new optimization strategy proposed which was based on using different coating temperatures during the same extraction process was found to be an excellent alternative approach to improve the extraction of both volatiles and semi-volatiles in a given mixture. The multivariate approach was chosen because it provides information on the interaction of two or more parameters on the system under study.

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