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

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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.

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, ΔT 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 ΔT 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 μ 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).