

Coating of Solid-Phase Microextraction Fibers with Chemically Bonded Silica Particles: Selective Extraction of Polycyclic Aromatic Hydrocarbons from Drinking Water Samples

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Abstract

In this study, solid-phase microextraction fibers coated with modified silica particles (5 μm dp) bonded to methyl (C_1), hexyl (C_6), octyl (C_8), and polymeric octadecyl (C_{18}) groups are prepared and evaluated. Selective extraction of polycyclic aromatic hydrocarbons (PAHs) from river water is used to demonstrate the selective behavior of the fibers as a function of the alkyl chains bonded to the silica phase. Scanning electron micrography suggests that the coating structure consists in a monolayer of particles bonded to the surface of the fiber. The behavior of the fibers upon the extraction of PAHs from water samples is compared with the use of standard polydimethylsiloxane fibers that are commercially available.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are present in several complex environmental matrices such as crude oils and sediment extracts, often in association with other organic compounds (1). Increased attention has recently been paid to these compounds, both in organic geochemistry because PAHs are indicators of the maturation/origin of the sedimentary organic matter (2) and in environmental chemistry because of the mutagenic character of some of these molecules (3). Despite the selectivity of modern analytical techniques, it is necessary to develop appropriate separation to gain access to specific compounds of interest. Current techniques for the extraction and concentration of PAHs from water samples include liquid-liquid extraction and solid-phase extraction. Both of these techniques require the use of toxic organic solvents (4,5).

In the 1990s, chemists have paid considerable attention to solid-phase microextraction (SPME), which is a solvent-free alter-

native to classic extraction methods for the analysis of trace organic components in a variety of matrices. This technique has provided an interesting alternative to the selective extraction of several compound classes, including PAHs (6). SPME is a modern sample preparation technique that combines extraction, concentration, and sample introduction into a single step (7). This simple and relatively inexpensive extraction technique has found numerous applications in environmental analysis since its development. It is based on the partitioning of the analytes between the extracting phase immobilized on a fused-silica fiber substrate and the analyte matrix (8). The first coating fiber commercially available was polydimethylsiloxane (PDMS), which is a nonpolar coating. This coating has already been successfully used for the extraction of a variety of compounds (including PAHs), but the disadvantage of the PDMS coating is its general-purpose extracting character demonstrating little selectivity (9). The development of selective fibers increased its scope in analysis by gas chromatography (GC), and selective extraction of the analyte of interest can be easily achieved. Selectivity is used in this context to indicate the differences in the interaction of the analyte between the sample and the coating during the extraction; the structure of the coating contributes very much to this interaction (8,9). Thus, it is an indicator of the extraction power of the SPME process, being that high selectivity is almost always required for the extraction of complex mixtures whose contents are very similar compound groups. Selective fibers for the extraction of PAHs can be prepared by fixing silica particles onto the fused-silica capillary. Silica particles provide a large specific area; therefore, the different chemical groups that can be bonded on the silica surface will provide the required selectivity. The advantages of solid sorbents include a higher selectivity and capacity for apolar analytes (10,11).

This study describes the preparation of selective fibers coated with silica particles (5 μm dp) bonded with methyl (C_1), hexyl (C_6), octyl (C_8), and octadecyl (C_{18}). The selectivity of these phases was evaluated by analyzing PAH's priority pollutants in river

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water, being that the results compared with that obtained using a commercially available PDMS-coated fiber.

Experimental

Chemicals

Polymeric C₁₈, C₈, C₆, and C₁ bonded silica particles (5 μm dp) with a 100-Å pore size were obtained from Alltech (Deerfield, IL). ChemService (West Chester, PA) supplied the PAH's analytical standards. All solvents were analytical grade and used as obtained from Mallinckrodt (Xalostoc, NM). Stock solutions of each PAH were prepared by weighing and dissolving them in methanol, and they were stored in a freezer. Working solutions of PAHs were prepared daily by solubilizing the stock solution in river water to obtain the desired concentrations.

Fiber preparation

SPME fibers were individually coated with the chemically bonded silica particles containing C₁, C₆, C₈, and polymeric C₁₈ groups. Fused-silica capillaries (7.5–8.0 cm) were obtained from MicroQuartz (Munich, Germany). These were obtained already externally coated with polyimide and had an outer diameter of 0.30 mm. The polyimide coating on a 1-cm tip of fused silica was removed by burning off the tip. This was done carefully because the fused silica becomes fragile when the polyimide is removed. The exposed tip was washed with an excess of acetone and methanol and then air-dried at room temperature. The bonded-phase silica particles were immobilized on the fused-silica capillary surface using high-temperature cement from CIBA (New York, NY). The coated fused-silica fiber was preheated at 100°C for 1 h, at 150°C for 1 h, and finally at 180°C for 1 h. Then, the fiber was conditioned at 270°C into a GC injector for 2 h, being that it was ready for use.

SPME materials and procedure

The SPME holder employed during the manual extractives and a PDMS fiber (30 μm) were obtained from Supelco (Bellefonte, PA) and used for comparison purposes. The fiber was conditioned according to the instructions provided by the supplier. A magnetic stirrer from Corning PC-320 (New York, NY) was used for stirring the samples during extraction.

Preparation of the samples

Prior to analyses, river water was filtered through a 0.45-μm membrane filter Framex 389³ from Schleich&Schull (Dassel, Germany). Spiked river water samples were prepared by adding the appropriate volume (1–3 mL) of the analytical standard solution to the natural river waters to obtain the desired concentrations. River water samples from Ribeirão Feijão (São Carlos, SP, Brazil) and Ribeirão Anhumas, Ribeirão das Cruzes, and Córrego do Paiól (Araraquara, SP, Brazil) were investigated and successfully analyzed using the described approach.

SPME procedure

All of the extractions were performed at 27°C. The fiber was immersed into the sample (5-mL glass vial with a triangular stir

bar) for 40 min under stirring (1120 rpm). After extraction, the fiber was thermally desorbed (7 min) into the glass liner of a split/splitless GC injector maintained at 260°C. The injection was performed in the splitless mode for 1 min and then the split valve was opened for the rest of the analytical run.

Instrumental conditions

The GC used was a Shimadzu 17A (Kyoto, Japan) fitted with a flame ionization detector equipped with a 30-m × 0.25-mm-i.d. fused-silica capillary LM-5 column (5% phenyl–dimethylpolysiloxane, 0.3-μm film thickness) obtained from L&M Scientific (São Carlos, SP, Brazil). The initial column temperature was 90°C for 1 min, and then it was programmed to increase at a rate of 8°C/min to 300°C (7 min). The injection port and detector temperatures were maintained at 260°C and 300°C, respectively. Hydrogen was used as a carrier gas with an average linear velocity of 43.5 cm/s.

Scanning electron microscopy

The fibers were coated with a 20-Å thickness film of gold and then analyzed using a LEO-440 scanning electron microscope (SEM) (Oberkochen, Germany) (20 kV accelerating potential).

Results and Discussion

Fibers characterization

Four different silica-bonded phases (all having a 5-μm particle size diameter and a 100-Å pore size) containing C₁, C₆, C₈, and polymeric C₁₈ groups were used for the preparation of the SPME fibers. Figure 1 shows the resulting SEMs of a typical C₁₈-type SPME fiber. The silica particles were immobilized on the fused-silica capillary using proper cement. The knowledge of the final structure of the fibers seems necessary for understanding their detailed behavior during the extraction. Although the morphology of the coating shows that it is not an ideal bed of uniform spherical microparticles because the particle size of the silica moiety is clearly not uniform (Figure 1B), the micrographs suggest that the structure of the coating consists of a monolayer of particles bonded to the surface of the fiber.

When the SPME fiber that was coated with chemically bonded silica particles was exposed to river water, the analytes were adsorbed onto the surface of the silica layer. This process involves the transfer of the analyte from the bulk solution of the outer surface coating by molecular and convective diffusion processes. The transfer of the analyte from the outer surface into the interior of the coating occurs by diffusion through the macropores between and inside the particles (10). The larger the pore size of the silica, the faster the diffusion process is. According to this model the analytes will be immersed in the coating in a way similar to a partition process (12). Thermal desorption of the analytes in the GC injector is the reverse process of adsorption. Analytes, which were adsorbed by the silica fiber, diffused from the pore of the silica particles into the carrier gas. Because the mass transfer of the analytes into the carrier gas is very fast, the diffusion on the silica particles is a low-energy process and does not influence the desorption process, and the desorption rate is very fast (11).

The diameter of the coating fibers was approximately 27 μm , being that the reproducibility from fiber to fiber was fairly good with differences in the coating thickness within 13%. The higher surface area of silica coating should also provide an enhanced extraction efficiency in SPME. The smaller coating thickness should help faster mass transfer during extraction as well as the analyte desorption process. The fibers could be used for up to 100 extraction cycles without a significant reduction of extraction performance. However, because the fibers were very brittle the lifetime of the fibers was mainly limited by breakage.

Extraction yields (obtained with proposed fibers) were compared with a commercial PDMS (30 μm) coated fiber under the same extraction conditions. Higher extraction yields for naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene were obtained for the homemade silica fibers (C_8 and C_6 fiber) compared with the commercial PDMS fibers. The silica fiber capacity depends on each individual compound, because the adsorption of each analyte occurs in different ways on specific sites.

Selectivity of PAH extraction

Adsorption of PAHs from aqueous solution (in the SPME coating) depends on the interaction between the analytes and the coating. The structure of the SPME coating contributes very much to these interactions and, consequently, the selectivity for

the coating (13). The mass of the PAHs adsorbed in the extraction process on the fiber coating can be expressed as (14):

$$N_s = \frac{KV_s \cdot V_{aq} \cdot C_{aq}}{KV_s + V_{aq}} \quad \text{Eq. 1}$$

where N_s is the number of moles extracted by the solid phase at equilibrium; V_{aq} and V_s are the volumes of the sample and the coating, respectively; C_{aq} is the concentration of the analyte in the sample; and K is the distribution coefficient of analyte between the coating and water.

The mass adsorbed on the fiber is dependent on the surface area of the coating and the distribution coefficient; therefore, the selective extraction of PAHs should be possible by using a selective silica-bonded stationary phase because each of the chemically bonded alkyl groups offers a different interaction for the PAHs.

In general, the distribution coefficient of analytes is dependent on the intermolecular interactions between the solute and the coating, which includes hydrogen-bonding, acid–basic, dipole interactions, and Van der Waals forces. For the hydrophobic alkyl stationary phase, the interaction is mainly through Van der Waals forces (15). According to this theory hydrophobic interaction results from repulsive forces between a polar solvent (water matrix) and the nonpolar solute and stationary phase. The driving force in the binding of the solute to the stationary phase is the decrease in the area of the nonpolar segment of the solute molecule exposed to the solvent (16). Stated differently, it is the repulsion of the solute and the polar mobile phase rather than the weak nonpolar interactions between the solute and the nonpolar stationary phase, which is responsible for the interaction of the PAHs and the coating (17). The characteristics of the fiber used can affect the sorption behavior of the PAHs. The extraction profile for four SPME fibers (C_1 , C_6 , C_8 , and C_{18}) was compared with the PDMS fiber. The peak area of each PAH was percent normalized, taking into consideration that the corresponding peak area obtained with the PDMS fiber was equal to 100. The area of each

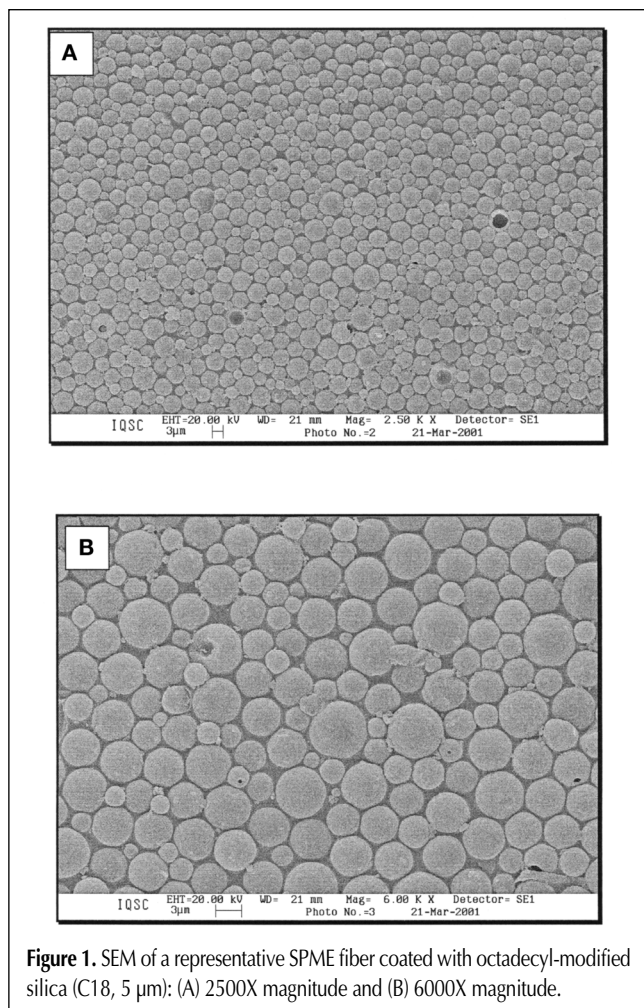


Figure 1. SEM of a representative SPME fiber coated with octadecyl-modified silica (C_{18} , 5 μm): (A) 2500X magnitude and (B) 6000X magnitude.

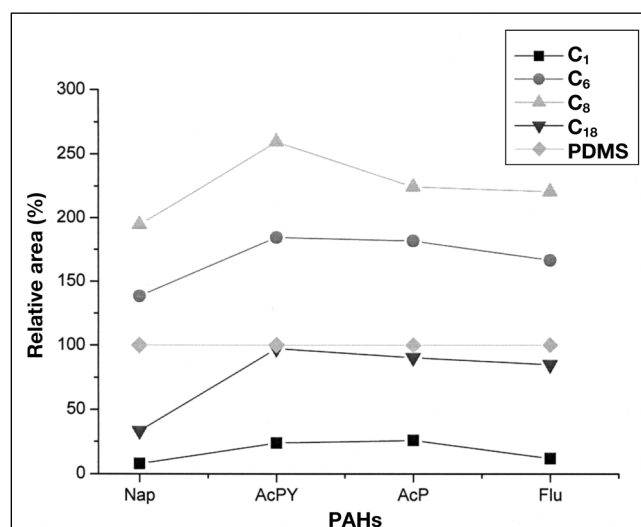


Figure 2. Extraction profile (relative to PDMS fiber normalized to 100%) of the low-molecular-weight EPA priority PAHs (MW = 128 and 170) as a function of the side alkyl chain of the chemically bonded silica fibers: naphthalene, Nap; acenaphthylene, AcPY; acenaphthene, AcP; and fluorene, Flu. See text for details.

PAH with each fiber was normalized versus the corresponding peak area obtained with the PDMS fiber. This approach was adopted to investigate the influence of the alkyl chain in the profile extraction of 16 U.S. Environmental Protection Agency (EPA) PAHs in water samples. Figure 2 shows the extraction profile normalized of the low-molecular-weight PAHs (MW = 128–70) as a function of the alkyl chain chemically bonded to the silica obtained with the different fibers versus PDMS.

We can observe that for all of the examined compounds that possessed a molecular weight below 170 Da and two rings, higher extraction yields can be obtained through the C₈ fiber. The extraction profile for these compounds as a function of the alkyl groups bonded to the silica is very similar, but the extracted amount (yield) for each one is a function of the molecular structure. The amount extracted by the C₈ fiber increased with the carbon number (except for the fluorine) and as a function of the molecular structure of the PAHs (the chemical structures are shown in Table I). For naphthalene (which presents two fused aromatic rings) the extracted amount was smaller than the other three compounds, which in addition to the aromatic group presents a cycle pentane ring conjugated to the aromatic ones. Acenaphthene and acenaphthylene presented similar behavior, being that the extracted amounts were approximately the same (a little bit higher for the latter), which is in accordance with their structural similarity. The amount extracted for acenaphthylene was higher in all of the alkyl-silica fibers, because the double bond of the cycle between the aromatic groups differs in relation to the acenaphthene (Table I).

For compounds of molecular weight between 178 and 202 Da mainly showing three rings (Table I), the extracted amount was higher on the C₆ fiber. The profile of the extraction for these compounds as a function of the alkyl chain shows a clear similarity on

the behavior of the isomeric compounds (Figure 3). For phenantrene and anthracene (both having three fused aromatic rings and the same molecular weight) the extracted amount varied with the position of the aromatic ring, being that the extraction of phenantrene was more favorable with the exception of the C₁ fiber. The compounds with four-ring PAHs were the most adsorbed. However, for fluoranthene and pyrene the extracted amount was similar for all silica fibers with the exception of the C₁ fiber whose extracted amount varied as a function of the structural differences between the two isomers, being that the more condensed compound (pyrene) was easier to extract in all of the alkyl-silica fibers (when compared with fluoranthene).

Therefore, for this group of compounds the extracted amount was higher in C₆ fibers and depended on the interaction between the alkyl chain of the stationary phase and the structural conformation of the molecule of the analyte.

The interactions between the alkyl groups of the stationary phase and the analyte that have molecular weights between 228 and 252 (mainly four-ring PAHs, shown in Table I) were more selective on the C₆ phase among the alkyl phases investigated. In this phase, the profile of the extraction of the isomeric compounds (benzo[*a*]anthracene and chrysene as a group of isomers and benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and benzo[*a*]pyrene as the other group) is similar, and for the other evaluated alkyl-silica phases the profile of the extraction is nearly the same for all of the compounds (Figure 4). Table I shows the structure and the molecular weight of these PAHs.

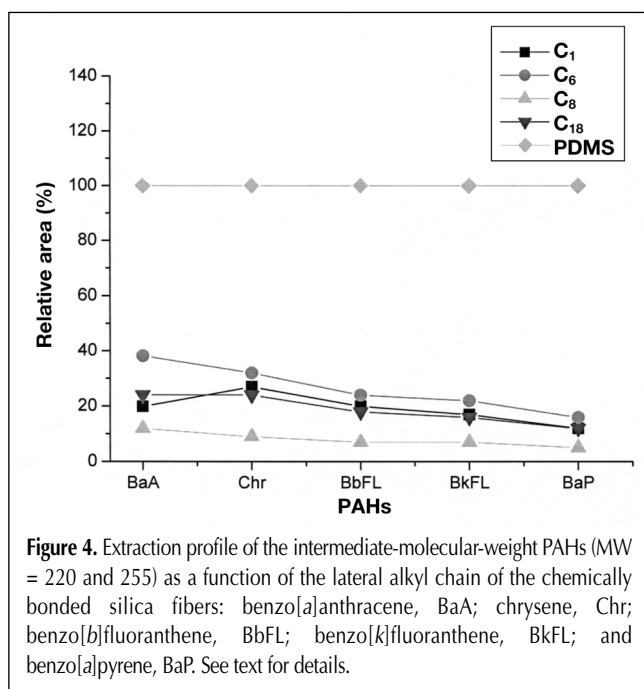
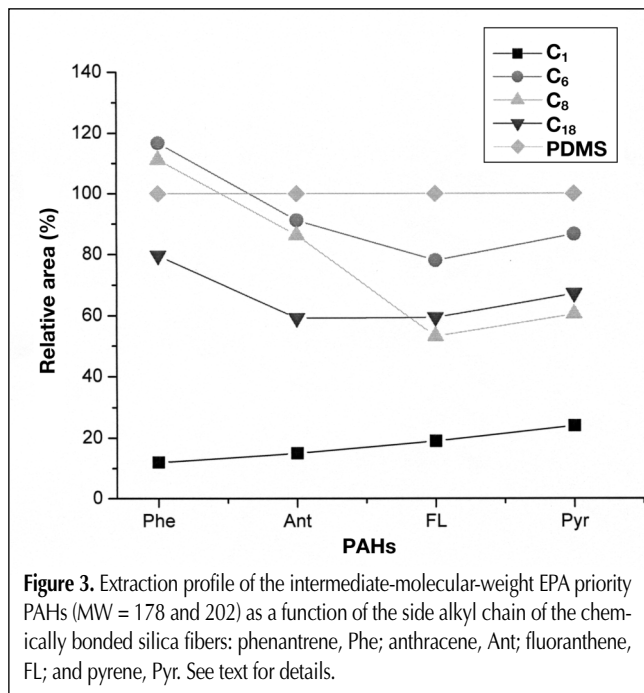
For compounds with a molecular weight of 276 to 278 (higher molecular weight and more condensed PAHs) the efficiency of the alkyl-silica phases was nearly similar for all of the investigated compounds (Figure 5). Although they have similar extraction profiles as a function of the alkyl phase, these compounds are not

Table I. Structure and Molecular Weight of PAHs Studied

Compounds	Structure	MW	Compounds	Structure	MW
Naphtalene		128.17	Chrysene		228.29
Acenaphthylene		152.19	Benzo[<i>a</i>]anthracene		228.29
Acenaphthene		154.21	Benzo[<i>b</i>]fluoranthene		228.29
Fluorene		166.22	Benzo[<i>k</i>]fluoranthene		228.29
Phenantrene		178.23	Benzo[<i>a</i>]pyrene		252.31
Anthracene		178.23	Indeno[1,2,3- <i>cd</i>]pyrene		276.00
Fluoranthene		202.25	Dibenzo[<i>a,h</i>]anthracene		278.35
Pyrene		202.25	Benzo[<i>ghi</i>]perylene		276.33

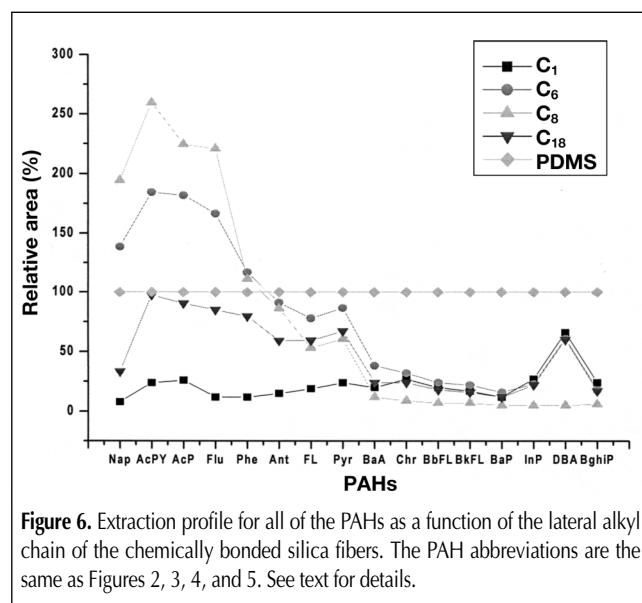
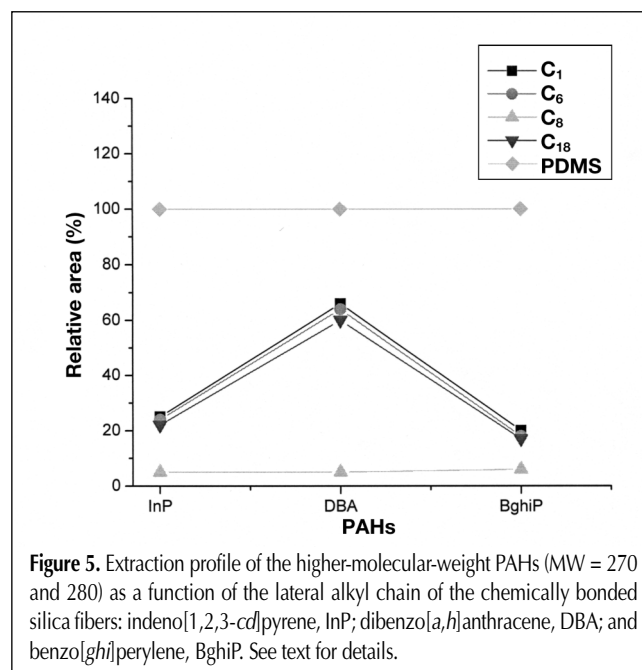
isomers (being discriminated (a little) only in the C₈ fiber).

Figure 6 illustrates the extraction profile of the 16 PAHs obtained with the C₁, C₆, C₈, and C₁₈ fibers normalized versus the PDMS fiber. As expected, the extraction profile varied as a function of the structural characteristics for each compound and of the alkyl chain bonded to silica. The extraction profile for the two-ring PAHs was similar for all of the silica fibers and were the most extensively adsorbed in the C₈ fiber following the order: C₈ > C₆ > C₁₈ > C₁. This means that an SPME fiber with octyl-silica coating is more suitable for the extraction of low-molecular-weight PAHs. However, the extraction amounts of three, four, and five rings were higher for the hexyl-silica coating, and the order of the recovery varied as a function of the ring numbers. For the three



rings the order of the recovery was C₆ > C₈ > C₁₈ > C₁ and for four rings was C₆ > C₁₈ > C₈ > C₁. Thus, with the increase of the number of rings from three and four rings, the extraction efficiencies for the octyl-silica coating decreases. Therefore, the behavior of five rings was similar to that of six rings except for octyl-silica coating, which showed low recovery with five- and six-ring PAHs. The C₆ fiber showed the higher recovery for these PAHs with the exception of indeno[1,2,3-*cd*]perylene, dibenzo[*a,h*]anthracene, and benzo[*ghi*]pyrene, whose relative area with C₁ were rather surprisingly 27, 66, and 24, respectively, and whose relative area with C₆ were 23, 61, and 18, respectively.

It is interesting to compare the efficiency extraction for the C₈ and C₁ fibers for all of the PAHs. The recovery for these fibers differed very widely from naphthalene to dibenzo[*ghi*]pyrene, the C₆ fiber was more suitable for the extraction of low-molecular-weight PAHs and C₁ for the higher-molecular-weight PAHs. The



profile for the other fibers (C_6 and C_{18}) were quantitatively similar for all compounds.

The selectivity of the alkyl-chain chemically bonded silica can be explained using the same theory used to explain the retention of analytes on the stationary phases in high-performance liquid chromatography (HPLC). An empirical model of extraction termed the "slot model" can explain the interaction between the PAHs and alkyl chain. According to this model, the stationary phase is viewed schematically as an environment consisting of slots into which a PAH's molecules can penetrate. Because slots can be thought of in finite heights and widths, a PAH's interaction (penetration) will vary depending upon the shape characteristics. Our results suggest that a similar behavior was observed in the SPME extraction of the PAHs, because by increasing the molecular size of the analyte they were better extracted by the small-chain alkyl-containing phases. The results show that longer chains appear to restrict the access of the bulkier molecules (larger PAHs) to the full extent of the hydrophobic surface as observed in HPLC in which the structure of the alkyl chain plays a definitive role in the control of retention and possibly selectivity. An increased chain length results in longer retention (16,18). As a consequence, and as shown in this study, the containing phase did not show to be the best phase for the extracting C_{18} for any of the 16 investigated PAHs.

Conclusion

The selective extraction of PAHs can be obtained using fibers coated with chemically bonded silica particles. The selectivity of the extraction is a function of the structure and molecular weight of the PAHs. Using a commercially available PDMS, 30- μm fiber for comparative purposes, selective extractions of the PAHs were not possible to carry out, being that the main advantage of this fiber was the higher extraction yield of higher-molecular-weight PAHs when compared with those fibers coated with alkyl silica. For lower-molecular-weight PAHs the lower alkyl chain presented a higher extraction yield than the obtained one using the PDMS fiber. Further studies on the effect of particle size, pore size, and surface coverage will allow for the optimization of the alkyl-silica fibers in order to increase the extraction yield because their selectivity is already demonstrated in this study.

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