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Helical Sorbent for Fast Sorption and Desorption in Solid-Phase Microextraction-Gas Chromatographic Analysis

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A new technique for solid-phase microextraction (SPME) of analytes using a helical solid sorbent followed by thermal desorption into a gas chromatographic injector is reported. The main factors that affect the mass transport of analytes in sorption and thermal desorption process using a poly(dimethylsiloxane) (PDMS) helical sorbent are described. The sorption and thermal desorption were achieved in a few seconds, being very close by the theoretical prediction. Both processes were very fast by the reduction of the thickness of boundary layer between sorbent and gaseous sample as a result of a turbulent rotational flow of the headspace air on the surface of sorbent, which is generated by the helical configuration of the sorbent. The thermal desorption was also reduced by improving heat transfer into a thin boundary layer and by increasing the temperature of the heat transporter (carrier gas). The sorption and desorption with PDMS helical sorbent were compared with those of the PDMS silica rod. The extraction time was as much as 15 times faster with the PDMS helical sorbent than with the PDMS silica rod. The desorption with the PDMS helical sorbent was very fast, giving narrow peaks without tailing and a high efficiency of separation in comparison with PDMS silica rod.

A wide range of sample preparation methods are used before chromatographic analysis, but the extraction has become the most popular for collection, purification, and concentration of analytes from complex sample matrixes. Classical liquid extraction is an equilibrium process based on the differential distribution of analytes between the phase of the sample matrix and an immiscible liquid phase. The separation of analytes is not exhaustive, uses large amounts of neat solvents, is time-consuming, and is often tedious. It also is difficult to remove a large volume of solvent if a supercritical fluid is not used. Although the time and the consumption of solvent were reduced recently by liquid−liquid segmented extraction,[1,2] liquid extraction into a single drop,[3] and accelerated solvent extraction,[4] these disadvantages persist.

A very attractive alternative to liquid extraction in terms of quantities of expensive organic solvent, time required, sensitivity, selectivity, precision, and relative simplicity is solid-phase extraction, which already has thousands of applications for gaseous[5] and liquid [6] samples or for analytes from the headspace of condensed samples.[7] This extraction involves the sorption of analytes from the sample matrix onto a solid sorbent as the extractant. The solid extractant is a solid material, such as particles in a small tube[5,6] or small rods and tubes,[8−10] with sorption properties like those for analytes or coated with a specific stationary phase. In solid-phase extraction, the analytes can be retained completely in a temporarily dynamic and nonequilibrium process by loading the solid sorbent with a discrete volume of liquid sample or retained partially in a dynamic and equilibrium process. The desorption from the solid sorbent can be performed by extraction with a volume of optimum elution solvent or by heating the solid sorbent. The desire to reduce the amount of organic solvent used for desorption in solid-phase extraction has led to the use of small volumes of solid sorbent.[8−11] Thermal desorption[8−10,12−15] was successfully applied for the elimination of organic solvent needed for the desorption of volatile and semivolatile analytes from solid sorbents and for introducing them into a gas chromatograph.

The total time required for collecting, concentration, and injection into an analytical instrument by solid-phase extraction is shorter than with liquid extraction. However, solid-phase extraction with a porous sorbent, which is performed in four steps,[6] suffers from low reproducibility if the particle size distribution and physicochemical properties of the pores are not reproducible. A rod or a tube[8−10] with a smooth surface covered with a thin layer of stationary phase avoids this variation in the blank value. Moreover, extraction with these sorbents is faster, because they need only sorption and desorption steps and sometimes a

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conditioning. The time-determining step in this case is given by the diffusion of analytes from the sample matrix to the solid sorbent and back. The parameters that affect this mass transport of analytes and especially the diffusion through boundary layer on the surface of the sorbent can reduce significantly the extraction time.

This paper reports a new technique for solid-phase extraction that uses a helical solid sorbent. The technique is solvent-free in thermal desorption and reduces the time of sorption and desorption in dynamic extraction by generating a rotational flow of analytes and turbulence on the surface of the sorbent due to its helical configuration, reducing dramatically the diffusion time of analytes in the boundary layer.

EXPERIMENTAL SECTION

Regents and Materials. Benzene, toluene, ethyl benzene, o-xylene, and p-xylene used in a BTEX mixture were analytical grade from Merck (Darmstadt, Germany). All other solvents were reagent grade. Commercially available 30-μm bounded and 100-μm nonbounded film thicknesses of poly(dimethylsiloxane) (PDMS) on 0.1-mm fused-silica rod (Supelco, Bellefonte, PA) were used. On the basis of the coating dimensions reported by the manufacturer, the volumes and surface area of 30-μm PDMS solid phase were 0.122 mm^3 and 5.024 mm^2, respectively, and for 100-μm PDMS were 0.628 mm^3 and 9.421 mm^2, respectively. All PDMS silica rods were cleaned for at least 30 min at 300 °C before each solid-phase microextraction. PDMS used for helical sorbent was OV-1 stationary phase (Alltech, Hoogeveen, The Netherlands). The density of the PDMS material (952 kg/m^3) was obtained by measuring the mass and the volume of the polymer.

Instrumentation. An HRGCC-5300 gas chromatograph (Carlo Erba, Milan, Italy) was used for all experiments. The instrument was equipped with a flame ionization detector (FID) and 30 m × 0.25 mm i.d. fused-silica coated with a 0.25-μm film thickness DB-1 (J&W Scientific, Folson, CA). The GC oven temperature was programmed from 50 to 70 °C with 4 °C/min. The carrier gas was helium (Linde, Timisoara, Romania) at 1 mL/min. The injections with PDMS silica rods and PDMS helical sorbent were done manually through direct injection. The points in the extraction and desorption graphs are the mean value from seven injections.

Measurement of the air velocity inside the sampling vials was performed by the hot wire principle with an air velocity meter model HHF-51 from Omega (Stanford, CT). The wire of the meter device was maintained at 1200 °C, and the current across the wire was processed to give a direct digital reading of the air velocity.

Preparation of Helical Solid Sorbent. The helical solid sorbent can be a solid material with any geometrical form in cross section, arranged in any type of helical line, having sorption properties as such or coated physically or chemically with a sorbent material. The helical support for the coating material was made by wrapping with a constant pitch a wire around a straight wire with the same diameter. When the wrapping was finished, the straight wire was removed and the helical support was cut to a length (10−15 mm) determined experimentally as a function of the type of injector. In these experiments, the wire was made from a chromium−aluminum alloy (AB Kanthal, Hallstahammer, Sweden) and had a 0.07-mm diameter. The helical support was first cleaned with a mixture of water and detergent and rinsed with sufficient water to remove the trace of detergent. Afterward, it
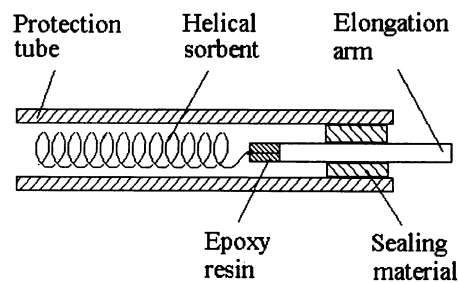

Figure 1. Sectional view of a helical sorbent.

was cleaned with a mixture of acetone and chloroform (1:1 v/v) in an ultrasonic bath for 30 min at room temperature and then was dried in air at 110 °C for 20 min. The surface of the helical support was coated with a multilayer of PDMS by immersion of the helical support in a solution of 60%/30% PDMS in chloroform. After each coating, the solvent was evaporated by heating the helical sorbent at 100 °C for 30 min. The thickness of the final coating of polymer depended on the concentration of the PDMS solutions and the number of coatings. The helical sorbent was weighted after each coating to obtain approximately the same PDMS-material-like PDMS fused-silica fiber. The wire (34-mm length) wrapped in a helical configuration was uniformly coated with approximately four layers of PDMS. The volume and surface area of the PDMS sorbent layer with 50-μm thickness were 0.631 mm^3 and 18.152 mm^2, respectively.

Helical Sorbent Holder Device. The helical sorbent was introduced into a tube (Figure 1) for to protect the sorbent from damage during storage and introduction of helical sorbent through the sample vial and the GC injector septa.

The helical sorbent was attached to an elongation arm by introduction of one end of the helical sorbent into a stainless steel tube, where it was fixed with 353ND high-temperature epoxy resin (Epoxy Technology, Billerica, MA). The elongation arm and the helical sorbent were moved inside and outside of the protection tube (0.52-mm i.d. and 0.60-mm o.d.), which had an opened end and another one plugged with a sealing material. The protection tube with helical sorbent inside was attached to a device to perform longitudinally movement of the helical sorbent (Figure 2). In this helical sorbent holder device, the elongation arm was connected to a plunger with a handle on the end. The plunger was equipped with a spring around it, and it was kept in the retracted position by a stopper. The protection tube could be moved through the hole of a guide plate fixed by three guide rods that had three springs around them. The guide rods slid through a guide connector that could be moved up and down on the external screw thread of a barrel. The movement of guide rods was adjustable by nuts and a limitation nut screwed onto the barrel.

Solid-Phase Microextraction Procedure. Two vials with screw caps and septums of 35 and 125 mL were used as sample containers. Stock volumetric mixture of benzene, toluene, ethyl benzene, o-xylene, and p-xylene (1:1:1:1:1) and stock solutions of 0.04 mg/mL of individual BTEX components in methanol were prepared. Appropriate amounts of this stock mixture or individual components were spiked into 15 and 50 mL, respectively, of distilled water using a 1-μL syringe to give different concentrations of analytes. A magnetic stirrer with a speed up to 1400 rpm was
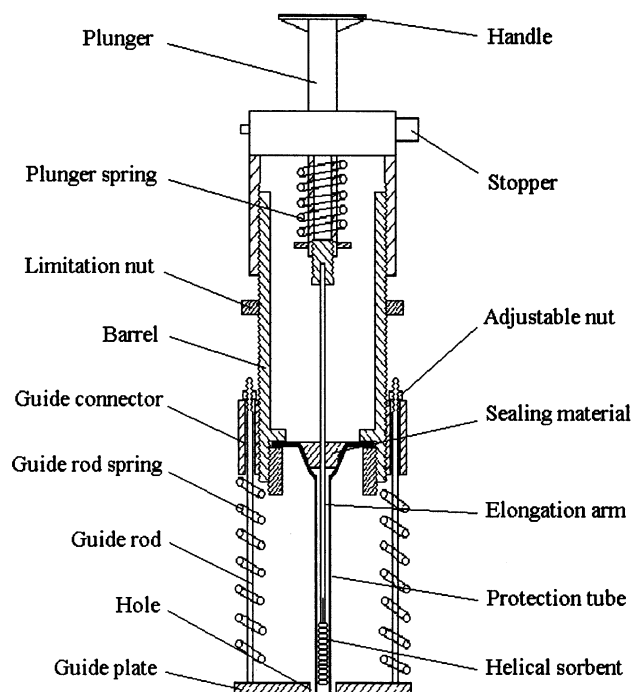
Figure 2. Schematic partial sectional view of a helical sorbent holder device.

used to agitate the analytes solution. The vials were thermostated at 25°C, and the agitation of the sample was started before sampling.

Solid-phase microextraction with the helical sorbent holder device involved a few simple steps. The tip of the protection tube with the helical sorbent retracted was adjusted with adjustable nuts or with a guide connector to be inside the guide plate hole. The guide plate was laid on the vial screw cap. The vial septum was pierced by the protection tube with helical sorbent retracted by pushing the barrel with the springs of the guide rods compressed. For headspace analysis, the length of penetrated guide tube was adjusted with a limitation nut to avoid contact with the surface of the solution. By pushing the plunger stopper, the plunger spring was released, and the helical sorbent was pushed down from the protection tube into the headspace. Releasing the spring of the guide rod immediately retracted the protection tube from vial. When the extraction was finished, the barrel was pushed down, and the protection tube was inserted again into the vial. The plunger was pulled up to the stopper position, and the helical sorbent was retracted into the protection tube. Stopping to push down the barrel completely removed the protection tube with the retracted helical sorbent from the vial. The extraction time was defined as the period from the insertion of the helical sorbent into the headspace until it was retracted into the protection tube.

Similar steps were used for introduction and removal the helical sorbent into and out of a GC injector port.

RESULTS AND DISCUSSION

A small rod or tube coated with a sorbent material for collection and extraction of the analytes from a sample matrix followed by their introduction into a gas chromatographic injector for analysis
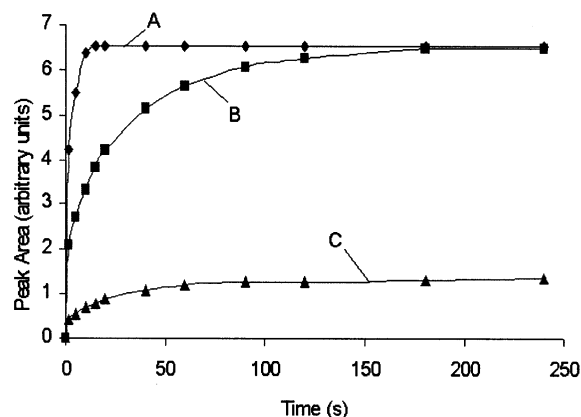

Figure 3. Extraction profile of benzene from headspace with a helical sorbent and a silica road coated with nonbounded PDMS: (A) helical sorbent with 50-μm coating thickness, (B) silica rod with 100-μm coating thickness, and (C) silica rod with 30-μm coating thickness. Conditions: 0.1 μg/mL benzene in water; 15 mL of solution in a 35-mL vial; the velocity of headspace flux on the surface of the coating was 0.05 m/s.

was applied for the first time by Palm.[8] Later, this technique was improved by Pawliszyn's group[9] and many other researchers.[16,17]

Figure 3 shows the extraction time profile of benzene from headspace with a helical sorbent and silica rod coated with PDMS. In both cases, it was a dynamic extraction based on an equilibrium process of the analytes in a three-phase system. The equilibrium of analytes between the liquid phase and the headspace can be ignored, since it was reached very quickly by stirring. The equilibrium process of the analytes between sample headspace and sorbent involves the following mass transport steps: (1) diffusion of analytes from the headspace to the boundary layer on the surface of the sorbent, (2) diffusion of analytes through the boundary layer, (3) adsorption of analytes onto the surface of the sorbent, (4) diffusion of analytes into the layer of sorbent. The diffusion in the boundary layer or in the sorbent can be the rate-controlling factor because steps 1 and 3 are very fast processes. The mass flow rate (F) of analyte from the headspace to coating surface should be equal to the mass flow rate from the coating surface to its inner layers for balanced mass transfer. Fick's first law of diffusion can be express as follows for this continuous-flow system,

$$F = -D_1(dC_h/dz) = -D_2(dC_c/dz) \tag{1}$$

were C_h and C_c are the molar concentrations of the analyte in the headspace and in the coating film, respectively; z is the distance in the direction of diffusion; D_1 is the diffusion coefficient of the analyte in the boundary layer at the coating-headspace interface; and D_2 is the diffusion coefficient of the analyte in the coating film. Taking into account the mass balance before and at equilibrium and the distribution equilibrium of the analytes between the headspace and coating sorbent, the number of moles of analytes absorbed by the coating sorbent at equilibrium (M_a)

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is given by equation

$$M_a = (KV_h V_c C_h^0)/(KV_c + V_h) \qquad (2)$$

where C_h^0 is the initial concentration of analyte in headspace, V_h and V_c are the volumes of headspace and sorbent coating, respectively, and K is the distribution constant. It should be noted that the amount of analyte extracted at equilibrium is directly proportional to the volume of sorbent material. This is in agreement with the results from Figure 3. The amount of analyte extracted at equilibrium with 50 μm of PDMS on the helical support was approximately the same given by 100 μm of PDMS on a silica rod, since the volumes of PDMS coating were practically the same.

The main disadvantage of the coated-silica rod has been a relatively long time for the extraction of analytes. The helical sorbent with a 50-μm PDMS coating had a film thickness twice as thin as the 100-μm PDMS rod, and the coating surface area was 1.92 times larger. These characteristics of the PDMS helical sorbent could increase until 4 times the speed of extraction, as compared to the 100-μm PDMS rod but could not explain why the extraction time at steady state was reduced more than 15 times. Moreover, the extraction time for the helical sorbent with the 50-μm PDMS coating was more than 15 times shorter, even in comparison with a thinner coating thickness, than the 30-μm PDMS silica rod. Similar results were obtained for toluene, ethyl benzene, o-xylene, and p-xylene. The only explanation of this huge difference in extraction time could be found in the improvement of the mass transfer of analytes in the boundary layer of the helical sorbent.

The boundary layer stems from the friction between the sample fluid and the surface of the sorbent, and it is practically a static layer where the mass transport is performed by molecular diffusion. The profile of the flow path lines around a silica rod coated with PDMS was similar to that already presented in the literature[18] and was monitored when the silica rod was placed in the vial so that the fluid flow was perpendicular to the axis rod. On ~50% of the rod surface, the flow was laminar, and on the other 50%, the erratic path lines were developed far from the surface of the sorbent, generating a thicker boundary layer. With a helical sorbent, the flow had a rotational motion around the helix,[19] and as a function of the velocity of the fluid and the pitch of the helix,[20] turbulence was generated on the surface of the sorbent. In a transition and turbulent flow, the thickness of the boundary layer was reduced to a thinner boundary layer called the laminar sublayer in which the mass transfer was also controlled by diffusion. The thickness of the boundary layer was defined as the distance from the sorbent surface at which the local concentration and velocity reach 99% of their values in the undisturbed stream[21] and depended on the type of surface, the interaction between the surface and the fluid, and the velocity of the sample fluid on the surface of the sorbent being calculated with semiempirical relationships for each type of surface. In all cases, an increase in velocity resulted in a decrease in the
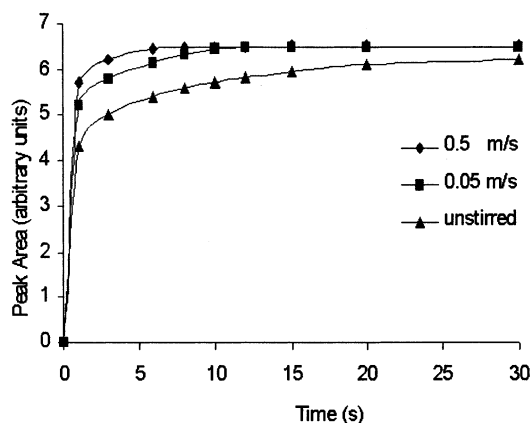
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Figure 4. The effect of the velocity of the headspace flux on the surface of the sorbent on the extraction profile of benzene with helical sorbent coated with 50 μm PDMS. Conditions: 0.1 μg/mL benzene in water, 50 mL of solution in a 125-mL vial.

boundary layer thickness. Figure 4 shows that the extraction time profile with helical sorbent coated with PDMS was affected by the velocity of the headspace air in the vial. It can be seen that the longest extraction time at steady state was obtained for the unstirred solution. However, the high amount of analyte extracted in the first second for unstirred solution was caused by the movement of the helical sorbent in the headspace when it was introduced and withdrawn from the vial and was due to the movement of molecules by thermal convection. The increase in the headspace flux velocity on the sorbent surface from 0.05 to 0.5 m/s gave a decrease in the extraction time from 12 to 8 s. These results suggested that the limiting step in the extraction process would be the diffusion through the boundary layer rather than the film thickness. It can be predicted that, under perfect conditions of agitation, the speed of the extraction process will be determined only by the diffusion of analyte in the PDMS coating. The average time (t) of diffusion of the analyte through the PDMS film is given by[22]

$$t = d^2/2D \qquad (3)$$

where d is the thickness of the PDMS layer, and D is the diffusion coefficient of the analyte in the PDMS layer. A silica rod coated with 100 μm of PDMS had the average time of diffusion of benzene in a polymer layer, ~18 s at 25 °C, for a diffusion coefficient[23] of 2.8×10^{-6} cm^2/s. For a helical sorbent coated with 50 μm of PDMS, the average time of diffusion was ~5 s. As can be seen from Figure 4, the extraction time with the helical sorbent was 8 s, which is very close to perfect agitation. This very fast extraction time was the result of the turbulent rotational flow of headspace air on the surface of the sorbent created by the helical configuration of the sorbent. This helical flow decreases significantly the boundary layer thickness. Practically, a perfect agitation cannot be reached, because the boundary layer can be reduced but cannot be eliminated.

Thermal desorption of the analytes from the sorbent in the GC injector is the reverse process of sorption involving only three

(22) Crank, J. *Mathematics of Diffusion*, 2nd ed.; Clarendon Press: Oxford, U.K., 1989; p 14.
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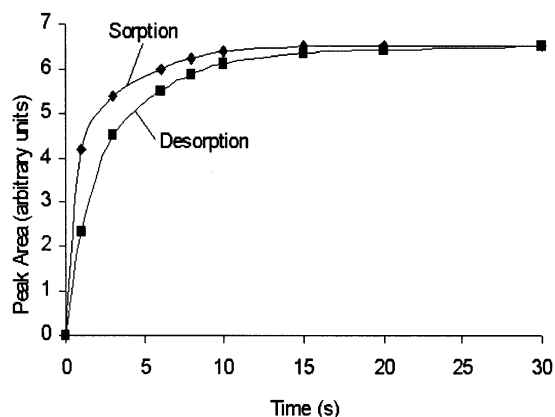
Figure 5. Sorption and desorption profile of benzene extracted from headspace with the helical sorbent coated with 50 μm of PDMS. Conditions: 0.1 μg/mL benzene in water; 15 mL of solution in a 35-mL vial; the temperatures for sorption and desorption were 25 °C; the velocity of headspace flux and carrier gas on the surface of the coating was 0.02 m/s.

Figure 6. Effect of temperature on the desorption profile of benzene extracted from headspace with a 50-μm PDMS helical sorbent. Conditions: 0.1 μg/mL benzene in water; the sorption time was 20 s; the velocity of headspace flux and carrier gas on the surface of the coating was 0.02 m/s.

basic steps: (1) the diffusion of analyte from the layer of sorbent to the boundary layer, (2) the diffusion of analyte through boundary layer, and (3) the diffusion of analyte from the boundary layer into the carrier gas. Since the mass transfer of the analytes into the carrier gas is very fast, the desorption from the PDMS coating is a diffusion-limited process in the PDMS coating and in the boundary layer on the surface of the coating. Figure 5 shows the profile of sorption and desorption of benzene with a helical sorbent coated with 50 μm of PDMS. The desorption was performed at approximately atmospheric pressure using a very short (0.5 m × 0.5 μm) deactivated fused-silica capillary in a GC oven. Both the sorption and desorption curves are linear in the initial stage and then are concave to the abscissa axis until a steady state. Under the same experimental conditions, the desorption process occurred at a lower speed in comparison with sorption, which would be in agreement with the sorption−desorption curves of hydrocarbons in polymers.[24] This difference between sorption and desorption is generated by the fast attachment of the analyte to the sorbent surface in the adsorption step of the sorption process, which does not occur in the desorption process.

Figure 6 shows the desorption profile of benzene at three different desorption temperatures. The time of desorption and the speed of desorption of the analyte were decreased by increasing the temperature in GC injector. The temperature of desorption was limited by the thermal stability of the analytes and sorbent. The time for desorption of benzene was 6 s with PDMS the helical sorbent at 250 °C. The thermal desorption process can be faster by improving the mass transfer of analytes in the boundary and sorbent layers and the heat transfer from the carrier gas to the sorbent. The diffusion of analytes in the boundary layer was faster with a thinner boundary layer, which was created by a turbulent rotational flow on the surface of the coating as a result of helical configuration of sorbent. The turbulence was limited by the carrier gas flow in the GC capillary column and was lower than in the sorption step. The diffusion of analytes in the sorbent layer was faster when the temperature of the sorbent was increased because the diffusion coefficient increased with the increase in temperature
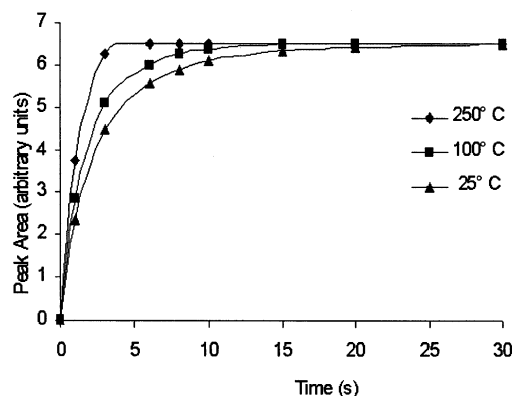
in accordance with the following equation[25]

$$D = D_0 \exp(-E/RT) \qquad (4)$$

where D_0 is the preexponential factor, E is the activation energy, R is the gas constant, and T is the temperature. The change in the diffusion coefficient with the temperature should be interpreted as an increasing zone of activation with increasing temperature and as being related to the increase in the free volume of the polymer sorbent with temperature. The temperature of the sorbent was increased as a result of heat transfer, which was a result of direct contact between the hot carrier gas and the cold sorbent. In the GC injector, the heat transport was by forced convection. The rate-controlling step of this process is the transfer through the boundary layer between the carrier gas and sorbent, where the heat transfer has a submicroscopic mechanism. Since the boundary layer was reduced by the turbulent rotational flow of the carrier gas generated by the helical configuration of sorbent, the heat transfer was rapid in this step, and the temperature of the sorbent increased very rapidly.

Gas chromatograms from Figure 7 show the influence of the temperature of desorption on the shape of the peaks. The helical sorbent was introduced into the GC injector for desorption of the analytes using the holder from Figure 2. This holder avoids the diffusion of the analytes into the protection tube of the helical sorbent during the extraction step, thus avoiding the thermal degradation and carryover for compounds with higher boiling point from the BTEX mixture. By desorption at 150 °C, the analytes extracted with the PDMS silica rod at equilibrium gave broad peaks with significant tailing (Figure 7C). When the extraction was performed with PDMS helical sorbent at equilibrium, the peaks generated by desorption at 150 °C (Figure 7B) were ~50% narrower than those were extracted with the PDMS silica rod. The separation between ethyl benzene and *p*-xylene was bad with the PDMS silica rod, but was very good with the PDMS helical sorbent, because the desorption with the PDMS

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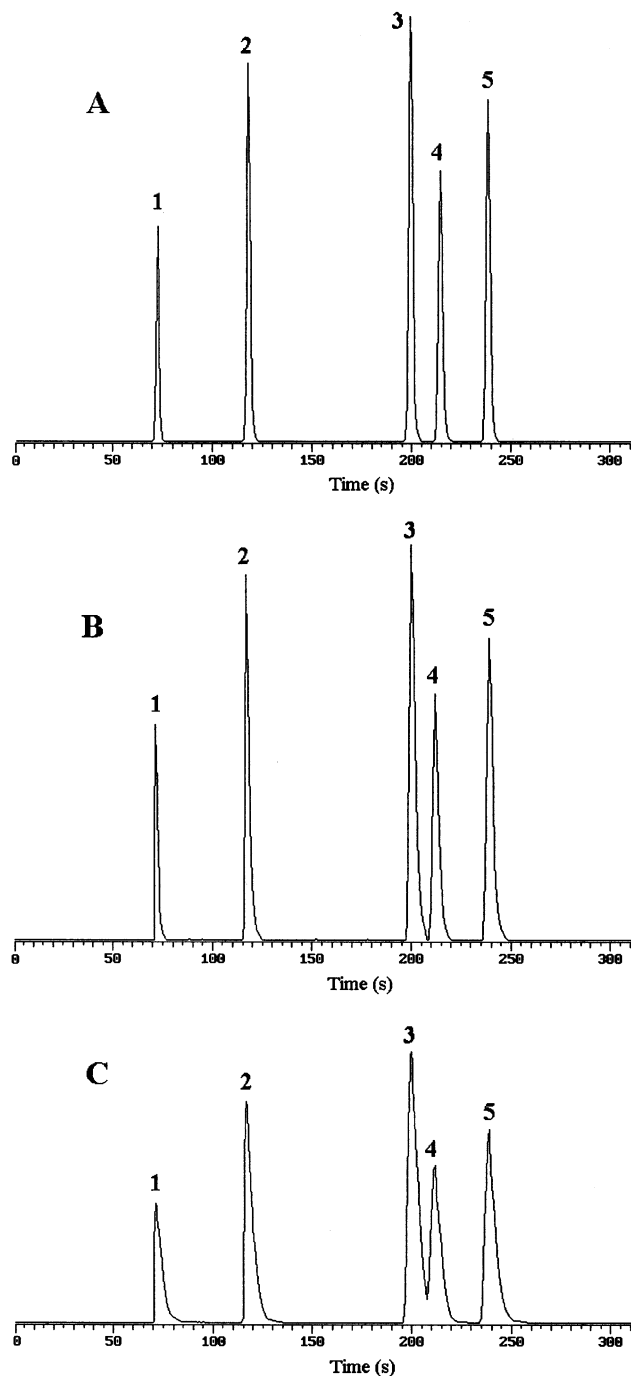(26) Ciucanu, I. Patent Application, PCT/RO 00209, 2001.

Figure 7. Gas chromatogram of BTEX from headspace solution using (A) 20-s extraction with 50-μm PDMS helical sorbent and desorption at 250 °C, (B) 20-s extraction with 50-μm PDMS helical sorbent and desorption at 150 °C, and (C) 10-min extraction with a 100-μm PDMS silica rod and desorption at 150 °C. Peaks: (1) benzene, (2) toluene, (3) ethyl benzene, (4) *p*-xylene, and (5) *o*-xylene. Conditions: 0.1 μg/mL from each analyte; 15 mL of solution in a 35-mL vial; the temperature of extraction was 25 °C; 1200 rpm stirring rate. For chromatographic conditions, see the Experimental Section.

helical sorbent was very fast as a result of the turbulent rotational flow on the surface of the sorbent, which generates narrower and sharper peaks. The higher peaks produced by the helical sorbent were a sign that the limit of detection can be improved using helical sorbent desorption. Increasing the temperature of desorption to 250 °C (Figure 7A), the speed of desorption in the PDMS layer of the helical sorbent was faster than at 150 °C, the peaks had no tailing and were narrower, and the separation between ethyl benzene and *p*-xylene was perfect for quantitative evaluation. Therefore, the efficiency of separation by gas chromatography was greatly improved using a helical sorbent for introduction of the analytes into the GC injector. This advantage of the helical sorbent can be used for introduction of thermosensitive analytes at low temperature into a GC column without losing the efficiency of separation.[26]

CONCLUSION

The results of this study clearly show that a helical sorbent is an ideal solution for fast sorption and desorption in dynamic solid-phase extraction-gas chromatographic analysis. The sorption of analytes in the extraction process became very rapid when the mass transfer of analytes in the boundary layer between the sorbent and gaseous sample was increased. The thickness of the boundary layer was reduced by the generation of a turbulent rotational flow of the headspace air on the surface of the sorbent as a result of the helical configuration of the sorbent. The sorption time at equilibrium was very close to the theoretical prediction for diffusion in the sorbent, being achieved in a few seconds. The extraction time at steady state was more as 15 times faster with the PDMS helical sorbent as it was with the PDMS silica rod.

The desorption of the extracted analytes into a GC injector was also achieved in a few seconds because of the improvement of the mass and heat transfer in the sorbent−sample boundary layer and in the sorbent layer by a turbulent rotational flow of the carrier gas on the surface of the sorbent generated by the helical configuration of the sorbent. The increase in the temperature in the GC injector increased the diffusion coefficient of the analytes in the sorbent, and the desorption was faster. A very fast desorption of analytes gave narrow peaks without tailing, and the separation was significantly improved. This made the helical sorbent ideal for injection of thermosensitive analytes at low temperatures with a good efficiency of separation. The presence of narrow, sharp peaks improved the limit of detection of the method. No carryover was noticed, even for analytes with low volatility, when the sorption and desorption were accomplished with the protection tube of the helical sorbent outside the sample vial and injector.

A possible application of the helical sorbent, either mobil or fixed inside of a protection tube, can be for fast collection and concentration of analytes by solid-phase microextraction followed by their fast desorption in a liquid chromatograph for analysis.