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High-performance polyethylene glycol-coated solid-phase microextraction fibers using sol–gel technology

Zhenyu Wang, Chuhua Xiao, Caiying Wu*, Huimin Han

Department of Chemistry, Wuhan University, Wuhan 430072, China

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Abstract

The sol–gel method is applied for the preparation of solid-phase microextraction (SPME) fibers. An electron microscopy experiment suggested a porous structure for Superox-4 (polyethylene glycol, PEG) coating. SPME–GC analyses provided evidence that the sol–gel fibers have some advantages, such as high velocities of mass transfer, efficient extraction rates, high thermal stability, long life span, and spacious range of application for both polar and non-polar analytes. Efficient SPME–GC analyses of benzene–toluene–ethylbenzene–xylenes, phenols, phthalic diesters, naphthalene congeners and pesticides were achieved using sol–gel-coated PEG fibers.

Keywords: Solid-phase microextraction; Extraction methods; Sol–gel chemistry; Headspace analysis; Poly(ethylene glycol); Benzenes; Toluene; Xylenes; Phenols; Pesticides; Naphthalenes; Phthalates; Chlorophenols; Nitrophenols

1. Introduction

The solid-phase microextraction (SPME) technique, introduced by Berladi and Pawliszyn [1], is a convenient and solvent-free extraction method which combines extraction, concentration and sample introduction in one step. Typically, a fused-silica fiber, which is coated with a thin layer of polymeric stationary phase [such as polydimethylsiloxane (PDMS) and polyacrylate (PA)], is used to extract analytes from water, soil and gaseous samples. Then, the extracted analytes are thermally desorbed in the injector of a gas chromatography (GC) system for analysis. This technology can be much quicker and simpler than the conventional methods. It is also sensitive, inexpensive and portable.

SPME is normally followed by GC. Currently, SPME has also been interfaced with other separation techniques, including high-performance liquid chromatography (HPLC) [2], capillary electrophoresis (CE) [3], and supercritical fluid chromatography (SFC) [4]. SPME has been successfully applied to the analysis of many complicated samples, such as soil, food [5], blood, urine [6] and other biological samples.

To date, several polymer-coated fused-silica fibers for SPME have been commercially available [7]. The PDMS fiber shows excellent selectivity for non-polar compounds, such as benzene–toluene–ethylbenzene–xylenes (BTEX) [8], polycyclic aromatic hydrocarbons (PAHs) [9], polychlorinated biphenyls (PCBs) [10]. The PA fiber which has an obviously more hydrophilic coating facilitates the extraction of polar analytes such as phenols [11], organophosphorous pesticides [12] and nitrogen-containing her-

*Corresponding author.

E-mail address: cywu@whu.edu.cn (C. Wu).

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bicides [13]. Compared with the upper temperature limit for the same stationary phases used in a GC column, the commercial 100 μm and 30 μm PDMS fibers have relatively low recommended operating temperatures and generally remain within the range of 200–270°C. Two factors are responsible for this [14]. First, the thickness of the stationary phase coating on SPME fiber is nearly one- to two-orders of magnitude higher than that of the stationary phase film in a GC column. Stabilization of SPME films is much more difficult than that of sub-μm thick films used in GC columns. Second, the lack of proper chemical bonding of the stationary phase coating with the silica surface is also responsible for the low thermal stability of the 100 μm and 30 μm PDMS fibers.

Sol–gel chemistry offers a simple and convenient pathway for synthesizing the advanced material systems and for applying them as surface coatings [15]. Sol–gel chemistry can efficiently incorporate organic compounds into the inorganic polymeric structures in solution under extraordinarily mild conditions. Among the many inherent advantages of sol–gel technology, the highlight is that it can provide strong adhesion of the coating to the substrate due to chemical bonding. Malik and co-workers have applied sol–gel coating technology to open tubular column GC [16], CE [17]. They also have used the sol–gel coating technique for a SPME fiber which was a bonded ~10 μm PDMS layer [14]. There were several advantages: high thermal stability, porous structure and large surface area. Sol–gel coating technology has high degree of flexibility in coating composition. By varying the proportion of the sol solution ingredients or using a deactivation reagent, one can change the composition of the layer which therefore will have different selectivity. In this paper, we use Superox-4 (polyethylene glycol, PEG) as the main sol ingredient to prepare a novel high-performance SPME fiber. To both polar and non-polar compounds, it shows a high sample capacity.

2. Experimental

2.1. Instrumentation and reagents

The SPME holder for manual sampling and SPME fibers were obtained from Supelco (Bellefonte, PA, USA). Four commercially available SPME fibers differing in stationary phase coating [100 μm and 7 μm PDMS, 85 μm PA, 65 μm Carbowax–divinylbenzene (CW–DVB)] were tested and compared in this study. Analyses were carried out in a Hewlett-Packard 6890 GC system equipped with an electron-capture detection (ECD) system, a WenLing 9790 GC system equipped with a flame ionization detection (FID) system (Zhejiang, China) and a Shimadzu C-R3A data processor. A 25 m×0.2 mm I.D., 0.33 μm HP-5 coating fused-silica capillary column (Hewlett-Packard) was used. Nitrogen was used as the carrier gas for both ECD and FID, at a linear velocity of 13–14 cm/s. The GC split valve was set to open after 2 min of insertion. The temperatures of injector and detector were maintained in the ranges of 250~300°C and 300°C, respectively. To analyze the BTEX, GC was programmed to hold at 40°C for 2 min, then heated at 7°C/min to 110°C, and then heated at 20°C/min to 130°C, for 1 min. To analyze the phenols, GC was programmed to hold at 80°C for 2 min, then heated at 4°C/min to 250°C. A JEM-1200/DX scanning electron microscope was used for the investigation of the fiber surface.

Methyltrimethoxysilane was purchased from WuDa Chemical Reagent (Wuhan, China), Superox-4 (PEG) was purchased from Alltech (Deerfield, IL, USA), trifluoroacetic acid (TFA) was purchased from Aldrich (Allentown, PA, USA). All solvents used in this study were analytical-reagent grade. Five kinds of stock solution are prepared. Solutions of BTEX (benzene, toluene, ethylbenzene, *o*-xylene, *p*-xylene), phenols (phenol, 2-chlorophenol, *o*-cresol, *p*-cresol, 2,6-dimethylphenol, 2-nitrophenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 1,2-benzenediol, 3-nitrophenol), phthalic diesters (diethyl phthalate, di-*n*-butyl phthalate, diamyl phthalate, diisohexyl phthalate, di-*n*-hexyl phthalate, di-*n*-octyl phthalate, dinonyl phthalate), naphthalene congeners (naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, biphenyl) were prepared by dissolving 10 mg of each compound in 10 ml methanol in a volumetric flask. The stock solution of organochlorine pesticides: 1,3,5- and 1,2,3-trichlorobenzene (135-TCB, 123-TCB), 1,2,3,5- and 1,2,3,4-tetrachlorobenzene (1235-TTCB, 1234-TTCB), α-, β-, γ- and δ-hexachlorocyclohex-

ane (α-HCH, β-HCH, γ-HCH and δ-HCH), hexachlorobenzene (HCB), aldrin, dieldrin, oystrene were prepared as 1 mg/ml in concentration. In our study, all samples were diluted with deionized water to give the required concentration.

2.2. Headspace extraction procedure

NaCl (3 g) was added to a standard 20 ml headspace (HS) vial containing a magnetic spin bar and 10 ml water sample. To prevent sample evaporation, the vial was sealed with a septum. During extraction, the septum vial was pierced with the protecting needle and the fiber was exposed to the gas. The organic analytes were adsorbed from the gas onto the fiber, then the adsorbed analytes were thermally desorbed by inserting the fiber into the injector of the GC system.

2.3. SPME fiber preparation

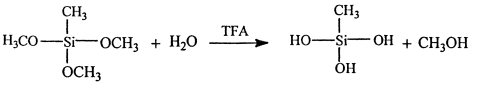
The sol solution was prepared as follow: 400 μl of methyltrimethoxysilane, 200 mg Superox-4 (PEG), 200 μl acetone and 150 μl of 95% TFA (containing 5% water) were thoroughly vortex-mixed in a plastic tube and centrifuged. The top clear sol solution was removed for fiber coating.

Prior to sol–gel coating, the protective polyimide layer was removed from a 1-cm segment of the fiber at one of its ends. This was accomplished by dipping it into acetone for several hours. After drying, it was dipped into the sol solution which was kept at 30°C. After ~30 min, a sol–gel coating was formed on the outer surface of the fiber. Then it was placed in a desiccator at room temperature.

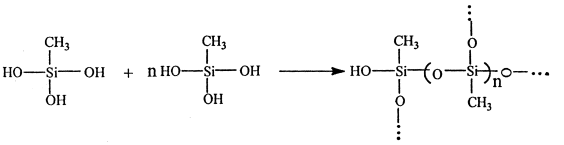
The sol–gel PEG fiber, 40 μm thick and 9 mm long, was conditioned at 300°C under nitrogen for approximately ~2 h. The SPME devices used in this study were modified from a commercial SPME fiber holder (Supelco). The sol–gel fiber was inserted through a septum-piercing needle with a brass ferrule and a sealing septum.

3. Results and discussion

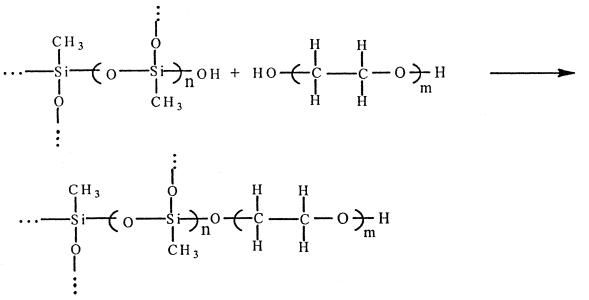
Two major sets of reactions take place during sol–gel processing [15]: (1) hydrolysis of the precursor and (2) polycondensation of the hydrolyzed products. These reactions are catalyzed by acids or bases and lead to the formation of a polymeric network. In this study, we use methyltrimethoxysilane as the precursor and TFA as the catalyst. There are several steps during the sol–gel processing. The first step is the hydrolysis reaction of the precursor under the acid catalyst:



The second step is that the hydrolyzed products undergo polycondensation reactions to produce a three-dimensional polymer network [15]:



In our study, we use PEG as a coating ingredient. Selection of this polymer aimed at chemically binding the PEG stationary phase to the growing silica network:



The silanol groups on the fused-silica fiber surface can also join in the condensation reactions and provide chemical anchorage to the polymeric network with the surface of the fuse silica fiber [15]. Thus a surface-bonded polymeric coating is formed. In the preparation of a capillary GC column, the column surface deactivation is an important step. It is because that there are some silanol groups on the fused-silica capillary inner walls and the polar compounds are prone to undergo adsorption interactions with the silanol groups. So in conventional column technology, deactivation is usually carried out as a separate step to derive the surface silanol groups. But in the preparation of an SPME fiber with

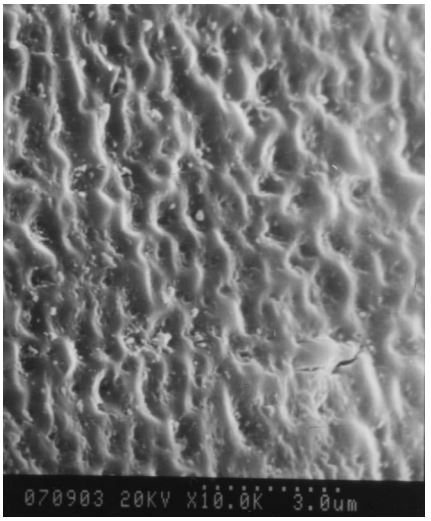


Fig. 1. Scanning electron micrograph of the sol–gel PEG fiber.

sol–gel technology, we can use these silanol groups as the chemical anchorage for the evolving sol–gel coatings. The hydroxy-terminated polymer can chemically bind with the silanol groups of the silica fiber surface.

3.1. Extraction and analysis of BTEX

During the HS-SPME procedure, distribution and adsorption equilibrium of the analytes must be established between the aqueous and gaseous phase, and between the gaseous and solid phase. The equilibrium is affected by various factors, such as the nature of the fiber, the identity of the analytes, the extraction time, and the extraction temperature. The optimal experimental conditions should be investigated for each compound and for the fiber selected.

Fig. 1 represents the micrograph of the sol–gel fiber obtained by scanning electron microscopy (SEM). As can be seen from the graph, the sol–gel coating possesses a porous structure. A high surface area will be able to provide large stationary phase loading and therefore, high extraction capacity.

Fig. 2 shows the extraction time profile of the sol–gel PEG fiber for 10 ng/ml BTEX under agitated sampling conditions. For HS-SPME, stirring may be beneficial because it facilitates the mass transfer from the liquid to the gaseous phase. The results indicate that the equilibration time for the agitated headspace extraction is very short, approximately 30 s for benzene and toluene, 40 s for ethylbenzene and *p*-xylene, 90 s for *o*-xylene. Under

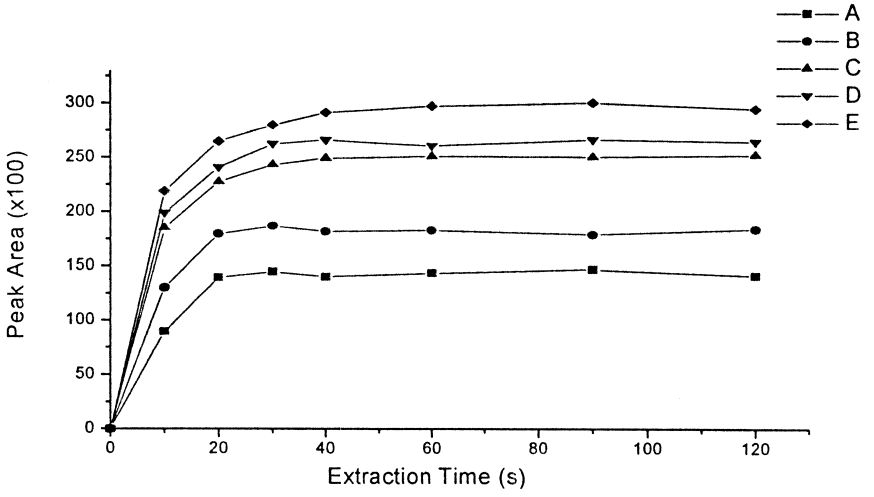


Fig. 2. The extraction time profile for 10 ng/ml BTEX (constant stirring at room temperature, stirring speed, 75% of maximum). A, benzene; B, toluene; C, ethylbenzene; D, *p*-xylene; E, *o*-xylene. GC conditions: 40°C for 2 min, then programmed at 7°C/min to 110°C and then at 20°C/min to 130°C for 1 min; injection temperature, 280°C; FID, 300°C; desorption time, 20 s.

the same conditions, the commercial 100 μm PDMS fiber needed several minutes to reach equilibration. The porous structure helps faster mass transfer during extraction, so the equilibration time is shorter. The desorption time profile is illustrated in Fig. 3. Analytes which were adsorbed by the porous layer diffuse from fiber into the carrier gas rapidly. As Fig. 3 shows, the desorption process is very fast and can be completed within 20 s at 280°C. Such short extraction and desorption equilibration times arise from the porous structure of the sol–gel PEG fiber and result in a short analysis time. From Fig. 4 we can see that with increase of injection temperature from 240°C to 300°C, the desorption quantities were not affected by changing of exposure temperature during sample introduction. The porous coating structure significantly increases the available surface area on the fiber. It is able to provide enhanced stationary phase loading and, therefore, high sample capacity. The comparisons of different fibers are shown in Fig. 5. As we forecast, the porous sol–gel-coated fiber has the maximal extraction quantities (unit volume of the coating) for these non-polar compounds. It is known that, at higher desorption temperature the compounds desorbed more quickly. Being a porous structure, the sol–gel PEG fiber has high mass-transfer rate, so even at a comparatively low desorption temperature, it also can desorb completely in a short time.

It should be noted that the maximum temperature of 65 μm CW–DVB is 265°C, and that for 100 μm PDMS is 280°C, but sol–gel-coated PEG fibers did not show any sign of bleeding even at the high temperature of 300°C. Such a high operating temperature is beneficial for one of the advantages of sol–gel technology: strong adhesion of the coating to the substrate through chemical bonding. In the sol–gel reaction, the silanol groups on the fused-silica fiber surface take part in the condensation reactions and provide anchorage to the polymeric network in the immediate vicinity of the fiber surface [18]. Being chemically bonded to the substrate, sol–gel-coated fibers are inherently stable when exposed in higher temperature. The high thermal stability of the sol–gel PEG fiber has another advantage: it is easy to eliminate the sample carryover problem. The fiber can provide efficient desorption of extracted analytes without carryover by using a high injection temperature.

The life span of a sol–gel PEG fiber was also evaluated. We have used the coating more than 150 times at 280°C, as can be seen in Table 1, it is still stable and reusable (but the commercial fiber can only be used for 50 to 100 analytes). Such long

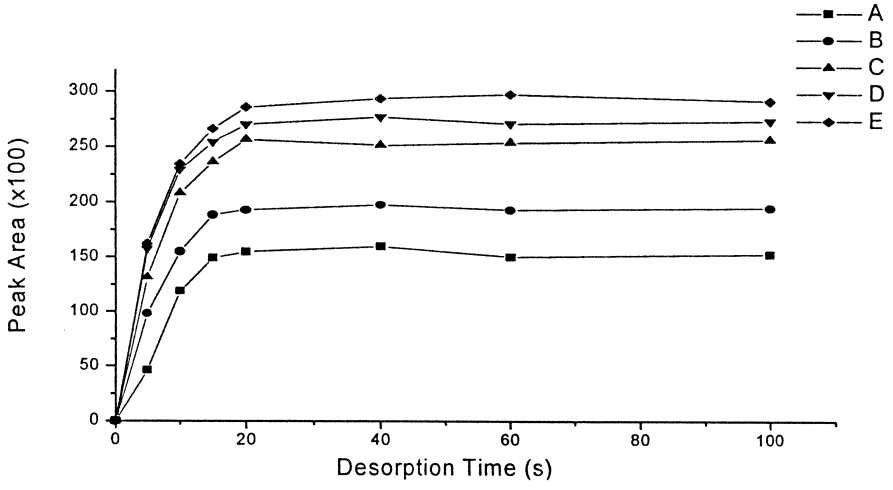


Fig. 3. The desorption time profile for 10 ng/ml BTEX. A, benzene; B, toluene; C, ethylbenzene; D, *p*-xylene; E, *o*-xylene. Conditions as in Fig. 2.

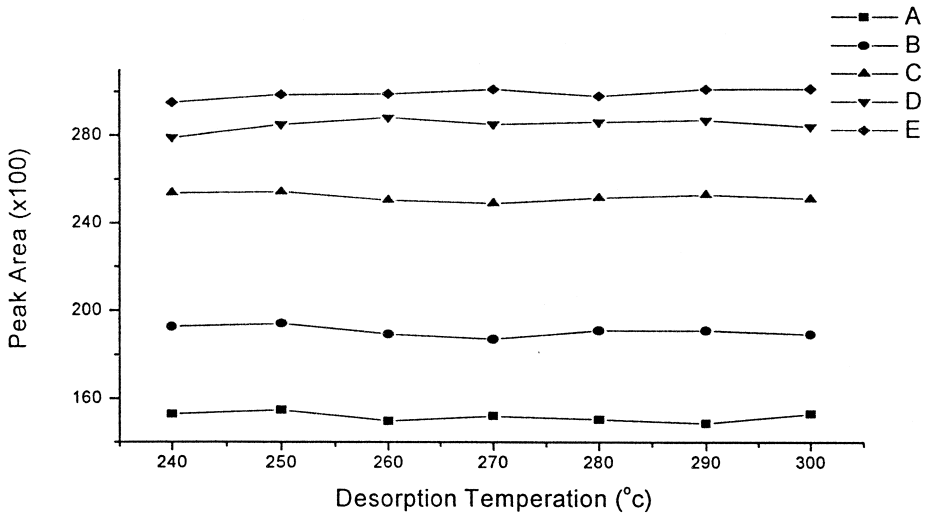


Fig. 4. The desorption temperature profile for 10 ng/ml BTEX. A, benzene; B, toluene; C, ethylbenzene; D, *p*-xylene; E, *o*-xylene. Conditions as in Fig. 2.

service lives are also due to the strong chemical bonding between the sol–gel-generated organic–inorganic composite coating and the silica fiber surface.

Detection limits (LODs), linearity and precision were also studied (see Table 2). For all compounds, the LODs are between 10 and 50 pg/ml. Comparing these results with other literature data [19] shows

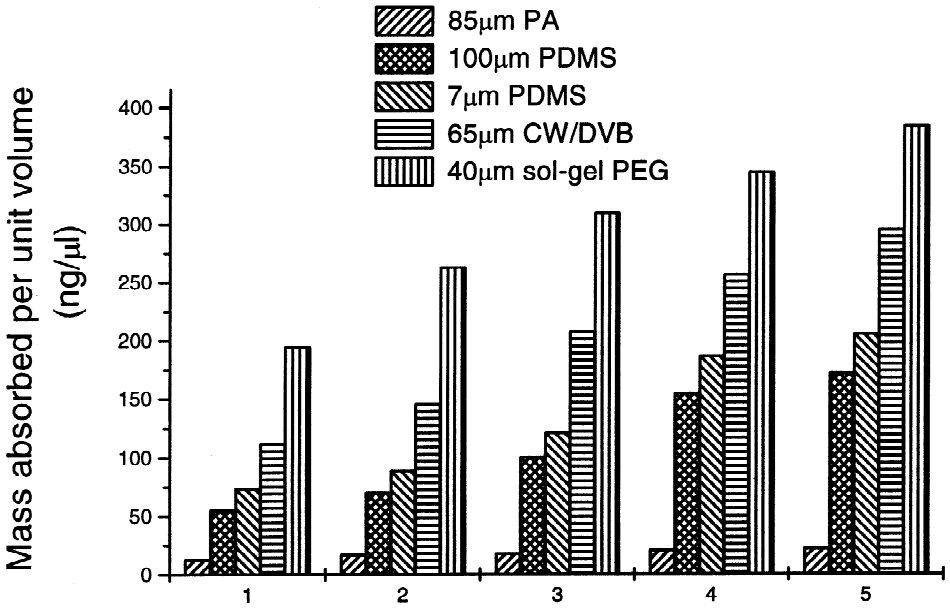


Fig. 5. The comparison of mass absorbed in unit volume using five different fibers for 10 ng/ml BTEX. 1, benzene; 2, toluene; 3, ethylbenzene; 4, *p*-xylene; 5, *o*-xylene. Extraction time, 10 min; injection temperature, 260°C; desorption time, 3 min. Other conditions as in Fig. 2.

Table 1
The extraction precision of the sol–gel-coated PEG fiber at 280°C under different periods

Compound	Extraction period							
	10th		50th		100th		150th	
	M.P.[a]	RSD (%)	M.P.	RSD (%)	M.P.	RSD (%)	M.P.	RSD (%)
Benzene	14 355	6.2	14 210	5.3	14 307	5.7	14 345	5.8
Toluene	18 301	5.9	18 219	5.7	18 269	6.1	18 247	6.0
Ethylbenzene	25 220	4.7	25 341	5.1	25 274	5.3	25 297	4.9
p-Xylene	26 691	3.9	26 536	4.4	26 598	3.7	26 674	4.1
o-Xylene	29 732	4.4	29 775	4.1	29 826	4.7	29 793	3.9

[a] M.P. means mean peak area ($n=3$).

that these very low detection limits are remarkable. The linearity of the compounds was studied over a vast concentration range. The linearity is ideal in the dynamic range: 100 to $5\cdot10^3$ pg/ml for benzene, 50 to $5\cdot10^3$ pg/ml for toluene, and 50 to 10^4 pg/ml for ethylbenzene and xylene. These results enabled quantitative analysis to be performed by the external standard method. The precision of the method for replicate analyses of aqueous solutions is also summarized. For the solution containing 10 ng/ml of each compound in BTEX, the relative standard deviation (RSD) was approximately 4% which shows acceptable precision. These results exhibit that the sol–gel-coated fiber used in this study has a good chemical, mechanical and thermal stability.

3.2. Extraction and analysis of phenols

The analytical determination of phenol and its derivatives is necessary because of their toxicity and their widespread use in industry. These compounds show a high polarity, and the 85 μm PA SPME fiber was available for the extraction of phenols [11]. If the fiber is exposed directly to samples, material from the matrix could coat the solid phase and interfere with the extraction. To avoid this, in our study the headspace extraction above the liquid is used. The success of this method depends on the transfer of analytes from the aqueous phase to the headspace. The phenols have low Henry's law constant values. Most of the phenols could be forced into the headspace by decreasing their solubility in the aqueous phase through saturating with sodium chloride and acidifying to below pH 1 with a few drops of concentrated acid [11].

For this experiment, a standard 20-ml headspace vial with 10 ml of 0.1 mol/l HCl saturated with 3 g of NaCl was used. All samples were stirred at 75% of the maximum stirring rate of the stirrer.

Fig. 6 is a typical gas chromatogram of a HS-SPME using a sol–gel PEG fiber for 0.1 μg/ml phenols under the optimized extraction and chromatographic conditions. Fig. 7 shows the extraction time profile of the sol–gel fiber for 0.1 μg/ml phenols under agitated conditions. It takes ~40 min for phenol, 2-nitrophenol, 2,4-dimethylphenol, and

Table 2
Limits of detection (LODs), linear range, correlation coefficients, and precision for the analysis of BTEX with headspace SPME–GC using the sol–gel PEG fiber

Compound	Retention time (min)	LOD[a] (pg/ml)	Linear range (pg/ml)	Correlation coefficient	RSD (%, $n=3$) 10 ng/ml
Benzene	4.425±0.02	50	100–$5\cdot10^3$	0.9991	3.1
Toluene	6.672±0.02	20	50–$5\cdot10^3$	0.9989	4.2
Ethylbenzene	9.163±0.01	20	50–10^4	0.9872	4.0
p-Xylene	9.383±0.03	10	50–10^4	0.9903	2.9
o-Xylene	10.047±0.03	10	50–10^4	0.9964	2.7

[a] Limit of detection (signal-to-noise=3).

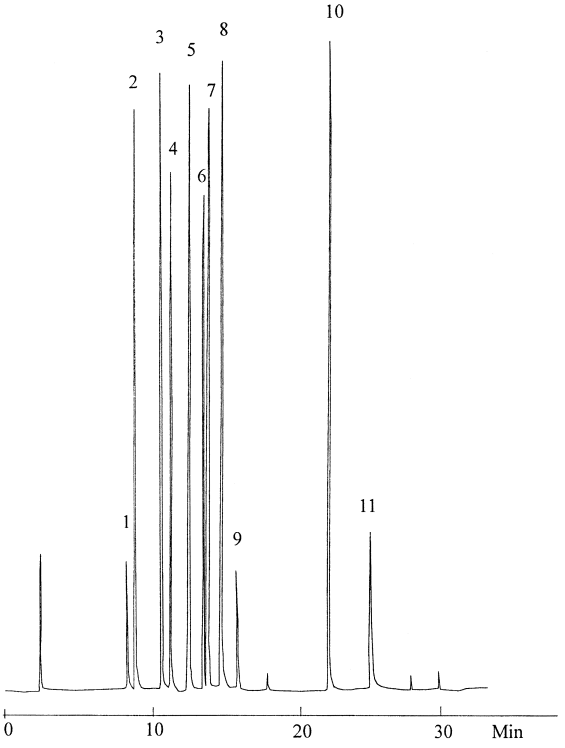


Fig. 6. SPME–GC analysis of 0.1 μg/ml phenols using the sol–gel PEG fiber and GC–FID system. Conditions: 80°C for 2 min, then programmed at 4°C/min to 250°C; injection temperature, 280°C; FID, 300°C; extraction time, 40 min (constant stirring at room temperature, stirring speed, 75% of maximum); desorption time, 3 min. 1, Phenol; 2, 2-chlorophenol; 3, *o*-cresol; 4, *p*-cresol; 5, 2,6-dimethylphenol; 6, 2-nitrophenol; 7, 2,4-dimethylphenol; 8, 2,4-dichlorophenol; 9, 1,2-benzenediol; 10, 2,4,6-trichlorophenol; 11, 3-nitrophenol.

~50 min for 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol to reach equilibrium. Extraction temperature has a double impact: at higher temperature, diffusion coefficients in water are higher, the equilibrium distribution of analytes between liquid and gaseous phase establishes more rapidly, so the extraction time is shorter; on the other hand, at higher temperature, the adsorbed quantities of compounds decrease, which is most probably a result of the exothermic process of adsorption. So there is an optimal extraction temperature at which one can get ideal adsorbed quantities and rapid equilibrium time. From Fig. 8, we can see 30°C is the optimal extraction temperature for phenols.

The data in Fig. 9 show that the PDMS fiber was not suitable for all of the polar analytes studied. As is known, conventional PDMS coating consists of a film of polydimethylsiloxane which is non-polar in nature, therefore, affinity of this non-polar coating toward polar compounds is low and cannot serve as an effective extraction medium for polar analytes. The figure shows that, both PA and sol–gel PEG fibers are efficient for the extraction of most of the analytes. From the experiment above, we can see that, for highly polar compounds, phenols, the sol–gel PEG fiber also has good extraction capacity. The reason is: one molecule PEG has two terminal hydroxyl groups, these hydroxyl groups are prone to bind with the terminal silanol groups of the sol–gel network through a condensation reaction (in the third step of reaction). But the chemical bonding requires only one hydroxyl group per molecule. So the other

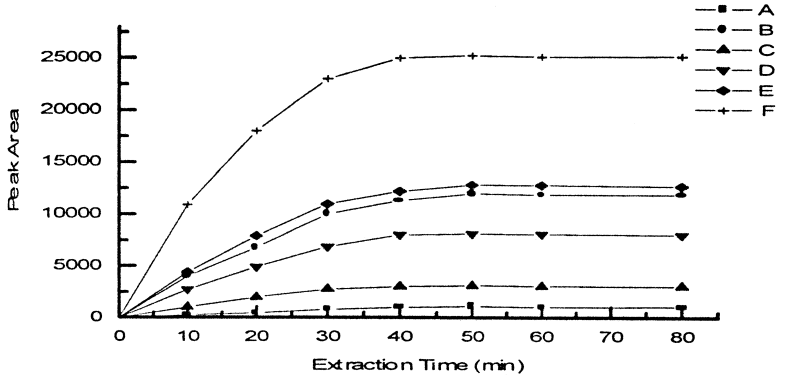


Fig. 7. The extraction time profile for 0.1 μg/ml phenols (constant stirring at room temperature, stirring speed, 75% of maximum). A, phenol; B, 2-chlorophenol; C, 2-nitrophenol; D, 2,4-dimethylphenol; E, 2,4-dichlorophenol; F, 2,4,6-trichlorophenol. Conditions as in Fig. 6.

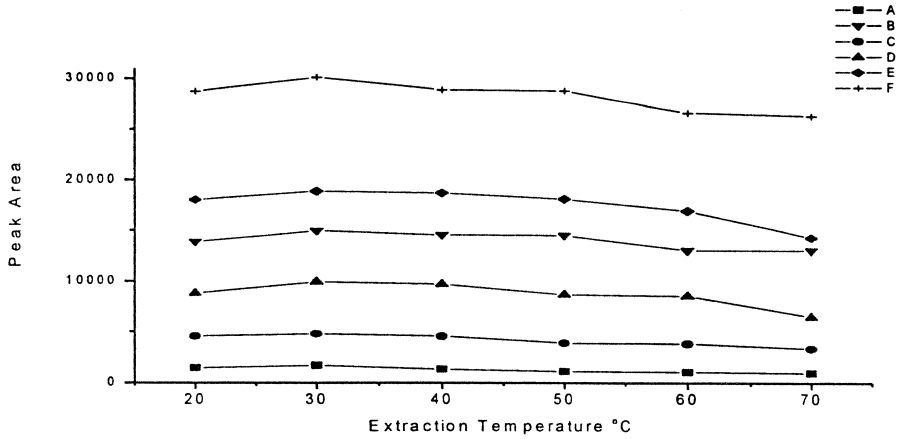


Fig. 8. The extraction temperature profile for 0.1 μg/ml phenols. (constant stirring, stirring speed, 75% of maximum). A, phenol; B, 2-chlorophenol; C, 2-nitrophenol; D, 2,4-dimethylphenol; E, 2,4-dichlorophenol; F, 2,4,6-trichlorophenol. Conditions as in Fig. 6.

hydroxyl group may be free, at least for some of the bonded PEG molecules (a condensation reaction may take place between the hydroxyl groups of some PEG molecules). In SPME, moderate degrees of –OH groups can enhance the polarity of the fiber, thus enhancing the selectivity for polar compounds. During the sol–gel reaction, we did not use deactivation reagent to derive the –OH groups in order to

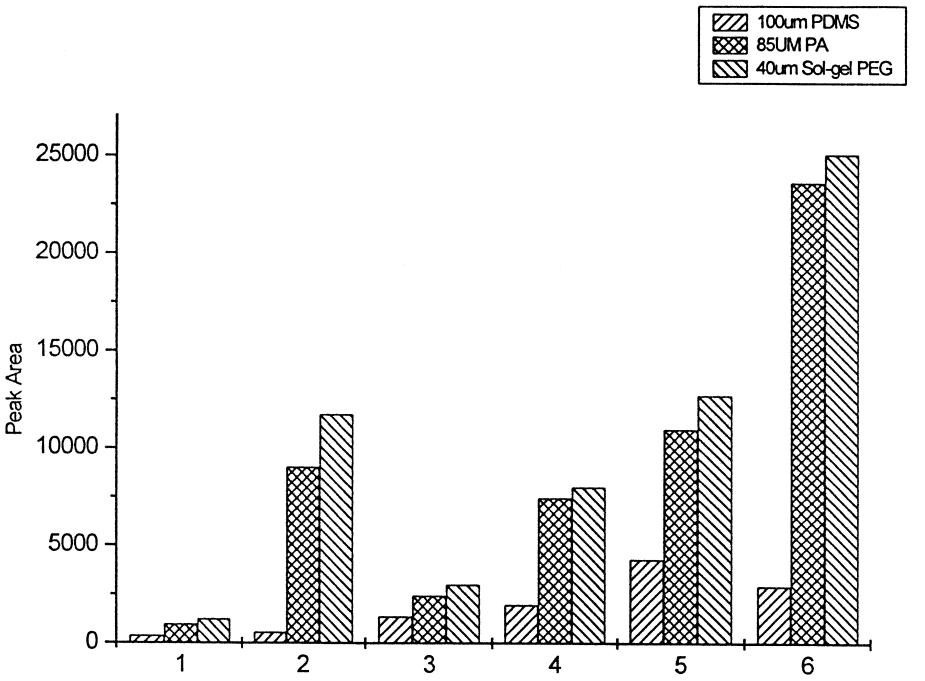


Fig. 9. The comparison of extraction quantities using three different fibers for 0.1 μg/ml phenols. 1, phenol; 2, 2-chlorophenol; 3, 2-nitrophenol; 4, 2,4-dimethylphenol; 5, 2,4-dichlorophenol; 6, 2,4,6-trichlorophenol. Extraction time, 90 min; injection temperature, 260°C; desorption time, 5 min. Other conditions as in Fig. 6.

Table 3
Limits of detection (LODs), linear range, correlation coefficients, and precision for the analysis of phenols with headspace SPME–GC using the sol–gel PEG fiber

Compound	Retention time (min)	LOD[a] (ng/ml)	Linear range (μg/ml)	Correlation coefficient	RSD (%, $n=3$) 0.1 μg/ml
Phenol	8.643±0.02	10.0	0.05–1	0.9865	3.7
2-Chlorophenol	9.075±0.03	0.5	0.01–1	0.9914	3.4
2-Nitrophenol	13.197±0.02	5.0	0.02–1	0.9923	4.1
2,4-Dimethylphenol	13.441±0.03	1.0	0.01–1	0.9898	4.0
2,4-Dichlorophenol	14.868±0.04	0.1	0.005–1	0.9904	5.3
2,4,6-Trichlorophenol	22.183±0.04	0.1	0.005–1	0.9877	5.9

[a] Limit of detection (signal-to-noise = 3).

retain the fiber with an ideal selectivity for polar compounds. After conditioning at 300°C for ~2 h, we found the fiber had a stable selectivity and extraction capacity during the experiments.

Detection limits, linearity and precision were also studied (see Table 3). For these compounds, LODs are between 0.1 and 10 ng/ml. For the solution containing 0.1 μg/ml of phenols, the RSDs were less than 6%, which shows acceptable precision.

Table 4 illustrates the comparisons of some basic characters of four commercial fibers and the sol–gel PEG fiber.

3.3. Analysis for phthalic diesters, naphthalene congeners and pesticides

Fig. 10 is the chromatogram of 1 μg/ml phthalic diesters for the sol–gel-coated fiber. A 20-ml headspace vial with 10 ml deionized water and 3 g NaCl were used. The fiber was exposed in the headspace of the vial at 90°C for 30 min, without stirring. Fig. 11 is the chromatogram of 1 μg/ml naphthalene congeners. All extraction conditions are the same for phthalic diesters, except for the extraction temperature, which is 50°C. Organochlorine pesticides were dissolved in deionized water in a headspace vial, 0.1 μg/ml of each compound. The target analytes were extracted by HS-SPME at 70°C, for 3 min. Fig. 12 illustrates that sol–gel-coated PEG fibers show sufficient selectivity for organochlorine compounds. The three results above are also consistent with the hypothesis that the sol–gel PEG fiber is suitable for the efficient extraction of both polar and non-polar compounds.

4. Conclusion

Sol–gel chemistry offers a simple and convenient method for the coating of SPME fibers. Because of chemical bonding between the sol–gel-coated PEG and the fused-silica surface, these sol–gel-coated

Table 4
Comparisons of some commercial fibers and the sol–gel PEG fiber

Stationary phase	Film thickness (μm)	Maximum temperature (°C)	Description	Life span[a] (analyses)	Application
PDMS	100	280	Non-bonded	50–100	For volatile, low-, mean-boiling and non-polar compounds
PDMS	30	280	Non-bonded	50–100	For volatile, low-, mean-boiling and non-polar compounds
Polyacrylate	85	320	Partially crosslinked	50–100	For volatile, semi-volatile and polar compounds
CW–DVB	65	265	Partially crosslinked	50–100	For volatile, low-, mean-boiling and polar compounds
Sol–gel PEG	40	≥300	Chemically bonded	≥150	For both polar and non-polar compounds

[a] The life span of the fibers depends on the particular application and the care that they are given.

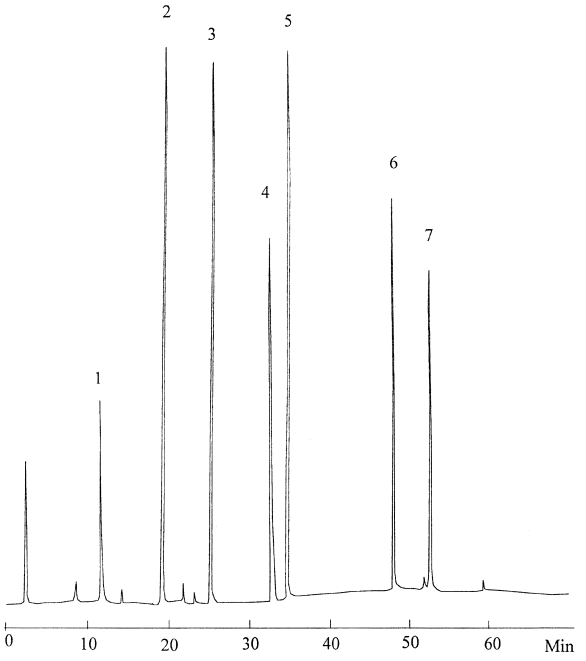


Fig. 10. SPME–GC analysis of 1 μg/ml phthalic diesters using the sol–gel PEG fiber and GC–FID system. Conditions: 80°C for 2 min, then programmed at 20°C/min to 200°C and then at 2°C/min to 260°C for 30 min; injection temperature, 300°C; FID, 300°C; extraction time, 30 min (without stirring); extraction temperature, 90°C; desorption time, 5 min. 1, Diethyl phthalate; 2, di-*n*-butyl phthalate; 3, diamyl phthalate; 4, diisohexyl phthalate; 5, di-*n*-hexyl phthalate; 6, di-*n*-octyl phthalate; 7, dinonyl phthalate.

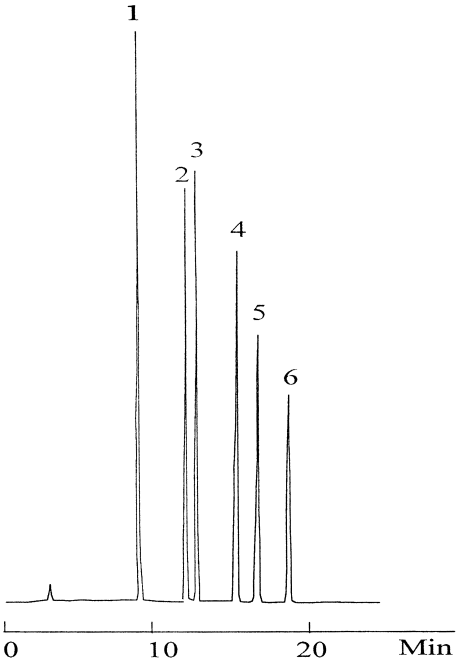


Fig. 11. SPME–GC analysis of 1 μg/ml naphthalene congeners using the sol–gel PEG fiber and GC–FID system. Conditions: 120°C for 2 min, then programmed at 3°C/min to 150°C for 10 min; injection temperature, 300°C; FID, 300°C; extraction time, 30 min (without stirring); extraction temperature, 50°C; desorption time, 3 min. 1, Naphthalene; 2, 2-methylnaphthalene; 3, 1-methylnaphthalene; 4, biphenyl; 5, 2,6-dimethylnaphthalene; 6, 2,3-dimethylnaphthalene.

PEG fibers exhibit higher thermal stability, the maximum temperature is 300°C. Enhanced thermal stability sol–gel-coated fibers allow one to overcome the sample carryover problem. In addition, high thermal stability allows the use of high-injection temperatures for efficient desorption of less-volatile analytes, so a great number of less-volatile compounds can be analyzed by SPME–GC. As can be seen from the electron micrograph of the coated surface, the sol–gel coating possesses a porous structure. It increases the surface area on the fiber, therefore, even a thin coating will be able to provide enhanced stationary phase loading and high sample capacity. The porous structure also increases the speed of extraction and desorption. The thickness of the chemically bonded polymeric layer can be controlled by varying the dipping time and the concentration of the sol solution. Higher film thicknesses can be achieved through repeated dipping operations. By varying the proportions of the sol solution ingredients or using deactivation reagent, we can change the composition of the coating, which will give the possibility of selectivity change in SPME fiber technology. The presented experimental results clearly demonstrate that the sol–gel-coated PEG fibers are suitable for an extended range of analytes, for both polar and non-polar compounds.

Acknowledgements

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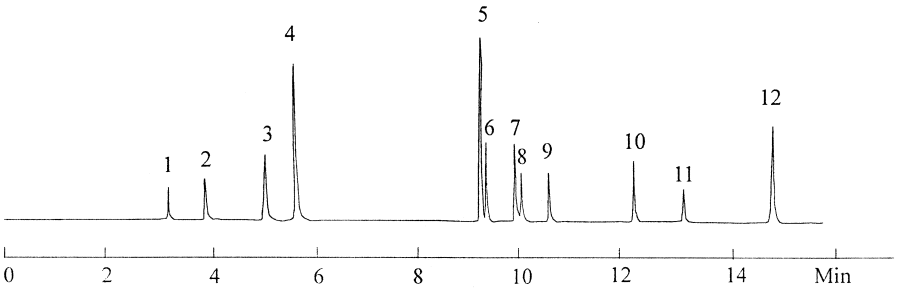

Fig. 12. SPME–GC analysis of 0.1 μg/ml organochlorine pesticides using the sol–gel PEG fiber and GC–ECD system. Conditions: initial temperature 100°C, initial time 0 min, then programmed at 10°C/min to 190°C for 10 min; injection temperature, 280°C; ECD, 290°C; extraction time, 3 min (without stirring); extraction temperature, 70°C; desorption time, 1 min. 1, 135-TCB; 2, 123-TCB; 3, 1235-TTCB; 4, 1234-TTCB; 5, α-HCH; 6, HCB; 7, β-HCH; 8, γ-HCH; 9, δ-HCH; 10, aldrin; 11, oystrene; 12, dieldrin.

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