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Preparation and characteristics of sol–gel-coated calix[4]arene fiber for solid-phase microextraction

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Abstract

5,11,17,23-Tetra-*tert*-butyl-25,27-diethoxy-26, 28-dihydroxycalix[4]arene/hydroxy-terminated silicone oil coated fiber was first prepared and applied for solid-phase microextraction (SPME) with sol–gel technology. The possible sol–gel mechanism was discussed and confirmed by IR spectra. It showed wonderful selectivity and sensitivity to polar (aromatic amines), nonpolar (benzene derivatives, polycyclic aromatic hydrocarbons) and high boiling point compounds (phthalates) and the extraction equilibria were reached quite fast. The coating has high thermal stability (380 °C) and solvent stability (organic and inorganic), thus its lifetime is longer than conventional fibers. In addition, it has surprising fiber-to-fiber and batch-to-batch reproducibility. The detection limits were quite low and the linear ranges were pretty broad for all analytes.

Keywords: Sol–gel; Solid-phase microextraction; Calixarenes; Polynuclear aromatic hydrocarbons; Amines, aromatic; Phthalates; Benzene; Ethylbenzene; Toluene; Xylenes

1. Introduction

Since its introduction, solid-phase microextraction (SPME) [1] has gained great interest of scientists due to its simple, solvent-free, time-efficient and selective properties. Up to now, it has been used to determine benzene derivatives [2,3], chlorinated hydrocarbons [4], herbicides [5,6], polycyclic aromatic hydrocarbons (PAHs) [7–9], phenols [10], aromatic amines [11,12], polychlorinated biphenyls (PCBs) [13], organometals [14–18] and so on. SPME is based on the partitioning of analytes between the sample and the extraction phase, which is fixed on the surface of a fused–silica fiber. In addition to sampling conditions and analytes properties, the type of fiber coating is one of the most crucial aspects in optimization. The nonpolar poly(dimethylsiloxane) (PDMS) fiber was the first polymer being used for SPME. However, it does not extract polar compounds very well. To achieve more selective determination of different compounds classes, the variety of different coating materials for SPME has increased. Polyacrylate (PA) and some mixed-phase films, such as PDMS–divinylbenzene (DVB), Carbowax (CW)–DVB, Carboxen–PDMS, also became available. Recently, some novel fibers, nonpolar silica particles bonded with C_8, C_{18} [19], inorganic Carbopack [20], gold [21], pencil lead [22], graphite [23], activated charcoal [24], polypyrrole (PPY) [25], molecularly imprinted polymer (MIP) [26], alkyldiol-silica (ADS) particles [27] and some laboratory-made PDMS coated fibers [28] have been prepared. To overcome the fragility of the fused-silica fibers, the metal wire substitutes for the brittle fiber, as anodized alumina wire [29] and PPY-coated platinum fiber [25]. Nevertheless, all these fibers are generally prepared by mere physical deposition of the polymer coating on the surface of the fibers. Lacking proper chemical bonding of the stationary phase coating with the fiber surface may take the most responsibility for the low thermal and chemical stability of conventionally coated fibers, and these lead to a short lifetime of the coating.

Sol–gel coating technology [30–32], established by Malik and co-workers, has solved the difficulty. It offers a simple and convenient pathway for the syntheses of advanced material systems and for applying them as surface coatings. It effectively combines surface treatment, deactivation, coating and stationary phase immobilization into a single step. A

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wall-bonded coating results due to condensation of the surface silanol groups with the sol–gel network evolving in their vicinity. Because of the direct chemical bonding to the fused silica surface, sol–gel coatings possess higher thermal and solvent stability than conventional coatings.

In our group, crown ether [10] and poly(methylphenylvinylsiloxane) (PMPVS) [3] coated fibers had been first prepared with this technique. Owing to their inherent multifunctional properties and the features of sol–gel chemistry, these coatings revealed good thermal and solvent stability as well as long lifetime. Compared with conventional SPME stationary phase, they showed better selectivity and sensibility toward polar and nonpolar aromatic analytes such as phenols [10], aromatic amines [11], benzene derivatives, PAHs and phthalates [3]. Particular attention should be paid to the hydroxyl–crown ether fiber. It shows us a good application respective "because of its good selectivity resulting from its cavity structure and the strong electronegative effect of heteroatoms on the crown ether ring".

Calixarenes are regarded as the third generation of supramolecules next to crown ethers and cyclodextrins. They are a class of cyclic oligmers prepared from formaldehyde and *para*-substituted phenols via cyclic condensation under alkaline conditions. Considering the outstanding capacity of the calixarene as receptors mainly based on their variable chemical modification potential and their conformational pliability allowing a kind of induced fit to the shape of suitable guest molecules, they have been widely used in ion-selective electrodes [33], phase-transfer agents [34], catalysts [35], molecular recognition [36], and liquid membranes [37]. Most of all, their applications as high-performance liquid chromatography (HPLC) stationary phase [38] and gas chromatography (GC) open-tubular capillary coating [39] have interpreted special selectivity. Relative work had been done previously in our laboratory [39,40]. However, to the best of our knowledge, the application of calixarene as SPME coating has not yet been explored.

In this paper, the synthesized 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene (C[4]) blending with hydroxy-terminated silicone oil (OH-TSO) coated SPME fibers (C[4]–OH-TSO) were prepared with sol–gel technology and their characteristics were investigated by the analysis of benzene, toluene, ethylbenzene and xylenes (BTEX), PAHs, aromatic amines and phthalic acid esters (phthalates, PAEs).

2. Experimental

2.1. Apparatus

The experiments were carried out on SP-6800A capillary GC system (Shandong, China) equipped with a capillary split/splitless injector system and flame ionization detection (FID) system. Online data collection and processing was done on Chromatopac model SISC-SPS (Beijing, China). To mix various solution ingredients thoroughly, an Ultrasonator model SY-1200 (Shanghai Ultrasonic Instrument Factory) was used. A Centrifuge model TGL-16C (Shanghai Anting Instrument Factory, Shanghai, China) was used to separate the sol solution from the precipitate. The fused-silica fiber (120 μm, o.d.) with protective polyimide coating was obtained from Academy of Post and Telecommunication, Wuhan, China. A magnetic stirrer DF-101B (Leqing, China) was employed for stirring the sample during extraction. A laboratory-made SPME syringe was used to transfer the extracted sample to the GC injector for analysis. The commercially available PDMS (100 μm), PA (85 μm), PDMS–DVB (65 μm) and CW–DVB (65 μm)-coated fibers for comparison were obtained from Supelco (Bellefonte, PA). IR spectra were done on IR instrument model FTIR-8201PC (Shimadzu).

2.2. Reagents

C[4] was synthesized by referring to the reported method [41]. OH-TSO was purchased from Chengdu Center for Applied Research of Silicone (Chengdu, China). 3-(2-Cyclooxypropoxyl)propyltrimethoxysilane (KH-560), tetraethoxysilane (TEOS), and poly(methylhydrosiloxane) (PMHS) were obtained from the Chemical Plant of Wuhan University. Trifluoroacetic acid (TFA) and trimethylchlorosilane were purchased from Shanghai Chemical Factory, China. All solvents used in this study were analytical-regent grade.

2.3. GC conditions

The separation for BTEX was carried out on a capillary column (30 m × 0.25 mm i.d.) coated with OV-1701. Temperatures were maintained at 250 °C for the injection port, 250 °C for the FID detector and 80 °C for the column. For PAHs and aromatic amines a capillary column (25 m × 0.25 mm i.d.) coated with SE-54 was used. When PAHs were analyzed, the temperatures were 300 °C for the injector, 180 °C for the column, and 260 °C for the FID; while they were 250, 140, and 250 °C for aromatic amines, respectively. A capillary column (20 m × 0.25 mm i.d.) coated with OV-1 was used for the separation of phthalic acid esters. The column temperature program was: 260 °C for 2 min, 260–300 °C at 12 °C/min, and hold for 6 min. The temperatures were 340 °C for the injection port and 320 °C for the FID system. Nitrogen was used as the carrier gas at a linear velocity of 12–15 cm/s in the 1:100 split mode for all the analyses.

2.4. Preparation of C[4] fiber

Preparation of the sol–gel SPME fiber involves the following steps: (1) pretreatment of the fused-silica fiber; (2) preparation of the sol solution; (3) sol–gel coating of SPME fiber; and (4) thermal conditioning of the SPME fiber.

Table 1
The types of fiber used in this study

Fiber	Coating	Film thickness (μm)
PDMS	Commercially available PDMS	100
PA	Commercially available PA	85
CW–DVB	Commercially available CW/DVB	65
PDMS–DVB	Commercially available PDMS/DVB	65
OH-TSO	Laboratory-made fiber coated with a sol–gel layer of OH-TSO	65
C[4]–OH-TSO (20 mg)	Laboratory-made fiber coated with a sol–gel layer of C[4]–OH-TSO	55
C[4]–OH-TSO (30 mg)	Laboratory-made fiber coated with a sol–gel layer of C[4]–OH-TSO	60
C[4]–OH-TSO (40 mg)	Laboratory-made fiber coated with a sol–gel layer of C[4]–OH-TSO	57.5

Prior to sol–gel coating, the protective polyimide layer of a 6 cm-long fused-silica fiber including a 1 cm end segment was removed by dipping it in acetone for 3 h. Then the fiber was dipped in 1 M NaOH solution for 2 h, to expose the maximum number of silanol groups on the surface of the fiber, and cleaned with water. Finally, it was placed in 0.1 M HCl solution for 2 h to neutralize the excess NaOH, cleaned again with water and air-dried at room temperature. The sol solution was prepared as follows: 30 mg of C[4] was dissolved in 200 μl of methylene chloride, and then 90 mg of OH-TSO, 100 μl of TEOS, 50 μl of KH-560 and 10 mg of PMHS were added and mixed thoroughly by ultrasonic agitation in a plastic tube. A 38 μl volume of TFA containing 5% water was sequentially added to the resulting solution with ultrasonic agitation for another 3 min. The mixture was centrifuged at 12,000 rpm for 8 min. The top clear sol solution was used for fiber coating. After the treated fiber was dipped vertically into the sol–gel solution for 30 min, a sol–gel coating was formed on the bare outer surface of the fiber end (about 1 cm). For each fiber, this coating process was repeated several times until the desired thickness of the coating was obtained. The fiber was then placed in a desiccator at room temperature for 12 h and then conditioned at 280–380 °C under nitrogen for 2.5 h in the GC injection port. After that, the fiber was dipped in methylene chloride and water for 3 h, respectively. The final thickness of the fiber was gained. Some other C[4]–OH-TSO fibers were coated with the same procedures except that the mass of C[4] was 20 and 40 mg, respectively. A OH-TSO fiber was also coated for comparison by sol–gel technique with an almost identical preparation procedure except that the C[4] was not added into the sol solution. Table 1 lists the types of fiber used in this study.

2.5. Preparation of aqueous standard solution for extraction by SPME

BTEX [benzene (B), toluene (T), ethylbenzene (E), *o*-xylene (O), and *m*-xylene (M)] were dissolved in methanol to make stock solution at a concentration of each 1 mg/ml. PAHs [indene (Ind), naphthalene (Nap), biphenyl (Bip), acenaphthylene (Ace), fluorene (Flu), and phenanthrene (Phe)] and PAEs (dimethyl, diethyl, dibutyl, diamyl, di-*n*-octyl, diisooctyl, dinonyl, didecyl) phthalate (respectively designated DMP, DEP, DBP, DAP, *n*-DOP, *i*-DOP, DNP and DDP) were prepared by dissolving 10 mg of each compound in a 10 ml acetone in a volumetric flask as stock solution. For all analyses, a 10 μl portion of this standard solution was diluted with 5 ml of deionized water in 10 ml amber vials to give 2 μg/ml BTEX, or PAHs aqueous solution, respectively. When PAEs were analyzed, a 10 μl portion of the standard solution was diluted with 8 ml of deionized water in 10 ml amber vials to give 1.25 μg/ml PAEs aqueous solution. Stock solution of aromatic amines [aniline (A), *o*-toluidine (OT), 2,4-dimethylaniline (2,4DMA), 3,4-dimethylaniline (3,4DMA), *N*-ethyl-*m*-toluidine (NEMT), and *N*,*N*-diethylaniline (N,NDEA)] were dissolved in acetonitrile to get a concentration of each 1 mg/ml. A 10 μl sample of this standard solution was diluted with 5 ml 0.1 M NaOH solution to give aqueous solution of 2 μg/ml in concentration. All stock solutions were stored at 4 °C.

2.6. Headspace SPME (HS-SPME) procedure

Before the first usage, the fibers were conditioned according to the recommendations of the producer. Each day, before analysis, the fibers were conditioned for 30 min in the GC injector held at 250–380 °C and then, prior to starting set of experiments, a blank analysis was performed to verify that no extraneous compounds were desorbed from the fiber. To prevent the analytes from being adsorbed on the glass wall, the amber vials were acid washed and silanized with trimethylchlorosilane prior to the experiments. A 10 μl portion of the standard solution, 5 ml of distilled water and 2 g NaCl were added in a 10 ml vial containing a magnetic spin bar (PTFE). When the aromatic amines were analyzed, a 5 ml 0.1 M NaOH solution substitutes for the 5 ml distilled water to ensure all of the amines were in their neutral form. To avoid sample evaporation, the vials were closed with butyl rubber stoppers wrapped with PTFE sealing tape, and then sealed with aluminum caps. The extraction was performed by exposing the coated fiber end to the headspace of the vial for an appropriate time. The fiber was then immediately inserted into the heated GC injection port for thermal desorption. Throughout the study, no analytes residues were found to be left on the C[4]–OH-TSO SPME fibers after each re-conditioning.

2.7. Direct SPME (Dir-SPME) procedure

PAEs were analyzed by direct SPME. For the SPME process, 8 ml of distilled water spiked with 10 μl of standard working solution were placed into the amber vials. The concentration of NaCl in the aqueous solution was 0.25 g/ml. In the extraction process, the fiber was directly introduced into the sample solution for 60 min at 40 °C. The samples continuously stirred at a constant speed with a magnetic stirrer. Finally, the compounds were thermally desorbed from the fiber in the gas chromatograph injector at 340 °C. The fiber remained in the injector for 8 min.

3. Results and discussion

3.1. Possible mechanism of the coating process

There are five major reaction processes that occur during the sol–gel formation [10]: (1) ring-opening polymerization first takes place between KH-560 and C[4] catalyzed by TFA; (2) both the product and TEOS are hydrolyzed by mixing it with water; (3) condensation and polycondensation among the products of (2) and OH-TSO form a 3D sol–gel network (3D network); (4) the polymeric networks chemically bind with the silanol groups exposed on the fiber surface to create a surface-bonded polymeric coating; (5) PMHS is added to the solution to deactive the fiber coating since the dried gel still contains a very large concentration of chemisorbed hydroxyl on the surface, which may influence the reproducibility of the fiber. Thus, a surface-bonded polymeric coating (C[4]–OH-TSO) is formed and the chemical structure is shown in Fig. 1. The percent of amount of C[4] incorporated in the resulting gels of a 30 mg C[4]–OH-TSO fiber is 11%.

The IR spectra of the stationary phase after rinsing with methylene chloride and water can confirm the successful binding of C[4] to the stationary phase. Fig. 2 shows the IR spectra of pure C[4], sol–gel-derived C[4]–OH-TSO stationary phase and sol–gel-derived OH-TSO stationary phase (OH-TSO). The feature identified by C[4]: 3047.9 cm^{-1} ($\nu_{Ar\text{-}H}$), 1485.7 cm^{-1} ($\nu_{ArC\text{-}C}$), 870.1 cm^{-1} ($\delta_{Ar\text{-}H}$) also appeared in C[4]–OH-TSO.

3.2. C[4] coating characterization

In this study, OH-TSO was selected as one of the mixed coating ingredients because it can lengthen the silica network leading to increased surface area of the fiber and can help to spread the stationary phase on the glass surface uniformly. Fig. 3 shows the extraction capability of our laboratory-made sol–gel coated OH-TSO fiber and C[4]–OH-TSO fiber with the identical preparation procedure. The C[4]–OH-TSO fiber gave rather higher response to BTEX than the OH-TSO

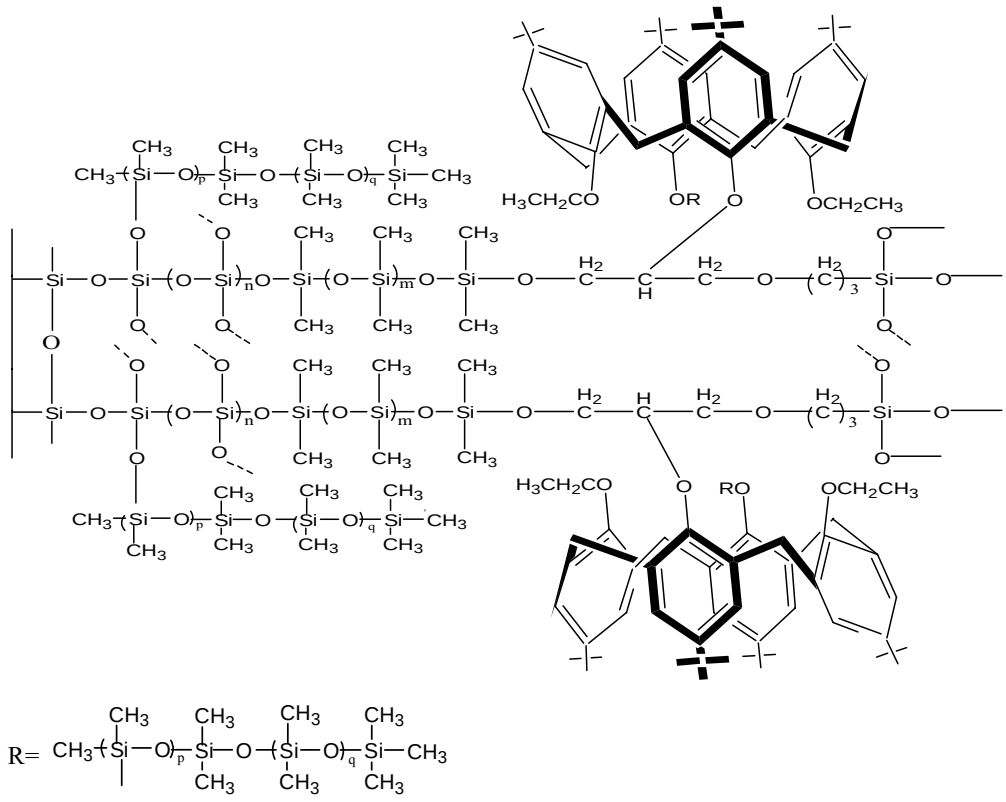

Fig. 1. The chemical structure of C[4]–OH-TSO coatings.

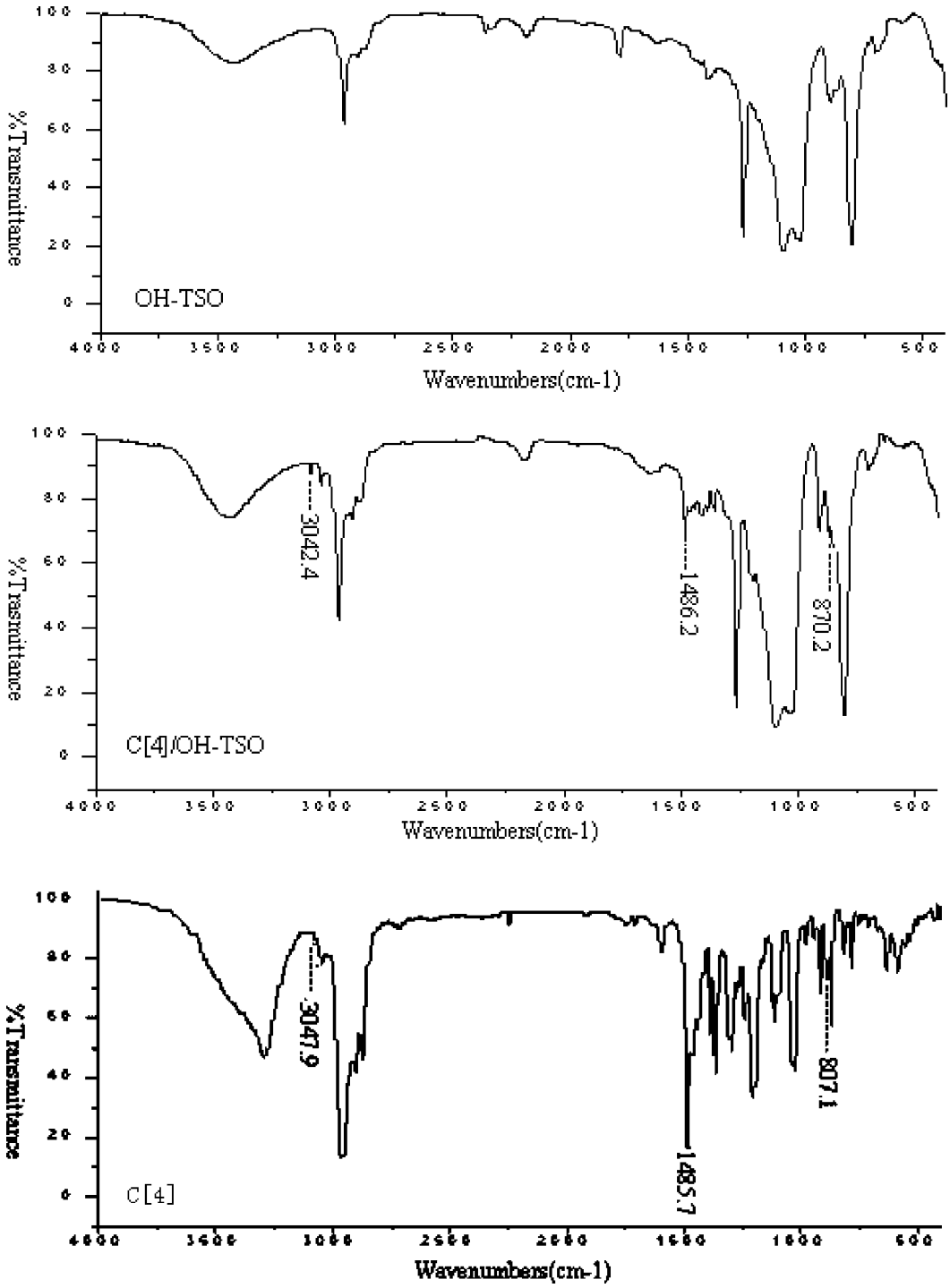

Fig. 2. IR spectra of pure C[4], sol–gel-derived C[4]–OH-TSO and sol–gel-derived OH-TSO.

fiber. Undoubtedly, C[4] plays an important role in the extraction. Similar experiments reveal that C[4]–OH-TSO fiber also shows better selectivity to PAHs and aromatic amines.

Optimization of the mass of C[4] in sol–gel solutions was done by preparing fibers from sol–gel solutions containing 20, 30, and 40 mg C[4], respectively. Fig. 4 illustrates the extraction efficiency for BTEX of C[4]–OH-TSO fibers containing different mass of C[4]. It shows that 30 mg C[4] coated fiber gained the best extraction performance. The sol–gel solution containing 40 mg C[4] are likely to precipitate during the fiber coating because the sol–gel solution may lack enough dissolubility for C[4]. Then 30 mg C[4]-contained fiber was chosen to carry out all the experiments.

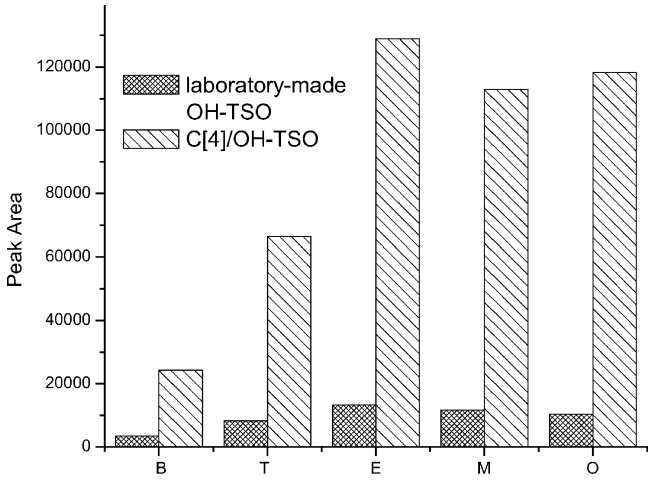

Fig. 3. Comparison of the extraction capability of 2 μg/ml BTEX extracted per unit volume (μl) by use of our laboratory-made sol–gel coated OH-TSO fiber and C[4]–OH-TSO fiber with the identical preparation procedure. Conditions: carrier gas, nitrogen; split ratio, 100:1; injection temperature, 250 °C; FID temperature, 250 °C; column temperature, 80 °C; extraction time, 1 min; extraction temperature, 14.5 °C; desorption time, 3 min; saturated out with NaCl; constant stirring.

3.3. Selectivity of the fiber

Since C[4] contains phenyl and a cavity, it is expected to extract non-polar aromatic compounds easily through π–π interaction, hydrophobic interactions and cavity-shaped cyclic molecular structure. The results for BTEX and PAHs are consistent with this hypothesis. Table 2 contrasts with the extraction capability of C[4]–OH-TSO and PDMS fibers for analysis of BTEX and PAHs. For all compounds examined, C[4]–OH-TSO coating shows a superior extraction selectivity and sensitivity in compared with PDMS. At the same time, these interactions should be increased with approximately increasing the aromatic rings and molecule size to be encapsulated within the cavity. In order to compare, the ratios are adopted by comparing the areas of C[4]–OH-TSO fiber with the corresponding areas of commercial PDMS fiber. From Table 2, we find the extraction responses for BTEX with C[4]–OH-TSO fiber are twice more than that with PDMS fiber. While the ratios for PAHs are from 4.0 to 6.1, except phenanthrene. Taking the extraction time (Fig. 5) and the desorption time (Fig. 6) of PAHs into account, the extraction equilibrium was reached quite slowly for phenanthrene while it desorbed quite fast. It seems that phenanthrene does not been encapsulated by C[4].

Table 2
Comparison of the quantities of BTEX and PAHs (each 2 μg/ml) extracted per unit volume (μl) by C[4]–OH-TSO and commercial PDMS

Component	C[4]–OH-TSO[a]	PDMS[a]	Ratio[b]
Benzene	24186	10897	2.2
Toluene	66443	31280	2.1
Ethylbenzene	128958	61326	2.1
m-Xylene	112866	54759	2.1
o-Xylene	118276	58994	2.0
Indene	35941	8929	4.0
Naphthalene	81954	16303	5.0
Biphenyl	167055	28865	5.8
Fluorene	66167	15529	4.3
Acenaphthylene	99031	16176	6.1
Phenanthrene	33986	17802	2.0

SPME–GC conditions for BTEX are the same as in Fig. 3. and for PAHs are: concentration, 2 μg/ml; carrier gas, nitrogen; split ratio, 100:1; injection temperature, 300 °C; FID temperature, 260 °C; column temperature, 180 °C; extraction time, 20 min; extraction temperature, 40 °C; desorption time, 8 min; saturated out with NaCl; constant stirring.

[a] All the numerical values were shown as mean with $n = 3$.

[b] The ratios are adopted by comparing the areas of C[4]–OH-TSO fiber with the corresponding areas of commercial PDMS fiber.

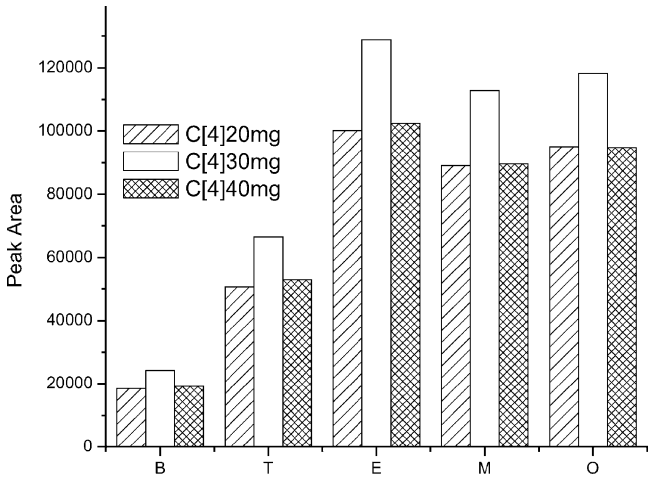

Fig. 4. Extraction efficiency for 2 μg/ml BTEX extracted per unit volume (μl) by use of C[4]–OH-TSO fibers containing different mass of C[4]. SPME–GC conditions are the same as in Fig. 3.

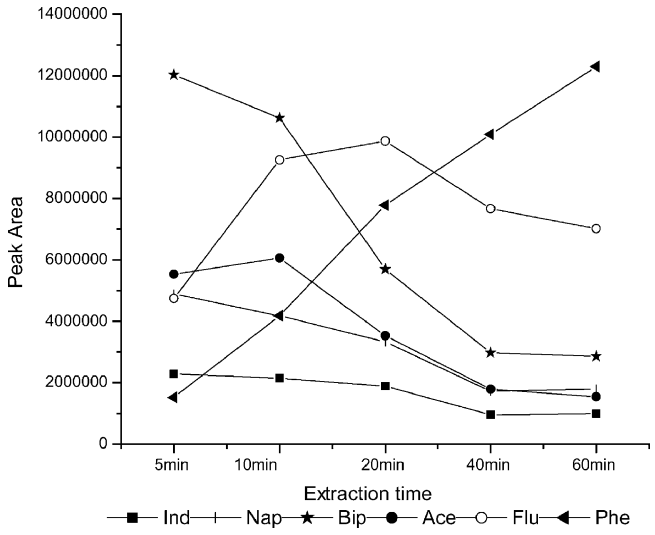

Fig. 5. The extraction time profile for 2 μg/ml PAHs. Conditions: carrier gas, nitrogen; split ratio, 100:1; injection temperature, 300 °C; FID temperature, 260 °C; column temperature, 180 °C; extraction temperature, 40 °C; desorption time, 8 min; saturated out with NaCl; constant stirring.

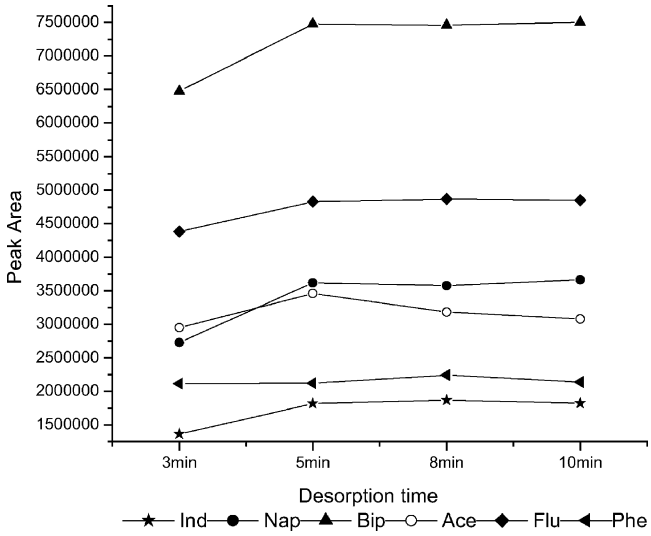

Fig. 6. The desorption time profile for 2 μg/ml PAHs. Conditions: carrier gas, nitrogen; split ratio, 100:1; injection temperature, 300 °C; FID temperature, 260 °C; column temperature, 180 °C; extraction time, 20 min; extraction temperature, 40 °C; saturated out with NaCl; constant stirring.

C[4]-OH-TSO fiber also shows good application for the analysis of polar compounds. Fig. 7 represents the extraction ability of different fibers (PDMS, PA, CW–DVB, PDMS–DVB and C[4]–OH-TSO) to aromatic amines. Under the same extraction and desorption conditions, the extraction capability of C[4]–OH-TSO, PA and CW–DVB fibers are almost identical to the strong polar compounds, such as aniline and *o*-toluidine, which suggests that C[4]–OH-TSO fiber shows good extraction ability to polar aromatic amines through hydrogen bonding and dipole-dipole interactions. At the same time, C[4]–OH-TSO fiber reveals bigger responses to less polar aromatic amines

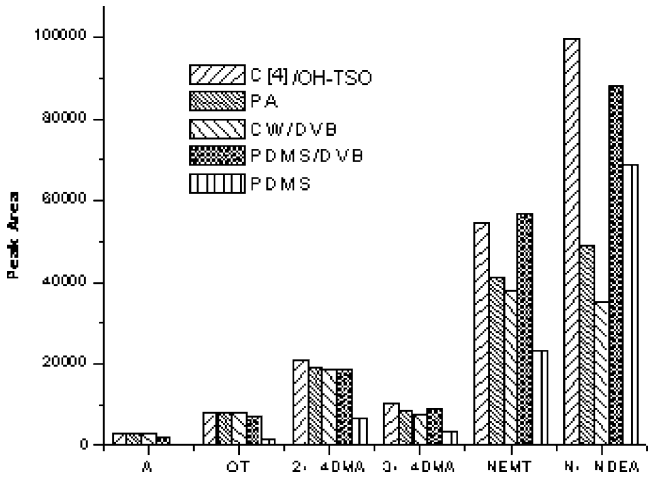

Fig. 7. Comparison of the extraction capability of 2 μg/ml aromatic amines extracted per unit volume (μl) by use of four different coatings. Conditions: carrier gas, nitrogen; split ratio, 100:1; injection temperature, 250 °C; FID temperature, 250 °C; column temperature, 140 °C; extraction time, 30 min; extraction temperature, 30 °C; desorption time, 5 min; saturated out with NaCl; constant stirring.

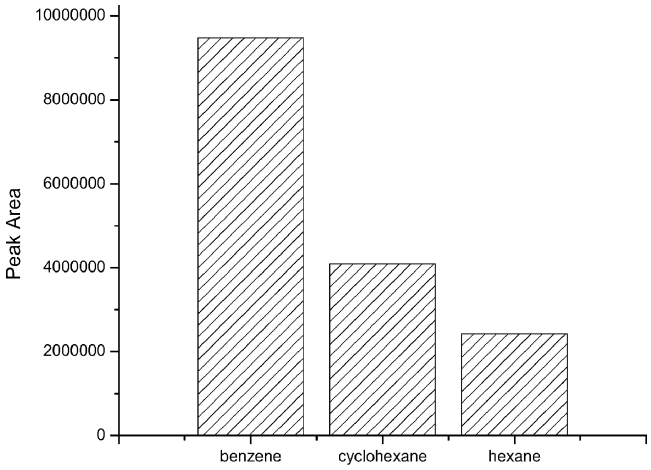

Fig. 8. The extraction efficiency of the 30 mg C[4]–OH-TSO fiber (60 μm) to benzene, cyclohexane and hexane with a concentration of each 4 μg/ml. SPME–GC conditions are the same as in Fig. 3.

(2,4DMA, 3,4DMA, NEMT, N,NDEA) than PDMS–DVB fiber. And the extraction capability of both the two fibers is superior to that of PDMS, PA and CW–DVB. The high extraction selectivity and sensitivity of C[4]–OH-TSO fiber to these compounds is due to the π–π interaction, hydrophobic interactions and cavity-shaped cyclic molecular structure. In the meantime, this becomes possible also thanks to the outstanding material properties of sol–gel coating. The organic–inorganic nature of the sol–gel C[4]–OH-TSO coating provides sorption sites for both the polar and nonpolar analytes.

Fig. 8 represents the extraction efficiency of a C[4]–OH-TSO fiber to benzene, cyclohexane and hexane with a concentration of each 4 μg/ml. The fiber exhibits the highest selectivity to benzene and produces rather poor results to cyclohexane and hexane. These results give a further test that the fiber shows extraordinarily sensitivity to aromatic compounds.

3.4. Extraction equilibrium

A short extraction time is very important for analysis. C[4]–OH-TSO fibers provide a short exposure time and a relatively low temperature for SPME. Fig. 9 and Fig. 5 explain the extraction-time profiles for BTEX and PAHs, respectively. It is evident that the extraction equilibrium was reached quite fast, approximately 15 s for benzene and toluene, 60 s for ethylbenzene and xylene (at room temperature, which is best for BTEX [3]). Wittkamp et al. [42] reported the extraction time was 30–45 min using a 100 μm PDMS fiber to extract BTEX from water. The maximum peak amounts were obtained by C[4]–OH-TSO fiber only in 5 min for indene, naphthalene and biphenyl, 10 min for acenaphthylene, and 20 min for fluorene at optimized temperature, 40 °C. Nguyen and co-workers [28] reported that with HS-SPME of PAHs using their laboratory-made PDMS

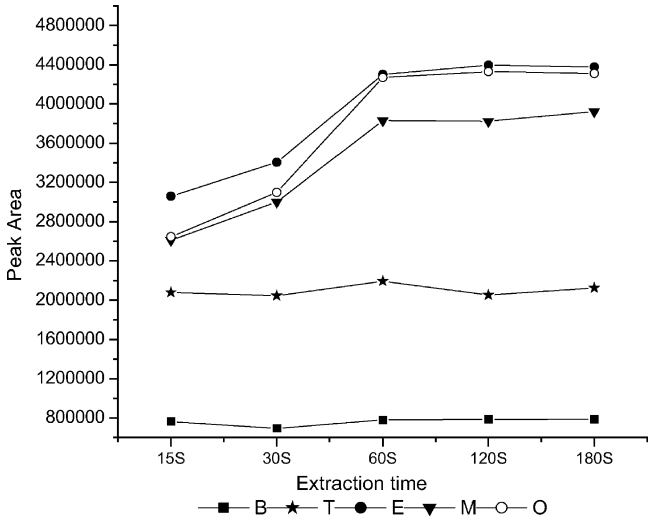

Fig. 9. The extraction time profile for 2 μg/ml BTEX. Conditions: carrier gas, nitrogen; split ratio, 100:1; injection temperature, 250 °C; FID temperature, 250 °C; column temperature, 80 °C; extraction temperature, 14.5 °C; desorption time, 3 min; saturated out with NaCl; constant stirring.

fiber the adsorption time was at least 1–2 h to reach equilibrium. The same phenomenon can be found when it extracted aromatic amines (Fig. 10). Enhanced surface area of the sol–gel coating [30] is a contributing factor to this faster mass transfer during extraction as well as analyte desorption processes during sample introduction, which quickened the partitioning of the analytes from the headspace to the fiber. The extraction time and temperature were chosen to ensure most of analytes were extracted in our study, 1 min and 14.5 °C for BTEX, 20 min and 40 °C for PAHs, 30 min and 30 °C for aromatic amines, 60 min and 40 °C for PAEs.

Table 3
Thermal stability of sol–gel-coated C[4]–OH-TSO SPME fiber

	r^a (/320 °C)					
	280 °C	300 °C	320 °C	340 °C	360 °C	380 °C
Indene	0.91	0.96	1.00	1.13	1.11	1.09
Naphthalene	0.89	0.95	1.00	1.10	1.13	1.11
Biphenyl	0.93	0.97	1.00	1.11	1.08	1.10
Fluorene	0.95	0.97	1.00	1.01	1.02	1.04
Acenaphthylene	0.86	0.90	1.00	1.02	0.99	1.01
Phenanthrene	0.88	0.96	1.00	1.03	1.01	0.99

All the numerical values were shown as mean with $n = 3$, SPME–GC conditions are the same as in Table 2 except that the desorption temperature is variable.

[a] The ratio (r) of PAHs are obtained by comparison of the peak areas at each temperature with that at 320 °C.

3.5. Thermal stability of the coating

Table 3 illustrates the thermal stability of sol–gel-coated C[4]–OH-TSO SPME fiber. The fiber was conditioned for 1h at 280, 300, 320, 340, 360 and 380 °C, successively. The ratio (r) of PAHs are obtained by comparison of the peak areas at each temperature with that at 320 °C. As we can see in Table 3, the values of r did not significantly decrease after the fiber was conditioned at 340, 360, 380 °C. Sol–gel SPME typically uses a fused-silica fiber coated with sol–gel stationary phase, which is chemically bonded to the substrate. Thanks to this chemical bonding, sol–gel coatings have remarkable temperature-stability advantages over physically coated conventional fibers.

3.6. Solvent stability of the coating

Fig. 11 represents the solvent stability of the C[4]–OH-TSO fiber. The extraction ability had no obvious change

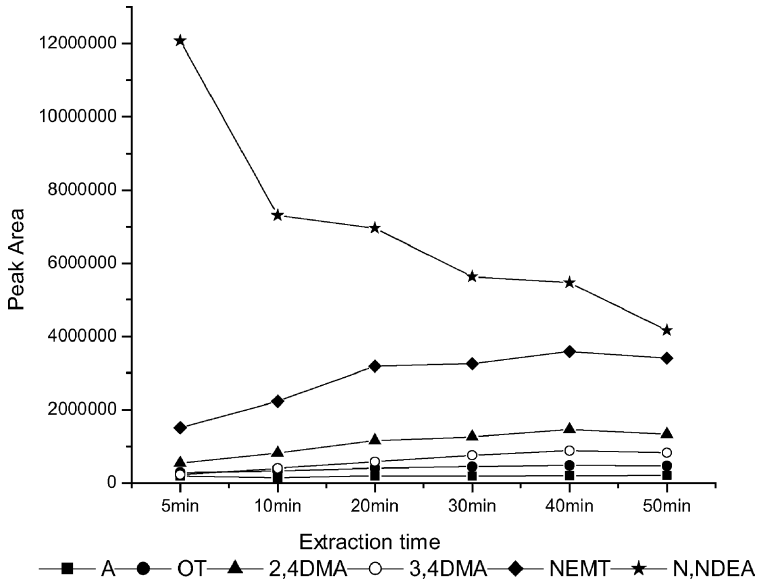

Fig. 10. The extraction time profile for 2 μg/ml aromatic amines. Conditions: carrier gas, nitrogen; split ratio, 100:1; injection temperature, 250 °C; FID temperature, 250 °C; column temperature, 140 °C; extraction temperature, 30 °C; desorption time, 5 min; saturated out with NaCl; constant stirring.

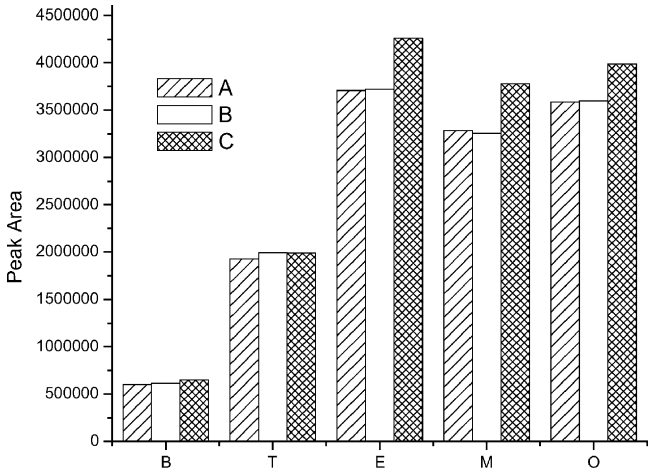

Fig. 11. Influence of solvent on the sol–gel-coated C[4]–OH-TSO fiber on the areas of BTEX (2 μg/ml) extracted. SPME–GC conditions are the same as in Fig. 3. (A) Before dipping in methylene chloride and water; (B) dipping in methylene chlorierde; (C) dipping in water.

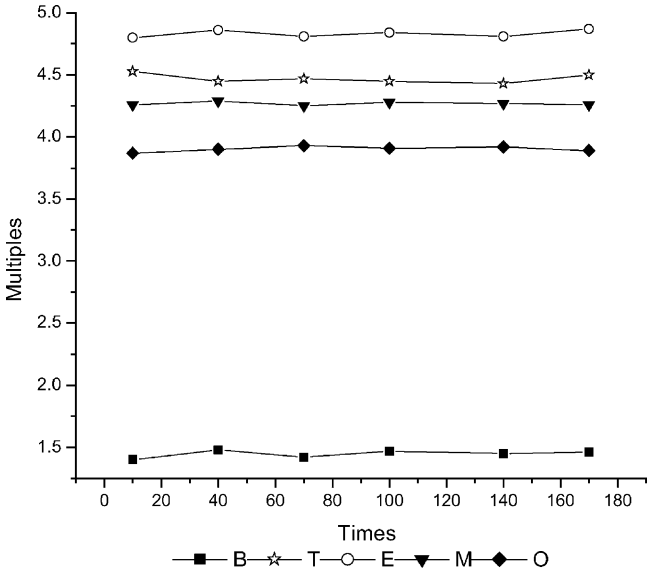

Fig. 12. Lifetime profile of sol–gel C[4]–OH-TSO fiber. SPME–GC conditions are the same as in Fig. 3.

after the fiber was dipped in methylene chloride for 12 h. Being chemically bonded to the fiber surface, sol–gel-coated fibers are inherently stable in operations requiring their exposure to organic solvents. It should be mentioned that commercial SPME fibers are not normally recommended to be exposed to organic solvent media. The extraction amounts were slightly increased after its dipping in water for 12 h, as small molecules not polymerized were dissolved with water, which enlarged the porous layer surface area. All the sol–gel-coated fibers were dipped in methylene chloride and water before used in the following experiments.

3.7. The lifetime of the coating

Fig. 12 reveals the extraction ability of C[4]–OH-TSO fiber after it had been used for 10, 40, 70, 100,140, 170 times. To ensure the comparability of the results, the ratios gained by the comparison of the areas in the chromatogram measures by HS-SPME with the corresponding peak areas obtained by direct injection of 2 μl of a solution with the same concentration. As can be seen in Fig. 12, the response has no obvious decline after being used for 170 times. The C[4]–OH-TSO coating was still stable and reusable. However, the lifetime of commercial fibers can only be used about 40–100 times [43].

3.8. Reproducibility of the coating

Table 4 explains the fiber-to-fiber and batch-to-batch reproducibility of the C[4]–OH-TSO fibers. Six sol–gel-coated C[4]–OH-TSO fibers prepared in the same batch and three identically prepared C[4]–OH-TSO fibers in three batches (each thickness was 60 μm) were tested for the analysis of BTEX. It showed C[4]–OH-TSO fibers have a marvelous reproducibility not only between the same batch but also between different batches, which is a significant improvement in the development of SPME technology.

3.9. Linear range, detection limits and precision

Table 5 lists the linear range, detection limits and precision of BTEX, PAHs and aromatic amines with C[4]–OH-TSO fiber.

The HS-SPME procedure with sol–gel-coated C[4]–OH-TSO fiber showed extraordinarily wide linear ranges with correlation coefficients better than 0.9990. The linear ranges were 1.5–15 000 μg/l for BTEX, 2–2000 μg/l for PAHs and 5–6 orders of magnitude for aromatic amines. The injection split ratio was 40:1 to the entire set of analyses. Such wide linear ranges make it suitable for analysis of both high-concentration samples and low-concentration samples.

The precision of the method was determined by performing six consecutive fiber extractions from an aqueous solution with a concentration of 2.0 μg/ml for BTEX and aromatic amines, and 0.2 μg/ml for PAHs under optimum conditions. The corresponding standard deviation was then

Table 4
Reproducibility data for BTEX (2 μg/ml) using C[4]–OH-TSO fiber containing 30 mg C[4] with the same thickness(60 μm)

Compound	R.S.D. (%)	
	Fiber-to-fiber ($n = 6$)	Batch-to-batch ($n = 3$)
Benzene	1.10	0.44
Toluene	0.96	1.19
Ethylbenzene	0.65	0.69
m-Xylene	1.58	1.26
o-Xylene	0.48	1.34

Table 5
Linear ranges, detection limits[a], and precisions

Compound	LOD (ng/l)	R.S.D.% ($n = 6$)	Linear range (μg/l)	Linear regression equation
B	35.2	3.0	1.5–15000	$y = 763.8x + 31243$, $r = 0.99999$
T	4.7	8.3	1.5–15000	$y = 2158.3x + 154526$, $r = 0.99997$
E	17.7	2.3	1.5–15000	$y = 3835.7x + 251683$, $r = 0.99992$
M	8.3	3.3	1.5–15000	$y = 3886.5x + 268424$, $r = 0.99992$
O	15.3	3.2	1.5–15000	$y = 4338.9x + 87265$, $r = 0.99999$
Ind	51.4	2.2	2–2000	$y = 9217.7x + 432451$, $r = 0.9996$
Nap	2.5	1.0	2–2000	$y = 17806.0x + 819664$, $r = 0.9997$
Bip	1.2	7.1	2–2000	$y = 30477.3x + 2.49372E6$, $r = 0.9990$
Flu	15.2	1.2	2–2000	$y = 15608.0x + 1.25074E6$, $r = 0.9992$
Ace	5.6	4.5	2–2000	$y = 23415.4x + 3.45743E6$, $r = 0.9990$
Phe	8.0	3.8	2–2000	$y = 16368.7x + 5.01598E6$, $r = 0.9997$
A	34.2	2.8	2–200000	$y = 64622.9x + 102685$, $r = 0.9991$
OT	72.4	1.2	2–20000	$y = 328273.3x + 109726$, $r = 0.9992$
2,4DMA	66.8	3.4	2–20000	$y = 1.04298E6x = 214173.8$, $r = 0.9993$
3,4DMA	26.1	5.3	2–20000	$y = 692975.8x + 138429$, $r = 0.9993$
NEMT	49.2	2.6	2–20000	$y = 7.66644E6x + 713600$, $r = 0.9997$
N,NDEA	15.6	3.9	0.2–20000	$y = 1.59047E7x + 788371$, $r = 0.9999$

[a] Detection limits were estimated on the basis of 3:1 signal to noise ratios.

calculated for these extractions and expressed as a percentage. The relative standard deviation (R.S.D., $n = 6$) values obtained were ≤8.5% in all cases, ranging from 2.3 to 8.5% for BTEX, 1.0–7.1% for PAHs and 1.2–5.3% for aromatic amines.

Limits of detection (LODs) were estimated on the basis of 3:1 signal to noise ratios. Owing to the high selectivity and sensitivity of C[4]–OH-TSO coating, low detection limits (ng/l) were achieved for most of the analytes. The LODs varied from 4.7 to 35.2 ng/l for BTEX, from 1.2 to 51.4 ng/l for PAHs and from 15.6 to 72.4 ng/l for aromatic amines.

Figs. 13–15 represent typical HS-SPME–GC–FID chromatograms of extraction of BTEX, PAHs and aromatic amines, respectively by sol–gel-coated C[4]–OH-TSO fiber.

PAEs are pollutants in the environment, but the determination of them are much difficult because they (especially those with long-chain) are not likely to diffuse into the gas phase. The use of Dir-SPME with C[4]–OH-TSO fibers exhibits many advantages attributing to their characteristics. Fig. 16 represents the GC–FID chromatogram obtained after direct SPME of 1.25 μg/ml phthalic acid esters. The C[4]–OH-TSO fiber was used at least 140 times for Dir-SPME of PAEs and still showed excellent selectivity.

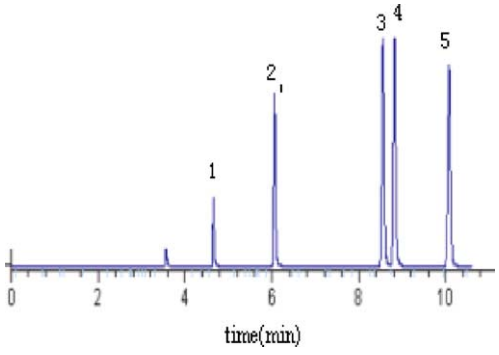

Fig. 13. Typical HS-SPME–GC–FID chromatogram of extraction of 2 μg/ml BTEX. SPME–GC conditions are the same as in Fig. 3. Peaks: (1) B; (2) T; (3) E; (4) M; (5) O.

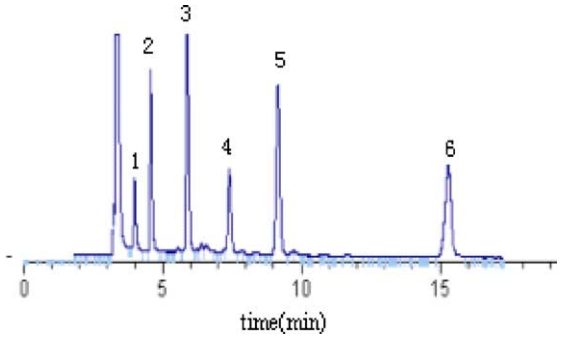

Fig. 14. Typical HS-SPME–GC–FID chromatogram of extraction of 2 μg/ml PAHs. SPME–GC conditions are the same as in Table 2. Peaks: (1) Ind; (2) Nap; (3) Bip; (4) Ace; (5) Flu; (6) Phe.

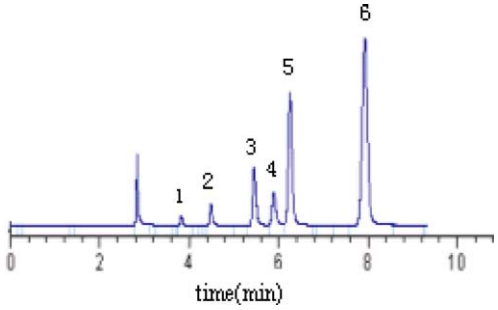

Fig. 15. Typical HS-SPME–GC–FID chromatogram of extraction of 2 μg/ml aromatic amines. SPME–GC conditions are the same as in Fig. 7. Peaks: (1) A; (2) OT; (3) 2,4DMA; (4) 3,4DMA; (5) NEMT; (6) N,NDEA.

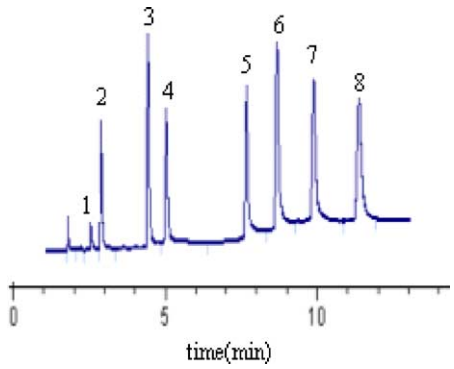

Fig. 16. Typical direct-SPME–GC–FID chromatogram of extraction of 1.25 μg/ml phthalic acid esters. Conditions: carrier gas, nitrogen; split ratio, 100:1; injection temperature, 340 °C; FID temperature, 320 °C; oven programming: 260 °C for 2 min, then programmed at 12 °C/min to 300 °C for 6 min; extraction time, 60 min; extraction temperature, 40 °C; desorption time, 8 min; NaCl, 0.25 g/ml; constant stirring. Peaks: (1) DMP; (2) DEP; (3) DBP; (4) DAP; (5) *i*-DOP; (6) *n*-DOP, (7) DNP; (8) DDP.

4. Conclusions

The sol–gel-coated 5,11,17,23-tetra-*tert*-butyl-25,27-diethoxy-26,28-dihydroxycalix[4]arene SPME fiber was prepared and investigated for the first time. It exhibits high selectivity and sensitivity and fast extraction equilibrium. Good thermal and solvent resistance, marvelous reproducibility and long lifetime, broad linear ranges and low detection limits are all its characteristics. Since calixarenes are easy to modify with different functional groups, the application of calixarene fibers will undoubtedly improve the development of SPME technology.

Acknowledgements

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