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Hydroxyfullerene as a novel coating for solid-phase microextraction fiber with sol–gel technology

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Abstract

Hydroxyfullerene (fullerol) as a novel coating for solid-phase microextraction (SPME) fiber was first prepared by a sol–gel technology. The coating procedure involving sol solution composition and conditioning process was presented. A fullerene polysiloxane surface-bonded porous coating on the fused-silica fiber surface was obtained and confirmed by IR spectra and scanning electron microscopy. The coating has stable performance at high temperature (even to 360 °C) and solvents (organic and inorganic) because of the properties of fullerene and the chemical binding between the coating and the fiber surface. The extraction properties of the new coatings to less volatile organic compounds, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons and polar aromatic amines were investigated using headspace SPME coupled with GC–electron-capture detection and GC–flame ionization detection. In addition, compared with commercial SPME stationary phases, the new coatings showed higher sensitivity, faster velocities of mass transfer for aromatic compound, and possessed planarity molecular recognition for PCBs. Moreover, this fiber was firm, inexpensive, durable and can be prepared simply. The fiber-to-fiber reproducibility was very good.
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Keywords: Solid-phase microextraction; Sol–gel; Hydroxyfullerene; Fullerene; Fullerol

1. Introduction

Solid-phase microextraction (SPME), developed by Pawliszyn and coworkers (e.g., Ref. [1]), is a convenient, solvent-free, and efficient extraction method. In recent years, the applications of SPME have been widely extended from volatile organic compounds, semi-volatile chemicals to non-volatile inorganic pollutants in different fields, including the environment, food, natural products, pharmaceuticals, biology, toxicology, forensics, etc. [2]. SPME has been coupled with various techniques to achieve different analytical goals, such as gas chromatography (GC), GC–mass spectrometry (MS), high-performance liquid chromatography (HPLC), Raman spectrometry [3] and capillary zone electrophoresis [4].

Typically, SPME uses a polymeric-coated fused-silica fiber to extract target compounds from different sample matrices, therefore, the key part of the SPME device is the fiber coating. At first, only poly(dimethylsiloxane) (PDMS) and polyacrylate (PA) coatings were commercially available. PDMS is a nonpolar phase that extracts nonpolar analytes very well while PA fibers have a great affinity for polar

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compounds. Later, mixed-phase coatings, PDMS–divinylbenzene (DVB), Carboxen–PDMS, Carbowax–DVB, and Carbowax–template resin which have composite properties compared with PDMS and PA also became available. Recently, some new types of fibers, such as nonpolar silica particles bonded with C_8, C_{18} [5], and inorganic Carbopack [6], gold [7], pencil lead [8], graphite [9], activated charcoal [10], poly(3-methylthiophene) [11], Nafion perfluorinated resin [12], polypyrrole [13], anodized aluminum wire [14] and molecularly imprinted polymer (MIP)-coated fiber [15] have been prepared. However, almost all these fibers coated with polymer are generally prepared by mere physical deposition or partial crosslink of the polymer coating on the surface of the fused-silica fibers. The lack of proper chemical bonding between the polymer coating and fused-silica fiber surface may be responsible for the low thermal and chemical stability. Furthermore, the price of commercially available SPME fibers is high due to their preparation process requiring expensive equipment. Up to now, there are still few fibers with strong conformation selectivity and molecule recognition for some particular analytes of interest. These limiting factors have hindered the development of SPME.

Sol–gel coating technique offers important advantages compared with conventional coating techniques, (1) strong adhesion between the coating and the bare fused-silica surface because of chemical bonding which is important for enhancing operation stabilities involving temperature and solvents, (2) the porous surface structure of sol–gel coating which can provide high surface areas and allow for high extraction efficiency, (3) relative ease of change the composition of the coating which therefore will have different selectivity. Malik and co-workers have applied sol–gel coating technology to open tubular column GC [16], capillary electrophoresis (CE) [17]. They also have used the sol–gel coating technique for a SPME fiber (10 μm PDMS) [18]. We have applied sol–gel coating technology to prepare sol–gel polyethylene glycol (PEG) fibers for the determination of both polar and non-polar compounds [19]. Fullerene has a unique spherical shape, conjugated three-dimensional π-electronic system, and it used as stationary phase for LC [20] and GC [21], has shown wide operational temperature, good thermal stability and good selectivity for aromatic compounds, especially exhibited strong affinity for planar polychlorinated biphenyl (PCB) molecules.

In this paper, a novel containing hydroxyfullerene (fullerol)–hydroxy-terminated silicone oil (OH-TSO) coated SPME fiber was prepared, and its features were investigated by the analysis of 12 PCBs (four tetrachlorobiphenyls and eight pentachlorobiphenyls), 10 polycyclic aromatic hydrocarbons (PAHs) and 21 aromatic amines. The new SPME–GC method was applied to the analysis of some practical environment samples.

2. Experimental

2.1. Instrumentation and reagents

The SPME devices for manual sampling and a 30-μm commercially available PDMS coated fiber for comparison were obtained from Supelco (Bellefonte, PA, USA) and were also prepared by modification of a commercial SPME fiber holder and assembly. SPME–GC experiments were carried out on a Hewlett-Packard 6890 GC system equipped with a capillary splitless injector system, an electron-capture detection (ECD) system and a flame ionization detection (FID) system and a HP-3396 Integrator. A 30 m×0.32 mm I.D., 0.25 μm HP-5 coating fused-silica capillary column was used. Nitrogen was used as the carrier gas for both ECD and FID. A Hitachi Model CT6D centrifuge (Hitachi, Japan) was used to separate the sol solution from the precipitate. To mix various solution ingredients thoroughly, a Branson Model 8210 Ultrasonator (Yamato, Japan) was used. The fused-silica fiber (140 μm, O.D.) with protective polyimide coating was obtained from Academy of Post and Telecommunication, Wuhan, China. The Hitachi X-650 scanning electron microanalyzer and Bio-Rad FTS 175 Fourier transform (FT) IR spectrometer were used for the investigation of the fiber surface.

Fullerol was synthesized by the reaction of C_{60} with aqueous NaOH and H_2O_2 in the presence of tetrabutylammonium hydroxide (TBAH) [22]. Methyltrimethoxysilane (MTMOS) and OH-TSO were purchased from the Chemical Plant of Wuhan

University. Trifluoroacetic acid (TFA) was purchased from Aldrich (Allentown, PA, USA). All solvents used in this study were analytical-reagent grade. The stock solutions of PCBs: PCB 52, PCB 44, PCB 66, PCB 77 and PCB 104, PCB 100, PCB 101, PCB 103, PCB 87, PCB 114, PCB 118, PCB 126, were prepared by diluting 100 μg/ml (from Chem Service) of each compound to 1.0 μg/ml concentration with *n*-hexane in a volumetric flask. The stock solutions of PAHs were prepared by dissolving 10 mg of each standard in a 10-ml vial with methanol. Stock solution of 21 aromatic amines with 2 mg/ml in methanol was purchased from Dikma. The working standard solutions were prepared to the corresponding concentration by diluting stock standard solutions with solvent.

2.2. SPME fiber preparation

Preparation of the sol–gel SPME fiber involved the following steps: (1) pretreatment of the fused-silica surface, (2) preparation of the sol–gel solution, (3) coating of the retreated fused-silica surface and (4) conditioning of the coated surface. Prior to sol–gel coating, the protective polyimide layer on a 1 cm tip of a 10 cm piece of fused-silica was removed by dipping it in acetone for 3 h. Then the fiber was dipped in 1 *M* NaOH solution for 1 h, to expose the maximum number of silanol groups on the surface of the fiber, and cleaned with water. Then it was placed in 0.1 *M* HCl solution for 30 min to neutralize the excess NaOH, cleaned again, and air-dried at room temperature. Care is required in these experiments because the fused-silica becomes fragile when the polyimide is removed. The sol–gel solution was prepared as follows: 20 mg of fullerol was dissolved in 100 μl of water, and then 400 μl of MTMOS, 100 μl of OH-TSO were added and mixed thoroughly for 20 min by ultrasonic agitation in a plastic tube. A 200-μl volume of TFA was sequentially added to the resulting solution with ultrasonic agitation for another 5 min. The mixture was then centrifuged at 6000 rpm for 3 min. The precipitate at the bottom of the tube, if any, was removed and the top clear sol solution was used for fiber coating. The treated fiber was dipped vertically into the sol–gel solution for 30 min, during which a sol–gel coating was formed on the bare outer surface of the fiber end. For each fiber, this coating process was repeated several times, using a freshly prepared sol solution each time until the thickness of the coating wanted was obtained.The fiber was placed in a desicator at room temperature for 24 h. This was followed by the conditioning process. The fiber was initially conditioned by placing it in a GC injector port kept at a temperature of 150 °C with a gentle N_2 flow (~10 p.s.i.; 1 p.s.i.=6894.76 Pa) for 2 h, and then conditioned again at 250–350 °C for another 6 h. After removal from the injector, the fiber was cooled to room temperature, and it was ready for SPME and SPME–GC experiments. The final thickness of the fiber was 30 μm; the other three fibers with each thickness of 30 μm were also coated for comparison.

2.3. Headspace extraction procedure

A 15-μl portion of each above stock standard solution was diluted with 15 ml of distilled water in 20-ml headspace (HS) vial containing a magnetic spin bar (PTFE). To avoid sample evaporation, the vial was sealed with a headspace aluminum cap with a PTFE-faced septum. During extraction, the septum vial was pierced with the protecting needle and the fiber was exposed to the headspace over the water. The organic analytes were adsorbed from the headspace onto the fiber, then the adsorbed analytes were thermally desorbed by inserting the fiber into the injector of the GC system. To prevent the analytes from being adsorbed on the glass wall, all the glassware used for these analyses was silanized prior to use, as described previously [23].

3. Results and discussion

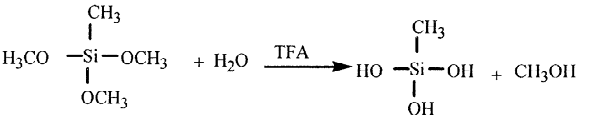
3.1. Optimization of the sol–gel process

The sol–gel process was affected by varying the mass of fullerol, altering precursors and by changing the drying time of sol–gel coating, etc. Usually tetraethoxysilane (TEOS) is used as a precursor in the sol–gel process. In this work, however, we

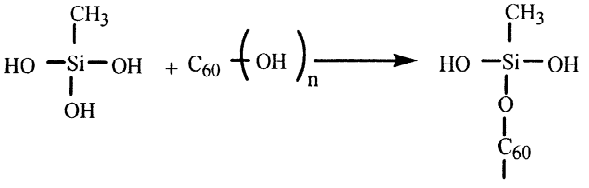
decided to use MTMOS that can overcome some inherent problems during the gel-drying process associated with cracking and shrinkage of the coating. This problem becomes more significant for sol–gel coatings with greater thickness. OH-TSO is added into this system not only to lengthen the silica network leading to the increased surface area of the fiber but also to help to spread the stationary phase on the fiber uniformly. C_{60} molecules in the sol–gel network are selectors for compounds with conjugate π electric system and planar structure. Therefore, the mass of fullerol added in the sol–gel solution is to determine the conformation selectivity of the coating. In this study, optimization of the mass of fullerol in sol–gel solutions was done by preparing fibers from sol–gel solutions containing 0, 10 and 20 mg fullerol. A mass of fullerol greater than 20 mg in sol–gel solution leads to precipitation because the sol–gel solution may lack enough dissolubility for fullerol.

3.2. Major reaction of the coating process

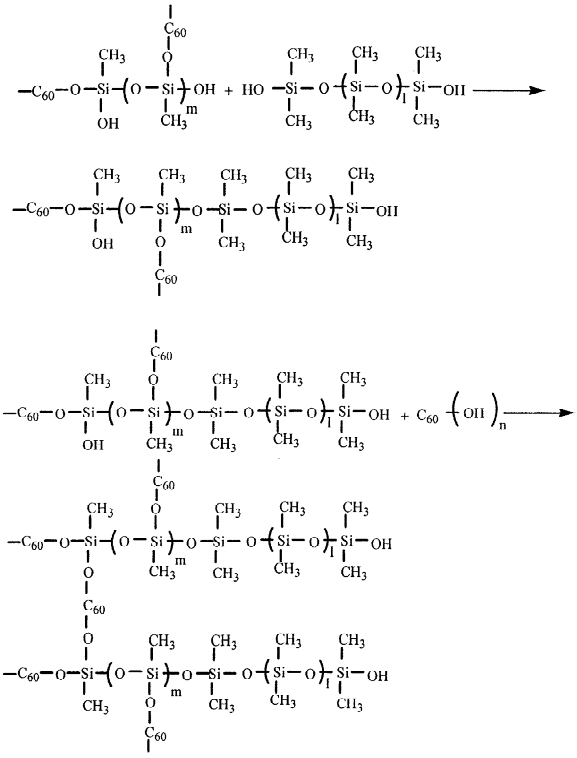
There are four major reaction processes that occur during the sol–gel formation, (1) catalytic hydrolysis of MTMOS:



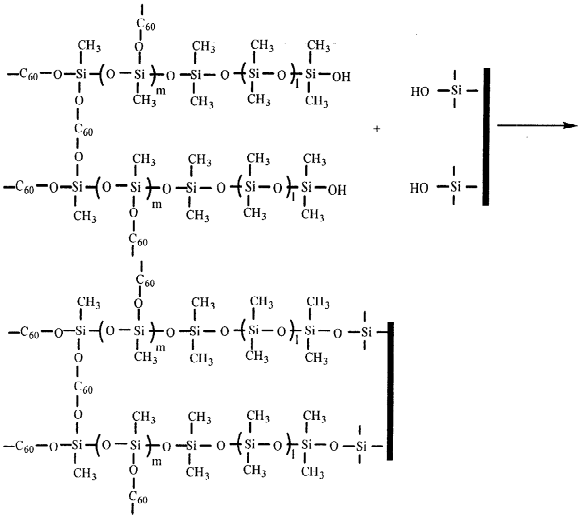
(2) Condensation of the hydrolyzed products with fullerol:



(3) Polycondensation of the condensation products into a three-dimensional sol–gel network, chemical bonding of OH-TSO and fullerol to the evolving sol–gel network:



and (4) chemical anchoring of the evolving sol–gel polymer to the surface of the fiber to create a surface-bonded polymeric coating:



The IR spectra data of the fiber coatings contain

the feature identified by 1102 cm^{-1} (C_{60}–O–Si) that confirm the successful bonding of fullerol to the stationary phase.

3.3. Surface structure of the coating

As can be seen from the scanning electron micrograph of the fullerol-coated surface presented in Fig. 1, the sol–gel fullerol coating possesses a porous structure. Such a porous structure should significantly increase the available surface area on the fiber. This can improve the kinetics of the extraction process and, therefore, enhance extraction efficiency.

3.4. Thermal stability of the coating

Fig. 2 illustrates the thermal stability of sol–gel-coated fullerol SPME fiber. It was seen that the extraction peak areas of four tetrachlorobiphenyls did not significantly decrease after they were conditioned for 1 h at 280, 300, 310, 320, 330, 340, 350 and 360 °C, successively, which is due to the special nature of fullerene and the strong chemical bonding provided by sol–gel technology. It should be noted that the performance of the fiber was not affected even at a temperature of 360 °C, which is one of the highest operational temperature of SPME fiber up to now. Such high thermal stability can expand the SPME application range toward higher boiling-point compounds.

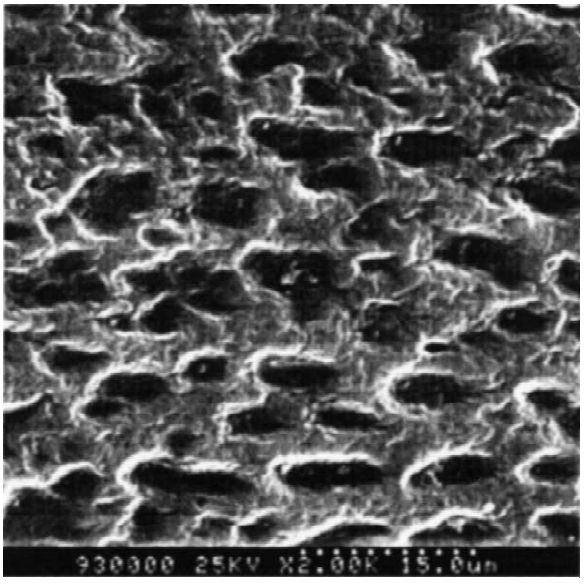


Fig. 1. Scanning electron micrograph of sol–gel fullerol fiber at 2000-fold magnification.

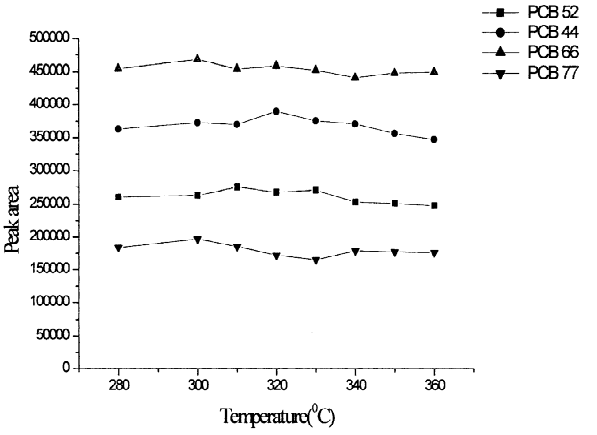


Fig. 2. Effect of temperature on sol–gel fullerol fiber (30 μm) on the amounts of four tetrachlorobiphenyls extracted. Extraction time, 30 min; extraction temperature: 80 °C; desorption time, 5 min; distilled water with no salt; constant stirring. HP-5, 30 m × 320 μm I.D. capillary; splitless injection, injector and ECD temperature: 300 °C. Oven programming: 120 °C for 1 min, then programmed at 6 °C/min to 280 °C for 5 min.

3.5. Effect of solvents

Being strongly adhesive to the coating of the fiber surface due to chemical bonding and wrapped by the three-dimensional network, the sol–gel fullerol coating hardly swells in solvents and cannot slip off the fused-silica substrate. Fig. 3 shows that the extraction ability had no obvious decrease after the fiber was dipped in different polar solvents, *n*-hexane, methylene chloride, acetone, distilled water for 1 h, respectively. The stability of the coating was also studied under the same methylene chloride solvent for periods of up to 12 h. The relative standard deviations (RSDs) of the extraction peak areas determined at concentration of 50 ng/l were less than 5%, and they showed the extraction efficiencies did not degrade. Thus, the stability in

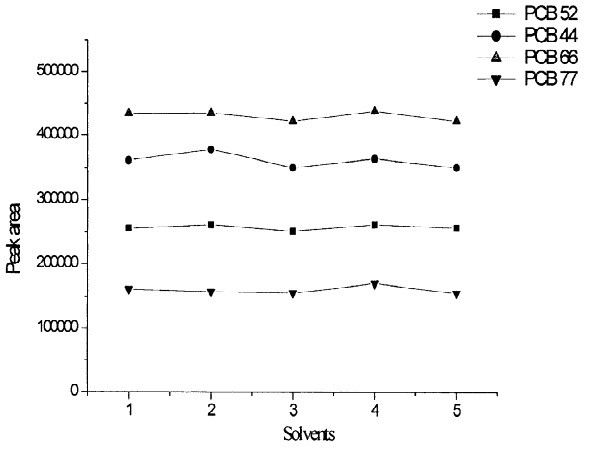


Fig. 3. Influence of solvent on the sol–gel fullerol fiber (30 μm) on the amounts of four tetrachlorobiphenyls extracted. Extraction temperature, 80 °C. Solvents: 1, not dipped in solvent; 2, *n*-hexane; 3, methylene chloride; 4, acetone; 5, distilled water. Other conditions as in Fig. 2.

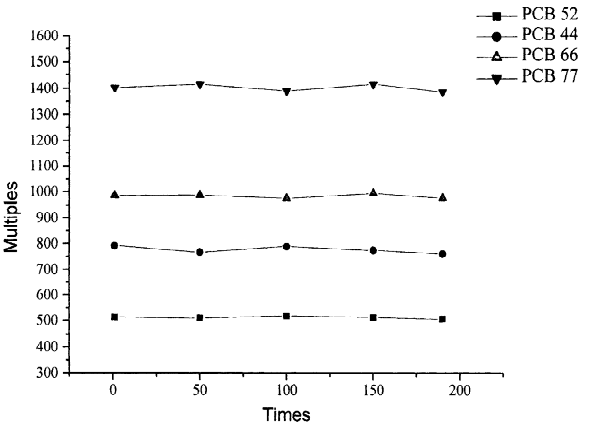


Fig. 4. Lifetime profile of sol–gel fullerol fiber. SPME–GC conditions as in Fig. 2.

solvents of the sol–gel fullerol coatings make it suitable for the coupling of SPME with many more techniques, such as HPLC and supercritical fluid chromatography (SFC).

3.6. The lifetime of the coating

A coating's lifetime is important for practical application. The coating is damaged mainly by high temperature of the injection port of the gas chromatograph and/or solvent in the matrix. The sol–gel-coated fullerol SPME fiber is characterized by its high thermal and solvent stability. Thus, the lifetime of this fiber is longer than that of commercial fibers. The fiber can be used nearly 200 times while all commercial fibers can only be used about 40~100 times. Fig. 4 shows the change of extracting performance of this fiber. In order to ensure comparability of the result, the ratios of areas obtained by the comparison of the areas in the chromatogram measured by HS-SPME with the corresponding peak areas gained by direct injection of 1 μl of a solution with the same concentration, were used for representing the extracting performance of the fiber. Fig. 4 shows that the ratios have no obvious decline after being used 190 times.

3.7. Conformation selectivity

PCBs are a group of stable, persistent, lipophilic contamination compounds, which occur widely in many media and organisms and consist of 209 distinct chlorine-substituted congeners. Studies of structure–activity relationships suggest the non-*ortho*, coplanar PCBs such as PCB 77, PCB 126, substituted with chlorine atoms in both *para* and at least one *meta* position, and their mono-*ortho* analogues such as PCBs 66, 114 and 118 have biological properties similar to the well-known 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) [24]. Therefore, specific analyses of these higher toxicity congeners in environmental samples are important for analytical chemists. Fig. 5 shows the extraction quantities of PCBs in each fiber coating. Within the group of isomers, a strong increase of extraction quantities was observed in going from tetra-*ortho* to non-*ortho*-substituted PCBs when fibers B and C were used. The data of PCB 77, PCB 126 are the biggest, respectively, among four tetrachlorobiphenyls and among eight pentachlorobiphenyl molecules. It shows that the novel SPME fiber coatings provide excellent planar conformation selectivity and molecule recognition. The higher selectivity can be seen from the figure with larger mass of fullerol in the coating. The strong extraction capabilities of the fullerol fiber for planar PCB congeners may be caused by charge-transfer between the PCBs

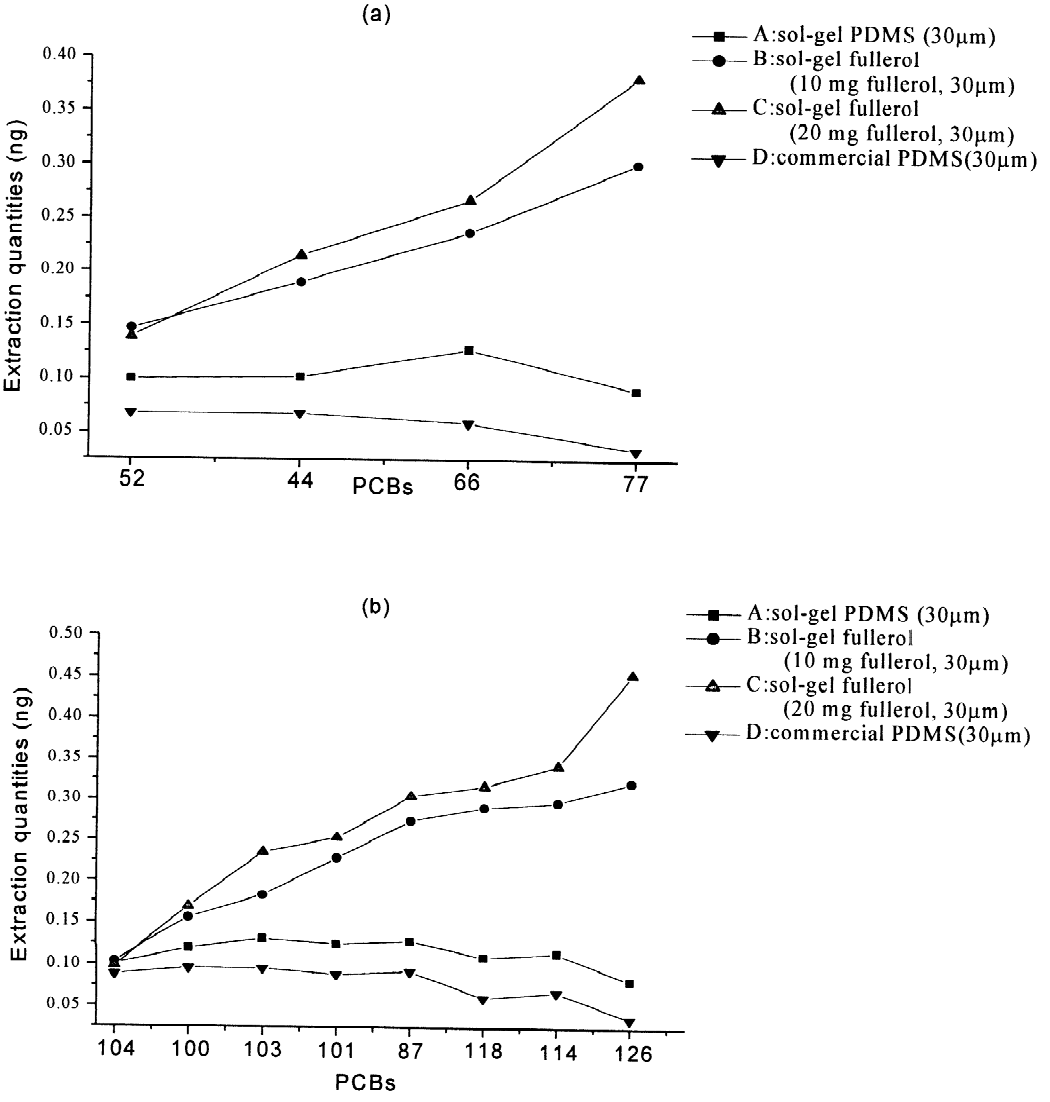


Fig. 5. The comparison of extraction quantities of four different fibers for (a) 0.1 ng/ml four tetrachlorobiphenyls and (b) 0.1 ng/ml eight pentachlorobiphenyls. Extraction time, 30 min; extraction temperature, 100 °C. Other conditions are the same as in Fig. 2.

and the fullerol coating and by the structure matching because the planar PCBs isomers contain a partial structure similar to that of the C_{60} molecules. Thus, the fullerol coating shows increased affinity with increasing planarity of the PCB molecules. However, when there is no fullerol in the coating, extraction quantities for PCBs decrease significantly for the commercial PDMS (fiber D) and laboratory-made sol–gel PDMS (fiber A), while extraction capabilities of laboratory-made sol–gel coated fibers are much higher than that of commercial PDMS, which is because the surface area of sol–gel-coated fiber is higher due to its porous structure.

3.8. Extraction and analysis of PCBs

As mentioned above, the sol–gel fullerol fiber shows unique selectivity for PCBs. Thus it may be

applied to the selective enrichment and analysis of the highly toxic PCBs. According to the literature [25], HS-SPME offered higher sensitivity than direct-SPME at higher temperature for the determination of PCBs in water. Furthermore, HS-SPME can avoid the interruption of matrix of sample. Thus, in our study, all findings were obtained by the HS-SPME method. During the HS-SPME procedure, distribution and adsorption equilibrium of the analytes must be established between the gaseous and solid phase. The equilibrium is affected by various factors, such as the nature of the fiber, the identity of the analyses, the extraction time, and the extraction temperature. The optimal experimental conditions should be investigated for each compound and for the fiber selected. In general, the equilibrium is compound dependent and can vary significantly among the different compounds. The equilibrium times were longer for the PCBs because of their higher molecular mass and boiling point. The equilibration time is about 50 min for PCB 52, PCB 104, PCB 44, PCB 100, PCB 103, approximate 80 min for other PCBs. Under similar conditions, the commercial 100 μm PDMS fiber needed even several days to reach equilibration [25]. The porous structure helps faster mass transfer during extraction, so the equilibration time is shorter. But the time is still long for a routine analysis. To be a viable analytical method and keep a reasonable sampling time, operation under nonequilibrium conditions is necessary. Recently, Ai [26] has proposed a dynamic model for the SPME adsorption process. One of the conclusions of this model is that the amount of analyte adsorbed onto the fiber is proportional to the initial concentration in the sample matrix, once the agitation conditions and the sampling time are held constant, and hence, SPME quantitation is feasible under nonequilibrium conditions. In our studies, this conclusion is also confirmed by use of the polysilicone fullerene (PF) coating [27]. Here, the sampling time was fixed at 30 min. Extraction temperature has a double impact, so there is an optimal extraction temperature at which one can obtain ideal adsorbed quantities and rapid equilibrium time. With an increase in temperature, the extraction ability of the fiber increased (to 80 °C), which is because increasing temperature can significantly increase analyze evaporation rates (distribution constants) and mass transfer at the water–gas interface (distribution velocity). It is apt for the analytes to enter the gas phase and coating. However, a significant decrease in adsorption capacity with increasing temperature was observed (up to 100 °C), resulting from the partition coefficient between the coating and the headspace decreasing because adsorption is generally an exothermic process. The optimal extraction temperature is not the same for distinct PCBs. As a whole, we chose to extract and enrich at 80 °C. Because the boiling points of PCBs are very high, the desorption process is relatively slow, but, here, all these PCBs can be determined within 5 min at 300 °C. Such short desorption times arise from the porous structure of the sol–gel fullerol fiber and result in a short analysis time. Table 1 summarizes the limits of detection (LODs), RSDs, and linear ranges for the extraction of PCBs using the fiber. The LODs were estimated to be the concentrations of the PCBs that produce signals three times of the background noise. It can be seen that LODs were 0.013–0.051 ng/l for all the PCBs which are much lower concentrations, sufficient to meet the demands of environmental monitors, food supervision, and so on. The HS-SPME procedure showed wide linear range, 10^3 or over 10^3 and the correlation coefficients (r^2) were between 0.9983 and 0.999. The repeatability is very good, and the RSD determined at 50 ng/l is 1.8–4.6%.

The proposed SPME method was applied to determine the concentration of PCBs in a contaminated sediment sample. Fig. 6 shows the chromatogram of extractions of the sediment using this sol–gel fiber coupling with GC–ECD. Only 1.0 g fine powder sediment was used and the analytical process took less than 2 h. It was found to contain 0.3031 ng/g PCB 66, 1.033 ng/g PCB 77, 0.9750 ng/g PCB 87, 0.4336 ng/g PCB 114, 0.6258 ng/g PCB 126, 0.1630 ng/g PCB 156 and 0.0521 ng/g PCB 189. The apparent recovery defined as $C_{\text{test}}/C_{\text{spike}}$ (the percentage of determination results to the spiked concentration) study was carried out by spiking 0.75 ng of each of the above PCBs into 1.0 g of non-contaminated soil. The calculated average recoveries were PCB 66: 101.9% (RSD, 2.9%, $n=6$), PCB 77: 102.5% (3.6%), PCB 87: 92.3% (2.0%), PCB 114: 89.0% (3.7%), PCB 126: 98.2% (6.0%), PCB 156: 87.1% (5.2%) and PCB 189: 103.6% (3.1%). It can

Table 1
The linear range, LOD, RSD, correlation coefficient (r^2) and linear regression equation of sol–gel fullerol fiber for the determination of PCBs

Compound	Linear range (ng/l)	LOD (ng/l)	RSD (%, $n=6$)	Correlation coefficient (r^2)	Linear regression equation (x: ng/l)
PCB 52	$1–10^3$	0.051	3.5	0.9986	$y=2203.5x+41\,419$
PCB 104	$1–10^3$	0.038	2.1	0.9983	$y=2758.1x+55\,446$
PCB 44	$1–10^3$	0.026	1.8	0.999	$y=3392x+57\,348$
PCB 100	$0.5–10^3$	0.019	2.6	0.9989	$y=4394.9x+74\,852$
PCB 103	$0.5–10^3$	0.021	1.8	0.9991	$y=5085.9x+76\,720$
PCB 66	$0.5–10^3$	0.023	2.0	0.9995	$y=3963.1x+74\,144$
PCB 101	$1–10^3$	0.013	3.3	0.9988	$y=4034.2x+81\,859$
PCB 87	$0.5–10^3$	0.018	1.1	0.9997	$y=6401.7x+65\,852$
PCB 77	$0.5–10^3$	0.030	2.5	0.9993	$y=1018.1x+25\,770$
PCB 118	$1–10^3$	0.025	3.9	0.9998	$y=3024x+36\,195$
PCB 114	$1–2\cdot10^3$	0.022	2.5	0.999	$y=5848.3x+13\,333$
PCB 126	$1–2\cdot10^3$	0.021	4.6	0.9996	$y=1218.7x+8755$

be seen that the sol–gel fullerol fiber has obvious advantage for the determination of PCBs.

3.9. Extraction and analysis of PAHs

PAHs are the ubiquitous contaminants in the environments. Due to their potential or proven carcinogens, the concentration of PAHs in the environment must be determined and controlled. Doong et al. [28] compared five kinds of commercial SPME fibers and found the PDMS was the most suitable for the determination of PAHs by the HS-SPME method. In our study, the sol–gel fullerol fiber was used to extract and analyze 10 kinds of PAHs by the HS-SPME method. The comparison of extraction quantities of commercial PDMS and the novel sol–gel fullerol fiber for 0.010 μg/ml PAHs is represented in Fig. 7. The result revealed the new coating had a better efficiency for PAHs than commercial PDMS did. The coating also had conformation selectivity for planar PAHs molecules just as Xiao et al. had discussed [27].

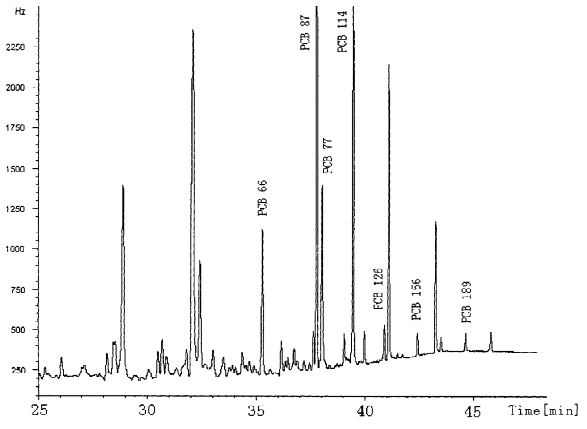


Fig. 6. The chromatogram of the contaminated sediment sample by SPME–GC–ECD. SPME and GC conditions as in Fig. 2.

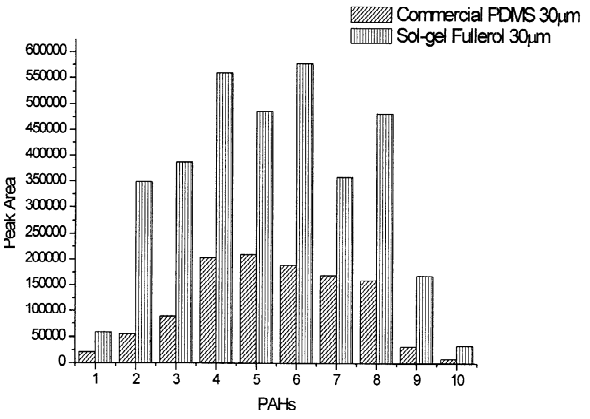


Fig. 7. The comparison of extraction quantities of commercial PDMS and the laboratory-made sol–gel fullerol fiber for 0.010 μg/ml PAHs. Peaks: 1, naphthalene, 2, biphenyl, 3, acenaphthylene, 4, fluorene, 5, anthracene, 6, phenanthrene, 7, fluoranthene, 8, *m*-terphenyl, 9, *p*-terphenyl, 10, pyrene. Extraction time, 30 min; extraction temperature: 60 °C; desorption time, 90 s; saturated solution with NaCl; constant stirring. HP-5, 30 m×320 μm I.D. capillary, splitless injection, injector and FID temperature: 280 °C. Oven programming: 100 °C for 1 min, then programmed at 8 °C/min to 280 °C for 5 min.

Table 2
The linear range, LOD of sol–gel fullerol fiber for the determination of PAHs

Compound	Linear range (ng/ml)	LOD (ng/ml)	RSD (%, $n=6$)	Correlation coefficient (r^2)	Linear regression equation (x: ng/ml)
Naphthalene	$0.1–10^2$	0.039	3.8	0.9985	$y=4573x+11\,123$
Biphenyl	$0.05–10^2$	0.0066	2.0	0.9997	$y=31\,161x+7078.4$
Acenaphthylene	$0.1–10^2$	0.010	3.1	0.999	$y=20\,441x+35\,634$
Fluorene	$0.05–10^2$	0.0068	2.3	0.9997	$y=30\,708x+35\,202$
Anthracene	$0.05–10^2$	0.0067	1.9	0.9997	$y=25\,637x+23\,367$
Phenanthrene	$0.05–10^2$	0.0061	3.7	0.9992	$y=15\,989x+24\,015$
Fluoranthene	$0.1–10^2$	0.0081	4.2	0.9999	$y=12\,976x+8091.5$
m-terphenyl	$0.1–10^2$	0.0049	3.3	0.9999	$y=10\,106x+5246.1$
p-terphenyl	$1–10^2$	0.0096	5.8	0.988	$y=459.9x+14\,874$
Pyrene	$1–10^2$	0.125	8.9	0.9996	$y=93.4x+1066.6$

Table 2 illustrates the linearity, precision and detection limits of PAHs with the sol–gel fullerol fiber. The HS-SPME procedure showed wide linear range, 10^3 or over 10^3 for low-ring PAHs, 10^2 for *p*-terphenyl, pyrene. The correlation coefficients (r^2) were between 0.988 and 0.999. The precision of the method was determined by performing six consecutive fiber extractions from an aqueous solution with a concentration of 1 ng/ml under the optimal conditions. At 60 °C, the reproducibility is expressed as the RSD of the fiber. The RSD obtained using the sol–gel fullerol fiber ranged from 1.9 to 8.9%. In general, the higher RSD values were determined for compounds having higher molecular masses resulting from the low water solubility and long equilibrium times of these compounds. The LODs of PAHs ranged from 0.0049 to 0.125 ng/ml ($S/N=3$).

The fiber was also applied to analyze PAHs in waste water sample. A 12-ml volume of water sample and 3.0 g NaCl were used. The SPME–GC–FID chromatogram of the sample is shown in Fig. 8. There are 2.62 μg/l biphenyl, 0.57 μg/l anthracene

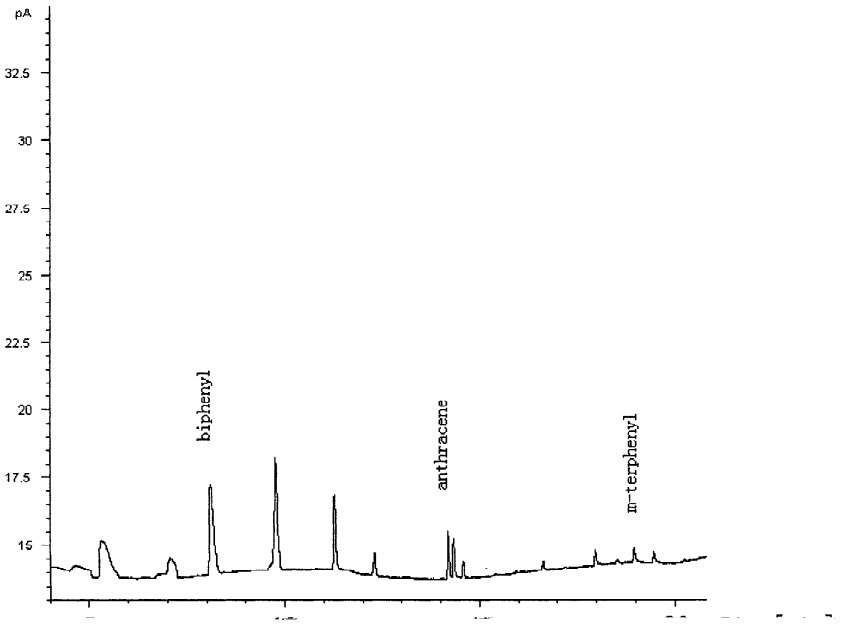


Fig. 8. SPME–GC analysis of PAHs in waste water using the sol–gel fullerol fiber and GC–FID system. SPME and GC conditions as in Fig. 7.

perature and solvent resistance, firmness, and long durability are the main advantages of this fiber. It shows excellent extraction characteristics for both less volatile organic compounds and polar substances, especially for planar molecules.

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