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Preparation of stir bars for sorptive extraction using sol–gel technology

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Abstract

A sol–gel coating method for the preparation of extractive phase on bars used in sorptive microextraction is described. The extraction phase of poly(dimethylsiloxane) is partially crosslinked with the sol–gel network, and the most part is physically incorporated in the network. Three aging steps at different temperatures are applied to complete the crosslinking process. Thirty-micrometer-thick coating layer is obtained by one coating process. The improved coating shows good thermal stability up to 300 °C. Spiked aqueous samples containing *n*-alkanes, polycyclic aromatic hydrocarbons and organophosphorus pesticides were analyzed by using the sorptive bars and GC. The results demonstrate that it is suitable for both aploar and polar analytes. The detection limit for chrysene is 7.44 ng/L, 0.74 ng/L for C_{19} and 0.9 ng/L for phorate. The extraction equilibration can be reached in less than 15 min by supersonic extraction with the bars of 30 μm coating layer.
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Keywords: Sol–gel; Stir bar sorptive extraction; Supersonic sorptive extraction; Extraction methods; Alkanes; Polynuclear aromatic hydrocrabons; Pesticides; Organophosphorus compounds

1. Introduction

Sorptive extraction (SE) provides a simple, effective, and solvent-free sample preparation technique for selective adsorption and enrichment of target compounds in sample matrix [1,2]. Many modes of SE have been developed to date, such as fiber-SE [3–6], in-tube SE [7–10] and stir bar sorptive extraction (SBSE) [11–15], that have been applied to a great variety of matrices: gas [3,4], liquid [5–7] and solid [16–19], and extended to a wide range of analytes from volatile to nonvolatile compounds [3–9,16–19]. Because the recovery of an analyte from the sample is determined by the partitioning coefficient and the phase ratio between the extraction phase and the aqueous sample, low recoveries are obtained for compounds with low coefficients, which is improved by SBSE technique using stir bars of 10 mm and 40 mm length coated with 50–200 μL of poly(dimethyl siloxane) (PDMS) [11–15]. The phase ratio of SBSE is about 100–400 times lower than that in other modes of solid phase microextraction, resulting in much higher recoveries, especially for volatile compounds with higher octanol–water partition coefficients ($K_{o/w}$) [12].

In SE, the coating technology of extraction phase is vitally important to the performance of the device. To date, static coating technology [20,21] and sol–gel coating technology [22,23] are commonly used in SE. Compared to static coating technology, sol–gel technology may be much more suitable for the preparation of thick film. Because of strong adhesion between the coating and the surface of bare fused silica or glass by chemical bonding, the phase exhibits low bleeding, good repeatability and long lifetime in SE [24,25].

In conventional SBSE, a slice of special PDMS tubing, which covers on a glass tube with a magnetic core, has been used as the extraction phase. To date there is no satisfaction method for the preparation of SBSE coating directly on the glass bar.

In this paper, an improved sol–gel method for the preparation of coating on the bars was investigated and two modes of extraction were examined. One mode is SBSE and the other is supersonication sorptive extraction (SSE).

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2. Experimental

2.1. Equipment

A Trace GC 2000 capillary GC system (ThermoQuest CE Instruments, USA) equipped with a capillary split/splitless injector and flame ionization detection (FID) system was used to analyze *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs). The analysis of organophosphorus pesticides (OPPs) was performed on a CP 3800 GC system (Varian, USA) system equipped with thermal specified detector. A home-made thermal desorption system (TDS), consists of a quartz liner and heaters, two gas flow controllers, temperature control units, and a sample transfer line. A 90 mm long stainless steel cylinder of 6.7 mm i.d. and 12 mm o.d. is used to hold the desorption liner and the transfer line. One of the gas flow controllers provides purge gas for the desorption from the top of the liner, and another flow controller provides sweep gas from the bottom of the liner to avoid diffusion and adsorption of the sample outside the quartz liner. The transfer line was inserted directly through the injector septum into the GC pre-column about 20 cm deep.

A JEM-1200EX scanning electron microscope (JEOL, Japan) was used to examine the sol–gel PDMS coatings (including the surface and thickness of the sol–gel coating). A SK-1 quick blend machine (Zhengji Machine Co., Jiangsu, China) was used for thorough mixing of various ingredients in the sol solution. SB3200 ultrasonic bath (Shanghai Branson, China) was used in SSE. The bared glass bar (30 mm × 1.8 mm o.d.) used for the preparation of sorptive stir bar contains an iron bar inside the glass tube, and the one used for supersonic sorptive bar contains no iron bar. The water used in this experiment was Wahaha purified water (Wahaha, Hangzhou, China).

2.2. Reagents

Hydroxy-terminated PDMS was obtained from Keguang New Material Co. (Nantong, Jiangsu Province, China). Methyltrimethoxane (MTMS) was purchased from Danyang Organic Silane Co. (Jiangsu Province, China). Poly(methylhydrosiloxane) (PMHS) was obtained from the Chemical Plant of Wuhan University (Wuhan, China). Trifluoroacetic acid (TFA) was purchased from Shanghai Chemical Plant (Chinese Medicine Group, China). HPLC-grade methylene chloride was purchased from Tedia (USA). Chromatography grade *n*-alkanes (C_{12-19}) were from National Research Center for CRMs (Beijing, China). The PAH mixture and OPPs were purchased from J&K Acros Organics (Beijing, China).

2.3. Preparation of sorptive bars

2.3.1. Pretreatment of bars

The bars were sequentially cleaned by water and methylene chloride, followed by 1 mol/L NaOH and 0.1 mol/L HCl for 8–12 h, respectively. After being washed by water, the bars were purged with N_2 at 120 °C in a 40 mm × 10 mm i.d. stainless steel tube.

2.3.2. Preparation of sol solution

The sol solution was prepared as follows: 200 mg of hydroxy-terminated PDMS was thoroughly dissolved in 300 μL methylene chloride; then 50 μL MTMS and 50 mg PMHS were added. The mixture was vortexed thoroughly by quick blend machine. After this, 50 μL TFA (containing 5% water) was added, and vortexed quickly until the mixture was a clear solution which was used for bar coating. The bars were immersed into the solution for a given time that controlled the thickness of coating. For coatings over 30 μm, the above coating procedure should be repeated with fresh sol. The coated bars were then placed into a vacuum desiccator for 8 h for coating gelation.

2.3.3. Conditioning of the bars

The sol–gel PDMS coated bars were conditioned in the stainless steel tube described in Section 2.3.1 under N_2 purge. The tube was put into a GC oven, and was heated under temperature programming. The oven temperature is from 40 °C to 120 °C at 1 °C/min, held for 180 min, then to 240 °C at the same ramp and held for 180 min, and finally to 300 °C at 1 °C/min and held for 240 min. The bars were then extracted by boiling methylene chloride for 4 h. Before being used for extraction, the bars were purged under a N_2 stream at 300 °C for 2 h.

2.4. Extraction mode

Stirring extraction and supersonic extraction modes were studied. For SBSE the stir bar was in a 50 mL sample vial at room temperature. For SSE the sorptive bar was in 50 mL sample vial, which was put into an ultrasonic bath.

2.5. Thermal desorption of extracted analytes in thermal desorption systems

Thermal desorption of the extracted analytes from the sol–gel bars was performed in the laboratory-made desorption unit. Brief drying of the bars with tissue paper before desorption is recommended. Desorption temperature was 260 °C and 280 °C, respectively, for *n*-alkanes and PAHs. The set temperature of desorption unit was reached in 2 min and held for 5 min for complete desorption. The thermally desorbed analytes were focused at the head of the analytical column, which was kept at 40 °C during the thermal desorption process.

2.6. Preparation of aqueous standards

A 10-μL portion of the stock solutions of all PAHs was diluted with methanol in a 10-mL volumetric flask at room

Table 1
Contents of PAHs stock solution and diluted methanol solution

Component	Content of stock solution (μg/mL)	Content of diluted methanol solution (ng/mL)	Content of spiked water sample solution (pg/mL)
Acenaphthene	994.0	994.0	994.0
Acenaphthylene	2001.0	2001.0	2001.0
Anthracene	100.0	100.0	100.0
Benz[*a*]anthracene	99.5	99.5	99.5
Benzo[*a*]pyrene	99.8	99.8	99.8
Benzo[*b*]fluoranthene	201.0	201.0	201.0
Benzo[*ghi*]perylene	197.2	197.2	197.2
Benzo[*k*]fluroanthene	101.0	101.0	101.0
Chrysene	100.2	100.2	100.2
Dibenz[*a,h*]anthracene	197.2	197.2	197.2
Fluoranthene	197.0	197.0	197.0
Fluorene	201.2	201.2	201.2
Indeno[1,2,3-*cd*]pyrene	100.0	100.0	100.0
Naphthalene	1001.0	1001.0	1001.0
Phenanthrene	100.0	100.0	100.0
Pyrene	100.4	100.4	100.4

temperature. The content of the stock solution and diluted methanol solution was showed in Table 1. A 50 μL portion of the diluted solution was diluted further with 50 mL purified water. Stock solution of *n*-alkanes was prepared by dissolving 2.00 mg of each compound in a 100-mL volumetric flask methanol at room temperature to give a 20 μg/mL solution. A 1-μL portion of which was dissolved in 50 mL purified water to give 400 pg/mL *n*-alkanes sample. A 1-mL portion of 10 μg/mL OPPs was diluted to 1 μg/mL by methanol, which was then diluted further to 200 pg/L spiked water sample.

2.7. Chromatographic conditions

2.7.1. Conditions for the analysis of n-alkanes and PAHs

A 5 m × 0.53 mm i.d. deactivated capillary column was connected to a 30 m× 0.53 mm i.d. 0.6 μm SE-54 analytical column by a press fit connector. The temperatures of injector and detector were all 300 °C for *n*-alkanes analysis, and were 260 °C and 300 °C, respectively, for PAHs analysis. Hydrogen was used as the carrier gas at a linear velocity of 30 cm/s. The injector was maintained in the splitless mode. Column temperature is as follows: for analysis of *n*-alkanes, 30 °C for 5 min, then to 280°C at a rate of 15 °C/min; For PAHs analysis, 40 °C for 5 min, program to 120 °C at a rate of 30 °C/min, then to 150 °C at a rate of 15 °C/min, and finally to 280 °C at a rate of 8 °C/min. The column temperature for the bar test is the same as that of *n*-alkanes.

2.7.2. Conditions for the analysis of OPPs

A 5 m × 0.53 mm i.d. deactivated capillary column was connected to a 30 m × 0.25 mm i.d. 0.25 μm SE-54 analytical column by a press fit connector. The temperatures of injector and detector were 260 °C and 300 °C, respectively. Nitrogen was used as the carrier gas at a linear velocity of 13.6 cm/s. The injector was maintained at splitless mode. Column temperature ramp is as follows: 40 °C for 5 min, then to 110 °C at a rate of 30 °C/min, and finally to 260 °C at a rate of 10 °C and held for 20 min.

3. Results and discussion

Because the coating layer of sorptive stir bar/supersonic sorptive bar is rather thick, it is very important to have a stable and long lasting stationary phase having a low bleeding at high temperature. Conventional coating technologies used in the preparation of fiber SPME, in-tube SPME, and GC columns are not fit for sorptive stir bar/supersonic sorptive bar.

Sol–gel approach to column technology for analytical microseparations is highlighted in recent years. This technology can be applied to a wide range of microseparation and sample preparation techniques including capillary gas chromatography, solid phase microextraction, capillary electrophoresis, and capillary electrochromatography.

The main obstacle in the creation of film by sol–gel method is cracking. The use of alkyl or aryl derivatives of tetraalkoxysilanes as precursors and drying control chemical additives (DCCAs) can release the capillary stress generated during drying of the coated surface.

3.1. The sol–gel chemistry involved in the creation of coating layer

The sol–gel process starts with the hydrolysis of the sol–gel precursor, followed by polycondensation of hydrolyzed products into a sol–gel network. At the same time the hydroxyterminated PDMS is partially bonded to the network because of the large molecular size ($M_W \geq$ 40,000), which prohibits complete bonding of OH-PDMS. The sol–gel polymer is bonded to the silanol groups on the

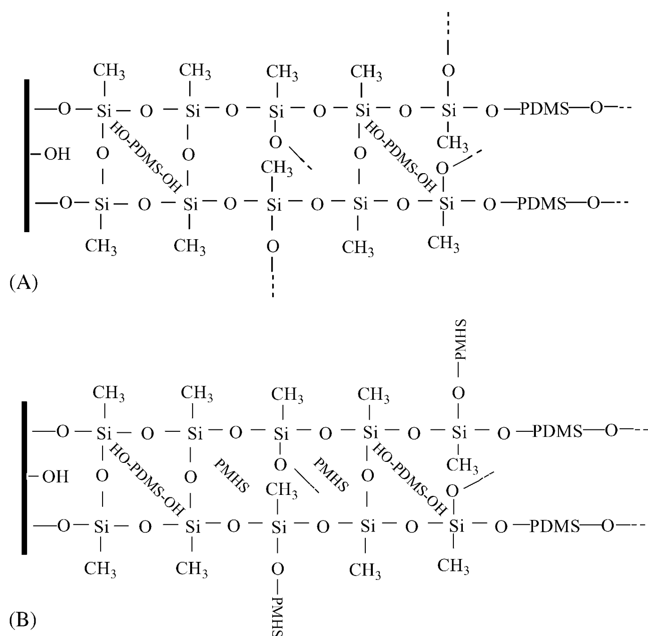

Fig. 1. (A) Physical incorporation of hydroxy-teminated PDMS into the sol–gel network. (B) Deactivation of sol–gel network with PMHS and its incorporation into the sol–gel network.

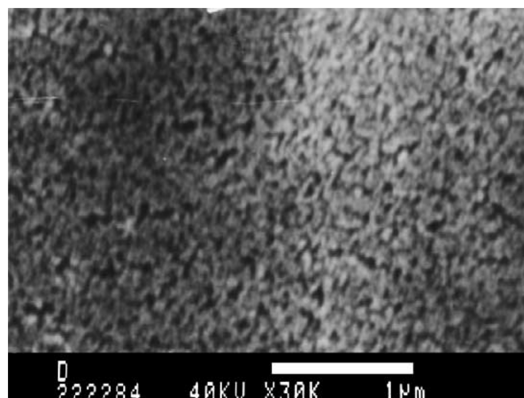

Fig. 2. The scanning electron microscopy image of the surface structures of a sol–gel PDMS coating on the wall of glass bar. Magnification 30,000×.

glass surface of bars. The major part of OH-PDMS is physically incorporated and entangled with sol–gel network, as depicted in Fig. 1A. The mechanism of the coating process, therefore, is not the same as reported before [21,22,27]. In order to increase the surface area and expose most of the surface silanol groups, the bars are treated with 1 M NaOH and 0.1 M HCl [29]. The precursor in this sol–gel process is much less than that of reported previously [22,26,28], in which a compact sol–gel is created and vortexed thoroughly before adding catalyst TFA, resulting molecular level mixing. A loose sol–gel network is formed because of the incorporation of more OH-PDMS after adding TFA. The pore diameters are relatively large and the degree of cracking is much less during the drying process.

The role of PMHS is deactivation of surface and network. The active hydrogen atoms react with silanol groups at elevated temperatures to end-cap remaining silanol groups. Post-thermal conditioning of coating layer leads to

Table 2
Peak height repeatability data for analytes and their detection limits

Analytes	Peak height repeatability ($n = 5$)		Detection limit, S/N = 3 (pg/mL)
	Mean peak height	RSD (%)	
C_{12}	1.43	0.78	20.0
C_{13}	7.01	1.89	11.04
C_{14}	15.34	2.64	2.00
C_{15}	27.89	3.83	1.11
C_{16}	32.22	4.71	0.92
C_{17}	38.62	5.48	0.78
C_{18}	40.21	5.91	0.75
C_{19}	40.58	6.10	0.74
Acenaphthene	31.08	4.85	0.48
Acenaphthylene	20.15	1.26	0.83
Anthracene	3.87	2.33	0.37
Benz[*a*]anthracene	1.10	3.90	0.18
Benzo[*a*]pyrene	7.11	8.37	0.28
Benzo[*b*]fluoranthene	13.32	6.32	2.76
Benzo[*ghi*]perylene	1.59	10.32	0.45
Benzo[*k*]fluroanthene	6.17	5.43	0.25
Chrysene	10.07	2.18	0.19
Dibenz[*a*,*h*]anthracene	1.12	11.85	0.35
Fluoranthene	19.20	4.36	0.20
Fluorene	9.52	4.83	0.39
Indeno[1,2,3-*cd*]pyrene	2.85	9.67	0.24
Naphthalene	9.12	1.13	1.99
Phenanthrene	7.13	3.95	0.29
Pyrene	9.32	7.69	0.19

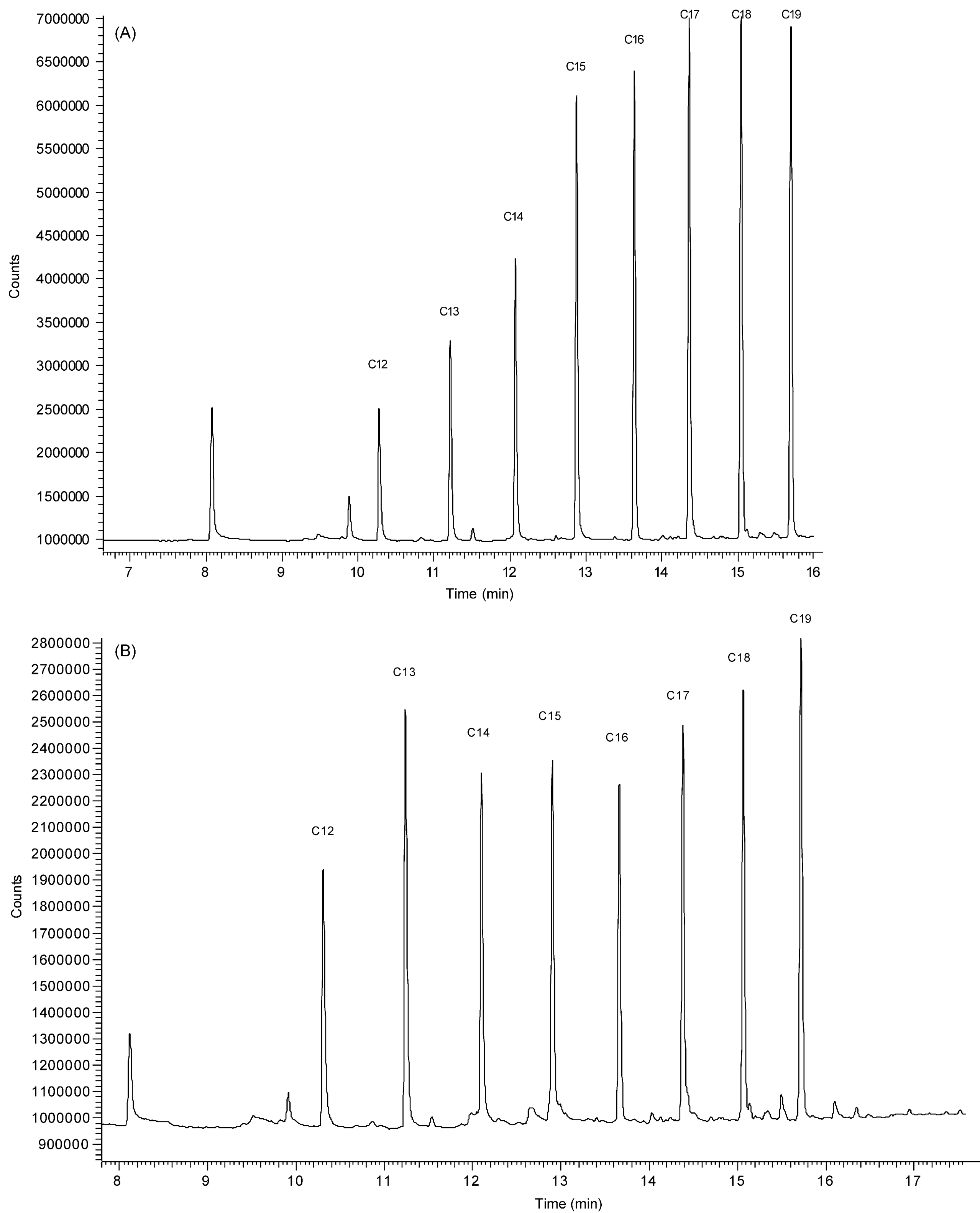

Fig. 3. Chromatograms of spiked *n*-alkanes aqueous sample. (A) SSE–cGC–FID; (B) SBSE–cGC–FID. Conditions see text. The concentrations of all analytes were 400 ng/L.

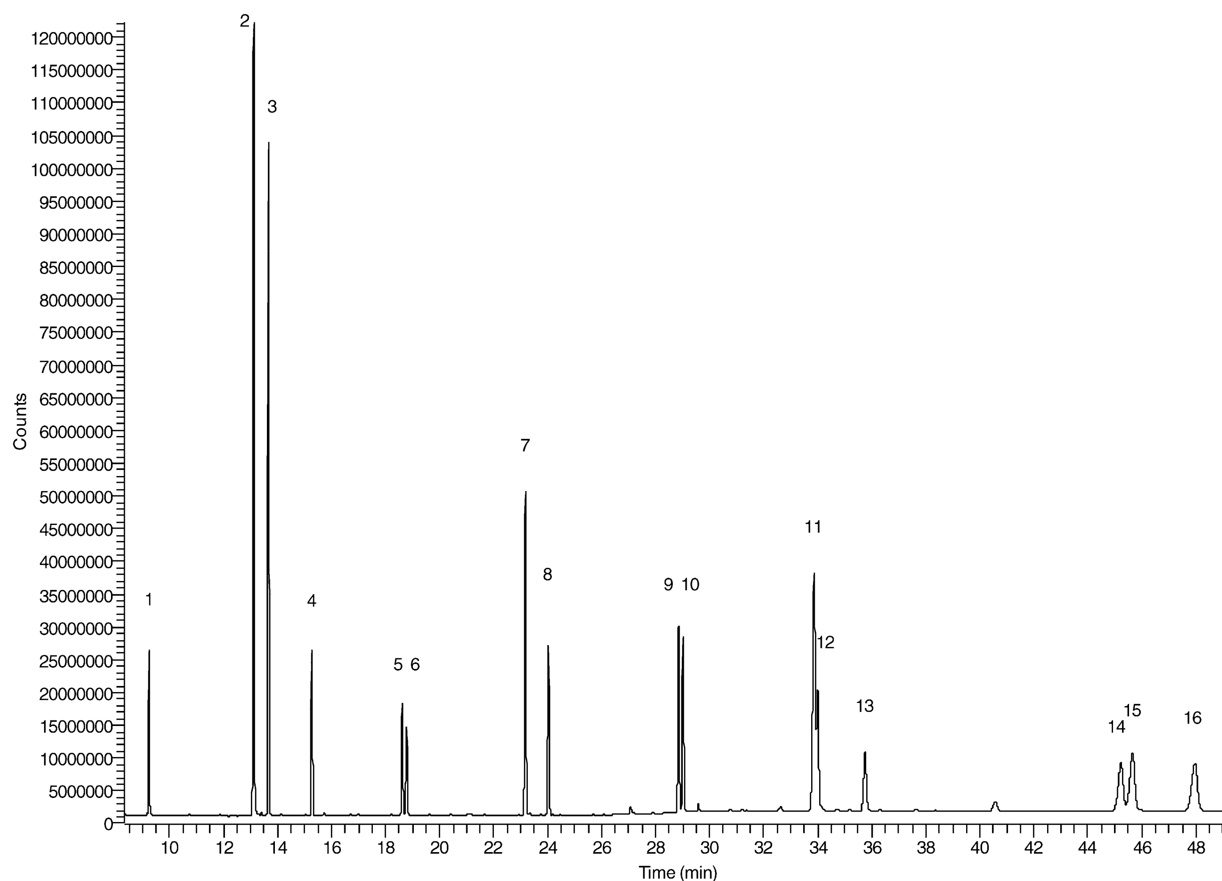

Fig. 4. Chromatogram of PAHs from the extraction of sorptive bar. Conditions: column conditions as in Fig. 3; injector: 260 °C; detector: 300 °C; column temperature: 40 °C for 5 min, programmed to 120 °C at a rate of 30 °C/min, then to 150 °C at 15 °C/min, and finally to 280 °C at 8 °C/min. Peak identities: 1, naphthalene; 2, acenaphthylene; 3, acenaphthene; 4, fluorene; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene; 9, benzo[*a*]pyrene; 10, chrysene; 11, benzo[*b*]fluoranthene; 12, benzo[*k*]fluroanthene; 13, benz[*a*]anthracene; 14, indeno[1,2,3-*cd*]pyrene; 15, dibenz[*a,h*]anthracene; 16, benzo[*ghi*]perylene. The concentrations of the analytes were shown in Table 1.

deactivation of the bars. In the sol–gel network PMHS has very similar chemical structure to that of PDMS, its incorporation in the coating structure as shown in Fig. 1B has a little effect on the characteristics of PDMS. The methyl group in the precursor of MTMS also plays the similar role as PMHS after polycondensation of hydrolysis [22].

Appropriate amounts of PMHS and OH-terminated PDMS in the solid phase improve the selectivity for polar compounds.

Because of the thick coating layer on sorptive bars, rather high temperature for thermal desorption has to be applied especially for apolar analytes. To achieve high thermal stability, the post-coating thermal conditioning is optimized to guarantee sufficient conditioning and avoid cracking of the coating layer. Three temperature ramps at a rate of 1 °C/min and maintaining at 120 °C, 240 °C, 300 °C for several hours was finally adopted.

Fig. 2 shows the coating layer structure by scanning electron microscopy (SEM). It shows that the sol–gel coating layer possesses porous structure, which enhances the surface area for solute–solid phase interactions and the extraction rate. The cross-section SEM image of the coated bar shows that the sol–gel PDMS coating layer is about 30 μm in thickness, and is very uniform.

The thermal stability of the coating of the bars was examined by thermal desorption in the TDS unit at 300 °C for

Table 3
The peak height repeatability of two extraction modes

Extraction mode	RSD (%) ($n = 5$)							
	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}
Supersonic extraction for 10 min	0.78	1.89	2.64	3.83	4.71	5.48	5.91	6.10
Stir bar sorptive extraction for 90 min	4.42	3.19	1.65	1.66	1.34	1.59	2.08	2.55

Table 4
The precision and detection limits of OPPs by SBSE–GC–TSD

Analyze	Peak area repeatability (n = 5)		Detection limit, S/N = 3 (pg/mL)
	Mean peak area	RSD (%)	
Methamidophos	5906.6	11.27	8.0
Dichlorvos	3413.3	9.85	6.4
Acephate	4171.0	4.58	7.6
Monocrotophos	18352.7	3.63	3.1
Phorate	45328.0	4.17	0.9
Parathionmethyl	11508.6	5.43	3.5
Malathion	22983.6	11.06	1.7
Fenitrothion	24236.3	12.20	2.1
Fenthion[a]	145311.0	8.49	0.3
Chlorpyrifos[a]			
Parathion[a]			
Methidathion	3360.0	6.37	6.1
Triazophos	42271.7	3.71	1.2
Ethaion	16013.3	11.35	2.8

[a] These three peaks overlapped.

5 min, followed by a capillary (cGC) run and FID. No ghost peak was observed in the chromatogram (chromatogram not shown).

3.2. Extraction modes

In our work, two modes of extraction were applied: SBSE and SSE. In supersonic extraction mode, the intensive supersonic vibration destroys the boundary layer between extraction phase and sample matrix. The control step of extraction rate, therefore, becomes the mass transfer rate from the surface to the body of the extraction phase. The lower the diffusion coefficient, or the thicker the extraction phase, the longer the extraction time will be.

Table 2 shows the results of run-to-run repeatability in peak height, retention time and the detection limits by using sol–gel sorptive stir bar and supersonic sorptive bar. The detection limit of *n*-alkanes is 0.74 ng/L for $n\mathrm{C}_{19}$, and of PAHs 0.19 ng/L for chrysene.

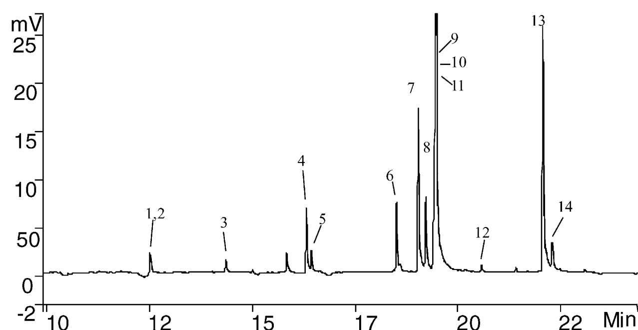

Fig. 5. Chromatogram of organophosphorus pesticides by SBSE–cGC–TSD. Conditions see text. Peak identities: 1, methamidophos; 2, dichlorvos; 3, acephate; 4, momocrotophos; 5, phorate; 6, parathion-methyl; 7, malathion; 8, fenitrothion; 9, fenthion; 10, chlorpyrifos; 11, parathion; 12, methidathion; 13, triazophos; 14, ethaion; concentration of each analyze was at 200 pg/mL.

Fig. 3A and B shows the GC chromatogram of *n*-alkanes by the extraction of sol–gel coated sorptive stir bar and supersonic sorptive bar. The extraction time for the stir bar and the sorptive bar is 90 min and 10 min, respectively. It can be seen from the two figures that peak heights in SSE mode are higher than those in SBSE, implying that the extraction efficiency of supersonic extraction is higher than that of stir bar sorptive extraction. The boundary layer in SBSE limited the mass transfer rates of the analytes with relative large molecular weight. Table 3 compares the repeatability data of peak heights by the two extraction modes, proving that both extraction modes give satisfaction results. The carryover of the extraction bar was also examined by second TDS of the same bar followed by chromatographic analysis. We found no peaks in the chromatogram (chromatogram not shown), demonstrating complete desorption of analytes.

Fig. 4 represents the GC chromatogram of PAHs by the extraction of sol–gel coated sorptive stir bar for 120 min. Supersonic sorptive extraction was also tested, and the same phenomena as those of *n*-alkanes are also observed. It proved that for the stable compounds being tested, supersonic extraction mode is prior to SBSE. No carryover problem is found at the desorption temperature of 280 °C for compounds tested.

Polar analytes were also tested in our study. The OPPs spiked water sample was extracted by stir bar for 120 min, followed by TDS-cGC analysis. The chromatogram of OPPs was shown in Fig. 5, and results were shown in Table 4. The detection limit of OPPs are in the pg/mL range, and is 0.9 pg/mL for phorate.

4. Conclusion

A sol–gel method is investigated for the preparation of extraction phase on bars used in SBSE and SSE. The extraction solid phase (hydroxy-terminated PDMS) not only

crosslinked with the sol–gel network created by the hydrolysis products of the sol–gel precursor but entangled within it. The aging process for the thick coating was also developed to avoid cracking of the film. Supersonic extraction mode was investigated and compared to SBSE mode, showing that the former has much higher mass transfer rate and shorter equilibration time, and higher extraction efficiency.

References

[1] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1987) 2145.
[2] H. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153.
[3] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller, Anal. Chem. 68 (1996) 144.
[4] R.J. Bartelt, Anal. Chem. 69 (1997) 364.
[5] K. Jinno, M. Kawazoe, Chromatographia 52 (2000) 309.
[6] C. Rivasseau, G. Vanhoenacker, P. Sandra, M.C. Hennion, J. Microcol. Sep. 12 (2000) 323.
[7] L. Nardi, Am. Lab. 34 (2002) 30.
[8] Y. Saito, M. Kawazoe, M. Hayashida, K. Jinno, Analyst 125 (2000) 807.
[9] Y. Gou, R. Eisert, J. Pawliszyn, J. Chromatogr. A 873 (2000) 137.
[10] H.W. Wang, W.M. Liu, Y.F. Guan, LC:GC North Am. 22 (2004) 16.
[11] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcol. Sep. 11 (1999) 737.
[12] D. Frank, B. Tienpont, P. Sandra, LC:GC North Am. 21 (2003) 1.
[13] J. Vercauteren, C. Peres, C. Devos, P. Sandra, F. Vanhaecke, L. Moens, Anal. Chem. 73 (2001) 1509.
[14] P. Popp, C. Bauer, L. Wennrich, Anal. Chim. Acta 436 (2001) 1.
[15] G.J. Andreas, H.H.L. Lauer, T. Heideman, P. Sandra, J. High Resolut. Chromatogr. 23 (2000) 644.
[16] J.J. Jimenez, F.J. Lopez, O. Cepria, F. Hernandez, J. Chromatogr. A 829 (1998) 269.
[17] M. Moder, P. Popp, R. Eisert, J. Pawliszyn, Fresenius J. Anal. Chem. 363 (1999) 680.
[18] A.A. Boyd-Boland, J. Pawliszyn, Analyst 121 (1996) 929.
[19] R. Hu, B. Hennion, L. Urruty, M. Montury, Food Addit. Contam. 16 (1999) 111.
[20] C. Haberhauer-Troyer, M. Crnoja, E. Rosenberg, Fresenius J. Anal. Chem. 366 (2000) 329.
[21] B.W. Wright, P.A. Peaden, M.L. Lee, T.J. Stark, J. Chromatogr. 248 (1982) 17.
[22] S. Chong, A. Malik, Anal. Chem. 69 (1997) 3889.
[23] T.P. Gbatu, Anal. Chim. Acta 402 (1999) 67.
[24] S.A. Rodriguez, L.A. Colon, Anal. Chim. Acta 397 (1999) 207.
[25] A.M. Siouffi, J. Chromatogr. A 1000 (2003) 801.
[26] Z.R. Zeng, W.L. Qiu, Z.F. Huang, Anal. Chem. 73 (2001) 2429.
[27] C. Shende, A. Kabir, E. Townsend, A. Malik, Anal. Chem. 75 (2003) 3518.
[28] A. Malik, Electrophoresis 23 (2002) 3973.
[29] Y. Guo, L.A. Colon, Anal. Chem. 67 (1995) 2511.