Preparation and Characteristics of New Coating for Solid-Phase Microextraction

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Abstract: Poly (methylphenylvinylsiloxane) (PMPVS) coating for solid-phase microextraction (SPME) was first prepared by using sol-gel approach and cross-linking of free radical initiation. The extraction properties of the novel coating for aromatic compounds were investigated using a self-made SPME device coupled with a gas chromatograph-flame ionization detector (GC-FID). The coating provided high surface areas and allowed high extraction efficiency. Compared with some commercial SPME stationary phases, the new phase showed better selectivity and sensitivity toward aromatic compounds. Furthermore, PMPVS coating showed good thermal stability and longer lifetime.

Key words: solid-phase microextraction; sol-gel process; poly(methylphenylvinylsiloxane); solid phase coating
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固相微萃取新型涂层的制备和特性

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摘要: 以聚甲基苯基乙烯基硅氧烷为主要成分,采用溶胶-凝胶技术和自由基引发交联反应的方法首次制备了一种固相微萃取新涂层,并与气相色谱联用,分析了芳香族化合物,考察了它的萃取性能。结果表明:该涂层提供了大的比表面积,可获得高的萃取效率。与相应的商用固相微萃取涂层相比,该涂层具有更好的灵敏度和选择性,且热稳定性好,使用寿命长。

关键词: 固相微萃取; 溶胶-凝胶法; 聚甲基苯基乙烯基硅氧烷; 固相涂层

Devised by Pawliszyn and his co-workers in late 1989[1], solid-phase microextraction (SPME) has become an increasingly popular sampling method for a variety of compounds and attracted more and more attention from researchers in chromatography. In SPME, the fiber coating is the most important factor that determines sensitivity and selectivity. However, conventionally coated SPME fibers have some considerable drawbacks, such as low operational stability, only a few varieties and short service life. New improvements were made with the appearance of new coatings that allowed an increase in the specificity of this extraction technique.

Commercially available poly (dimethylsiloxane) (PDMS) fiber is a non-polar phase that extracts non-polar analytes very well. One of the main difficulties limiting the wide application of SPME-gas chromatography (GC) is the absence of proper chemical bonding of the stationary phase coating with the silica surface, which is responsible for the low thermal stability of 100 μm and 30 μm PDMS fibers on which PDMS coatings are non-bonded phases[2]. As a result, they have relatively low recommended operating temperatures generally within the range of 200 ℃ – 270 ℃[3]. Its lifetime is about 40 – 100 times only. Sol-gel coating technique can overcome this problem by providing efficient incorporation of organic components into inorganic polymeric structure in solution under extraordinarily mild thermal conditions[3,4]. As we have recently demonstrated, the sol-gel approach can be effectively used to create surface-bonded coatings on the outer surface of SPME fiber[5,6]. Compared with conventional approach, sol-gel chemistry in the development of SPME fiber coatings has many

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advantages：(a) it effectively combines fiber surface treatment, deactivation, coating and stationary phase immobilization into a single step and provides a versatile way of designing organic-inorganic hybrid coatings with desirable extraction properties; (b) it creates chemical binding between the solid phase coating and the substrate surface, which is an important factor to facilitate stable performance of the coating under more crucial operating conditions involving temperature and solvents, thus expands the SPME-GC application range toward higher-boiling compounds and makes the coating fiber lasting longer; (c) the coating porosity provided by the sol-gel method enhances higher surface area and allows the use of thinner coatings to achieve acceptable stationary-phase loadings, sample capacities and fast mass transfer characteristics.

The commercial poly (methylphenylvinylsiloxane) (PMPVS) has been widely used for the stationary phase of a GC column. Our interests are to use PMPVS as fiber coating for SPME. It should show better extraction efficiency for aromatic compounds.

In this paper, we describe the preparation of fibers with PMPVS/OH-TSO coatings for SPME applications using sol-gel technique and cross-linking. Its extraction properties for aromatic compounds were evaluated and the comparison with commercial SPME stationary phases was also investigated.

1 Experimental

1.1 Reagents and apparatus

PMPVS and trifluoroacetic acid (TFA) were purchased from Shanghai Chemical Plant. OH-terminated silicone oil (OH-TSO) was purchased from Chengdu Center for Applied Research of Silicone. Vinyltriethoxylsilane (VTEOS), tetraethoxysilane (TEOS) and poly (methylhydrosiloxane) (PMHS) were obtained from the Chemical Plant of Wuhan University. All solvents used in this study were of analytical reagent grade. The fused-silica fiber (140 μm o.d.) was obtained from Academy of Post and Telecommunication, Wuhan.

An SC-7 GC gas chromatograph equipped with a split injector and flame ionization detector (FID) (Sichuan, China) was used throughout. On-line data collection and processing was done on a Chromatopac Model SC1100 (Kangzhi, Beijing). A self-made SPME syringe was used to transfer the extracted sample into the GC injector for analysis. The fiber coated with PMPVS/OH-TSO was inserted into the needle of a modified syringe and attached to the plunger. The commercial SPME holders for manual use and three kinds of different fibers: poly(dimethyl siloxane) (PDMS, 100 μm), polyacrylate (PA, 85 μm) and carbowax/divinylbenzene (CW/DVB, 65 μm) fibers for comparison were obtained from Supelco (Bellefonte, PA, USA).

1.2 Preparation of the fiber

Forty milligrams of PMPVS, 90 mg of OH-TSO, 100 μL of TEOS, 50 μL of VTEOS, 10 mg of PMHS and 8 mg of benzophenone were dissolved in 400 μL of methylene chloride. A 120 μL volume of TFA containing 5% (*V*/*V*) water was added to the resulting solution with ultrasonic agitation for 5 min. The mixture was centrifuged at 12 000 r/min for 5 min. The top clear sol solution was collected for the fiber coating. A sol-gel coating formed on the bare outer surface of the fiber end (1 cm), after the fiber was dipped vertically into the sol-gel solution for 30 min. For each fiber, this coating process was repeated several times using a freshly prepared sol solution until the thickness of the coating required was obtained. The fiber was irradiated under ultraviolet light for 30 min, and then placed in a desiccator at room temperature for 12 h and then conditioned at 250 ℃ − 350 ℃ for 2 h under nitrogen in the GC injection port.

1.3 Headspace (HS) SPME procedure

To prevent the analytes from being adsorbed on the glass wall, the vials were acid washed and silanized prior to the experiments. For all analyses, a 20 μL portion of the standard solution and 10 mL of doubly distilled water and 3 g NaCl were added into a 16 mL vial. The vial was covered with a cap wrapped with membrane after a stirring bar was added. During magnetic stirring, the fiber was inserted into the headspace of the vial for an appropriate time period and then placed into the injector of a gas chromatograph for thermal desorption.

1.4 GC conditions

To analyze some BTX (benzene, toluene, *o*-xylene, and *p*-xylene), GC separation was conducted using a 2,3,6-*o*-tributyl-β-cyclodextrin (TB-CD) column (20 m×0.25 mm i.d.) with a 0.25 μm film

thickness[6]. The column temperature was maintained at 110 ℃; injector and detector port temperatures were, respectively, 150 ℃ and 200 ℃. Some PAHs (naphthalene, biphenyl, fluorene, phenanthrene) analysis was performed using a 23 m×0.25 mm i.d. calixarene column with a 0.25 μm film thickness[7]. Separation conditions employed for the compounds were: column temperature, 180 ℃; injector temperature, 300 ℃; detector temperature, 250 ℃. A polymeric fullerene-polysiloxane column (13 m×0.25 mm i.d.) with a 0.25 μm film thickness[8] was selected to separate some PEs (dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), diamyl phthalate (DAP). Separation conditions employed for the compounds were: column temperature, 210 ℃; injector temperature, 280 ℃; detector temperature, 250 ℃. Throughout the separation, nitrogen was used as the carrier gas at a linear velocity of 12 $cm \cdot s^{-1}$ – 15 $cm \cdot s^{-1}$ and the injection split ratio was 80∶1.

2 Results and discussion

The main sol-gel reactions involved in the coating procedure are (Ⅰ) catalytic hydrolysis of the alkoxide precursor, (Ⅱ) polycondensation of the hydrolyzed products into a three-dimensional sol-gel network, (Ⅲ) chemical bonding of the coating ingredient to the evolving sol-gel network, and (Ⅳ) chemical anchoring of the evolving sol-gel polymer to the outer surface of the fused-silica fiber[3].

Unlike the common sol-gel process, in which only one metal alkoxide is used as the precursor to produce silica fiber, two different silicon monomers as co-precursors are used in our process. A commonly employed precursor for a glass matrix, TEOS, was hydrolyzed in conjunction with a second monomeric unit that contains a vinyl substituent. We conveniently selected VTEOS as the co-precursor to impart an organic character to the silica glass. Exposing to the ultraviolet light, vinyl group in both VTEOS and PMPVS will react to form the cross-linking with benzophenone as the catalyst for solidification reaction. Thus, a surface-bonded polymeric coating (PMPVS/OH-TSO) forms as schematically illustrated in Fig.1.

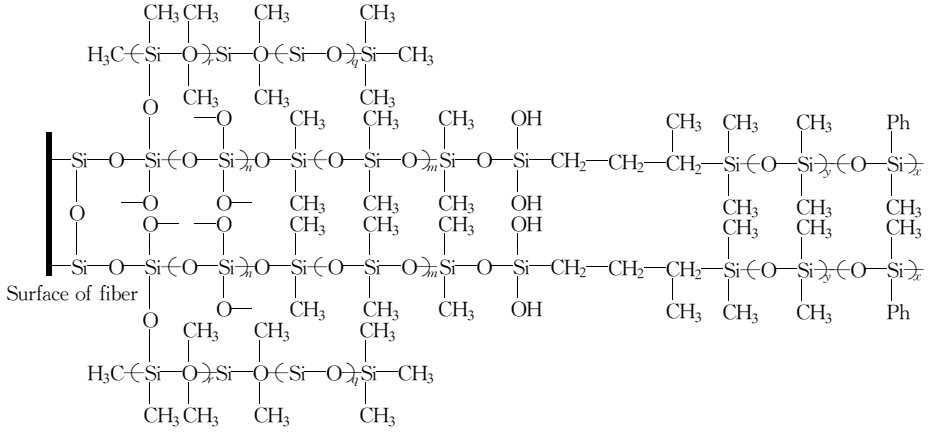

Fig.1 The structure of PMPVS/OH-TSO fiber coating

The IR spectra of the PMPVS, VTEOS and PMPVS/OH-TSO films were obtained. The characteristic absorption decline from C═C stretching (1 599.4 cm^{-1}) in PMPVS/OH-TSO shows that it had chemically bonded with other components.

OH-TSO was selected as one of the mixed coating ingredient 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[6]. In addition, an ultrasonic drying technique was applied in our work, which aimed at the solving of shrinkage and cracking problems in preparing coating of SPME fibers[3].

The PMPVS/OH-TSO fiber gave higher response to BTX (Fig.2) and PAHs (Fig.3) than the commercial PDMS and PA SPME fibers. It is because of the incorporation of phenyl groups into the polymer coating in which the polarizable phenyl groups in PMPVS/OH-TSO fiber can exhibit π-π interactions with BTX and PAHs, and 3-D network in the coating structure providing higher surface area and sample capacity. Furthermore, PMPVS/OH-

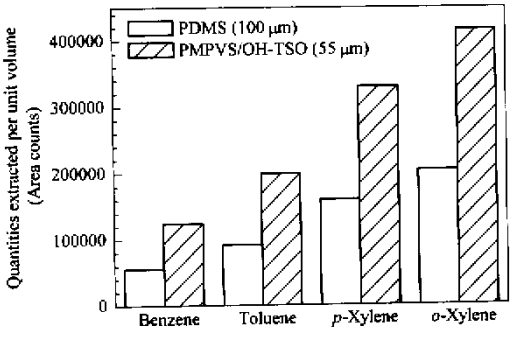

Fig. 2 Comparison of the quantities of BTX extracted by two different coatings

Concentration of each compound, 0.5 mg·L^{-1}; exposure time, 2 min; exposure temperature, 15 ℃; desorption temperature, 150 ℃; desorption time, 3 min.

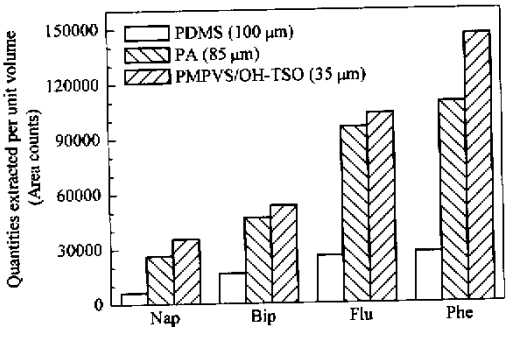

Fig. 3 Comparison of the quantities of PAHs extracted by three different coatings

Concentration of each compound, 0.1 mg·L^{-1}; exposure time, 60 min; exposure temperature, 60 ℃; desorption temperature, 300 ℃; desorption time, 8 min.

Nap: naphthalene; Bip: biphenyl; Flu: fluorene; Phe: phenanthrene.

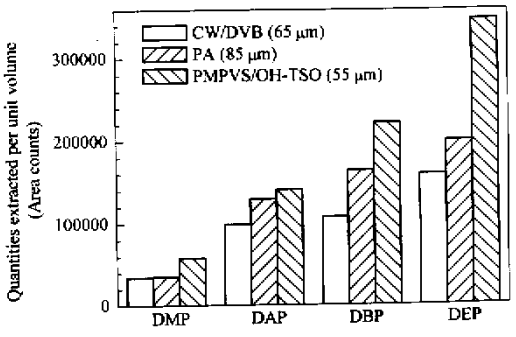

Fig. 4 Comparison of the quantities of phthalic acid diesters extracted by three different coatings

Concentration of each compound, 0.5 mg·L^{-1}; exposure time, 60 min; exposure temperature, 75 ℃.

DMP: dimethyl phthalate; DAP: diamyl phthalate; DBP: dibutyl phthalate; DEP: diethyl phthalate.

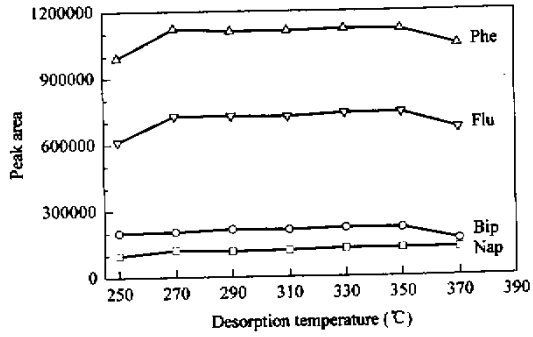

Fig. 5 The desorption temperature profile for 1 mg·L^{-1} PAHs

Conditions as in Fig. 3.

Nap: naphthalene; Bip: biphenyl; Flu: fluorene; Phe: phenanthrene.

TSO fiber also showed better selectivity than the commercial CW/DVB and PA SPME fibers toward more polar phthalic acid diesters (Fig. 4). These results demonstrate the selectivity of the coating (molecular/analyte recognition) can be modified by introduction of additional functional groups to the polymer.

In the SPME fiber technique, physically coated fibers cannot provide high operational stability for obvious reasons. Using the sol-gel approach and the cross-linking step, the operational stability of the SPME fiber can be enhanced[3,4,6]. Fig. 5 illustrates the thermal stability of PMPVS fibers. As can be seen from this figure, with the increase of injection temperature from 270 ℃ to 350 ℃, desorption quantities of the fiber coating to PAHs were not affected by the changing of exposure temperature during sample introduction. The performance of the fiber did not show any sign of bleeding even at this high injection temperature (350 ℃), whereas commercial PDMS fibers began to bleed at significantly lower temperatures (about 200 ℃). Such a high operating temperature of sol-gel fiber is due to strong adhesion of the coating to the substrate through chemical bonding.

Fig. 6 shows the change of extraction efficiency of sol-gel-derived PMPVS/OH-TSO fiber in extracting some PAHs from aqueous solution after being used for 1, 50, 100, and 150 times at 250 ℃ − 350 ℃. As can be seen in Fig. 6, the response has no obvious decline, and the PMPVS/OH-TSO coating is still stable and reusable after being used for 150 times.

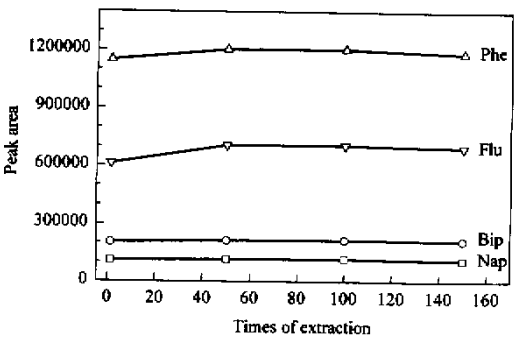

Fig. 6 Lifetime profile of PMPVS/OH-TSO fiber (35 μm)

Concentration of each compound, 1 mg·L^{-1}. Conditions as in Fig. 3.

Nap: naphthalene; Bip: biphenyl; Flu: fluorene; Phe: phenanthrene.

The extraction equilibrium for the BTX components was reached quite fast, approximately 60 s for benzene and toluene, 120 s for xylene (at 15 ℃). The desorption time required to desorb the analytes from the PMPVS/OH-TSO fiber was less than 40 s for all the BTX components at 150 ℃. The extraction and desorption processes is shorter because of the faster mass transfer of analytes in the gel structure.

The linearity of the method was tested with GC-FID by extracting aqueous standards, with increasing concentrations, in typical ranges of 0.5 μg·L^{-1} – 500 μg·L^{-1} for BTX, and 1 μg·L^{-1} – 1 000 μg·L^{-1} for PAHs. The HS-SPME procedure showed a good linear behavior in tested ranges with correlation coefficients better than 0.999 2. The precision of the method was determined by performing five consecutive fiber extractions from an aqueous solution with concentrations of 1 μg·L^{-1} for BTX and 10 μg·L^{-1} for PAHs under optimal conditions. The relative standard deviations (RSDs) obtained ranged from 1.5% to 7.7% for BTX and from 1.9% to 5.8% for PAHs. The limit of detection (LOD) is defined as the concentration of an analyte in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3. The LODs ranged from 0.01 μg·L^{-1} to 0.1 μg·L^{-1} for the BTX and from 0.05 μg·L^{-1} to 0.29 μg·L^{-1} for the PAHs.

3 Conclusions

In this study, the new SPME fiber coating with a mixture of PMPVS and OH-TSO has been successfully prepared by a sol-gel method and cross-linking of free radical initiation. Compared with some commercially available SPME fibers, the PMPVS/OH-TSO fiber has higher extraction efficiency for aromatic compounds, and also exhibits higher thermal stability (to 350 ℃) and longer service life (more than 150 times).

References:

[1] Berlardi R P, Pawliszyn J B. Water Pollut Res J Can, 1989, 24(1): 179

[2] Mills G A, Walker V. J Chromatogr A, 2000, 902(1): 267

[3] Chong S L, Wang D X, Hayes J D, *et al*. Anal Chem, 1997, 69(19): 3 889

[4] Wang Z Y, Xiao C H, Wu C Y, *et al*. J Chromatogr A. 2000, 893: 157

[5] Qiu W L, Zeng Z R, Peng Q, *et al*. Fenxi Kexue Xuebao (Journal of Analytical Science), 2001, 17(3): 198

[6] Zeng Z R, Qiu W L, Huang Z F. Anal Chem, 2001, 73: 2 429

[7] Zeng Z R, Guan N, Tang X H, *et al*. Analyst, 2000, 125: 843

[8] Zeng Z R, Ye H Y, Liu Y, *et al*. Chromatographia, 1999, 49: 293