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a Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China
b Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan 430072, P.R. China.

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SOL-GEL METHOD FOR THE PREPARATION OF SOLID-PHASE MICROEXTRACTION FIBERS

Key Words: Solid-phase microextraction, sol-gel method, gas chromatography, solid-phase coating.

Z.P. Zhou\textsuperscript{a}, Z.Y. Wang\textsuperscript{a}, C.Y. Wu\textsuperscript{a}, W. Zhan\textsuperscript{b}, Y. Xu\textsuperscript{b}

\textsuperscript{a}Department of Chemistry, Wuhan University, Wuhan 430072, P.R. China
\textsuperscript{b}Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan 430072, P.R. China.

ABSTRACT

A novel sol-gel method is applied for the preparation of solid-phase microextraction (SPME) fibers. Scanning electron microscopy experiments suggested a porous structure for the poly(dimethylsiloxane) (PDMS) coating. SPME-GC analysis provided evidence that the sol-gel fibers have some advantages, such as high thermal stability, efficient extraction rates, high velocities of mass transfer, and spacious range of application.
INTRODUCTION

Since its introduction by Pawliszyn and co-workers in 1989¹, solid-phase microextraction (SPME) has proliferated in the past few years². However, conventionally coated SPME fibers have some significant drawbacks, such as low operational stabilities (temperature, solvent, etc.), only a few varieties and short service lives. Therefore, future advancements in SPME technology depend greatly on developing new coating technologies for creating colorful SPME fibers of good selectivities, high stabilities, efficient extraction rates.

The sol-gel process is very well-adapted for thin-film fabrication by either spin-coating or dip-coating techniques³⁴. The sol-gel chemistry can efficiently incorporate organic components into inorganic polymeric structures in solution under extraordinarily mild thermal conditions. Among many inherent advantages of sol-gel technology, the highlight is it can provide strong adhesion of the coating to the substrate due to chemical bonding with a porous structure. Hence, sol-gel coating technology will be easily applied to the preparation of various SPME fibers with high stabilities, good sample capacities and long service lives. In this paper, we report a sol-gel coating technique for SPME fibers. Compared with conventionally coated fibers, sol-gel-coated fibers have some operational advantages.

EXPERIMENTAL

Equipment and reagents

Hewlett-Packard 6890 GC equipped with ECD and split/splitless injection port, SP-502 GC equipped with FID (Shandong, China), Shimadzu C-R3A chromatopac, SPME fiber assembly (Supelco, Inc., Canada).

135-TCB, 123-TCB, 1235-TTCB, 1234-TTCB, α-HCH, hexa-CB, β-HCH, γ-HCH, δ-HCH, Aldrin, Oystrene, and Dieldrin are CR, the other reagents are AR.
SPME fiber preparation

The sol solution was prepared as follows: 300μL of methytrimethoxysilane, 150mg of hydroxy-terminated poly(dimethylsiloxane) (PDMS), 30mg of poly(methylhydrosiloxane), and 200μL of 95% trifluoroacetic acid (containing 5% water) were thoroughly vortexed in a plastic tube and centrifuged. The top clear sol solution was removed for fiber coating.

A cleaned fused-silica fiber was dipped vertically into the sol solution which was kept at 70°C. After ~30min, a sol-gel coating was formed on the outer surface of the fiber. The coated fiber was dipped into a trimethylmethoxysilane/methanol solution (4:1 v/v) for 1min, and placed in a desiccator at room temperature.

The sol-gel PDMS fibers were conditioned at 310°C under nitrogen for approximately 1-2h. Seen from the scanning electron micrograph, the sol-gel coating possessed a porous structure, 40μm thick and 1cm long.

Analysis of BTEX aqueous solutions

Stock solutions of benzene, toluene, ethylbenzene and xylene isomers (BTEX) were prepared by dissolving 10mg of each compound in 10mL of methanol in a volumetric flask. This standard solution was diluted with deionized water to give 10mg/L and 0.1mg/L BTEX solutions. In SPME-GC-FID analysis, we prepared 10mg/L benzene aqueous solution to test the optimum desorption time (Fig. 1), and the 10mg/L BTEX solution was used to test the relationship of desorption amount with desorption time (Fig. 2); in the same way, the 0.1mg/L BTEX solution was used to test the limits of detection (LOD) of this kind of analytical method (Table 1).

Analysis of simulated polluted water

12 selected organochlorine compounds were dissolved in deionized water in a headspace tube, 0.1mg/L of each compound in concentration. The target analytes were extracted by headspace-SPME at 70°C. After 6min, the SPME assembly
Fig. 1: Extraction time profile of benzene absorbed by sol-gel coated PDMS fiber.

Fig. 2: Desorption time profiles of BTEX absorbed by sol-gel coated PDMS fiber.

<table>
<thead>
<tr>
<th></th>
<th>Conventionally coated fiber</th>
<th>Sol-gel coated fiber</th>
</tr>
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<tbody>
<tr>
<td>Benzene</td>
<td>8.0</td>
<td>0.65</td>
</tr>
<tr>
<td>Toluene</td>
<td>3.0</td>
<td>0.32</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>2.0</td>
<td>0.39</td>
</tr>
<tr>
<td>p-xylene</td>
<td>2.0</td>
<td>0.31</td>
</tr>
<tr>
<td>o-xylene</td>
<td>2.0</td>
<td>0.52</td>
</tr>
</tbody>
</table>
was removed out from the tube and put into the injection port for analysis. Figure 3.a and b were the gas chromatograms of sol-gel-coated PDMS fiber and commercial polyacrylate (PA) fiber, respectively.

GC conditions: column HP-5 (30m×0.32mm), injector 250°C, ECD 290°C, initial temperature 100°C, initial time 0, rate 10°C/min, final temperature 190°C, final time 10min.

CONCLUSION

Sol-gel-coated PDMS fibers have some advantages, such as fast mass transfer, high thermal stabilities and efficient extraction rates. As can be observed in Figure 1, to benzene, the optimum extraction time of sol-gel-coated PDMS fibers was 6min, which was much faster than that of conventionally coated PDMS fibers (15min); also, the optimum desorption time of sol-gel-coated PDMS fibers is only 20sec (Figure 2). In our experiments, we have operated sol-gel coated PDMS fibers at 300°C without negative consequences, such as solid-phase bleeding. As can be seen in Table 1, using 40μm sol-gel-coated PDMS fibers, the LODs of BTEX are about one order of magnitude lower than those using 56μm conventionally coated PDMS fibers, which indicates the sol-gel coatings can provide enhanced stationary-phase loadings and, therefore, higher fiber sample capacities. The reason why sol-gel-coated fibers have those advantages is that, in the sol-gel coating approach, the solid-phase coating molecules were incorporated to the fused silica surface through chemical bonding, so they could achieve higher stability than the fibers coated by conventional physical coating approach; at the same time, the sol-gel coating porosity can improve the extraction efficiency to organic compounds; on the other hand, it provides high surface area and allows for the use of much thinner coatings (compared with 100μm coatings for conventional PDMS fibers) to obtain acceptable sample capacities, thus, mass transfer rates are promoted.
Sol-gel-coated PDMS fibers can be applied to an extended range of analytes. They allow the extraction of both polar and nonpolar compounds. As can be seen from Table 1, the capabilities of sol-gel-coated PDMS fibers to extract nonpolar BTEX are superior to those of conventionally coated PDMS fibers; Figure 3.a and b illustrate, compared with commercial PA fibers, sol-gel-coated PDMS fibers show sufficient selectivity for polar organochlorine...
compounds. This results from the following: first, after bonded to the sol-gel network through condensation reaction, some hydroxy-terminated PDMS molecules might have free terminal silanol groups, the presence of those hydroxyl groups will make the coating more polar than conventional PDMS coating; second, in the sol-gel PDMS coating, the hydroxy-terminated PDMS molecules are attached to the polar silica network through chemical bonding, the polarity of inorganic and organic components of the composite sol-gel PDMS coating makes it suitable for the efficient extraction of polar compounds. In addition, high thermal stability allows the use of high injection temperature for efficient desorption of less-volatile analytes, so a great number of less-volatile compounds can be analyzed by SPME-GC.

REFERENCES


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