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Preparation of A New Fiber by Sol-gel Technology in Solid-phase Microextraction (SPME)

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Abstract: The sol-gel technology is applied for the preparation of solid-phase microextraction (SPME) fiber. The fiber demonstrates high thermal stability, efficient extraction rate and the selectivity for non-polar or low-polar analytes. Efficient SPME-GC-FID analyses of benzene-toluene-ethylbenzene-xylenes (BTEXs) and low-polar halocarbon were achieved by the sol-gel coated DSDA-DDBT-TiO_2 fiber. Some parameters of the SPME fiber for the determination of halocarbon in aqueous sample were investigated.

Keyword: Solid-phase microextraction, sol-gel technology, selectivity, polyimide (DSDA-DDBT).

The solid-phase microextraction (SPME) technique was first introduced by Arthur and Pawliszyn in 1990 and is widely accepted now [1,2]. It is an inexpensive, time-efficient and solvent free extraction technique, which combines extraction, concentration and sample introduction in one step. To obtain more selective determination of different compounds, different coating fibers for SPME have been found. In addition to some commercially available coatings, there are approximately twenty kinds of homemade coating[3,4]. To avoid contaminating the detector such as ECD and MS and to enhance the extraction capacity of the coating fiber, the high thermal stability of the SPME fiber must be satisfied. Therefore, the important characteristic of the SPME fiber is the thermal stability. For enhance the extracted amount of target organic compounds, the SPME fiber should also possess better selectivity.

In this study, the polyimide-TiO_2 coating prepared by sol-gel technology met the above needs. The coating not only has better selectivity for non-polar analytes but also has high stability (to 330°C for a long time, to 350°C for a few minutes), which was investigated by the following experiments. In this paper, the polyimide prepared by dimethyl-3,7-diaminobenzothiophene-5, 5′-dioxide(DDBT) and 3, 3′,4, 4′diphenyl-sulphone tetracarboxylic dianhydride (DSDA) as the main sol ingredient to prepare the new SPME fiber.

Experimental

The sol solution was prepared as follows: 10% polyimide (DSDA-DDBT) dimethylforma-

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mide solution, 1.5 mL tetrabutyl titanate, 2.2 mL *n*-butanol, 0.5 mL acetic acid and 0.1 mL deionized water were thoroughly vortex-mixed in a plastic tube for 40 min to obtain the clear yellow sol solution. The coating was created on the fiber surface by dipping its bare end into a sol solution. The coating thickness can be varied simply by controlled dipping time in the sol solution. Sol-gel coated fibers were thermally conditioned at 270°C under nitrogen for 180 min before using them in SPME analysis.

Results and Discussion

The surface of the DSDA-DDBT-TiO_2 coating was investigated by scanning electron microscopy (SEM). As can be seen from **Figure 1**, the sol-gel coating possesses a three-dimensional porous polymeric network structure. Porous and network structure enhanced surface area for the analyte to interact with the stationary phase. This should allow for the use of fiber with less coating thickness to achieve reasonable sample capacity, so the thickness of the DSDA-DDBT-TiO_2 coating stays at 18 μm.

The thermal stability of the DSDA-DDBT-TiO_2 coating was investigated by analyzing BTEXs from aqueous sample. Extraction quantities stay stable with the coating conditioned temperature from 270°C to 330°C for 30 min. The extraction capacity slightly declined, when the fiber conditioned 350°C for 30 min. Because the thermal stability of the sol-gel coating was controlled by the highest thermal stability of polyimide(DSDA-DDBT, 280°C) and the force between the polyimide and inorganic gel compounds. Therefore, the DSDA-DDBT-TiO_2 fiber may be used in 330°C for a long time.

To evaluate the selectivity of the DSDA-DDBT-TiO_2 fiber, a polar and non-polar mixture was spiked in deionized water, where the concentration of each analyte was 0.1

Figure 1 Scanning electron micrograph of the DSDA-DDBT-TiO_2 fiber (Under taken with gold coating 10,000-fold magnification and 20-kv acceleration)

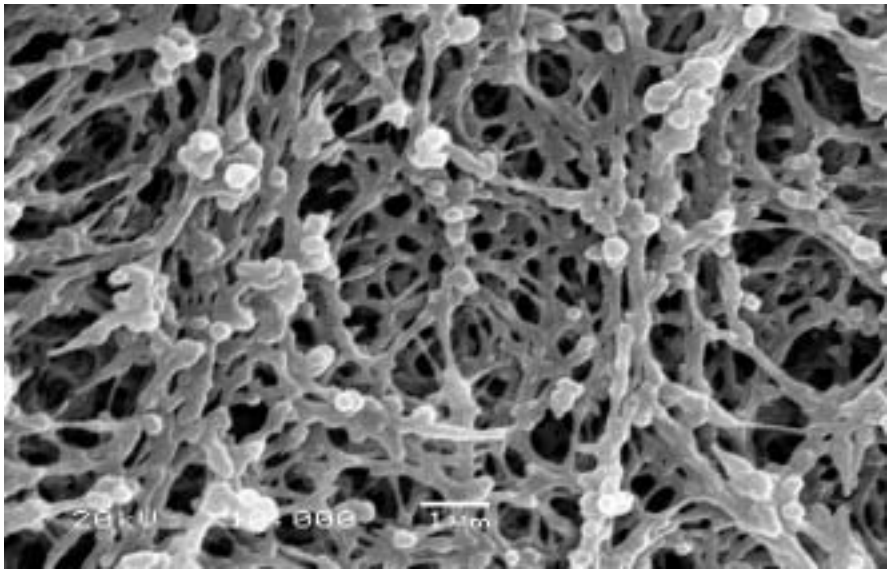
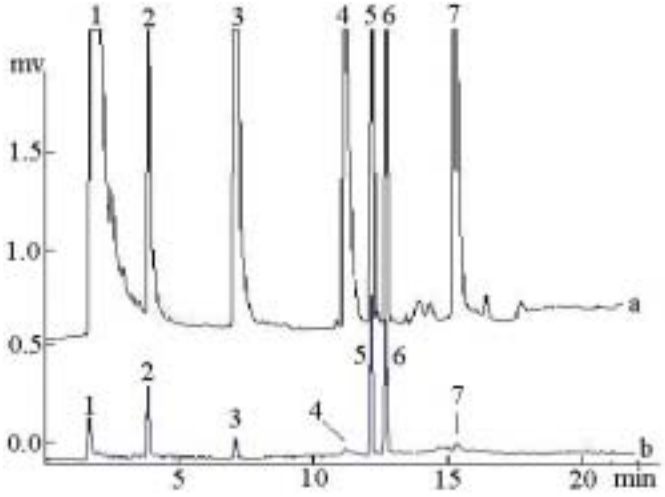


Figure 2 Comparative GC-FID chromatograms of mixture compounds



(a) The standard solution by directed sample injection (0.1uL, the concentration 1 g/L), (b) Typical SPME-GC-FID chromatogram extracted by DSDA-DDBT-TiO_2 fiber from the aqueous sample (0.1 mg/L). Column temperature programmed from 50°C (hold for 5min) to 150°C at a rate of 5°C/min; FID for 280°C; exposure time, 15 min; exposure temperature, 30°C; desorption time, 2 min; desorption temperature, 260°C;. Peaks: (1) solvent, methanol, (2) benzene, (3) 1-pentanol, (4) 1-hexanol, (5) 1,4-dichlorobutane, (6) *O*-xylene, (7) 1-heptanol.

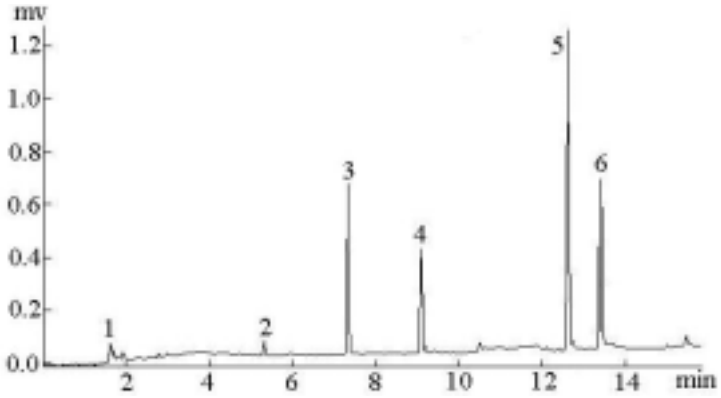
mg/L approximately. The comparison of extraction chromatogram obtained by SPME from aqueous sample and the standard solution (1 g/L) chromatogram obtained by 0.1 μL directed injection are shown in **Figure 2**. As can be seen from **Figure 2**, the DSDA-DDBT-TiO_2 fiber has higher extraction capacity to non-polar or low-polar analytes and lower adsorption to alcohols, which can be explained by the structure of polimide that has multi-phenyl and multi-thionyl, which shows better selectivity for non-polar and low-polar compounds through π-π action and dispersion force. Therefore, the DSDA-DDBT-TiO_2 fiber belongs to non-polar and low-polar selectivity coating.

The DSDA-DDBT-TiO_2 was used to investigate the low-polar halocarbon. The optimal experimental procedures including adsorption time, salt effect, desorption time, exposure temperature were studied and the method was then applied to determination of halocarbon from aqueous sample (see **Figure 3**). The reproducibility of the whole technique showed a relative standard deviation of 10%. The linearity was in the range of 0.0010 mg/L to 1.7 mg/L for the SPME of halocarbon from aqueous sample. The limits of detection was in the range 0.011 μg/L ~0.15 μg/L (S/N=5).

Conclusion

The DSDA-DDBT-TiO_2 fiber was prepared by sol-gel technology, which has better reproducibility. It exhibits high thermal stability (to 330°C) and better selectivity for non-polar or low-polar compounds. The characteristics of the DSDA-DDBT-TiO_2 will widen its application range. Further applications of the fiber are in progress.

Figure 3 The SPME-GC-FID chromatogram of halocarbon in the aqueous sample (1mg/L) extracted by the DSDA-DDBT-TiO_2 fiber.



Column temperature programmed from 50°C (hold for 5min) to 150°C at a rate of 5°C/min; FID for 280°C; exposure time, 15 min; exposure temperature, 30°C; desorption time, 2 min; desorption temperature, 260°C; NaCl, 20%. Peaks: (1) solvent, methanol, (2) 1,1,2-trichloroethane, (3) chlorobenzene, (4) 1,4-dichlorobutane, (5) *O*-dichlorobenzene, (6) *p*-dichlorobenzene.

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