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A novel fiber coating for solid phase microextraction and its application for the extraction of *n*-alkane from aqueous sample

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Abstract: Base on the previous work in laboratory, a novel polyaniline doped with polydimethylsiloxane coating was developed on a stainless steel wire for solid phase microextraction(SPME) by electroplating method. This electroplating method not only has advantages of ease preparation and simple equipments required, but also increases the lifetime of the SPME fiber. The composite fiber (polyaniline/polydimethylsiloxane(PANI/PDMS)) was evaluated by analyzing *n*-tridecane, *n*-tetradecane and *n*-pentadecane in aqueous sample. The new fiber coating showed comprehensive abilities to extract alkanes compounds. The relative standard deviations were found to be 6.8%—10.33%.

Keywords: solid phase microextraction; stainless steel wires; electroplating fiber preparation; polyaniline/polydimethylsiloxane; alkanes

Introduction

Solid phase microextraction (SPME) has gained more and more wide attentions since it was developed by Pawliszyn and his coworkers in 1989 (Berladi, 1989; Pawliszyn, 1999). SPME integrates sampling, extraction, and sample introduction into a single solvent-free step. The method saves preparation time and disposal costs and can improve detection limits. A whole SPME is assembled with holder and fiber. The coating on the fiber plays an important key role in the SPME procedure. So, until now more than one hundred papers dealing with preparation novel fiber coatings have been published. It is reported that all the coating have successfully applied to extract many kinds of environmental pollutants from different matrixes. In most papers, the fused silica fiber was used as the support phase for SPME. However, the fragility of fiber will limit the application of SPME. So, some polymers have been coated on metal wires as SPME fiber coating by chemical or electrochemical method (Wu, 2000a; 2000b; 2001; 2002a; 2002b). These coatings have been used to extract several kinds of compounds, including organic and inorganic compounds.

To exploit more applications of SPME, we have coated polyaniline on the stainless steel wire, and applied it to extract some aniline from aqueous sample successfully (Huang, 2004). In this article, to broaden the range of the application of conducting polymers on SPME and change the morphology of the coating, we prepared a new coating, polyaniline doped with polydimethylsiloxane (PANI-PDMS). To evaluate the new coating, three *n*-alkanes, including *n*-tridecane, *n*-tetradecane and *n*-pentadecane in aqueous sample were analyzed.

1 Experimental

1.1 Reagents

Polydimethylsiloxane (PDMS) was purchased from Shimadzu Corporation (Tokyo, Japan). Aniline (99.8%) was from Beijing Chemicals Reagent Factory (Beijing, China). Both the sulfuric acid and the phosphonic acid were purchased from Tianjin Dongfang Chemical Factory (Tianjin, China) and are both guarantee grade reagent. *n*-Tridecane (99.3%), *n*-tetradecane (99.5%) and *n*-pentadecane (99.9%) were all from Supelco (Bellefonte, PA, USA). Stock solutions of each *n*-alkane (0.1 mg/ml) were prepared with hexane as solvent, which was pesticide grade from Fisher Scientific (NJ, USA). All the solutions were stored at 4℃. Water used throughout the experiment was all purified by a Milli-Q system.

1.2 Apparatus

An Agilent HP-6890N GC with 5973 MS system (Agilent Technologies, DE, USA) was used and on-line data was collected and processed by a HP Chemstation (Agilent Technologies, DE, USA). The GC capillary column (HP-5 MS, 30 m × 25 μm × 25 mm) was purchased from Agilent (Agilent Technologies, DE, USA). The oven temperature was initially held at 50℃, programmed at 5 ℃/min to the temperature of 250 ℃ for 10 min. The injector was splitless and its temperature was set at 250℃. The carrier gas was high purity helium (99.999%). The column flow rate was set at 1.5 ml/min. A SPME manual holder was from Supelco (Bellefonte, PA, USA). A magnetic stirrer with heater (95-2 Model, Sile Instrument Factory, Shanghai, China) was used to stir the sample during extraction procedure.

1.3 Preparation of SPME fiber

The stainless steel wire was polished in the mixed solution of the sulfuric acid and phosphonic acid by electrochemical clean method before the electropolymerization process. A CHI Electrochemstation (CHI Instru, TX, USA) with three electrode system was used to control the electroplate process. An electrochemically polished stainless steel wire for solid phase microextraction, a calomel electrode and a platinum electrode were used as the working electrode, the reference electrode and the counter electrode respectively. The electrolyte was composed of 0.4 mol/L $HClO_4$ solution containing 0.1 mol/L aniline monomer (restilled before electropolymerization) and 0.05 g polydimethylsiloxane. A constant potential (1.1 V) was applied to the whole electrochemical process. The electroplate process was lasted for 24 h. After the black polymer film was formed on the surface of the stainless steel wire, it was subsequently washed with de-ionized water, then with methanol or acetone and was kept dried under nitrogen protection at room temperature. Finally, it was inserted into GC injector and conditioned at

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250℃ for 30 min before use. The surface of fiber was studied by Hitachi S-3000N model scanning electron microscopic (SEM) photography (Hitachi Science Systems LTD, Tokyo, Japan), and the elemental analysis was carried by an EDAX analyzer (NJ, USA).

1.4 Solid-phase microextraction procedure

To evaluate the extraction ability of the new fiber coating, 10 μl 0.1 mg/ml stock solution was added to 10 ml Milli-Q pure water in a glass vial. The SPME fiber protector pieced the cap of the vial and the fiber was pushed out above the sample. After 20 min, the fiber was retracted into the protector tube. Then the fiber was inserted into the GC injection for 5 min, where desorption of the analytes was carried out. And the analytes were delivered into the column for separation simultaneously. Before each extraction, the fiber should be desorbed for 3 min in the injection port to insure no carryover.

2 Results and discussion

2.1 Fiber properties

According to the reference (Dong, 1992), a smooth and clean surface of the stainless steel wire is essential for the electrochemical polymerization. After optimizing electrochemical-polishing process, a clean and smooth surface of the steel wire was obtained (Fig. 1). Fig. 2 is the SEM photography of the PANI-PDMS fiber surface. It is obvious that the coating is compact and its surface is rough. Fig.3 is the result of the elemental analysis. According to the percentage of the silicon, it is obviously that polydimethylsiloxane has been doped into the coating plentifully.

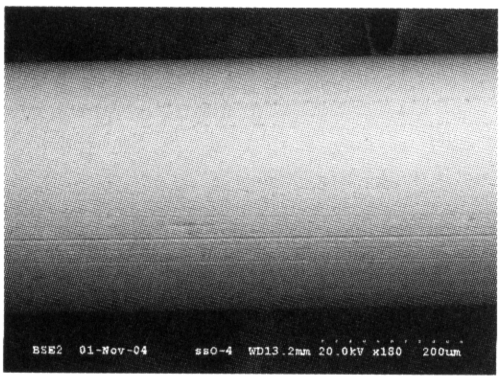

Fig.1 SEM of the surface of the stainless steel wire

2.2 Investigation of the fiber extraction ability by determination of *n*-alkanes in aqueous sample

To evaluate the new PANI-PDMS fiber, three *n*-alkanes (*n*-tridecane, *n*-tetradecane and *n*-pentadecane) in aqueous sample were analyzed. The concentration of the alkanes was about 100 μg/L. The extraction was carried under the room temperature. Fig. 4 shows that the PANI-PDMS fiber has good ability to extract the three alkanes and the retention time of *n*-tridecane, *n*-tetradecane and *n*-pentadecane were 14.20 min, 15.87 min and 17.63 min respectively. Table 1 lists the values of both peak height, peak area and *RSD*. of the three alkanes. We can draw a conclusion that the fiber showed best extraction ability to extract *n*-tridecane according to comparison its peak height with those of the other two alkanes. The reason was that *n*-tridecane was most volatile among these three alkanes. From Fig.4, we also can find

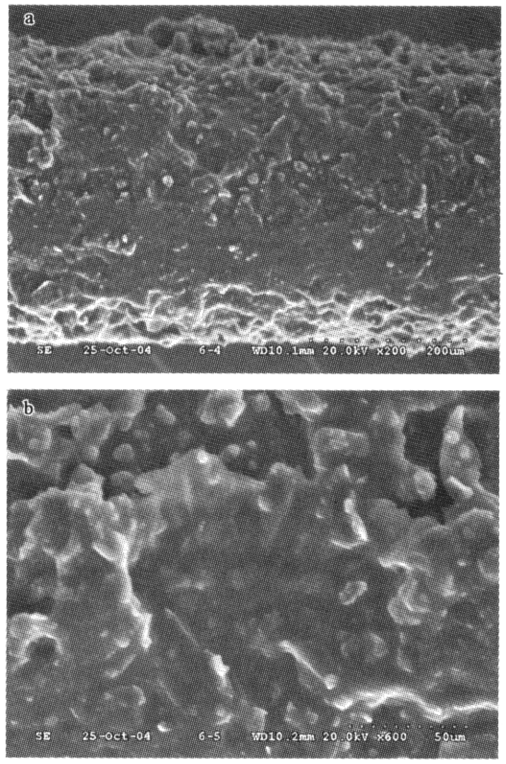

Fig.2 SEM of the surface of the PANI-PDMS coating
a: ×200; b: ×600

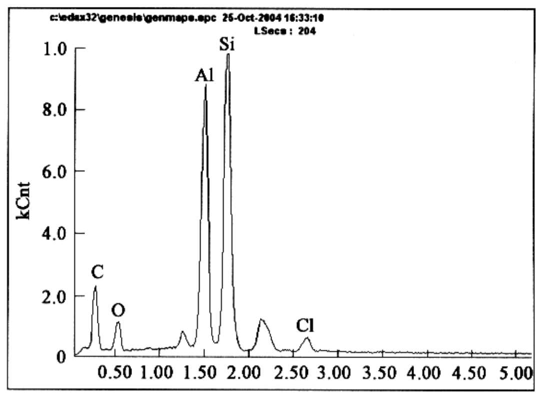

Fig.3 Result of the elemental analysis

some impurity in the chromatogram, which might caused by the thermal degradation of the polydimethylsiloxane. The polydimethylsiloxane was doped into polyaniline just by simple physical force (such as deposition). However, the fiber also showed good repeatability when it was used to extract the three analytes. For five repetitions, the values of relative standard deviation of *n*-tridecane, *n*-tetradecane and *n*-pentadecane were 6.89%, 6.96% and 10.3% respectively. The result showed that the fiber could be used to identify alkanes from aqueous sample.

Table 1 Extraction ability of *n*-alkanes (100 μg/L) by PANI-PDMS SPME fiber

n-alkanes	Retention time, min	Peak height	Peak area	*RSD*, %
n-tridecane	14.20	2011180	42565646	6.89
n-tetradecane	15.87	1024931	22242659	6.96
n-pentadecane	17.63	1390749	29336076	10.3

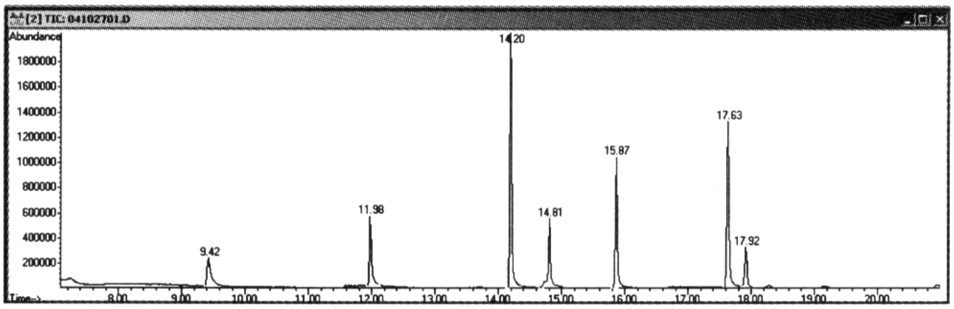

Fig.4 Chromatogram of the three alkanes extracted by the new SPME fiber

3 Conclusions

A new PANI-PDMS coating was prepared on stainless steel wire by electrochemical method. An ideal morphology of the coating was formed and the polydimethylsiloxane was doped by deposition. The performance of the novel fiber was evaluated by the extraction of n-tridecane, n-tetradecane and n-pentadecane in aqueous samples. It was found that the new fiber has good ability to extract the three alkanes. After five repetitions, good RSD. of three analytes were obtained with the new fiber. The new PANI-PDMS fiber might be used to identify some volatile compounds.

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