



# A strategy to enhance the antifouling property of coating for direct immersion solid phase microextraction



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## ABSTRACT

This paper presents a new approach for improving the antifouling property of solid-phase microextraction (SPME) coating. The SPME fiber was fabricated by electrodeposition of polyaniline (PANI) on stainless steel wire, followed by covering with an external layer of Nafion. The Nafion layer was able to block the interfering components in the matrix while the fiber was used for the direct extraction of several parabens. At the same time, the selectivity and stability of the SPME fiber was also improved. The adsorption coefficient and saturation-adsorption amount were determined, which showed that the extraction capability of the resulting fiber was similar to that of the original PANI fiber toward parabens. In addition, the fiber exhibited enhanced robustness in direct contact with complex matrix such as orange juice. After it was used for 110–150 adsorption–desorption cycles, its extraction efficiency decreased by 14–16% compared with the maximum measured value. This was a dramatic improvement when compared with the PANI fiber. Hence, the fiber was suitable for direct immersion SPME.

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## 1. Introduction

Solid-phase microextraction (SPME) is a widely used sample preparation technique, and it possesses many advantages over conventional sampling methods by integrating sample extraction, concentration and introduction into a single solvent-free step [1–4]. The mechanism of SPME is based on the distribution of analytes among different phases. Therefore, the exploitation of extraction coating is one of the most critical steps in SPME method development. In general, for different purpose corresponding coating should be prepared or adopted to achieve high adsorption ability and selectivity.

As for direct immersion SPME (DI-SPME) the fouling and chemical corrupt of matrix are generally met. To deal with these problems some pretreatment or cleanup steps are often adopted prior to SPME. Thus, the determination procedure becomes more complicated. Furthermore, some new problems may occur. To improve the situation some researchers devoted to developing new coatings with high selectivity and anti-fouling function, thus they could be coupled with gas chromatography (GC) analysis to well cope with complex matrix [5,6]. For example, Jahnke et al.

investigated the effect of nonvolatile matrix macromolecules on the polydimethylsiloxane (PDMS), and concluded that the sorptive properties of the PDMS were not modified and PDMS was suitable for sampling from complex matrixes [7]. Then Pawliszyn et al. modified the commercial polydimethylsiloxane/divinylbenzene (PDMS/DVB) coating with a thin layer of PDMS and used it for the DI-SPME of triazole pesticides in food matrix (i.e. whole grape pulp), the resulting coating achieved matrix-compatibility while retained the sensitivity of original coating [8].

Nafion has been extensively used in extraction, and it acts as a binder and support except for a sorbent [9,10]. Nafion is comprised of a rigid, highly hydrophobic Teflon-like backbone with hydrophilic perfluoroether side chains bearing terminal sulfonic acid groups. Its ionic groups can interconnect to form clusters, thus facilitating the transport of molecules [11,12]. Nafion coating suffers less from the irreversible fouling effect caused by the matrix components when compared with solid coatings [13,14]. Furthermore, besides its anti-fouling character, it has good mechanical performance. However, so far no report has concerned the use of Nafion as adsorptive phase in direct contact with complex matrixes.

In addition, the electrodeposited polyaniline (PANI) coating has been used for the DI-SPME-GC analysis of a wide range of analytes [15–17]. This coating presents high selectivity, increased retention capacity and high distribution coefficient. However, it suffers from irreversible fouling damage when directly contacts with complex

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matrix. This is very problematic as it can affect the uptake of analytes and the reproducibility of extraction, thus resulting in poor accuracy and decreased extraction efficiency upon repeated use. Besides PANI fiber coating, other conductive polymers based fibers, including polypyrrole and poly(thiophene) etc., also suffer from this problem.

With the aim to achieve matrix-compatibility while retain the extraction capability of original coating, PANI/Nafion fiber was fabricated. Herein, parabens were chosen as model analytes, and pure orange juice was chosen as a model of complex matrix. Based on the DI-SPME of PANI/Nafion fiber and afterward GC analysis, its extraction efficiency and robustness was evaluated.

## 2. Experimental

### 2.1. Reagents

All chemicals and reagents were analytical grade. Aniline (ANI) was purchased from the Reagent Factory of Shanghai (China). It was further purified by distillation before use. Nitric acid was obtained from the Reagent Factory of Shanghai. Nafion (5%, w/v, diluted with methanol) was purchased from Du Pont Company of Shanghai.

Parabens (i.e. methyl paraben, ethyl paraben, propyl paraben, butyl paraben) were purchased from the Reagent Factory of Shanghai. Individual solutions (100 mg/mL) of these parabens were prepared in methanol. The mixture stock solution contained 1 mg/mL of each paraben. Different working solutions (0.1–500 µg/L of each paraben) were prepared by dilution with methanol.

Pure orange juice was obtained from a local market (Wuhan, China). It was analyzed immediately after sampling with no sample pretreatment required.

### 2.2. Apparatus

A CHI 617A electrochemical workstation (CH Instrument Corp., Shanghai) was used for the electrodeposition of PANI. A conventional three-electrode system was adopted, including a stainless steel wire (2 cm × 250 µm O.D.) as working electrode, a Pt counter electrode (2.5 cm × 0.1 cm O.D.) and a saturated calomel electrode (SCE) as reference electrode. Commercial SPME fibers (i.e. 100 µm PDMS and 65 µm PDMS/DVB) were supplied by Supelco (Bellefonte, PA, USA). The heating and stirring of the samples were carried out by a heater-magnetic stirrer model S10-3 (Shanghai). Analysis of paraben preservatives was performed on a GC-2010 gas chromatography system (Shimadzu Corporation, Japan) fitted with a split/splitless injection chamber, HP-5 column (30 m, 0.25 mm i.d., 0.25 µm film thickness) (USA) and a flame ionization detector (FID). A GC solution chromatographic workstation program (Shimadzu Corporation) was used to process chromatographic data. Ultrapure nitrogen was used as carrier gas at a constant flow rate of 1 mL/min. Hydrogen and air flow rates were maintained at 40 mL/min and 400 mL/min, respectively. The temperatures of capillary splitless injector and detector were 260 °C. The column temperature program was initially set at 50 °C for 3 min, ramped at 10 °C/min to 140 °C, ramped at 5 °C/min to 200 °C, and then ramped at 20 °C/min to 220 °C and held for 2 min, giving a total run time of 27 min. The SPME device was laboratory-made.

### 2.3. Preparation of Nafion modified fiber

The PANI coating was directly electrodeposited on a stainless steel wire surface from a 10 mL 1 M HNO<sub>3</sub> aqueous solution containing 0.1 M ANI by using cyclic voltammetry (CV) technique. Prior to electrochemical polymerization, the stainless steel wire was ultrasonicated in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1 M NaOH and distilled water each for

15 min and then dried at room temperature. The CV was performed between –0.2 V and 1.5 V at a scan rate of 50 mV/s, and the number of scan cycle was set at 50. The obtained fiber was washed with distilled water to remove unwanted chemicals such as monomer and supporting electrolyte, and subsequently kept in a desiccator for 10 h at room temperature. Afterwards, it was aged in an electric furnace at 100 °C for 30 min and then at 260 °C for 2 h under a gentle stream of N<sub>2</sub>.

The coating procedure consisted of immersing the PANI fiber into the Nafion solution for 1 min and subsequently pulling out slowly. The coating/curing process was repeated twice to ensure complete and uniform coverage, considering the relatively low viscosity of Nafion. After the coating process, the coated fiber was placed in a desiccator at room temperature for 12 h. Then, the fiber was installed into the laboratory-made SPME device, which was a modified 5 µL syringe. Prior to use the fiber was conditioned in the GC injection port under N<sub>2</sub> flow at 260 °C for 30 min. The Nafion coating was 2 mm longer than the PANI, thus ensuring the complete isolation of the latter from the surroundings.

In order to examine the topography of the coating as well as the thickness of the Nafion layer, scanning electron microscopy (SEM) images were acquired using an LEO 1530 field emission SEM (Carl Zeiss NTS GmbH, Germany).

### 2.4. SPME procedure and GC determination

#### 2.4.1. Extraction of parabens from standard aqueous solution

This approach was employed to compare the extraction behavior of the PANI fiber and the Nafion modified fiber. A 10 mL aqueous solution of parabens (0.1–500 µg/L) was transferred in 15 mL vial. Extraction was performed at 30 °C under magnetic agitation at 500 rpm. The extraction time ranged from 10 to 300 min. Then, the fiber was placed in the GC injection port for desorption of 5 min at 260 °C. All extractions were performed in duplicate.

#### 2.4.2. Extraction of parabens from orange juice

As no parabens were detected by DI-SPME GC analysis, the orange juice was used for method evaluation. A 10 mL orange juice was added in a 15 mL vial with PTFE silicon septum, fortified at 100 µg/L. A 20 min extraction was performed at 30 °C under magnetic agitation. Following extraction, a rapid rinsing of the fiber in deionized water was implemented. It was observed that no significant loss of analyte occurred up to 30 s of rinsing; thus, it was chosen for further experiments. Subsequently, the fiber was placed in the GC injection port for desorption of 5 min at 260 °C. Every day, before the measurements, the fibers were conditioned in the GC injection chamber (at 260 °C) for 30 min. In addition, the column blank and fiber blank were recorded to determine the extent of any laboratory contamination.

## 3. Results and discussion

### 3.1. Characterization of PANI/Nafion coated fiber

It was necessary to optimize the coating method (spraying or dipping) and the overall parameters such as the number of coating cycle and duration of coating time. The spraying method resulted in highly irregular coatings, thus, dip-coating was adopted. The optimized procedure was that as presented in the Experimental Section. The optimized Nafion outer layer was obtained by dipping for two times, which resulted in optimum surface coverage of the original coating. Results showed that thinner coatings (e.g. one dip-coating) did not ensure total surface coverage, thus resulting in the inner PANI coating cannot get effective protection. In addition, thicker coatings (e.g. three dip-coating) resulted in nonuniform surface coverage in terms of thickness throughout the coating length.

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