



# Development of dual-templates molecularly imprinted stir bar sorptive extraction and its application for the analysis of environmental estrogens in water and plastic samples



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## ARTICLE INFO

### Article history:

Received 21 May 2014

Received in revised form 26 June 2014

Accepted 27 June 2014

Available online 3 July 2014

### Keywords:

Stir bar sorptive extraction

Dual-templates molecularly imprinted

Environmental estrogens

Bisphenol A

Sample preparation

## ABSTRACT

In this study, a novel dual-template molecularly imprinted polymer (MIP)-coated stir bar was prepared and coupled with high-performance liquid chromatography (HPLC) for the analysis of environmental estrogens in complex samples. Dual-template MIP coating was homogeneous and porous with an average thickness of 5  $\mu\text{m}$ . Moreover, it could be used for at least 50 times and be kept for at least 12 months in a dryer without any damage. The MIP-coated stir bar showed excellent selectivity to bisphenols and steroids. The method for the determination of bisphenols and steroids in complex samples via MIP-coated stir bar sorptive extraction coupled with HPLC was developed. The method was successfully applied in the analysis of five estrogens in lake and river water samples with recoveries of 71.2–96.4% and 62.8–98.0%, respectively. The method was also successfully applied to the analysis of five estrogens in three plastic samples with recoveries of 67.7–99.1%, 68.8–99.9%, and 74.8–101.8%. The limit of quantitation was 1.0–5.0  $\mu\text{g/L}$ . The proposed method is suitable for the simultaneous determination of multiple trace environmental estrogens in water and plastic samples.

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## 1. Introduction

Stir bar sorptive extraction (SBSE) was first introduced by Baltussen et al. in 1999 [1]. SBSE follows the same extraction theory as solid-phase microextraction. However, it has better extraction yield because of its larger volume and surface area. SBSE enriches analytes during self-stirring and avoids competitive sorption from an additional stirrer. The SBSE technique is now rapidly developing and is widely used in complex sample preparations [2–5]. Several novel coatings for stir bars have been proposed. These coatings include composite coatings [6–8], dual-phase stir bar coatings [9,10], polymeric phases [11–15], monolithic materials [16–19], restricted access material [20], cation-exchange coating [21], zirconia coating [22], and  $\text{C}_{18}$  coating [23]. Several novel styles for stir bar have also been proposed, such as stir cake [24], stir membrane [25], “dumbbell-shaped” stir bar [26], rotating-disk [27,28], and stir rod [29]. These novel stir bars have extended the application of SBSE, but the coatings are still non-selective sorbents.

Molecularly imprinted polymer (MIP) is a synthetic material with selective recognition ability. Given its advantages of high

selectivity, good capability of resisting disturbances, easy preparation, and low cost, MIP has been widely used in sample preparations [30–32]. However, only a limited number of studies on SBSE with MIP coatings have been conducted. Zhu et al. prepared monocrotophos [33] and L-glutamine [34] MIP-coated stir bars based on commercial PDMS stir bars via a phase inversion method. Yang et al. reported nicosulfuron molecularly imprinted stir bar for the selective enrichment of sulfonylurea herbicides [35]. Xu et al. developed ractopamine [36], sulfamethazine [37], trimethoprim [38], and metsulfuron-methyl [39] MIP for SBSE coatings. They were immobilized on the surface of silylated glass capillary via copolymerization. Moreover, terbutylazine [40] and prometryn [41] MIP for SBSE coatings have been prepared via the same method. In addition, chiral imprinted polymer SBSE coatings have been proposed for the analysis of (s)-citalopram from a racemic mixture in aqueous media [42].

Environmental estrogens are considered as endocrine disruptor compounds and can mimic or function as antagonists to the estrogens in the body. Considering their environmental effects, environmental estrogens have attracted attention. Environmental estrogen can be divided into two categories, namely, endogenous estrogens (17 $\beta$ -estradiol and estrone) and artificial estrogens (17 $\alpha$ -ethynylestradiol, diethylstilbestrol, bisphenol A, and other bisphenols) [43]. Bisphenols are widely used as additives

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to improve the properties of plastics. Bisphenols have estrogenic activity and are potentially carcinogenic and mutagenic to animals and humans [44]. Bisphenol A is a typical endocrine disruptor and is widely used in the manufacture of polycarbonate plastics and epoxy resins. However, its trace residue levels released through diffusion or degradation below levels that are normally considered safe still have adverse biological effects [45].

In the present study, dual-template molecularly imprinted stir bar sorptive extraction was conducted. The coatings were characterized via SEM. The extraction conditions were optimized and the extraction capability and selectivity of the dual-template MIP-coated stir bar were investigated. Furthermore, a method for dual-template MIP-coated SBSE coupled with high-performance liquid chromatography (HPLC) was developed and was applied for the analysis of bisphenols in plastic samples. The method was also successfully applied for the analysis of environmental estrogens in water and plastic samples.

## 2. Experimental

### 2.1. Chemicals and materials

Bisphenol A (BPA), bisphenol B (BPB), bisphenol F (BPF) and bisphenol S (BPS) were purchased from Wuhan Jinnuo Chemical Co. Ltd (Wuhan, China). Estradiol (E2), estriol (E3), estrone (E1) and diethylstilbestrol (DES) were purchased from Hubei Hengshuo Biochemical Co. Ltd (Wuhan, China). P-tert-octylphenol (PTOP) and p-tert-butylphenol (PTBP) were purchased from Aladdin Chemistry Co. Ltd, Shanghai, China). Tetracycline (TC) was purchased from Xiya Reagent (Shandong Xiya Reagent Chemistry Co. Ltd, Linshu, China). Acetonitrile and methanol (HPLC grade) were obtained from Xilong Chemical Co. Ltd (Shantou, China). Water used for HPLC was doubly distilled and filtered through a 0.45  $\mu\text{m}$  nylon filter. Other chemicals were analytical pure. Glass capillary (1 mm diameter, 100 mm length) was obtained from West China University of Medical Sciences Instrument Plant.

### 2.2. Instrumentation

DCY-12S nitrogen Evapoator (Haike, Qingdao, China) was used for the polymer reaction. An FEI Quanta 200 scanning electron microscope (FEI, Holland) was used to investigate the coating surface of the MIP-coated stir bar. An EQUINOX 55 Fourier transform infrared (FT-IR) spectrometer (Bruker optics, Germany) was applied to investigate the composition of the coating.

### 2.3. HPLC conditions

A Dionex-3000 HPLC (Dionex, USA) equipped with a DAD detector and a C18 column (250 mm  $\times$  4.6 mm i.d., 5  $\mu\text{m}$  packing, J & K Scientific LTD) was used for separation and detection. The flow rate was 1.0 mL/min and the column temperature was 30 °C. BPA, BPB, BPF, BPS, E2, E1, DES and phenol were determined at 230 nm and the mobile phase was acetonitrile/water (50:50, v/v). E3 was determined at 230 nm and the mobile phase was acetonitrile/water (40:60, v/v). PTOB and PTBP were determined at 225 nm and the mobile phase was methanol/water (77:23, v/v). TC was determined at 360 nm and the mobile phase was acetonitrile/0.01 mol/L sodium dihydrogen phosphate buffer solution (25:75, v/v).

### 2.4. Preparation of dual-templates molecularly imprinted polymer coated stir bar

The molecularly imprinted stir bar coatings were immobilized onto a glass capillary substrate via a previously reported method [36–39], which differs only by having two templates added in the

synthesis. The adding of two templates would generate two different kinds of specific binding sites and three-dimensional cavities which could recognize each template after elution. The preparation process of dual-templates MIP coating is shown in Fig. 1S. About 228.0 mg of BPA and 272.0 mg of E2 were dissolved in 20 mL of methanol–acetonitrile mixture (1:1, v/v). About 0.51 mL of methacrylic acid was then added. The solution was mixed thoroughly and kept for 12 h at room temperature. About 6.00 mL of ethyleneglycol dimethacrylate and 124.0 mg of azodiisobutyronitrile (AIBN) were added and degassed in an ultrasonic bath for 5 min. Afterward, 1.5 mL of the degassed solution was transferred into a test tube and deoxygenized with a nitrogen stream for 5 min. Subsequently, the silylated glass capillary was inserted into the test tube, and the polymerization was performed at 60 °C. When the polymer solutions solidified after 25 min, the silylated glass capillary was pulled out. The polymer coatings were then heated for 24 h in a nitrogen atmosphere. A suitable thickness was obtained by repeating the coating procedure. A 1.7 cm magnetic core was then inserted in a 2.3 cm glass capillary, which was coated with a 2.0 cm coating. The glass capillary was sealed using flame to generate a stir bar. A non-imprinted polymer (NIP) coated stir bar was prepared via the same procedure but without the template. The newly coated stir bars were eluted by 10% (v/v) acetic acid solution to remove the templates until it could not be detected by HPLC.

### 2.5. SBSE procedure

The stirring speed in stir bar sorptive extraction was 500 rpm at room temperature. The volume of sample was 15 mL. After extraction and solvent evaporation, the stir bar was inserted in a 200  $\mu\text{L}$  glass vial with a conical insert. About 150  $\mu\text{L}$  of 10% (v/v) acetic acid/water solution was then added followed by ultrasonication for 10 min. Subsequently, the stir bar was retrieved using a magnet, and 20  $\mu\text{L}$  of desorption liquid was injected into the HPLC equipment for analysis.

### 2.6. Sample preparation

The volume of each water sample was 15 mL. The water sample should be filtered by a syringe with a 0.45  $\mu\text{m}$  nylon filter before extraction. Each plastic sample was 0.1 g. It was cut into pieces and dissolved in and extracted using 2 mL of acetone for 12 h. The extraction solution was 25 mL of methanol. About 3 mL of the supernatant was drawn and dried at reduced pressure. The sample was then dissolved with 15 mL of water.

## 3. Results and discussion

### 3.1. Coating characterization

The dual-template MIP coatings were synthesized via copolymerization. The coating method was performed seven times, and a suitable thickness of about 5  $\mu\text{m}$  was obtained. The batch-to-batch reproducibility of dual-templates MIP-coated stir bar was evaluated by extraction of 50  $\mu\text{g/L}$  mixed standard solution. The RSD ( $n = 10$ ) of extraction amounts for BPA and E2 were 3.6% and 3.0%, respectively. The dual-template MIP-coated stir bar could be used for at least 50 times. After using more than 50 times, coating cracking might be occurred for long time sonication. The MIP-coated stir bar would not be used after apparent damage could be seen. The robustness of the MIP-coated stir bar was also characterized by extraction performance evaluation. After using 1, 10, 20, 35, 50 times, the extraction amounts of dual-templates MIP-coated stir bar to 50  $\mu\text{g/L}$  BPA and E2 were no obvious difference in extraction efficiency (Fig. S2). The MIP-coated stir bar could be kept in a dryer for at least 12 months.

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