



Water-compatible graphene oxide/molecularly imprinted polymer coated stir bar sorptive extraction of propranolol from urine samples followed by high performance liquid chromatography-ultraviolet detection



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ABSTRACT

Due to the high selectivity and stability, molecularly imprinted polymers (MIPs) have been successfully applied in stir bar sorptive extraction (SBSE) as a special coating to improve the selective extraction capability for target analytes. However, traditional MIPs usually suffer from incompatibility in aqueous media and low adsorption capacity, which limit the application of MIP coated stir bar in aqueous samples. To solve these problems, a water-compatible graphene oxides (GO)/MIP composite coated stir bar was prepared in this work by *in situ* polymerization. The prepared water-compatible GO/MIP coated stir bar presented good mechanical strength and chemical stability, and its recognition ability in aqueous samples was improved due to the polymerization of MIP in water environment, the adsorption capacity for target analytes was also increased by the addition of GO in MIP pre-polymer solution. Based on it, a method of water-compatible GO/MIP coated stir bar sorptive extraction combined with high performance liquid chromatography-ultraviolet detector (HPLV-UV) was proposed for the analysis of propranolol (PRO) in aqueous solution. The influencing factors of SBSE, such as sample pH, salt effect, stirring rate, extraction time, desorption solvent and desorption time, were optimized, and the analytical performance of the developed SBSE-HPLC-UV method was evaluated under the optimized conditions. The limit of detection (LOD) of the proposed method for PRO was about $0.37 \mu\text{g L}^{-1}$, and the enrichment factor (EF) was 59.7-fold (theoretical EF was 100-fold). The reproducibility was also investigated at concentrations of $5 \mu\text{g L}^{-1}$ and the relative standard deviation (RSD) was found to be 7.3% ($n=7$). The proposed method of GO/MIP coating-SBSE-HPLC-UV was successfully applied for the assay of the interested PRO drug in urine samples, and further extended to the investigation of the excretion of the drugs by monitoring the variation of the concentration of PRO in urine within 10 h after drug-taking.

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1. Introduction

Stir bar sorptive extraction (SBSE) is a novel environmentally friendly microextraction technique which was developed from solid phase microextraction (SPME) in 1999 [1]. The extraction mechanism of SBSE is similar to that of SPME, which is based on the partitioning equilibrium of target analyte between the extraction phase and the sample matrix [2]. The main difference between SPME and SBSE is that the extraction phase involved in SBSE is about 50–250 times larger than that in SPME, resulting in higher abso-

lute recoveries and higher sample capacity. Due to its advantages of simplicity, rapidity, sample clean-up ability and high extraction efficiency, SBSE has been successfully applied in environmental, food and biological samples. The selectivity and extraction efficiency of SBSE are mainly determined by the stir bar coatings. An ideal stir bar coating should be capable of enriching the target molecules with high enrichment factors, whilst leaving other interfering substances in the sample matrix [2]. However, only polydimethylsiloxane (PDMS), ethylene glycol (EG)-silicone and polyacrylate (PA) are the commercially available coatings for stir bar presently, limiting the application of SBSE in the real-world samples. Therefore, the development of novel stir bar coatings with high affinity and selectivity towards target analytes is of great interest.

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Molecularly imprinted polymers (MIPs) are stable polymers with selective molecular recognition abilities, provided by the template used during their synthesis [3]. Synthesis of MIPs involves three steps: (1) the template molecule integrates with the functional monomer by covalent or noncovalent binding forces; (2) the formed complexes react with a cross-linking agent to form the polymer material; (3) the template molecule is removed. Due to the high selectivity and stability, MIPs have been successfully applied in SBSE as a special coating to improve the selective extraction capability for target analytes. MIPs coated stir bar was first reported by Zhu et al. [4]. They applied the phase-inversion imprinting technique to prepare the MIP coated stir bar with a nylon-6 polymer solution. Compared with the conventional coating (non-MIP coating) based stir bars, the MIP coated stir bars showed not only high selectivity but also rapid adsorption dynamics. In the phase inversion imprinting system, the MIPs were casted from the polymer solutions of the template molecule rather than polymerized from monomers, while a commercial PDMS-coated stir bar is necessary as a substrate during the preparation. Li's research group [5–8] developed an *in-situ* synthesis method for linking the MIP to the stir bar by chemical bonding, which was realized through silylation of the substrate surface and then multiple co-polymerization reactions. The MIP coated stir bars were successfully applied to the determination of β_2 -agonists in animal-derived food samples [5], triazole herbicides in agricultural products [6], triazole fungicides in soil [7], and sulfa drugs in food samples [8], 2-aminothiazoline-4-carboxylic acid in forensic urine [9], and sulfonylurea herbicides in water and soil [10], respectively. The MIP coating chemically bonded to the glass bar was homogeneous and porous and showed good mechanical and chemical stability. Gomez-Caballero et al. [11] designed a chiral MIP-SBSE device for selectively extracting (S)-citalopram from a racemic mixture in aqueous media. The prepared MIP coated stir bar was proved to be significant for the pre-concentration of *enantio*-specific sample and subsequent analysis without the need of chiral chromatographic separation. To prevent the template bleeding problem, Sheng et al. [12] and Zhan et al. [13] prepared dummy MIP coated stir bars for bisphenol A (BPA) analysis using 3,3',5,5'-tetrabromobisphenol A (TBBPA) as dummy template molecule. Besides, our research group [14] also prepared an MIP coated stir bar with cyromazine as a dummy template for the determination of target melamine. The dummy-MIP coated stir bar showed better selectivity than the bars coated with PDMS or non-imprinted polymers in the extraction of target analytes.

Nowadays, numerous analytes of interest are mainly present in water, and the separation/pre-concentration needs to be carried out in aqueous environment, such as organic molecules in wastewater or body fluids. However, traditional MIPs are usually synthesized in an aprotic organic solvent, and exhibited good extraction performance only in a non-aqueous environment [15]. The possible main reason is that the recognition of template by the traditional MIPs is mainly mediated by hydrogen bonds between the template and the functional groups on the MIPs, and the nonspecific adsorption is mainly caused by the hydrophobic or ion-exchange sites of the materials. Therefore, it is necessary to develop water-compatible MIPs, which can bind target molecules in a specific and selective manner in aqueous samples. Haginaka et al. [16] specified that water molecular played an important role in target binding by MIPs in a water environment. To maintain target-specific binding and reduce the hydrophobic nonspecific interactions between the template and the polymer matrices in aqueous solution, a hydrophilic external layer surrounding the MIPs was formed in a water-based system by using a mixture of methanol and water as the porogenic solvent [17–22], which were demonstrated to be effective in the improvement of the recognition ability of template molecular in aqueous solution.

Except for the incompatibility in aqueous media, MIPs prepared by the conventional technique also present the disadvantage of low adsorption capacity. In recent years, carbonaceous nanomaterials, especially graphene and carbon nanotubes, have been used as MIPs supporters to improve the adsorption capacity due to their large surface area and unique structure [23–26]. Graphene oxide (GO) is a precursor to graphene (G) after reduction, which consists of a hexagonal carbon network bearing hydroxyl and epoxide functional groups on its “basal” plane [27,28]. The large surface area, high surface-to-volume ratio and rich oxygen-containing functional groups of GO make it possible to improve the binding kinetic properties and adsorption capacities in the adsorption process. Qiu et al. [29,30] prepared two kinds of graphene oxide-magnetite-molecularly imprinted polymers (GM-MIP) for selective determination of (L)-tryptophan and epinephrine, respectively. The addition of GO was confirmed to improve the adsorption capacity of MIPs, and the adsorption capacity of GM-MIP (11.4×10^{-5} mol/g) was much higher than common MIP (1.2×10^{-5} mol/g).

In this work, a GO/MIP coated stir bar was prepared by *in situ* polymerization for selective extraction of propranolol (PRO) as model analyte. To improve the selectivity in aqueous environment, the ratio of water and methanol was optimized for the water-compatible MIP polymerization. Besides, GO was uniformly doped in the preparation of MIP to improve the adsorption capacity. Due to the special binding sites on the GO/MIP coating, PRO could be selectively adsorbed in aqueous samples. Based on it, a method of GO/MIP-SBSE-high performance liquid chromatography-ultraviolet detector (HPLC-UV) was developed for the selective determination of PRO in urine samples, and further extended to the investigation of the excretion of the drugs by the monitoring of the variation of the concentration of PRO in urine. The prepared GO/MIP coated stir bar presented a good specific recognition ability, water compatibility and high adsorption performance.

2. Experimental

2.1. Reagents and standards

Propranolol (PRO) and other six cardiovascular drugs (xylocaine, XYL; metoprolol, MET; mexiletine, MEX; labetalol, LAB; carvedilol, CAR; propafenone, PPF) were all analytical grade and obtained from Aladdin Reagent Database Inc. (Shanghai, China). Among them, PRO was the target analyte and template for GO/MIP preparation, respectively; other six cardiovasculars were employed to investigate the selectivity of self-prepared GO/MIP coating for PRO. The structure, pK_a and $\log P$ of PRO and other six cardiovascular drugs are listed in Table S1. Each standard solution of target analytes (500 mg L^{-1}) was prepared in methanol. Working standard solutions were prepared by diluting the mixed standard solution with pure water to the required concentration. All standard stock solutions were kept in refrigerator at 4°C away from light.

Methacrylic acid (MAA) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Azodiisobutyronitrile (AIBN) was obtained from Shanghai No. 4 Reagent & H. V. Chemical Co., Ltd. (Shanghai, China). Ethylene glycol dimethyl acrylate (EGDMA) was obtained from Aladdin Reagent Database Inc. (Shanghai, China). γ -(Methacryloxypropyl) trimethoxysilane (KH-570) was obtained from WD Silicone Co., Ltd. (Wuhan, China). Methanol (CH_3OH), acetone (CH_3COCH_3), toluene ($\text{C}_6\text{H}_5\text{CH}_3$), dichloromethane (CH_2Cl_2), sodium dihydrogen phosphate (NaH_2PO_4), sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid (CH_3COOH , HAc), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were all analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). High purity deionized water was purified using a Milli-Q water purification system ($18.2 \text{ M}\Omega \text{ cm}$, Millipore, Mol-

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