

Preparation and Application of Polyimide Coated Stir Bar for Extraction of Phenols in Environmental Water Samples

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Abstract: A polyimide coated stir bar for sorptive extraction (SBSE) was prepared by immersion precipitation method and evaluated by using 5 phenols and chlorinated phenols as model samples. The highest extraction efficiency was achieved among all commercial extraction phases of SBSE reported. Experimental parameters including stirring speed, ionic strength, extraction temperature, extraction time, desorption temperature and time were optimized. Under the optimal conditions such as 100 mL of sample, 30% NaCl, extraction time of 30 min, stirring speed of 800 rpm and extraction temperature of 25 °C, the target compounds were recovered by thermal desorption at 300 °C for 4 min. More than two orders of magnitude of linearity were obtained ($R \geq 0.9995$). LOQs ($S/N = 10$) were 0.028–0.123 $\mu\text{g L}^{-1}$, and RSDs were in the range of 1.6%–9.7%. The polyimide SBSE coupled with gas chromatography-mass spectrometry was applied to the extraction and analysis of phenols in real samples, including tap water, sea water, and waste water. It was found that the polyimide SBSE showed high selectivity towards polar compounds and high thermostability up to 350 °C.

Key Words: Polyimide, Stir bar; Solid phase extraction; Thermal desorption; Phenols

1 Introduction

Phenols are prevalently existed in the environmental waters because of their wide use in industrial production^[1–3]. Due to the toxicity, bioaccumulation, persistence in the environment and carcinogenic properties, China, European Union (EU), and US Environmental Protection Agency (EPA) have classified phenol, chlorophenols, and cresols as priority pollutants^[4–6]. However, it is still challenging to quantify these phenols because of the low extraction efficiency due to their good water solubility, and high desorption temperature for some phenols with boiling points up to 360 °C.

Solid phase microextraction (SPME)^[7] and stir bar sorptive extraction (SBSE)^[8,9] are two kind of green sample preparation techniques, which eliminate the use of solvents, and combine sampling and enrichment in one step. In contrast with SPME, the volumes of extraction phase in SBSE stir bars (from 24 μL

to 126 μL) were tens to hundreds of times larger than that in SPME fibers (maximum 0.5 μL), which led to higher sample extraction capacity and better reproducibility, and was suitable for trace analysis^[8]. After extraction, the analytes extracted on the coated stir bar were desorbed by thermal or liquid desorption before chromatographic separation^[10]. Thermal desorption (TD) is the most commonly used technique, and the extracted compounds can be completely introduced into chromatographic system^[11,12]. Therefore, the thermostability of coatings is a crucial factor besides the extraction capacity and efficiency.

So far, the commercially-available coatings for SBSE are classified into three main types: (1) Polydimethylsilicone (PDMS), which is thermostable up to 320 °C and is widely used for extraction of apolar and weakly polar compounds. However, the PDMS phase showed low extraction efficiency towards phenols^[13] and steroid hormones^[14]. (2) Polyethylene glycol-modified silicone (EG Silicone Twister) and

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polyacrylate with a proportion of PEG (Acrylate Twister), their highest thermal desorption temperatures are under 200 °C and 220 °C, respectively^[15–19]. (3) Poly(phthalazinone ether sulfone ketone) (PPESK), which is thermostable up to 290 °C and has been successfully used for extraction of polar compounds and aromatic hydrocarbon^[20,21]. However, for the compounds with boiling points higher than 360 °C, there is lack of extraction phases with both excellent thermostability above 300 °C and good affinity towards polar analytes such as phenols.

As one kind of engineering plastics, polyimide (PI) possesses excellent physical and chemical properties. It can withstand up to 350 °C and chemical resistance to most organic solvents. Polyimide has the potential to be used as one kind of SBSE extraction phase for polar compounds based on π - π interaction and polar functional groups, such as imide-group and acyl-group polyimide coated stir bar was prepared by immersion precipitation technique, and was evaluated by stir bar sorptive extraction/thermal desorption-gas chromatography (SBSE/TD-GC) method with standard phenol samples and environmental water samples.

2 Experimental

2.1 Instruments and reagents

The following instruments were used: Shimadzu GC (2010 plus, Shimadzu) equipped with a FID, Shimadzu GC-MS (QP2010 plus, Shimadzu), magnetic stirring apparatus (DF-101S, Gongyi Yuhua Instrument Co., LTD, China), and homemade thermal desorption unit (TDU).

Polyimide (PI, 25% w/V, 50–80 Pa s, 150 kg mol⁻¹) was purchased from Changchun Gaoqi Polyimide Materials Co., Ltd., China. Dimethylsilicone and curing agent were obtained from DOW Coring (Michigan, UAS). Poly(phthalazine ether sulfone ketone) (PPESK) was purchased from Dalian Polymer New Material Co. (China). Standard solution containing 8 PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene, each at 2000 mg L⁻¹ in benzene/methylene dichloride (1:1, V/V)) was purchased from AccuStandard Inc (New Haven, USA). Hexadecane, heptadecane, octadecane and nonadecane were obtained from Shanghai Chemical Reagent Co. (China). 2-Chlorophenol (2-CP), 2,6-Dimethylphenol (2,6-DMP), 2-Nitrophenol (2-NP), 2,4-Dichlorophenol (2,4-DCP) and 2,4,6-Trichlorophenol (2,4,6-TCP) were purchased from Tianjin Guangfu Fine Chemical Research Institute (China). Mixed stock solution of phenols and *n*-alkanes each at 100 mg L⁻¹ was prepared in methanol and *n*-hexane, respectively. Mixed stock solution of PAHs at concentration of 100 mg L⁻¹ was prepared via dilution of the PAHs standard solution with methanol. All the stock solutions were stored at -21 °C. Working standard solutions were freshly prepared via dilution of the stock solutions with purified water (Wahaha Group Co.,

Ltd, Hangzhou, China).

Waste water was collected from the sewage outlet into sea (Dalian, China). Sea water was collected from Xinghai Bay (Dalian, China). Tap water was sampled in our laboratory. All the samples were stored at 4 °C for at most two days.

2.2 Chromatographic conditions

2.2.1 GC conditions

The separation of the test phenols was performed on a 30 m × 0.53 mm I.D. × 1 μ m, SE-54 capillary column (Dalian Scien-Tech Instrument Inc., Dalian, China). Nitrogen of 5N grade was served as carrier gas with a constant flow of 4 mL min⁻¹. The temperature of the injector and detector was maintained at 300 °C. The initial GC oven temperature was 40 °C for 1 min, and then programmed at a rate of 20 °C min⁻¹ to a final temperature of 260 °C and held for 5 min.

2.2.2 GC-MS conditions

Separation was performed on a 30 m × 0.32 mm × 1 μ m SE-54 capillary column (Dalian Scien-Tech Instrument Inc., Dalian, China). Helium of 5N grade was served as the carrier gas. Programmed pressure mode was used, and the initial pressure was 20 kPa for 1 min, then rose to 50 kPa at a rate of 100 kPa min⁻¹ and held for 5 min. The temperatures of the GC injector, GC to MS transfer line, and MS ion source were maintained at 300, 250, and 200 °C, respectively. The initial GC oven temperature was set at 40 °C for 1 min, and then programmed at a rate of 20 °C min⁻¹ to a final temperature of 250 °C and held for 1 min. The electron energy was set at 70 eV. Selected ion mode (SIM) with two characteristic ions for each compound was selected for quantitative analysis of phenols^[22], while scan mode was selected for qualitative analysis of waste water.

2.3 Preparation of stir bars

2.3.1 Polyimide coated stir bars

Polyimide coated stir bars were prepared by immersion precipitation technique. First, PI solution (15%, w/V) was prepared by diluting the polymer with DMF, the glass tube embedded with a iron bar was immersed into the prepared polyimide solution, and then put out with a tweezer at a speed of 2 mm s⁻¹, then the coating on the surface of stir bar was precipitated out by immersing it into water at room temperature for 12 h. Subsequently, the coated stir bars were dried under vacuum overnight at 100 °C to remove DMF in the coating, and then thermally aged under nitrogen purge in a quartz tube in a GC oven. The temperature program for the aging process was as follows: 40 °C for 20 min, 3 °C min⁻¹ to

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