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# Covalent immobilization of metal organic frameworks onto chemical resistant poly(ether ether ketone) jacket for stir bar extraction

Chenlu Wang<sup>a, b</sup>, Wei Zhou<sup>a</sup>, Xiaoyan Liao<sup>a</sup>, Xuemei Wang<sup>a</sup>, Zilin Chen<sup>a, b, \*</sup>

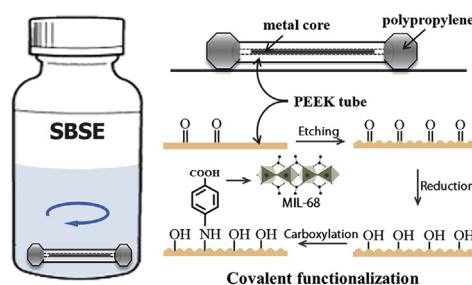
<sup>a</sup> Key Laboratory of Combinatorial Biosynthesis and Drug Discovery, Ministry of Education, Wuhan University School of Pharmaceutical Sciences, Wuhan, 430071, China

<sup>b</sup> State Key Laboratory of Transducer Technology, Chinese Academy of Sciences, Beijing, 10080, China

## HIGHLIGHTS

- PEEK material was first used as jacket for SBSE device.
- The PEEK jacket based SBSE device showed excellent physical and chemical stability.
- Covalent modification method was used to functionalize the PEEK material.
- MIL-68 crystals were *in situ* immobilized onto PEEK jacket as stationary phase.
- The developed SBSE device showed excellent extraction efficiency towards parabens.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Preparation of stir bar extraction (SBSE) device with high physical and chemical stability is important and challenging by date. A novel poly (ether ether ketone) (PEEK) tube with excellent mechanical property and chemical stability was firstly used as jacket of metal bar for preparation of stir bar. By employing covalent modification method, the inherent chemical resistant problem of PEEK which restricts the modification of sorbents was well solved. After functionalization, plenty of benzoic acid groups were formed onto the PEEK jacket. Metal organic frameworks of aluminium-based Materials of Institute Lavoisier-68 (MIL-68) was *in situ* immobilized onto the PEEK surface (MIL-68@PEEK) by the bonding with benzoic acid groups. Afterwards, a facile dumbbell-shaped structure was designed for reducing the friction between sorbents and bottom of container. Due to superior property of the PEEK jacket and the covalent modification method, the MIL-68 modified PEEK jacket SBSE device showed good robustness. After coupling with HPLC-MS/MS, the MIL-68@PEEK-based SBSE device was used to analyse of three parabens including methyl paraben, ethyl paraben and propyl paraben. The method had low limit detection up to 1 pg mL<sup>-1</sup> with good linearity ( $R^2 \geq 0.9978$ ) and good reproducibility (relative standard deviation  $\leq 9.74\%$ ). The method has been applied to the detection of parabens in cosmetics and rabbit plasma after painted with cosmetics with recoveries between 73.25% and 104.23%.

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\* Corresponding author. School of Pharmaceutical Sciences, Wuhan University, Wuhan, 430071, China.

E-mail address: [chenzl@whu.edu.cn](mailto:chenzl@whu.edu.cn) (Z. Chen).

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## 1. Introduction

High efficient and selective sample pretreatment is very

important for analysis of real sample. Stir bar sorptive extraction (SBSE) is a simple and green sample pretreatment technique which has the advantages like rapid, solvent-free, and economical when compared with commonly used liquid-liquid extraction and solid-phase extraction [1]. In comparison to solid phase microextraction (SPME), SBSE has larger extracting capacity (24–126  $\mu\text{L}$ ) than SPME fiber (maximum 0.5  $\mu\text{L}$ ), which contributes to its high capacity [2]. In the past few years, SBSE based method has been widely applied in environmental, food and biological research [3–9].

Commonly used SBSE devices are constituted by three major parts, including a magnetic stirring rod for stirring, a glass jacket for covering the rod and immobilized sorbents for extraction [8]. The glass jacket can prevent the oxidation of the metal rod, and provide active silanol groups for the modification of sorbents. However, the glass jacket is fragile and easy to be broken under ultrasonication or carelessly crashed [9]. The friction between stir bar and container will also destroy the sorbents [10]. To solve these problems, Ochiai et al. invented a SBSE method with two stir bars, the stable one was stirring at the bottom, and the unstable one was attached on the inner wall of the container [11]. Neng et al. developed a suspended stir bar by coating polyethylene hollow cylindrical tubes with adhesive film [12]. So during the sampling, the stir bar was suspended on the top of the solution, and the other magnetic stir bar was stirring at the bottom. Both of these designs are relatively complex and inconvenient. The previous work in our group developed a jacket-free SBSE device, in which the sorbents are directly immobilized onto the stainless steel wire by polydopamine functionalization method [9,13]. However, when using this device, the metal rod was exposed into sample solution, which would be corroded after long time use under acidic condition. And the polydopamine layer is not sufficiently stable in some extreme conditions. Developing a new SBSE device with high physical and chemical strength is important and challenging by date.

Poly (ether ether ketone) (PEEK) is a kind of plastic material and has been widely used in microfluidic devices and liquid chromatography due to its excellent properties like high strength, high chemical resistance, good flexibility and easy to be cut [14,15]. It is an ideal jacket material for SBSE, but the high chemical resistance of PEEK material makes it difficult to be modified. To the best of our knowledge, there is no work reported on using of PEEK jacket for the SBSE device. In the previous work, mussel-inspired polydopamine modification method can realize functionalization of PEEK material and used in in-tube SPME [16,17]. However, the non-covalent interaction between polydopamine layer and PEEK surface is not sufficiently stable in some organic solvents especially dimethyl formamide (DMF), which are usually used in the synthesis of metal-organic framework (MOFs). As we know, the chemical resistance of PEEK material is due to the low reaction activity of monomer (oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) and tight molecules packing [18,19]. Therefore, if an appropriate method is introduced to decrease the molecules packing density of PEEK material and reduce the carbonyl groups in monomer to hydroxyl groups, then we might be able to functionalize the surface of PEEK tube by covalent method, which may improve the stability of the modified layer.

MOFs, a new class of porous hybrid crystalline materials, was constructed by coordination bonds between metal ions and organic linkers. MOFs present good properties like uniform structured nanoscale cavities, high adsorption affinity, ease preparation and adequate chemical stability [20]. These features, along with the high specific area and good adsorption affinity, make MOFs to be satisfactory material for application in extraction, separation, energy conversion and storage [21–24]. Aluminium-based ( $\text{Al}^{3+}$ ) Materials of Institute Lavoisier-68 (MIL-68) is a kind of MOFs which assembled from the infinite straight chains of  $\text{AlO}_4(\text{OH})_2$  that are

connected with each other through hydroxyl groups and terephthalate ligands [25,26]. Compared with currently used extraction phase in SBSE device like PDMS, organic polymer and other small organic molecules, MIL-68 possesses porous structure and large specific area, which is beneficial to the adsorption in the SBSE process. Besides, the three-dimensional networks of MIL-68 with uniform structured nanoscale cavities (intensively distributed around 11 Å) are good for the selective extraction of small molecules. The MIL-68 has already shown high adsorption capacity towards many organic pollutants like aniline, nitrobenzene and phenol [27,28].

Parabens (alkyl esters of *p*-hydroxybenzoic acid) are extensively used preservatives in cosmetics and personal care products such as sunscreen cream, day cream and *anti*-perspirant deodorants [29]. They have an extensive antibacterial spectrum and wide pH range, which are often used for antifungal. However, the chemicals structure of parabens has weak estrogenic properties which can disrupt human endocrine system and lead to breast cancer by dermal contact [30]. The maximum total concentration of parabens allowed by Europe (EU) law in consumer products is 8 g of parabens per kg of cosmetic product (EU Cosmetics Directive 76/768/EEC) [31]. Simultaneous extraction and detection of trace amounts of commonly used parabens including methyl paraben, ethyl paraben and propyl paraben in consumer products and biological samples after painting with cosmetics is important for quality control and studying effect to our health. The three-dimensional networks of MIL-68 have two types of channels with triangular pores and hexagonal pores. The possible hydrophobic and host-guest interactions due to the similar hexagonal pores of MIL-68 and size of the three parabens inspired us to investigate using MIL-68 for high selective and effective extraction of parabens.

In this work, a dumbbell-shaped PEEK jacket SBSE device was first developed. We described a novel covalent modification method for the immobilization of MIL-68 crystal onto the chemical resistant PEEK jacket. Firstly, the PEEK material was etched by concentrated sulfuric acid for construction of porous surface with more exposed ketone groups. Through reduction and substitution reaction, benzoic acid group was bonded onto the surface, which can be the anchor for *in situ* covalent immobilization of MIL-68 layer. Afterwards, a facile dumbbell-shaped device was prepared by simply burning a pipette tip and dropping to the both ends of the PEEK tube. The dumbbell shape of the SBSE device can obviously decrease the friction between sorbents and container, which significantly improved the stability. Due to the special host-guest interaction between MIL-68 and three parabens, the developed MIL-68 modified dumbbell-shaped PEEK jacket (MIL-68@PEEK) SBSE device showed remarkable selectivity and good extraction efficiency. On the basis of the MIL-68@PEEK device, a high sensitive SBSE-HPLC-MS/MS method was developed for the analysis of three parabens including methyl paraben, ethyl paraben and propyl paraben in cosmetics and rabbit plasma after painted with cosmetics with low limit detection of 1–2  $\text{pg mL}^{-1}$ .

## 2. Experimental section

### 2.1. Materials and instrumentation

See [Supplementary material](#).

### 2.2. Functionalization of the PEEK jacket

A 3 cm PEEK tube (1/16 inch o. d., 750  $\mu\text{m}$  i. d.) was washed with acetone and methanol thoroughly and dried at 60 °C for 3 h. The etching of PEEK tube was according to our previous work [18]. PEEK tube was dipped in 98% concentrated sulfuric acid for 120 s, washed

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