



Multiple monolithic fiber solid-phase microextraction: A new extraction approach for aqueous samples



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ABSTRACT

A novel multiple monolithic fiber solid-phase microextraction (MMF-SPME) was designed and prepared. Two steps were involved in the preparation of MMF-SPME. Firstly, single thin fiber (0.5 mm in diameter) was prepared by co-polymerization of vinylimidazole and ethylene dimethacrylate. Secondly, several thin fibers were bound together to obtain the MMF assembly. The extraction and desorption dynamics of MMF-SPME with different numbers of fibers were studied in detail. In order to demonstrate the usability of the new MMF-SPME, the extraction performance of MMF-SPME for 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol was investigated in direct SPME mode. Results indicated that aqueous samples could form convection effectively within MMF-SPME because there were gaps between fibers. The extraction procedure was accelerated by the convection. At the same time, the MMF-SPME possessed high extraction capacity because more sorbent was employed. Under the optimized extraction conditions, low detection limits ($S/N=3$) and quantification limits ($S/N=10$) for the target analytes were achieved within the range of 0.13–0.29 $\mu\text{g/L}$ and 0.44–0.98 $\mu\text{g/L}$, respectively. The MMF-SPME also showed a very long lifespan and good repeatability. Finally, the MMF-SPME was successfully applied to the analysis of tap, lake and ground water samples with spiked recoveries in the range of 73.8–101%.

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1. Introduction

Solid-phase microextraction (SPME) is a robust, simple, relatively fast, low or solvent-free extraction and sampling method. Since the first introduced by Pawliszyn's group in the early 1990s [1], SPME has gained a remarkable progress and been widely applied in environmental, biological and pharmaceutical analysis [2–8].

In SPME, the essential part lies in the extraction medium, which determines the extraction performance and thus the sensitivity and precision of the analysis. Typically, the extraction medium is coated on fiber such as silica, platinum or gold materials [9–12]. Up to now, a series of commercial polymer-coated fibers including polydimethylsiloxane (PDMS), divinylbenzene (DVB), polyacrylate (PA) and their copolymers are available for SPME (<http://www.sigmaaldrich.com/china-mainland/zh/analytical-chromatography/sample-preparation.html>). Besides, a number

of lab-made coatings such as nanomaterials [13], molecularly imprinted polymers [14], ionic liquids [15], mesoporous silica [16] have been developed for SPME. However, the coated fibers suffered from insufficient chemical/thermal coating stability. More important, the extraction capacity of coated fibers was limited because the coatings were thin and low extraction media were employed. Recently, substrateless fibers such as pencil lead [17–20], graphene [21] and carbon [22] for SPME have been developed. Compared with coated fibers, more extraction media were used in these fibers. Therefore, the substrateless fibers possessed higher extraction capacity than coated fibers. However, in substrateless fibers, longer time should be spent in order to reach extraction equilibration because of the thick sorbents. Hereby, to further develop SPME technology, there is still a necessity to synthesize novel extraction materials and develop new formats, affording high extraction capacity, quick extraction speed, high stability and capital saving.

Monolith was first introduced by Hjerten et al. [23] in 1989 and subsequently investigated by other research groups [24–29]. Monoliths possess numerous outstanding advantages such as simple preparation, high reproducibility, versatile surface chemistries and fast mass transfer. Based on these outstanding characteristics,

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monoliths have been widely acted as stationary phase in HPLC, capillary HPLC and capillary electrochromatography (CEC). Moreover, monoliths also play an important role in sample preparation including SPME [30–32]. In 2007, molecularly imprinted polymeric fibers using silica capillaries as molds were first reported by Martin-Esteban [33]. The preparation of monolith-based fibers was very simple and easy. The results indicated that the recoveries increased with the increase of the thickness of fibers. However, in order to enhance the extraction performance, relatively long extraction time (60 min) was adopted in enrichment procedure. Lee et al. also synthesized imprinted polymeric fibers for SPME using fused silica capillaries (0.53 μm) as molds [34]. The results showed that extraction equilibrium did not reach until 60 min. The previous research well demonstrates that porous monoliths can act as the substrate-less extraction fibers for SPME. However, increasing the extraction capacity and shortening the extraction equilibrium time are still needed to be solved.

Chlorophenols (CPs) are widely distributed in the environment as a result of degradation of some pesticides [35] or during the chlorination of drinking water [36]. CPs are highly toxic including estrogenic, mutagenic and carcinogenic effects [36]. Therefore, a number of official regulatory organizations have set maximum environmental concentrations. For example, a maximum allowable concentration (MAC) has been established for pentachlorophenol (PCP) (1 $\mu\text{g/L}$) in inland and other surface waters by European Union [37]. China also set maximum concentration for PCP of 9 $\mu\text{g/L}$ in tap water [38]. Therefore, it is vital to develop simple and sensitive method to determine CPs in water samples.

In this study, a novel monolith-based extraction approach for aqueous samples was designed and prepared. The new approach was termed multiple monolithic fiber SPME (MMF-SPME). The MMF-SPME is consisted of four independent thin monolithic fibers. In MMF-SPME, the aqueous samples can form convection during extraction because there are gaps between fibers. The formation of convection accelerates the extraction procedure. At the same time, the total amount of sorbent in MMF-SPME is larger than that of single fiber. Therefore, the MMF-SPME possesses higher extraction capacity. In present study, MMF-SPME based on poly(vinylimidazole-ethylene dimethacrylate) monolith was prepared, and its extraction performance for four CPs was selected as a paradigm for the practical evaluation of MMF-SPME.

2. Experimental

2.1. Chemicals and materials

Vinylimidazole (VI) (99%) and ethylene dimethacrylate (EDMA) (97%) were supplied by Alfa Aesar (Tianjin, China); Azobisisobutyronitrile (AIBN) (97%, recrystallized before use), 1-propanol (97%), 1,4-butanediol (98%) (distilled before use) were purchased from Shanghai Chemical Co. (China); trifluoroacetic acid (TFA) (98%) was supplied by Xilong Chemical Co. (Guangzhou, China); HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia (Fairfield, USA); Water used throughout the study was purified using a Milli-Q water purification system (Millipore, USA). 2-Chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) were purchased from Aladdin Chemical Co. (Shanghai, China). Glass capillaries (10 cm in length, 1.0 mm or 0.5 mm in diameter) were supplied by Shanghai Xinpeng Glass and Instrumental Co. (Shanghai, China).

A standard solution of 100 mg/L of each compound was prepared in methanol and renewed monthly. The standard mixtures of CPs were prepared by dissolving 2.00 mg of each compound in methanol in 100 mL volumetric flask. The stock solution was stored at 4 °C and diluted with Milli-Q water to give the required concentration.

Tap, ground, and lake water samples were collected in Xiamen city and filtered through 0.45 μm membranes. All the samples were stored in brown bottles at 4 °C in the refrigerator.

2.2. Instruments

HPLC analyses were carried out on a LC chromatographic system (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20A). Sample injection was carried out using a RE3725i manual sample injector with a 20 μL loop (Rheodyne, Cotati, CA, USA), all experiments were performed at room temperature. The morphologies of monolithic materials were examined by a Model XL30 scanning electron microscopy (SEM) instrument (Philips, Eindhoven, The Netherlands).

2.3. Chromatographic conditions

The separation of CPs was performed on a Thermo Hyper-sil GOLD C18 column (5 μm particle size, 250 mm \times 4.6 mm i.d.). Optimum separation was obtained with a binary mobile phase composed of ultrapure water (solvent A, with 1.0% TFA) and ACN (solvent B). The gradient elution program was as follows: 0–8.0 min = 60% B, 8.0–8.1 min = 90% B and kept to 15 min, 15–20 min = 60% B and kept to 25 min. The detector wavelength was set at 280 nm for 2-CP and 295 nm for other CPs; the flow rate was 1.0 mL/min; and injection volume was 20 μL .

2.4. Preparation of MMF-SPME

The preparation procedure of MMF-SPME is very simple and convenient. It includes two steps. The first step is the synthesis of single thin poly(vinylimidazole-ethylene dimethacrylate) monolithic fiber (VEMF). AIBN was used as polymerization initiator (1% (w/w) of the total monomer amount) in all the polymerization reaction. The mixture of 40% (w/w) 1-propanol and 60% (w/w) 1,4-butanediol was used as porogen. In monomer mixture, the ratio of VI to EDMA was 30/70 (w/w). The ratio of monomer mixture (30% (w/w) VI and 70% (w/w) EDMA) to porogen was 60/40 (% (w/w)). The monomer mixtures, porogen and AIBN were mixed ultrasonically into a homogenous solution, and then the reactant solution was purged with nitrogen for 3 min. Subsequently, the reactant mixture was introduced into a glass capillary (0.5 mm in diameter and 10 cm in length) with the aid of a syringe. After that, both ends of capillary were sealed with two small pieces of rubber. The filled glass capillary was placed in an oven and heated at 70 °C for 12 h. After the polymerization, 2 cm length of glass capillary was cut off carefully with grindstone. Firm, integrated and elastic monolithic fiber (2 cm in length and 0.5 mm in diameter) (Fig. 1a) was obtained. Thick VEMF (1.0 mm in diameter) was synthesized as the same procedure described as above. In the second step, several thin VEMFs were carefully tied up with parafilm at the glass part of VEMF to form fiber bunch. It is worthy to notice that the part of monoliths should be aligned to the edges and it cannot be bound. Then, the fiber bunch was dipped in methanol for 24 h to remove the residual monomers, porogen and uncross-linked polymers. Finally, the fiber bunch was dried in air for 1 h to obtain the final MMF-SPME. Figs. 1a and b show the photos of single thin VEMF and MMF-SPME with four VEMFs, respectively.

2.5. MMF-SPME procedure

Stirring extraction and liquid desorption (LD) modes were used in this work. The MMF-SPME was activated with methanol and ultrapure water in sequence. A volume of 20 mL of sample solution was added into a 25 mL vial containing an 8 mm \times 2 mm stirring bar. MMF-SPME was performed by direct immersion of the fiber bunch

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