



Etched Stainless Steel Wire as Solid-Phase Microextraction Fiber for Determination of Polychlorinated Biphenyls in Water Sample

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Etched stainless steel wire was simply fabricated and used as a solid-phase microextraction fiber to determinate polychlorinated biphenyls in water sample. The morphology and structure of the proposed fiber was characterized and elucidated by scanning electron microscope. Experimental parameters, including the extraction mode, extraction temperature, extraction time, desorption time were examined and optimized. Under the optimized conditions, a good analytical performance was achieved and the etched stainless steel fiber displayed a better extraction capability than commercial fiber. Furthermore, the spiked recoveries at 80 ng L⁻¹ for real river water were in the range of 88.9-98.9 %, which confirmed the feasibility of the developed method.

Keywords: Solid-phase microextraction, Etched stainless steel wire, Polychlorinated biphenyls, Gas chromatography.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of synthetic hydrocarbon compounds in which hydrogen atoms on the biphenyl structure were substituted by chlorine atoms. Owing to the quality of chemical stability, inoxidizability, thermal stability and electric insulativity, polychlorinated biphenyls were broadly utilized for industrial applications [1,2]. Nevertheless, these compounds were classified as persistent organic pollutants and considered to be harmful to the environment and human health [3,4]. Polychlorinated biphenyls can be detected in environmental samples in spite of the fact that they have been banned since the 1970s. Hence, developing an appropriate analytical method to quantify polychlorinated biphenyls is desirable. Gas chromatography-electron capture detector (GC-ECD) and gas chromatography-mass spectrometry (GC-MS) were typical methods in determination of polychlorinated biphenyls [5,6]. It is notable that pretreatment process is necessary for trace analysis before separation by GC system. Traditional pretreatment techniques, *i.e.* liquid extraction [7] and solid phase extraction (SPE) [8], have been used for pre-concentration of polychlorinated biphenyls, even though they were complicated and time-consuming. In recent years, solid-phase microextraction (SPME) has also been employed due to its unique merits of solvent-free, time-saving and simplicity [9,10].

As a promising pretreatment technique, SPME integrates sampling, isolation and enrichment into one step and has been extensively applied in analysis of analytes at trace-level since appearing in 1990s [11]. In SPME device, fiber is the crucial part. Although several commercial fibers were available, their drawbacks (*e.g.*, mechanical fragility, low using temperature, solvents instability and high-cost) restricted the development of SPME [12]. To overcome these troubles, many efforts were made. The traditional fused silica support was replaced by metal wires with high mechanical stability, containing aluminum wire [13], platinum wire [14], zinc wire [15], NiTi alloy [16] and stainless steel wire [17], *etc.*

Stainless steel wire (SS) is a low-cost material with excellent mechanical stability and chemical stability. In previous reports, various sorbent coatings, especially organic coating [18] and nano-metallic materials [19] were prepared based on the surface of stainless steel wire. However, stainless steel wire still be used as extraction fiber without additional coatings. It was first reported by Yan *et al.* that stainless steel wire which was simply etched by hydrofluoric acid exhibited high affinity to polycyclic aromatic hydrocarbons (PAHs) [20]. Similarly, Zhao *et al.* [21] confirmed that the etched stainless steel wire was suitable to extract polybrominated diphenyl ethers (PBEDs).

Inspired by this, the etched stainless steel wire fiber was fabricated and its potential in extraction of polychlorinated

biphenyls was systematically studied in this work. We intended to develop a reliable, rapid method for the analysis of polychlorinated biphenyls in environmental water samples.

EXPERIMENTAL

The polychlorinated biphenyl congeners (2 g L⁻¹ for each), 3,3',4,4'-TeCB (PCB77), 3,4,4',5-TeCB (PCB81), 2',3,4,4',5-PeCB (PCB123), 2,3',4,4',5-PeCB (PCB118), 2,3,4,4',5-PeCB (PCB114), 2,3,3',4,4'-PeCB (PCB105), 3,3',4,4',5-PeCB (PCB126), 2,3',4,4',5,5'-HxCB (PCB167), 2,3,3',4,4',5-HxCB (PCB156), 2,3,3',4,4',5'-HxCB (PCB157), 3,3',4,4',5,5'-HxCB (PCB169) and 2,3,3',4,4',5,5'-HpCB (PCB189) were purchased from AccuStandard, Inc. (New Haven, CT, USA). A mixture of these polychlorinated biphenyls was prepared by diluting with acetone and then further diluting the acetone solution with distilled water. Commercial SPME device and 7 μm PDMS fiber was acquired from Supelco (California, USA). 5 μL micro-syringes and stainless steel wire (0.25 μm) were obtained from Gaoge Industrial and Trading Co., Ltd (Shanghai, China). All reagents used in this study were at least of analytical grade. Hydrochloric acid (HF, 40 %), methanol and acetone were provided by LingFeng Chemical Reagent Co., Ltd (Shanghai, China).

Chromatographic analyses were carried out on a Shimadzu GC 2010 gas chromatograph coupled with an electron capture detector (ECD). All analyses were performed in the splitless mode using a Rtx-5 (30 m × 0.25 mm i.d. × 0.25 μm) column. Nitrogen was employed as a carrier gas with a constant column flow rate of 1.73 mL min⁻¹. The analytes were thermally desorbed by exposing the SPME fiber to the GC injector at 280 °C. The column temperature was initially set at 120 °C for 30 s and then raised to 220 °C at 80 °C min⁻¹ and held for 10 min, followed by a secondary ramp from 220 to 280 °C at 10 °C min⁻¹ and maintained for 5 min. The temperature of electron capture detector was kept at 300 °C.

Fabrication of solid-phase microextraction fibers:

Etched stainless steel wire fibers were prepared *via* a chemical etching method similar to previous works [20,21]. The stainless steel wire of 16.5 cm in length was firstly ultrasonically cleaned in acetone and water for 5 min, respectively. Then one tip of the wire (1.5 cm) was placed in 40 % hydrofluoric acid solution at 40 °C for 15 min to etch the surface of the stainless steel wire. After this, it was sequentially washed by ultrasonication in acetone, then methanol and finally distilled water for 5 min and then air-dried at ambient temperature. The etched stainless steel wire fiber was finally assembled into a modified 5 μL micro-syringe.

Solid-phase microextraction procedure and gas chromatography analysis: Before the first usage, as-proposed stainless steel wire fiber was conditioned in the injector of GC for 0.5 h at 280 °C under nitrogen atmosphere to eliminate any contaminants. Meanwhile, commercial fiber was also conditioned at 320 °C for 1 h according to product manual. For extraction experiments, 5 mL water samples added with certain amounts of working standard solution were put in 15 mL glass vials capped with PTFE-coated septa. To control the extraction temperature, glass vial was placed in a water bath. Afterwards, the etched stainless steel wire fiber was exposed

to the head-space of the sample solution for a period of time. After extraction, the fiber was removed from the glass vial and transferred to GC injector for desorption.

RESULTS AND DISCUSSION

The scanning electron microscopy (SEM) images in Fig. 1 shows the surface morphologies of prepared fibers. A smooth surface can be found for un-etched stainless steel wire fiber as shown in Fig. 1a and 1b. Opposite, a rough surface morphology was observed for etched stainless steel wire fiber in Fig. 1c and 1d. Compared to un-etched stainless steel wire fiber, the surface of stainless steel wire fiber had been greatly changed after chemical etching, which results in bark-like morphology (Fig. 1d). This bark-like morphology should be responsible for the larger surface area of etched stainless steel wire and more active sets, which can greatly improve the extraction efficiency.

Optimization of solid-phase microextraction conditions:

There are two frequent used extraction modes in solid-phase microextraction method: direct immersing (DI) and head-space (HS). Generally, HS-SPME was often applied when analytes have high volatility and low polarity, while the opposite is true for DI-SPME [22]. Actually, HS-SPME was chosen as extraction mode in many reports, although polychlorinated biphenyls belong to semi-volatile and non-polar compounds [23,24]. Herein, the effect of extraction mode was investigated. The result in Fig. 2 showed that HS-SPME was more efficient than DI-SPME towards all polychlorinated biphenyls. In DI-SPME, water molecules may participate in competitive adsorption and dominate the extraction process, which is adverse to extraction of polychlorinated biphenyls. Besides, immersing in liquid for long time would destroy coatings. Considering all these reasons, HS-SPME mode was selected as final extraction mode for following experiments.

Temperature is one of the most important parameters affecting extraction efficiency in HS-SPME because it affects the distribution and diffusion coefficient of analytes [25]. Heating not only drives analytes from liquid into headspace but also alter the partitioning of analytes between headspace and the fiber [26]. Fig. 3 showed the influence of extraction temperature on extraction efficiency in the range of 30 to 90 °C. A substantial increase in the polychlorinated biphenyls adsorption occurs when extraction temperature increased from 30 to 60 °C. This could be attributed to the fact that increasing the extraction temperature increases the distribution constant of the analytes to the headspace and in turn, increases the headspace capacity [27,28]. However, the extraction capability was decreased when temperature was elevated over 60 °C based on the fact that high temperature is unfavourable for the exothermic adsorption of the analytes onto the SPME fiber [29].

Solid-phase microextraction is an equilibrium-based technique and there is a direct relationship between the extracted amount and the extraction time [30]. Extraction time ranging from 5 to 40 min was studied. As described in Fig. 4, polychlorinated biphenyls were quickly adsorbed in the first 20 min and longer extraction times have little effect on the extraction efficiency. To achieve a compromise between extrac-

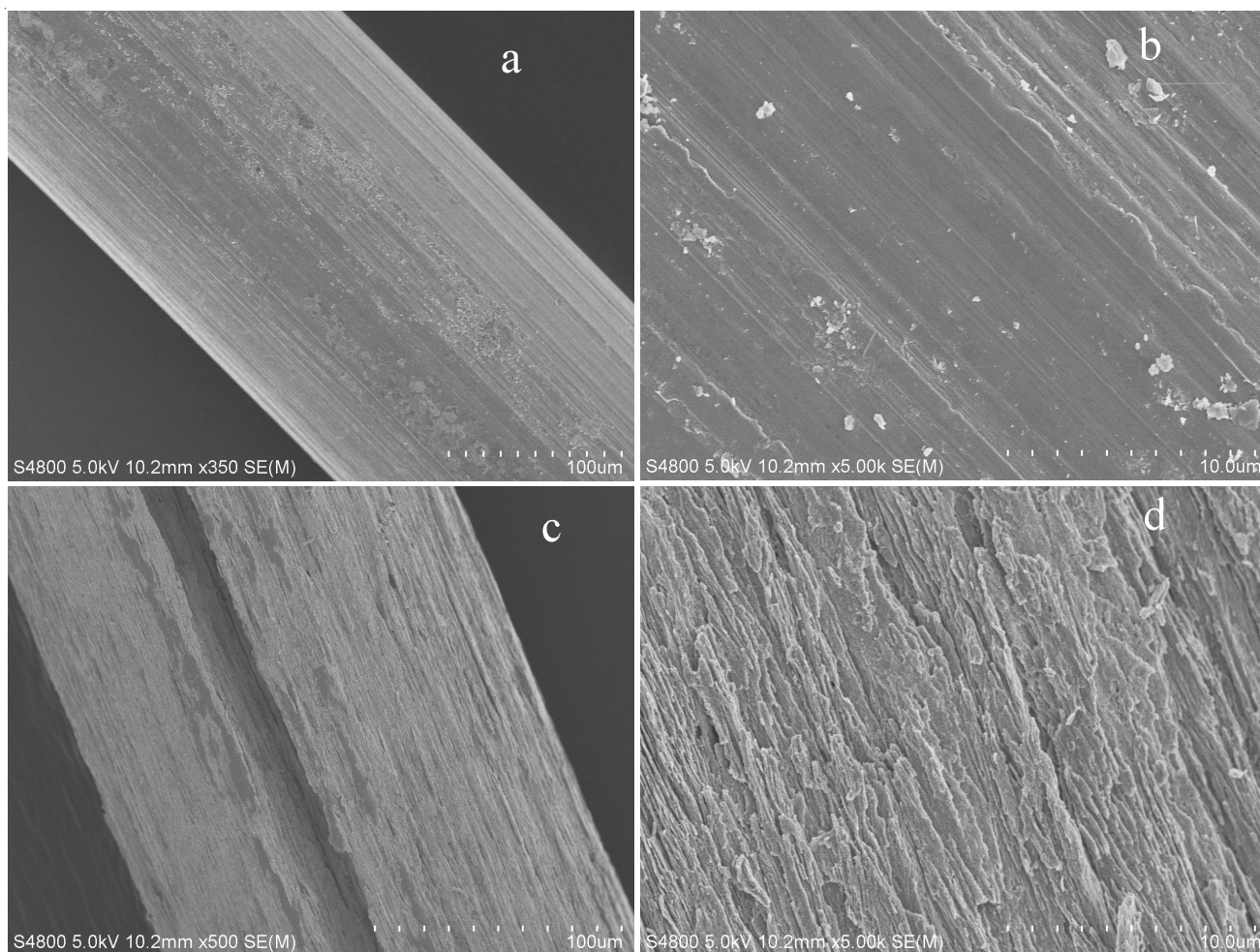


Fig. 1. SEM images of un-etched stainless steel wire fiber (a, b) and etched stainless steel wire fiber (c, d)

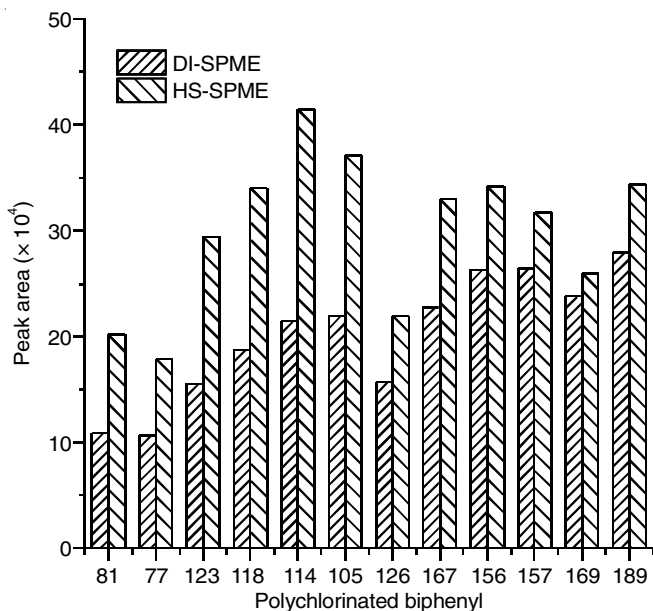


Fig. 2. Effect of extraction mode on the extraction efficiency of etched stainless steel wire fiber. SPME condition: extraction temperature, 60 °C extraction time, 20 min; desorption time, 3 min; concentration of polychlorinated biphenyls, 80 ng L⁻¹

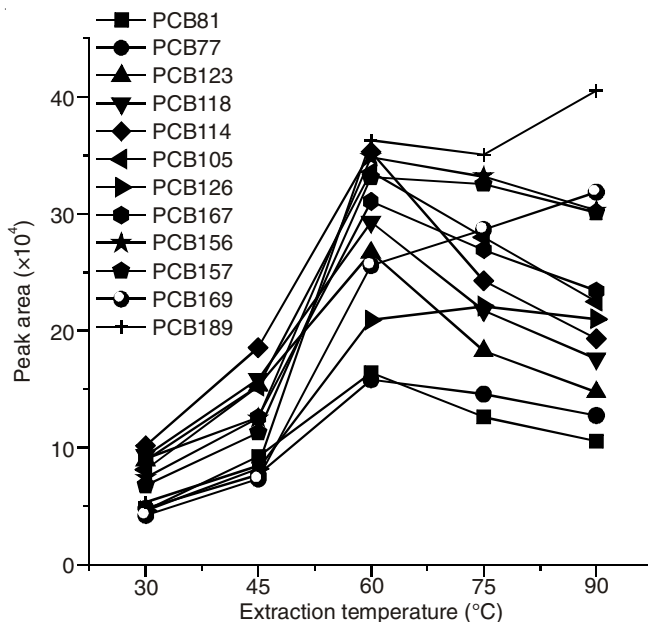


Fig. 3. Effect of extraction temperature on the extraction efficiency of etched stainless steel wire fiber. SPME condition: extraction mode, HS; extraction time, 20 min; desorption time, 3 min; concentration of polychlorinated biphenyls, 80 ng L⁻¹

tion efficiency and the time taken, 30 min was chosen as the most favourable extraction time.

Desorption time could affect the responses of the target analytes significantly, especially for compounds with high

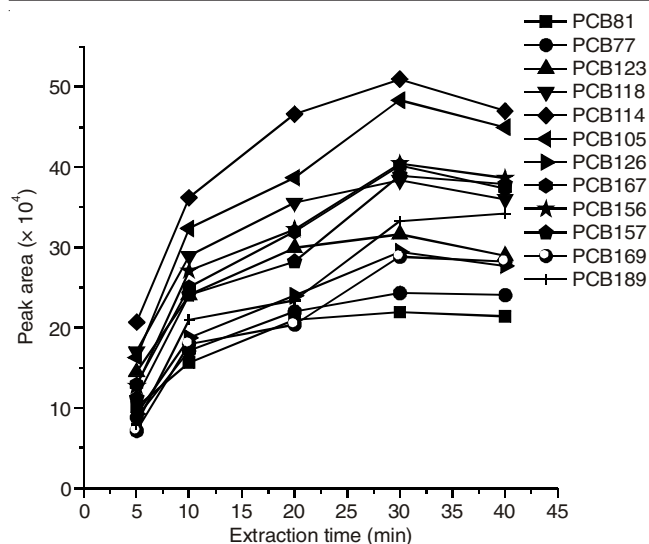


Fig. 4. Effect of extraction time on the extraction efficiency of etched stainless steel wire fiber. SPME condition: extraction mode, HS; extraction temperature, 60 °C; desorption time, 3 min; concentration of polychlorinated biphenyls, 80 ng L⁻¹

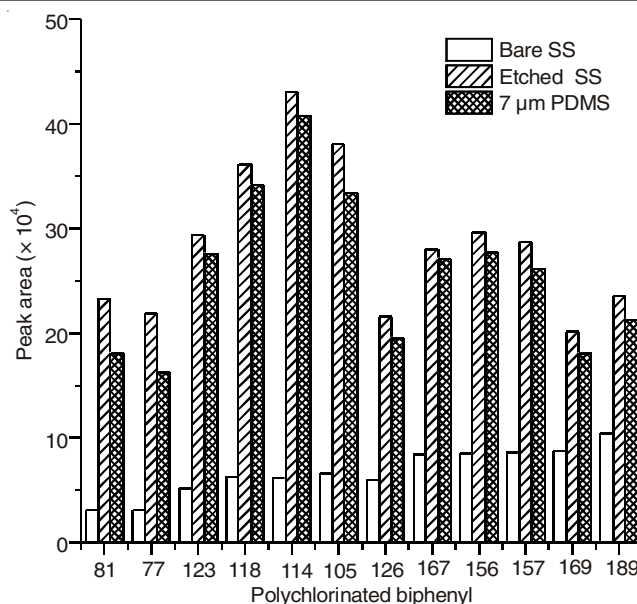


Fig. 5. Comparison of the etched stainless steel wire fiber with commercial PDMS and bare stainless steel wire

boiling point [29]. A proper extraction time would ensure thorough desorption of analytes. Thus, it is suggested that carry over effect could be prevented. The variation of extraction efficiency is not so significant with the increasing extraction time from 1 to 9 min. However, the best extraction efficiency was observed when desorption time was set at 5 min.

Consequently, the optimized parameters were set as following: extraction mode, head space; extraction temperature, 60 °C; desorption time, 5 min; extraction time, 30 min.

Comparison of extraction performance using different fibers: The extraction capability of the etched stainless steel wire fiber, bare (un-etched) stainless steel wire fiber and the commercial 7 μm PDMS fiber was compared. Fig. 5 showed that the extraction efficiency of the etched stainless steel wire fiber is much higher than that of bare stainless steel wire fiber owing to the enlarged specific surface area after etching. Moreover, the etched stainless steel wire fiber exhibited considerable extraction capability compared to 7 μm PDMS fiber. This result could be explained as the result of good affinity to aromatic compounds caused by cation-π interaction between metal oxides and aromatic ring [20].

Analytical evaluation of etched stainless steel wire fiber: At optimized extraction conditions, the analytical performance for the HS-SPME-GC method using etched stainless steel wire fiber for determination of polychlorinated biphenyls was determined and summarized in Table-1. Calibration curves were generated by adding the polychlorinated biphenyls concentration from 40 to 720 ng L⁻¹. All of the 12 polychlorinated biphenyls displayed good linearity at the tested concentration range with R² ranging from 0.9948 to 0.9990. The precision for one fiber was 3.6-7.9 %, while the reproducibility for three fibers was 4.7-10.4 %.

In order to evaluate the feasibility of proposed method, real water sample was studied. The water sample was collected in the River Huajin located in Anhui Normal University, China, on June 11th, 2015. Analytical results were listed in Table-2 and Fig. 6. No polychlorinated biphenyls was detected and

| Compd. | Line range (ng/L) | R ² | LOD (ng/L) | RSD (%; n = 3) | |
|--------|-------------------|----------------|------------|----------------|----------------|
| | | | | One fiber | Fiber to fiber |
| PCB81 | 40-720 | 0.9963 | 2.13 | 3.6 | 4.7 |
| PCB77 | 40-720 | 0.9961 | 10.04 | 5.0 | 7.2 |
| PCB123 | 40-720 | 0.9978 | 3.25 | 7.3 | 8.0 |
| PCB118 | 40-720 | 0.9983 | 3.28 | 5.9 | 6.3 |
| PCB114 | 40-720 | 0.9985 | 1.82 | 5.7 | 9.0 |
| PCB105 | 40-720 | 0.9980 | 4.46 | 6.8 | 9.9 |
| PCB126 | 40-720 | 0.9987 | 9.17 | 5.9 | 8.1 |
| PCB167 | 40-720 | 0.9974 | 2.36 | 7.9 | 9.6 |
| PCB156 | 40-720 | 0.9990 | 5.49 | 5.6 | 6.7 |
| PCB157 | 40-720 | 0.9988 | 0.75 | 5.2 | 6.9 |
| PCB169 | 40-720 | 0.9983 | 9.93 | 5.7 | 8.8 |
| PCB189 | 40-720 | 0.9948 | 2.28 | 6.9 | 10.4 |

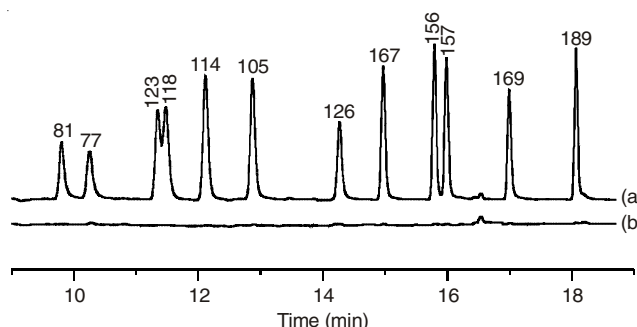


Fig. 6. Gas chromatogram obtained by the developed method: (a) blank river water (b) spiked river water 80 ng L⁻¹

recovery experiment was carried out to further estimate the accuracy of the results with the spiked concentration of 80 ng L⁻¹. The recoveries were calculated to be in the range of 88.2-98.9 % with RSDs within ± 13 % for all polychlorinated biphenyls, suggesting that HS-SPME method using etched stainless steel wire fiber was dependable for quantitative analysis of polychlorinated biphenyls in environmental water sample.

TABLE-2
ANALYTICAL RESULTS FOR DETERMINATION OF
POLYCHLORINATED BIPHENYLS (PCBs) IN WATER SAMPLE

| Compd. | Added conc. (ng/L) | Average recovery (%) | RSD (%, n=3) |
|--------|-----------------------|-------------------------|-----------------|
| PCB81 | 80 | 95.2 | 8.9 |
| PCB77 | 80 | 98.9 | 9.1 |
| PCB123 | 80 | 88.9 | 9.0 |
| PCB118 | 80 | 88.2 | 11.8 |
| PCB114 | 80 | 90.5 | 10.6 |
| PCB105 | 80 | 98.5 | 11.5 |
| PCB126 | 80 | 90.9 | 13.0 |
| PCB167 | 80 | 89.1 | 11.1 |
| PCB156 | 80 | 93.7 | 8.4 |
| PCB157 | 80 | 97.4 | 9.1 |
| PCB169 | 80 | 95.5 | 8.1 |
| PCB189 | 80 | 91.8 | 7.7 |

Conclusion

In this study, we prepared a simple, stable etched stainless steel wire fiber and successfully applied it to analysis of polychlorinated biphenyls in environmental sample. The experimental data demonstrated that the etched stainless steel wire fiber has a good affinity to polychlorinated biphenyls because of the large surface area and cation- π interaction. It was expected that etched stainless steel wire fiber might also play a role in determination of other aromatic compounds.

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