

Development of ZrO₂-Coated SPME Fibers for Detecting Benzotriazole Ultraviolet Filters in Water Samples

Abstract: In this study, the zirconium dioxide nanoparticles (ZrO₂NPs) were coated on the surface of stainless steel (SS) by cyclic voltammetry (CV) as solid phase microextraction fiber coating for detection of the benzotriazole ultraviolet filters (BUvFs) in different real water samples. The composition and images of the new SS@ZrO₂NPs fiber were characterized by scanning electron microscopy (SEM). The extraction capability of SS@ZrO₂NPs fiber was investigated for the enrichment and detection of benzotriazole ultraviolet filters (BUvFs) phthalate acid esters (PAEs) and polycyclic aromatic hydrocarbons (PAHs) coupled with HPLC. The fabricated SS@ZrO₂NPs fiber showed excellent extraction selectivity and good extraction capability for BUvFs. Under the optimized conditions, the SS@ZrO₂NPs-SPME method presented linear ranging from 0.15 to 200 µg/L with correlation coefficients of higher than 0.9982. Moreover the limits of detection (LODs) varied from 0.020 µg/L to 0.138 µg/L. Relative standard deviations (RSDs) with single fiber were below 7.78% and 8.91% for intra-day and inter-day measurements, respectively. The developed method was used to the detection of trace BUvFs in different real water samples.

Keywords: zirconium dioxide; solid phase microextraction; stainless steel; benzotriazole ultraviolet filters; high-performance liquid chromatography

1. Introduction

“Solid phase microextraction (SPME) is a very useful preparation technique. It integrate

sampling, extraction, enrichment and direct sample introduction into one step” [1]. “As an effective sample preparation technology, it had been applied to many fields such as environmental food, pharmaceutical and biological analyses” [2-6]. “Some commercial fibers show some defects such as fragility, the stripping of coatings, bending of the needle and easily swelling in an organic solvent. These limit its wide applications” [7]. Therefore, in the past two decades, the development of new fibers has become a hot topic in the field [8]. Thus, a large number of new materials with good adsorption properties are constantly being developed as SPME fiber coatings [9,10].

“ZrO₂ has the advantages of durability, corrosion resistance, wear resistance, strong adhesion to metal surface, non-toxic and so on, and is one of the most promising inorganic materials” [11]. “Due to good sorptive properties, ZrO₂ nanomaterials with various structures have been successfully applied as fiber coating for SPME” [12,13].

“As a class of benzotriazole derivatives, BUvFs are widely used in industrial products and personal care products to protect against ultraviolet radiation from sunlight” [14]. Because of their overuse, BUvFs have been found in environmental substrates such as surface water, biomes, wastewater and sediments [14-16]. “Some BUvFs have been reported to have endocrine-disrupting and estrogenic effects in organisms” [17, 18]. As a result, they have been recognized as emerging pollutants of concern, and their excessive use has been restricted in some countries and regions [18]. “However, BUvFs is present at trace or ultra-trace levels in environmental samples. Therefore, sample pretreatment is necessary for the analysis of trace analytes in complex substrates”. In this study, the SS@ZrO₂NPs fiber was prepared and used to the extraction and determination of BUvFs in environmental water

samples coupled with HPLC-UV.

2 Methodology

2.1 Reagents and Materials

Bare stainless steel was purchased from Gaoge. Zirconium (IV) oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) was obtained from Huawei Ruike (Beijing, China). Sodium chloride (NaCl) and Potassium chloride (KCl) were obtained from Shuangshuang Chemical Ltd (Shandong, China). Hydrofluoric acid (HF) was purchased from Shanghai Hunter Fine Chemicals Ltd. (Shanghai, China). The methanol with HPLC-grade was supplied from Yuwang Chemical Company (Shandong, China). 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol (UV-329), 2-(2'-hydroxy-5'-methylphenyl) benzotriazole (UV-P), 2-tertbutyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV-326), 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole (UV-320) and 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl) phenol (UV-234) were from AccuStandard (New Haven, CT, USA). Fluoranthene (Flu), benzo[a] pyrene (B[a]p), naphthalene (Nap), phenanthrene (Phe) and , di-(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DBP), dimethyl phthalate (DMP), di-n-octyl phthalate (DOP) were provided from Sigma-Aldrich (St. Louis, MO, USA)

2.2 Apparatus

Images of the prepared fibers were examined using Ultra Plus microscopy (Zeiss, Oberkochen, Germany), together with energy dispersive X-ray spectroscopy (EDX) analysis. Separation and determination of analytes were performed on Agilent 1260 Infinity LC system (Waldbronn, Baden-Württemberg, Germany) equipped with variable wavelength detector and a SB-C18 column. The data was collected with an Agilent ChemStation. Ultrapure water was

obtained from a XYG-60-H water purification system (Beijing, China).

2.3 Prepared of the SS@ZrO₂NPs fiber

The SS fibers were washed in an ultrasonic bath with acetone and ultra-pure water for 10 minutes, respectively. One end of the SS wire was pretreated in 40% (w/w) HF solution for 30 minutes and then rinsed in an ultrasonic water bath for 5 minutes. Thereafter ZrO₂ nanoparticles were deposited on the surface of SS by CV between 2.0 and 0 V (versus Ag/AgCl) at a scanning rate of 20 mV/s for 15 cycles. The electrolyte is composed of 0.005 mol/L ZrOCl₂ and 0.1 mol/L KCl. After deposition, the SS@ZrO₂NPs fiber was gently washed with ultrapure water and dried in air.

2.4 Extraction procedure

10 mL sample solution was added into a sample vial with a PEEK cap. The SS@ZrO₂NPs fiber was usually immersed in a stirred sample solution and extracted at a selected temperature for a specified time. After extraction, the SS@ZrO₂NPs fiber was removed from the sample vial and introduced into the SPME-HPLC interface for static desorption in corresponding mobile phase. The mobile phase of methanol/water with 95/5 (v/v), 90/10 (v/v) and 85/15 (v/v) was used for HPLC analysis to BUvFs, PAHs, PAEs, respectively. The flow rate was 1 mL/min. Corresponding detection wavelength were set at 340 nm, 254 nm and 280 nm. Before extraction, the SS@ZrO₂NPs fiber was washed with methanol for 5 minutes.

3. Results and discussion

3.1 Characterization of SS@ZrO₂NPs fiber

The surface images of SS@ZrO₂NPs fiber was characterized by SEM. As can be seen in Fig. 1B, bare SS fiber exhibited smooth surface microscopically at high magnification.

Moreover, EDX analysis shows that the main surface components of SS fiber are Fe, Ni, Cr and Si elements. After deposition, the uniform and porous nanoparticles were formed on the SS supports. EDX analysis (Fig. 2B) exhibited that the strong characteristic peaks of Zr and O elements appear. This result revealed the SS@ZrO₂NPs fiber was successfully fabricated.

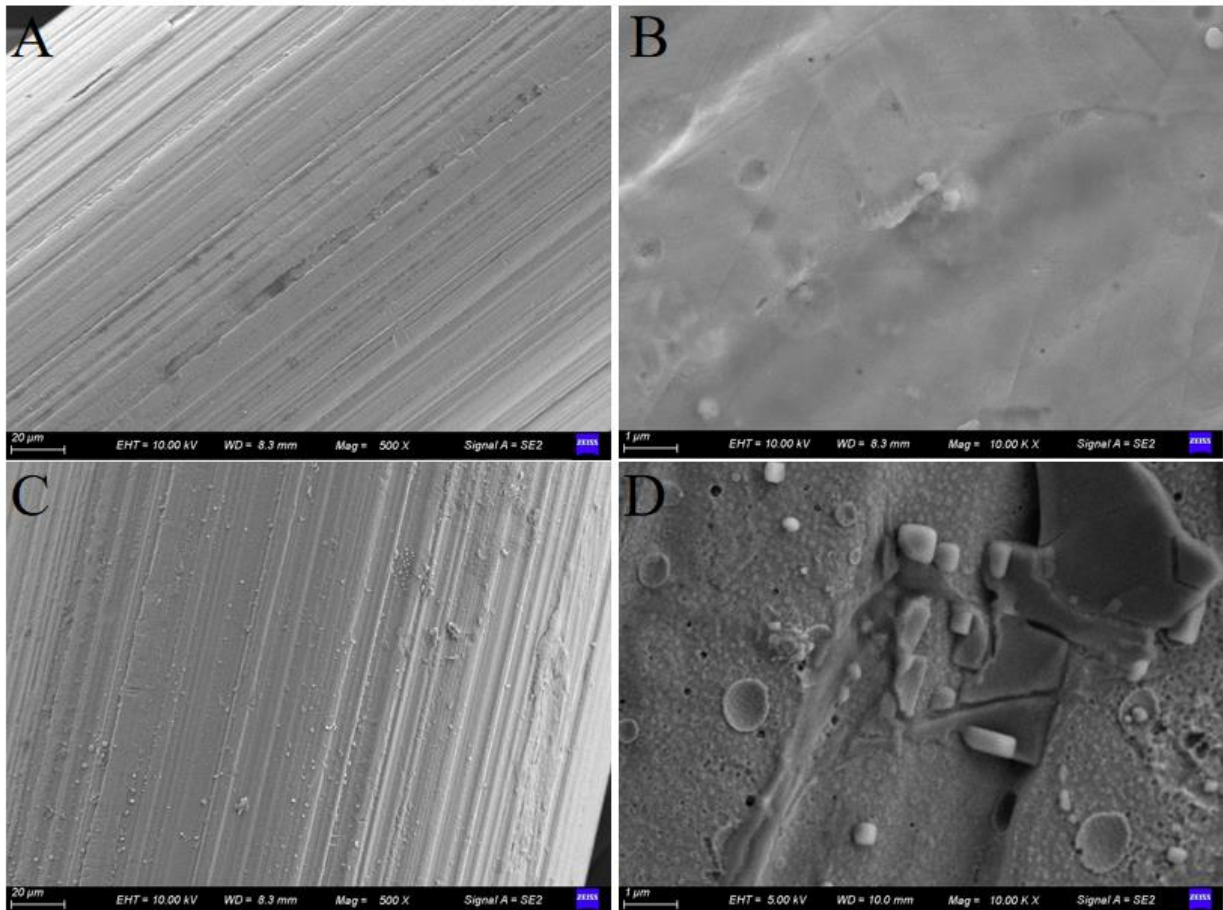


Fig. 1 SEM images of SS fiber (A) Bare SS wire ($\times 500$); (B) Bare SS wire ($\times 10,000$); (C) SS@ZrO₂NPs fiber ($\times 500$); (D) SS@ZrO₂NPs fiber ($\times 10,000$).

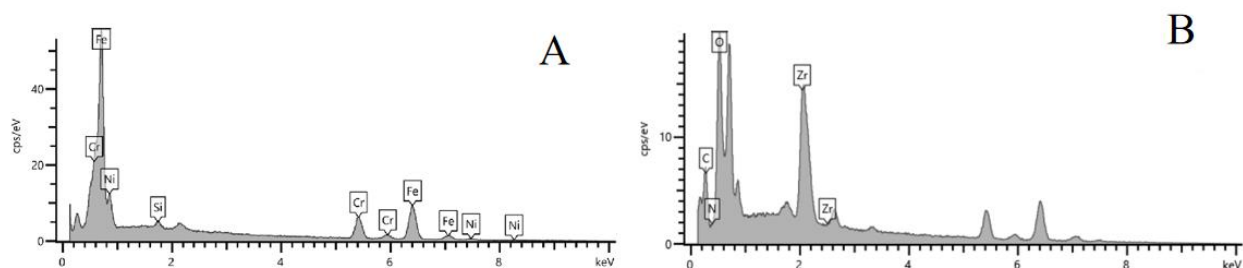


Fig. 2 EDX spectra of SS fiber. (A) Bare SS fiber; (B) SS@ZrO₂NPs fiber.

3.2 Extraction Selectivity

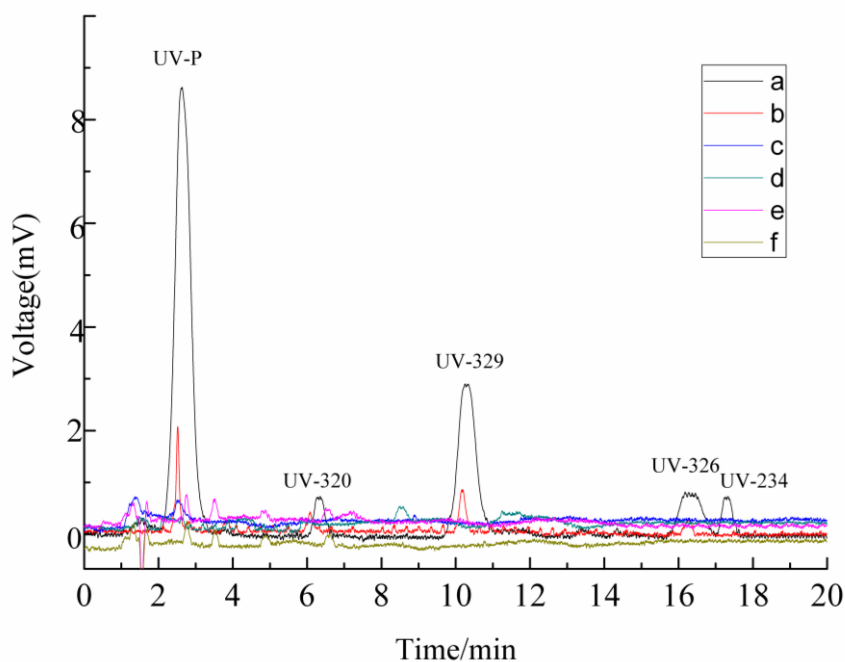


Fig. 3 Chromatograms of direct HPLC (a, c, e) and SPME-HPLC with the SS@ZrO₂NPs fiber (b, d, f). PAEs (a, b), PAHs (c, d) and BUvFs (e, f) at a spiking level of 50 μg/L for each analyte.

Fig. 3 shows the extraction selectivity of the SS@ZrO₂NPs fiber, which is estimated by three typical organic compounds including PAEs, PAHs and BUvFs. The SS@ZrO₂NPs fiber shows poor extraction capability for PAEs (Fig. 3(b)) and PAHs (Fig. 3(d)). However the

SS@ZrO₂NPs fiber displays good extraction capability for BUvFs (Fig. 3(f)). This result is attributed to the inherent chemical properties of the ZrO₂NPs coating. “Due to hydrophobic interactions between ZrO₂NPs coating and aromatic compounds, the SS@ZrO₂NPs fiber shows good extraction capability for BUvFs. Furthermore the strong Lewis acidic sites on the surface of ZrO₂ nanoparticles is expected to have a good affinity for target analytes with a Lewis basic character” [12].

3.3 Extraction conditions

The main SPME conditions including extraction time, temperature, stirring rate and ionic strength were studied and optimized. As can be seen in Fig. 4, the SS@ZrO₂NPs fiber showed excellent extraction capability for BUvFs at 30 °C for 40 min with a stirring rate of 500 r/min. Typically, adding NaCl to the sample solution can increase the ionic strength and reduce the solubility of BUvFs in the aqueous phase. Herein, NaCl concentration ranging from 0 to 25% (w/v) was added and the extraction efficiency of SS@ZrO₂NPs fiber for target BUvFs was investigated. As shown in Fig. 4(d), 5% (w/v) NaCl is added in the sample solution the optimal extraction capability of the novel fiber for BUvFs is reached. Therefore, 5% (w/v) NaCl is chosen as suitable salt concentration. In addition, 5 min was employed as desorption time.

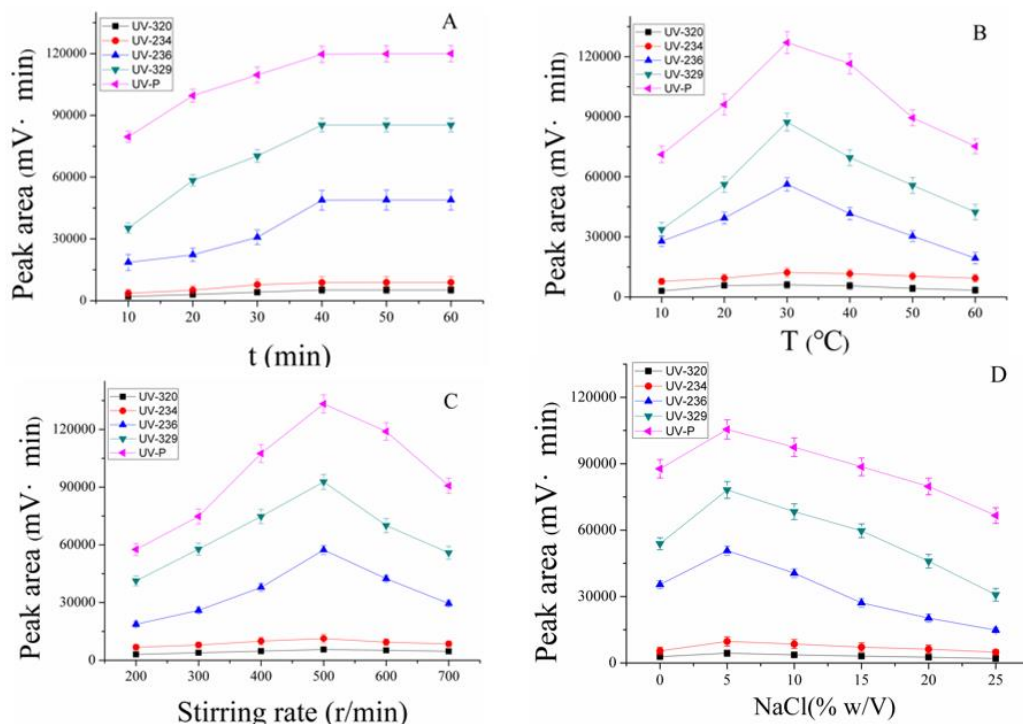


Fig. 4 Main SPME conditions. Extraction time (A); Temperature (B); Stirring rate (C) and Ionic strength (D).

3.4 Method validation

Under the optimized conditions, the analytical performance of the SPME-HPLC method with the SS@ZrO₂NPs fiber was investigated for BUvFs. The results are listed in Table 1. In the range of 0.15 ~ 200 µg/L, the linearity is good, and the correlation coefficient (r^2) is greater than 0.9982. Limits of detection (LODs) calculated with a signal-to-noise ratio of 3 (S/N=3) ranges from 0.020 µg/L to 0.138 µg/L. Relative standard deviations (RSDs) for BUvFs were less than 8.91% with a single fiber at the spiking level of 50 µg/L. These data indicated show that the SPME-HPLC-SS@ZrO₂NPs method has good accuracy, precision and sensitivity.

Table 1 Analytical parameters of the SPME-HPLC method with the SS@ZrO₂NPs fiber (n=5).

Analytes	Linear ranges ($\mu\text{g/L}$)	r^2	Recovery (%)	RSDs repeatability		LODs ($\mu\text{g/L}$)	LOQs ($\mu\text{g/L}$)
				Intra-day (%)	Inter-day (%)		
				UV-P	0.15-200		
UV-320	0.30-200	0.9990	96.7	7.78	8.91	0.067	0.221
UV-329	0.20-200	0.9992	98.2	7.47	7.75	0.049	0.162
UV-326	0.5-200	0.9982	97.5	6.47	7.49	0.124	0.410
UV-234	0.5-200	0.9990	96.9	7.08	7.64	0.138	0.453

3.5 Detection of real water sample

In order to verify the feasibility of the method, the prepared optical fiber is applied to the detection of target BUVFs in different water samples. All result were list in Table 2. To assess the accuracy of the results, standard BUVFs was added to the actual sample at levels of 15 $\mu\text{g/L}$ and 30 $\mu\text{g/L}$, respectively. The desired recoveries ranging from 91.7% to 100.0% was obtained. And the RSDs was less than 8.4%. These results show that the new SS@ZrO₂NPs fiber can be used for adsorption and sensitive detection of BUVFs in water samples in different environments.

Table 2. Analytical results of BUVFs in different real water samples (n=3)

Samples	Analytes	Original ($\mu\text{g/L}$)	Spiked with 15 $\mu\text{g/L}$			Spiked with 30 $\mu\text{g/L}$		
			Detected ($\mu\text{g/L}$)	Recovery (%)	RSDs (%)	Detected ($\mu\text{g/L}$)	Recovery (%)	RSDs (%)
River water	UV-P	ND ^a	13.98	93.2	6.6	28.53	95.1	7.3
	UV-320	ND	14.22	94.8	6.4	27.69	92.3	6.6
	UV-329	ND	14.65	97.6	6.0	28.11	93.7	6.7
	UV-326	ND	13.78	91.8	6.2	29.28	97.6	6.9
	UV-234	ND	13.89	92.6	7.2	28.97	96.5	7.2

Lake water	UV-P	ND	13.76	91.7	6.8	28.93	96.4	6.9
	UV-320	ND	14.19	94.6	7.0	29.09	96.9	6.9
	UV-329	ND	14.45	96.3	6.9	29.86	99.5	7.5
	UV-326	ND	14.78	98.5	7.5	28.40	94.6	7.1
	UV-234	ND	13.92	92.8	7.4	28.99	96.6	7.4
Wastewater	UV-P	0.72	15.04	95.4	8.0	30.20	98.2	7.2
	UV-320	0.64	14.97	95.5	7.8	29.22	95.3	8.0
	UV-329	ND	14.75	98.3	8.3	30.01	100.0	7.6
	UV-326	ND	14.74	98.2	7.2	29.68	98.9	8.1
	UV-234	ND	14.67	97.8	8.1	28.95	96.5	8.4

4. Conclusions

The SS@ZrO₂NPs fiber was successfully fabricated by cyclic voltammetry. Moreover the ZrO₂NPs coating possess porous and uniform structures. This special nanostructures facilitated the adsorption and extraction of analytes from the solution into the fiber coating. The SS@ZrO₂NPs fiber showed desired extraction capability for BUvFs. In addition, the SS@ZrO₂NPs fiber was successfully applied for the detection of BUvFs in real water samples.

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