Fabrication of ZrO_2 Coating For Highly Solid Phase Microextraction of Benzotriazole Ultraviolet Filters in different water samples

Abstract: In this study, the zirconium dioxide nanoparticals (ZrO_2NPs) were coated on the surface of stainless steel (SS) by cyclic voltammetry (CV) as solid phase microextractiom fiber coating for determination the benzotriazole ultraviolet filters in different environmental water samples. The images and composition of the fabricated SS@ZrO_2NPs fiber were characterized by using an Ultra Plus microscope equipped with semi-quantitative micro analysis by energy dispersive X-ray spectroscopy (EDX). The extraction performance of SS@ZrO_2NPs fiber was investigated for the concentration and detection of polycyclic aromatic hydrocarbons (PAHs), benzotriazole ultraviolet filters (BUFs)and phthalate acid esters (PAEs) coupled to HPLC with UV detection. The fabricated SS@ZrO_2NPs fiber exhibited exellent extraction selectivity and extraction capability for BUFs. Under the optimized conditions, the proposed method presented linear ranges from 0.15 to 200 g/L with correlation coefficients of higher than 0.9982 and limits of detection (LODs) from 0.020 g/L to 0.134 g/L. Relative standard deviations (RSDs) were below 7.78% and 8.91% for intra-day and inter-day measurements with the single fiber, respectively. The proposed method was successfully applied to the determination of trace target BUFs in different 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 powerful preparation technique and integrate sampling, extraction, concentration and direct sample introduction into one step [1]. Due to its imple, rapid, practical and effective sample preparation technology, it had been successfully applied to different fields such as food, pharmaceutical, environmental and biological analyses [2-6]. Some commercial silica-based fibers show some drawbacks such as fragility, the stripping of coatings, bending of the needle and easily swelling in an organic solvent which limit its widespread applications [7]. Therefore, the development of novel fibers has become popular in this field in the past two decades [8]. Thus, many new materials with good adsorption performance have been ceaselessly exploited as SPME fiber coatings [9,10].

ZrO_2 is one of the most promising inorganic material due to its durability, resistance to corrosion and wear, strong adhesion onto metallic surfaces and non-toxicity [11]. Based on its good sorptive properties, ZrO_2 nanomaterials with various structures have been successfully applied as fber coating for SPME [12,13].

As a class of benzotriazole derivatives, benzotriazole ultraviolet flters (BUvFs) are widely applied in industrial products and personal care products to prevent ultraviolet radiation from sunlight[14]. Because of excessive use for them, BUvFs have been found in the environmental matrices such as biota, sediment, wastewater, and surface water [14-16]. It has been repaorted that some BUvFs have endocrine disrupting and estrogenic efects in various organisms [17, 18]. Thus, they have been considered as emerging contaminants of concern and the excessive use of them is limited in some countries and regions [18]. However the content of BUvFs in environmental samples is at trace or ultratrace levels. Therfore sample pretreatment is process in the analysis of trace analytes in a complex matrix. In this study, the SS@ZrO_2NPs fiber was fabricated and used to extraction and determination of BUvFs in environmental water samples coupled with HPLC-UV.

2. Experimental

2.1 Materials and reagents

Stainless steel were purchased from Gaoge. Zirconium（Ⅳ）oxychloride octahydrate ($ZrOCl_2{\bullet}8H_2O$) was obtained from Huawei Ruike Chemical Co., Ltd. Potassium chloride (KCl) and sodium chloride (NaCl) were purchased from Yantai Shuangshuang Chemical Ltd (Shandong, China). Hydrofluoric acid was obtained from Shanghai Hunter Fine Chemicals Ltd. (Shanghai, China). HPLC-grade methanol was purchased from Yuwang Chemical Company (Shandong, China). 2- (2′-hydroxy-5′-methylphenyl) benzotriazole (UV-P), 2-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol (UV-329), 2-tertbutyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV-326), 2-(2H-benzotriazol-2-yl)-4,6- bis(1-methyl-1-phenylethyl) phenol (UV-234), and 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole (UV-320) were from AccuStandard (New Haven, CT, USA). Benzo[a] pyrene (B[a]p), fuoranthene (Flu), phenanthrene (Phe), and naphthalene (Nap) 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB-153), dimethyl phthalate (DMP), di-n-butyl phthalate (DBP), di-n-octyl phthalate (DOP), di-(2-ethylhexyl) phthalate (DEHP) were supplied from Sigma-Aldrich (St. Louis, MO, USA)

2.2 Apparatus

The morphologies of the fabricated fiber were examined by with an Ultra Plus microscope (Zeiss, Oberkochen, Germany) operating at 5 kV, where energy dispersive X-ray spectrometry (EDX) analysis was also carried out at the same time. Separation and determination of octadecylamine were performed on Agilent 1260 Infinity LC system (Waldbronn, Baden-Württemberg, Germany) with a G1314F variable wavelength detector and a Agilent Zorbax SB-C18 column. Data collection was obtained with an Agilent OpenLAB CDS ChemStation. Ultrapure water was obtained from a Pine-tree XYG-60-H water purification system (Beijing, China).

2.3 Fabricated of SS@ZrO_2NPs fiber

Bare SS wire was cleaned with acetone and ultrapure water in an ultrasonic bath for 10 min, respectively. One end (1.5 cm long) of the SS wire was pretreated in HF solution of 40% (w/w) for 30 min and subsequently rinsed in a sonicated water bath for 5 min. Thereafte ZrO_2 nanoparticles were deposited on the SS surface in the electrolyte of 0.005 mol L^{-1} $ZrOCl_2$ and 0.1 mol L^{-1} KCl by CV between 2.0 and 0 V (versus Ag/AgCl) at a scanning rate of 20 mV s^{-1} for 15 cycles. The as-fabricated fibers were gently rinsed with ultrapure water and dried in air.

2.4 SPME-HPLC procedure

Sample solution of 10 mL was transferred into a 15 mL sample vial with a Teflon septum and a PEEK cap. Typically the fabricated fiber was immersed in the stirred sample solution to reach extraction equilibrium at selected temperature. After extraction, the fiber was withdrawn from the sample vial and immediately introduced into the SPME-HPLC interface for static desorption in corresponding mobile phase. Subsequently the six-port valve was switched from load to inject position for chromatographic analysis. The mobile phase of methanol/water with 95/5 (v/v), 90/10 (v/v), and 85/15 (v/v) was used as for HPLC analysis to BUvFs, PAHs, PAEs, respectively. The flow rate was 1 mL·min^{-1}. Corresponding UV detection wavelength were set at 340 nm, 254 nm and 280 nm. Before next extraction, the novel SPME fber was washed with methanol for 5 minutes.

3. Results and discussion

3.1 Characterization of SS@ZrO$_2$NPs fiber

The surface morphology of SS@ZrO$_2$NPs fiber coating was characterized by SEM. As shown in Fig 1B, the SS wire exhibited smooth surface microscopically at high magnifcation. Moreover, EDX analysis revealed that the surface ingredients of SS wire consisted of the Fe、Ni、Cr and Si elements. After deposition, the uniform and porous nanoparticals were formed on the SS supports. EDX analysis (Fig. 2B) exhibited that the strong peaks of Zr and O elements appear. This result revealed the SS@ZrO$_2$NPs fiber coating was successfully fabricated.

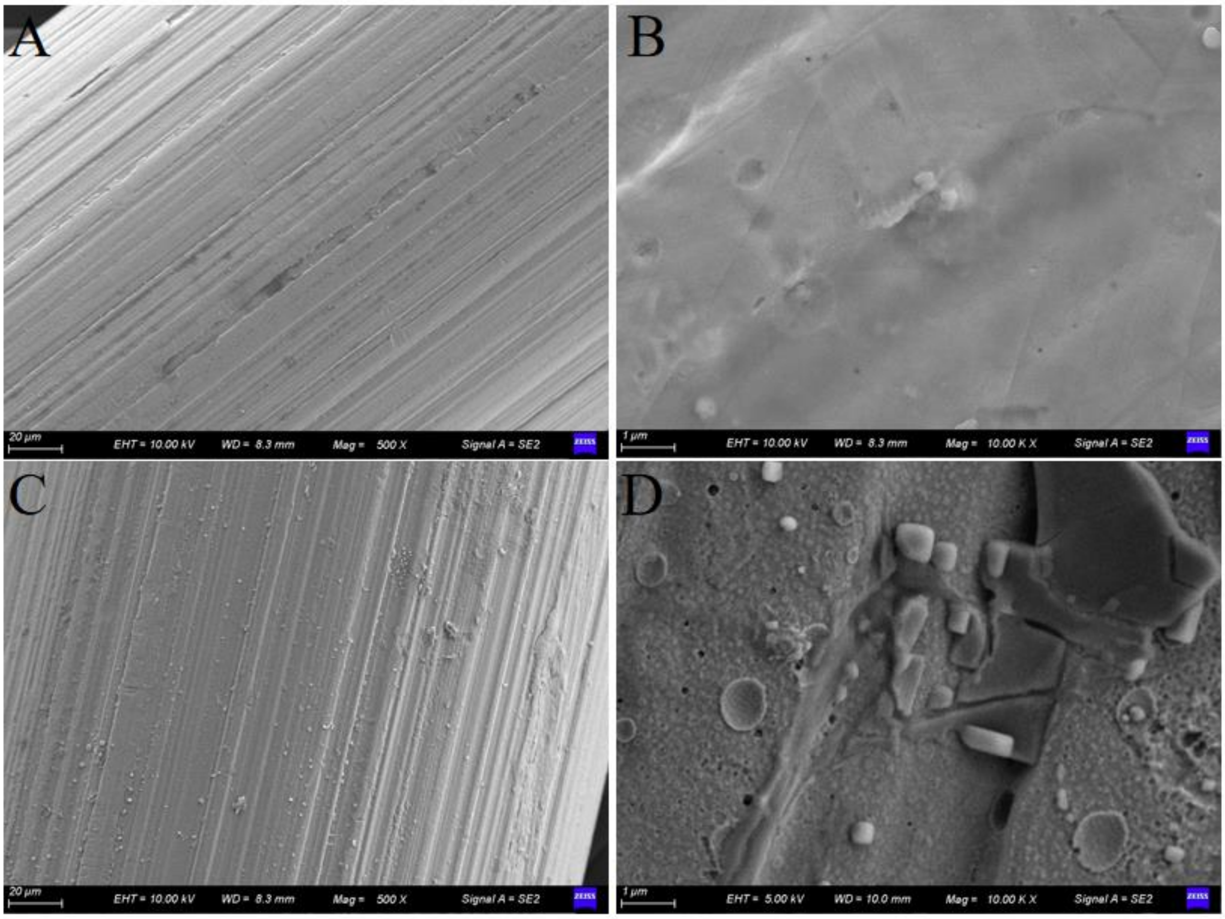

Fig. 1 SEM images of SS fiber substrate surface (A) Bare SS wire (×500); (B) Bare SS wire (×10,000); (C) SS@ZrO_2NPs fiber (×500); (D) SS@ZrO_2NPs fiber (×10,000).

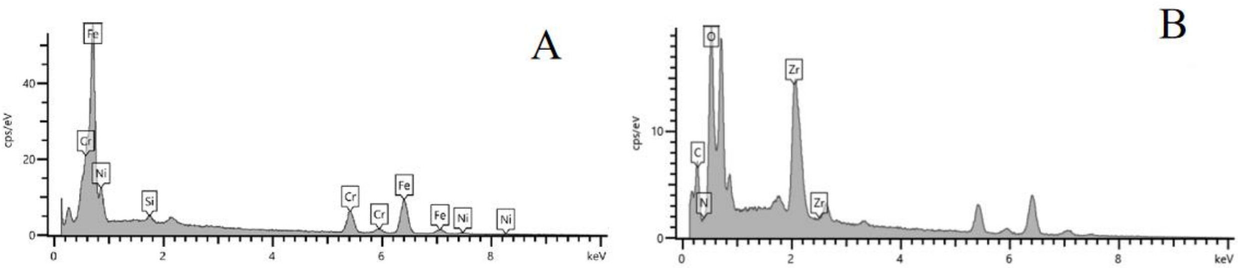

Fig. 2 EDX spectra of treated SS wires. (A) Bare SS wire; (B) SS@ZrO_2NPs fiber.

3.2 Extraction Selectivity

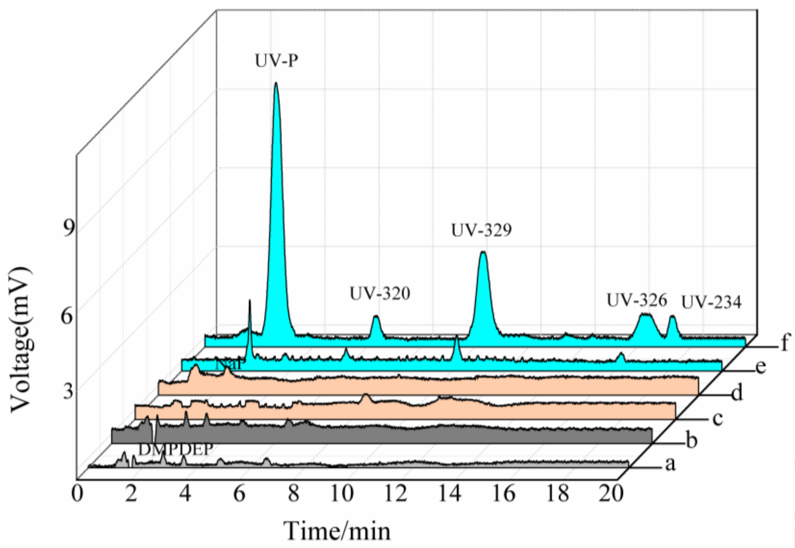

Fig. 3 Chromatograms of model analytes from direct HPLC

(a, c, e) and SPME-HPLC with the SS@ZrO_2NPs fiber (b, d, f).

PAEs (a, b), PAHs (c, d) and BUvFs (g, h) at a spiking level of 50 μg • L^{-1} for each analyte.

Fig. 3 shows the extraction performance of the SS@ZrO_2NPs fber, which is estimated by three typical compounds including PAEs, PAHs and BUvFs. The fabricated SS@ZrO_2NPs fiber shows poor extraction capability for PAEs (Fig. 3(b)) and PAHs (Fig. 3(d)). However the novel fiber displays good extraction capability for BUvFs (Fig. 3(f)) and the chromatographic peak areas of analytes are much larger than those of direct HPLC (Fig. 3(e)). This result may be attributed to the inherent chemical nature of ZrO_2NPs coating. Due to the hydrophobic interactions between ZrO_2NPs coating and aromatic compounds, the SS@ZrO_2NPs fiber displays desired extraction capability for BUvFs. Furthermore it is expected that strong Lewis acidic sites at the surface of ZrO_2 nanoparticles would show good affinity for target analytes with a Lewis basic character [12].

3.3 Optimization of SPME conditions

To obtain desired extraction capability, the main experimental conditions such as extraction time, temperature, stirring rate and ionic strthgth were further optimized. As shown in Fig. 4, the SS@ZrO_2NPs fiber showed desired extraction capability for BUvFs at 30 °C for 40 min with a stirring rate of 500 r/mim. Typically, addition of NaCl to sample solution can increase ionic strength and decrease the solubility of BUvFs in an aqueous phase. Herein, the extraction efciency of BUvFs with NaCl concentration ranging from 0 to 25% (w/v) was investigated. As shown in Figure 7(d), the optimal extraction capability of the novel fiber for BUvFs is reached when 5% (w/v) NaCl is added in the solution. Terefore, in this study, 5% (w/v) NaCl is chosen as suitable salt concentration. In addition, 5 min was employed as desorption time.

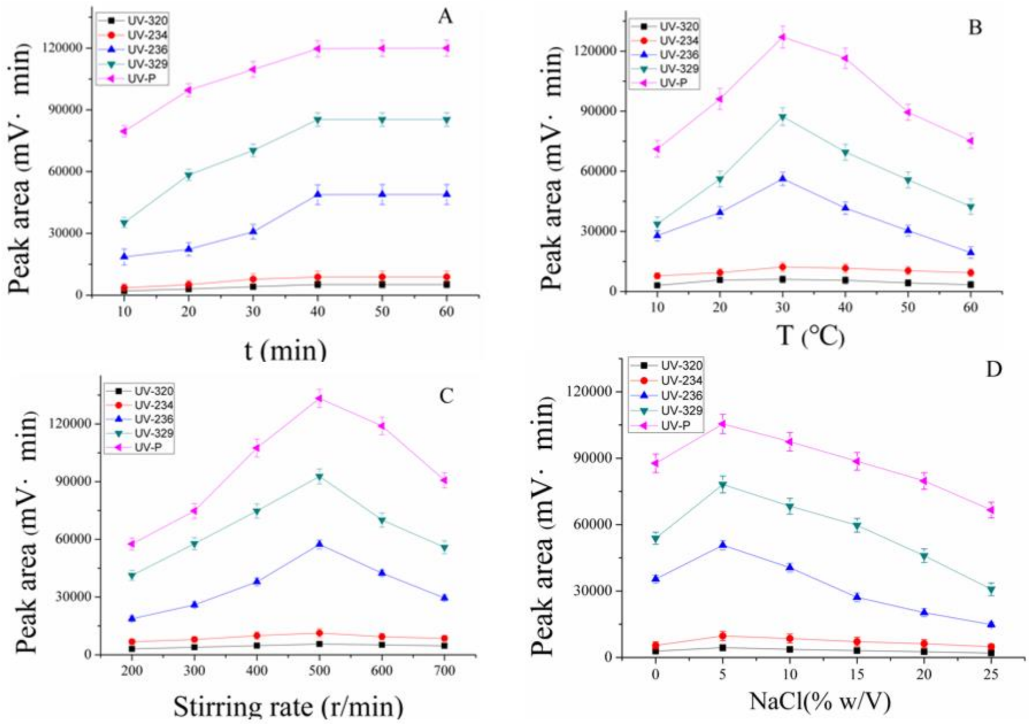

Fig. 4 Effect of (A) extraction time; (B) temperature; (C)stirring rate and (D) ionic strength on the extraction efficiency.

3.4 Method validation

Under the optimized conditions, the analytical performance of the proposed method with the SS@ZrO$_2$NPs fiber was investigated for BUvFs. The results are listed in Table 1. Good linearity was achieved in the range of 0.15-200 μg/L with correlation coefficients (r^2) above 0.9982. Limits of detection (LODs), calculated based on a signal-to-noise ratio of 3 (S/N=3), ranged from 0.020 g/L to 0.134 g/L. Relative standard deviations (RSDs) for five replicate extractions of BUvFs at the spiking level of 50 μg/L were less than 7.78% for a single fiber. These data indicated that satisfactory accuracy, precision and sensitivity were obtained for this method.

Table 1 Analytical parameters of the proposed method with the SS@ZrO$_2$NPs fiber (n=5).

Analytes	Linear ranges (μg/L)	r^2	Recovery (%)	RSDs for single fiber repeatability		LODs (μg/L)	LOQs (μg/L)
				Intra-day (%)	Inter-day (%)		
UV-P	0.15-200	0.9992	99.4	6.76	7.89	0.020	0.066
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 Analysis of real sample

To estimate the feasibility of the proposed method, the fabricated fiber was applied for the detection of target BUvFs in different real environmental water samples. The result were list in Table 2.To evaluate the accuracy of the results, standard BUvFs were spiked into the real sample at the levels of 15 μg/L and 30 μg/L, respectively. The recoveries ranged from 88.6% to 95.7% with the RSDs less than 8.4% for target BUvFs. These results demonstrated that the novel fiber was reliable and suitable for adsorption and sensitive detection of BUvFs in different environmental water samples.

Table 2. Analytical results of BUvFs in different environmental water samples (n=3)

Samples	Analytes	Original (μg·L^{-1})	Spiked with 15μg·L^{-1}			Spiked with 30 μg·L^{-1}		
			Detected (μg·L^{-1})	Recovery (%)	RSDs (%)	Detected (μg·L^{-1})	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@ZrO_2NPs fiber was successfully fabricated by CV cycles. Moreover the ZrO_2NPs caoting possess porous and uniform structure, which contributed to the adsorption and extraction of target analyte from sample solution to fiber coating. The fabricated SS@ZrO_2NPs fiber exhibited higher extraction capability for target BUvFs. In addition, the fabricated SS@ZrO_2NPs fiber was successfully applied for the detection of BUvFs in real water samples.

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