Development of ZrO$_2$-Coated SPME Fibers for Detecting Benzotriazole Ultraviolet Filters in Water Samples

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Original Research Article

ABSTRACT

In this study, the zirconium dioxide nanoparticles (ZrO$_2$NPs) 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@ZrO$_2$NPs fiber were characterized by scanning electron microscopy (SEM). The extraction capability of SS@ZrO$_2$NPs 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@ZrO$_2$NPs fiber showed excellent extraction selectivity and good extraction capability for BUvFs. Under the optimized conditions, the SS@ZrO$_2$NPs-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.

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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].

"ZrO_2 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, ZrO_2 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@ZrO$_2$NPs 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$_2$·8H$_2$O) 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). Fuoranthene (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@ZrO$_2$NPs 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 ZrO$_2$ 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 ZrOCl$_2$ and 0.1 mol/L KCl. After deposition, the SS@ZrO$_2$NPs 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.

3.2 Extraction Selectivity

Fig. 3 shows the extraction selectivity of the SS@ZrO₂NPs fber, 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].
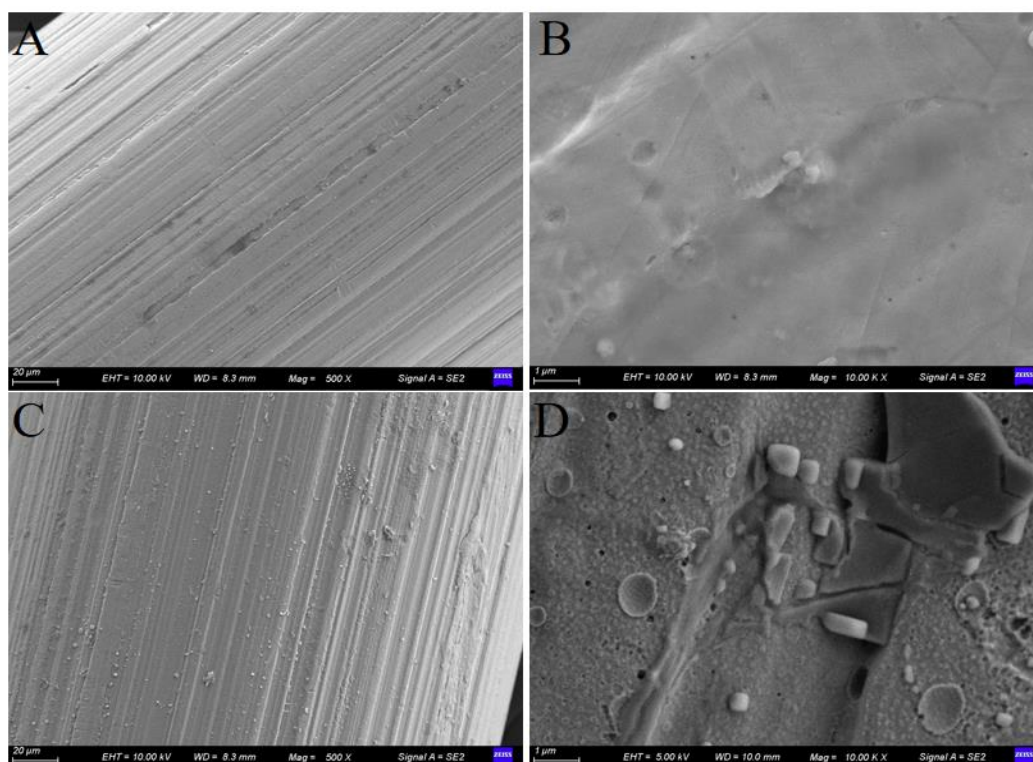

Fig. 1. SEM images of SS fiber (A) Bare SS wire (×500); (B) Bare SS wire (×10,000); (C) SS@ZrO₂NPs fiber (×500); (D) SS@ZrO₂NPs fiber (×10,000)
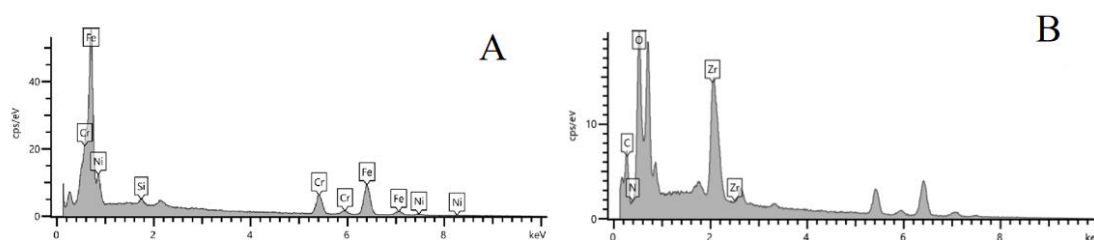
Fig. 2. EDX spectra of SS fiber. (A) Bare SS fiber; (B) SS@ZrO₂NPs fiber
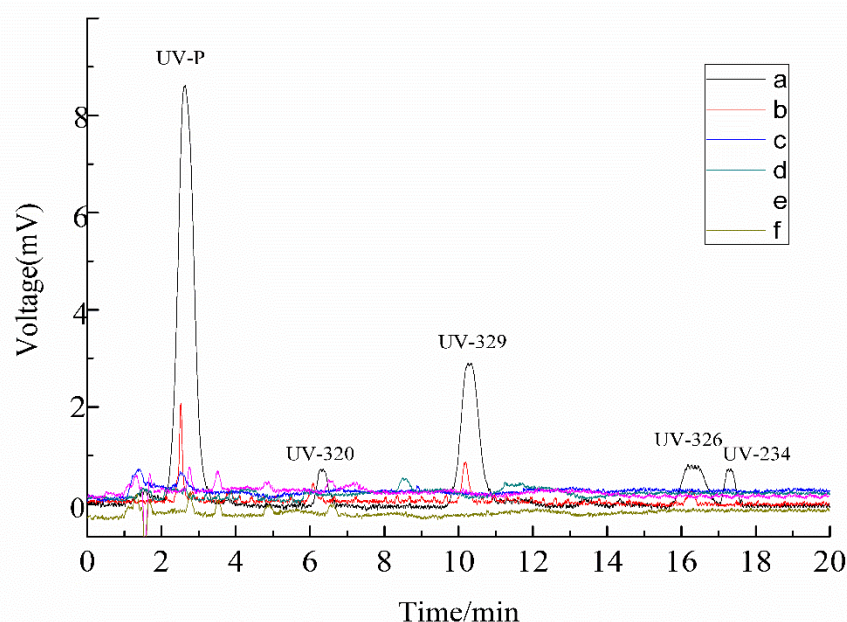

Fig. 3. Chromatograms of direct HPLC (a, c, e) and SPME-HPLC with the SS@ZrO₂NPs fiber (b, d, f). PAEs (a, b), PAHs (c, d) and BUvFs (e, f) at a spiking level of 50 µg/L for each analyte

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/mim. Typically, adding NaCl to the sample solution can increases the ionic strength and reduces 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.

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@ZrO$_2$NPs fiber (n=5)

Analytes	Linear ranges (µg/L)	r^2	Recovery (%)	RSDs 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

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

| Samples	Analytes	Original (µg/L)	Spiked with 15 µg/L			Spiked with 30 µg/L		
			Detected (µg/L)	Recovery (%)	RSDs (%)	Detected (µg/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
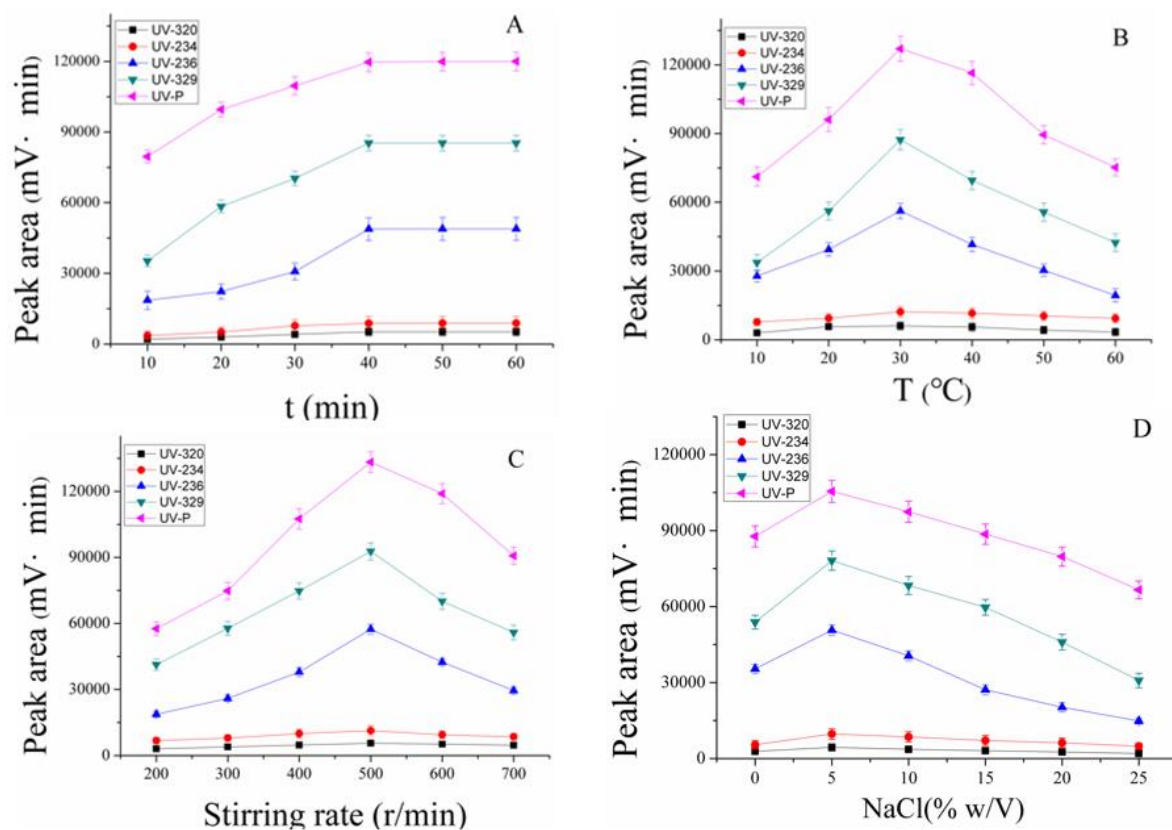
Fig. 4. Main SPME conditions. Extraction time (A); Temperature (B); Stirring rate (C) and Ionic strength (D)

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 μg/L and 30 μg/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.

4. CONCLUSIONS

The SS@ZrO₂NPs fiber was successfully fabricated by cyclic voltammetry. Moreover the ZrO₂NPs caoting 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.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of this manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Arthur CL, Pawliszyn J. Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem. 1990;62:2145-2148.

2. Ji JJ, Liu HH, Chen JM, Zeng JB, Huang JL, Gao LH, Wang YR, Chen X. ZnO nanorod coating for solid phase microextraction and its applications for the analysis of aldehydes in instant noodle samples, J. Chromatogr. A. 2012;1246:22-27.

3. Zhang X, Cai J, Oakes KD, Breton F, Servos MR, Pawliszyn J. Development of the space-resolved solid-phase microextraction technique and its application to biological matrices, Anal. Chem. 2009;81:7349-7356.

4. Zheng J, Kuang Y, Zhou S, Gong X, Ouyang GF. Latest improvements and expanding applications of solid-phase microextraction, Anal. Chem. 2023;95:218-237.

5. Napylov A, Reyes-Garces N, Gomez-Rios G, Olkowicz M, Lendor S, Monnin C, Bojko B, Hamani C, Pawliszyn J, Vuckovic D. *In Vivo* solid-phase microextraction for sampling of oxylipins in brain of awake, moving rats, Angew. Chem. Int. Ed. 2020;59:2392-2398.

6. Ouyang GF, Oakes KD, Bragg L, Wang S, Liu H, Cui S, Servos MR, Dixon DG, Pawliszyn J, Sampling-rate calibration for rapid and nonlethal monitoring of organic contaminants in fish muscle by solid-phase microextraction, Environ. Sci. Technol. 2011;45:7792-7798.

7. Es-haghi A, Hosseininasab V, Bagheri H. Preparation, characterization, and applications of a novel solid-phase microextraction fiber by sol-gel technology on the surface of stainless steel wire for determination of polycyclic aromatic hydrocarbons in aquatic environmental samples, Anal. Chim. Acta. 2014;813:48-55.

8. Es-haghi A, Baghernejad M, Bagheri H. Novel unbreakable solid-phase microextraction fibers on stainless steel wire and application for the determination of oxadiargyl in environmental and agricultural samples in combination with gas chromatography-mass spectrometry, Talanta. 2014;128:231-236.

9. Gholivand MB, Piryaei M, Abolghasemi MM. Anodized aluminum wire as a solid-phase microextraction fiber for rapid determination of volatile constituents in medicinal plant, Anal. Chim. Acta. 2011; 701:1-5.

10. Liu X, Wang X, Tan F, Zhao H, Quan X, Chen J, Li L. An electrochemically enhanced solid-phase microextraction approach based on molecularly imprinted polypyrrole/multi-walled carbon nanotubes composite coating for selective extraction of fluoroquinolones in aqueous samples, Anal. Chim. Acta. 2012;727:26-33.

11. Seabra B, Arantes-oliveira S, Portugal J. Influence of multimode universal adhesives and zirconia primer application techniques on zirconia repair, J. Prosthet. Dent. 2014;112:182-187.

12. Li Y, Yang YX, Liu HX, Wang XM, Du XZ. Fabrication of a novel Ti-TiO$_2$-ZrO$_2$ fiber for solid phase microextraction followed by high performance liquid chromatography for sensitive determination of UV filters in environmental water samples, Anal. Methods. 2014;6:8519-8525.

13. Budziak D, E.Martendal E. Carasek, Application of robust NiTi-ZrO$_2$-PEG SPME fiber in the determination of haloanisoles in cork stopper samples, Anal. Chim. Acta. 2008;629:92-97.

14. Salvador A, Benede JL, Chisvert A. Current trends on the determination of organic UV flters in environmental water samples based on microextraction techniques a review, Anal. Chim. Acta. 2018;1034:22-38.

15. Awonaike B, Lei YD, Parajulee A, Wania F. Phase partitioning, transport and sources of benzotriazole ultraviolet stabilizers during a runof event, Water research X. 2021;13:100115.

16. Denghel H, Leibold E, Goen T. Oxidative phase I metabolism of the UV absorber 2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol (UV 328) in an *In vitro* model with human liver microsomes, Toxicology *In vitro*. 2019;60:313-322.

17. Giokas DL, Salvador A, Chisvert A, UV flters: from sunscreens to human body and the environment, TRAC-Trend. Anal. Chem. 2007;26:360-374.

18. Peng XZ, Jin J, Wang CW, Ou WH, Tang CM. Multi-target determination of organic

ultraviolet absorbents in organism tissues by ultrasonic assisted extraction and ultrahigh performance liquid chromatography-tandem mass spectrometry, J. Chromatogr. A. 2015; 1384:97-106.

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