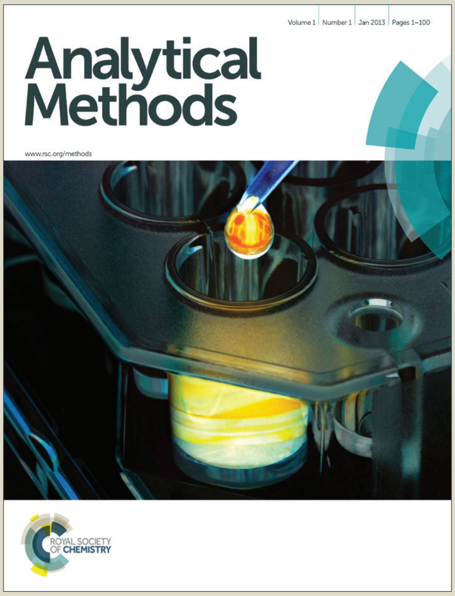
Analytical Methods

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

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

Yi Li [1], Yaoxia Yang [1], Haixia Liu [1], Xuemei Wang [1,2], Xinzhen Du [1,2*]

[1] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, P. R. China

[2] Key Lab of Bioelectrochemistry & Environmental Analysis of Gansu, Lanzhou 730070, P. R. China

A novel Ti-TiO_2-ZrO_2 fiber for solid-phase microextraction (SPME) was fabricated by chemical oxidization of a Ti wire substrate and subsequent electrodeposition of ZrO_2 nanoparticles coating. The chemically oxidized procedure afforded in situ fabrication of porous TiO_2 nanostructures on a Ti wire and provided a desirable substrate for further deposition of ZrO_2 nanoparticles coating. The best extraction capability was obtained by ZrO_2 nanoparticles with a size distribution of 20-30 nm and a coating thickness of about 4.5 μm after 10 cyclic voltammetry scans. The main parameters affecting the Ti-TiO_2-ZrO_2 fiber for SPME of ultraviolet (UV) filters were investigated coupled to high-performance liquid chromatography with UV detection. Good linearity was achieved in the range of 0.5-500 $\mu g\cdot L^{-1}$ with correlation coefficients higher than 0.996. Limits of detection were 0.032-0.082 $\mu g\cdot L^{-1}$ (S/N=3). The single fiber repeatability ranged from 4.3% to 12% and the fiber-to-fiber

---

[*] Corresponding author.

E-mail address: xinzhendu@yahoo.com (X.-Z. Du).

reproducibility from 4.3% to 11% for SPME of spiked water with 50 $\mu g \cdot L^{-1}$ UV filters (n=5). Furthermore this fiber has high stability, long service life and high extraction capability for UV filters compared to the commercially available polymeric fibers.

Keywords: ZrO_2 nanoparticles, porous TiO_2 nanostructures, electrodeposition, solid-phase microextraction, ultraviolet filters.

1. Introduction

Solid phase microextraction (SPME) is an attractive alternative to traditional sample preparation methods because it integrates sample extraction, concentration and introduction into one step.[1] It has been successfully applied to environmental,[2-5] biological,[6] crude oil[7] and food analysis[8] coupled with gas chromatography (GC) or high performance liquid chromatography (HPLC). However, commercial silica-based fibers are relatively expensive and show some drawbacks such as fragility, bending of the needle, the stripping of coatings, and easily swelling in organic solvent which limit its widespread applications.[9] Therefore, the development of novel microextraction fibers has become popular in this field in the past two decades.[10] Great efforts have directed to the development of metal-based fibers with thermally and chemically stable coatings that have high extraction performance and/or selectivity for the specified analytes.[11-20] With regard to inorganic materials, ZrO_2 is one of the most versatile ceramic materials due to its durability, resistance to corrosion and wear, strong adhesion onto metallic surfaces and non-toxicity.[21] It has been successfully used as a stationary phase in HPLC to analyze many analytes due to its high mechanical stability, good adsorption and excellent pH stability.[22] Budziak et al. also has carried out the electrodeposition of ZrO_2 on a NiTi wire as a fiber for SPME of halophenols in water samples.[23] This novel NiTi-ZrO_2 fiber showed a better extraction capability in comparison with the commercial fibers and a lifetime of over 300 extractions. Thus, it is a promising alternative for low-cost analysis due to its robustness and easy preparation.

Recently, nanostructured TiO_2-based SPME fibers were fabricated through the in situ oxidation of Ti wires with hydrogen peroxide[24] and the anodization of Ti wires in an electrolyte containing ethylene glycol and ammonium floride.[25] These novel TiO_2-based SPME fibers provide promising alternative substrates for further fabrication of highly efficient and rigid ZrO_2 coatings because they exhibit much larger surface area and better active sites. Electrodeposition can offer a rigid control of coating thickness, uniformity and deposition rate for ZrO_2 coatings. This technique is especially attractive for further deposition onto the substrates with complex shapes.[21]

Ultraviolet (UV) filters usually possess single or multiple aromatic structures conjugated with carbon-carbon double bonds and/or carbonyl moieties and are frequently used in a variety of cosmetics that mitigate the deleterious effects of direct sunlight exposure by absorbing UV radiation.[26] Their detection has shown that UV filters are directly or indirectly released into aquatic environment during bathing and washing activities via domestic wastewater.[27] A preliminary study reported that some UV filters are estrogenic, antiestrogenic, androgenic and antiandrogenic in vitro and in vivo.[28] For these reasons, more efforts were made to the development of accurate, convenient and robust methods to determine these emerging pollutants from different environmental matrices. To date, various pretreatment techniques such as solid phase extraction (SPE),[29] SPME,[27] single-drop microextraction (SDME),[30] hollow fiber supported liquid phase microextraction (HF-LPME),[31] dispersive liquid-liquid microextraction (DLLME)[32-35] have been successfully applied to extract UV filters from aqueous samples. In this work, a novel Ti-TiO_2-ZrO_2 fiber was fabricated using the cyclic voltammetry (CV) by a combination of the in situ fabrication of TiO_2-based nanostructure with subsequent electrodeposition of ZrO_2 nanoparticles coating at Ti wire surface. It was expected that strong Lewis acidic sites at the surface of ZrO_2 coating would show good affinity for UV filters with Lewis basic character. The microextraction conditions were examined and investigated. The extraction efficiency of ZrO_2 nanoparticles coating was compared with that of commercially available polydimethylsiloxane (PDMS) and polyacrylate (PA) fibers. The established procedure was successfully applied to the efficient preconcentration and sensitive determination of UV filters from the environmental water samples.

2. Experimental

2.1 Materials and reagents

Ti wire (purity 99.9%, ϕ0.127 mm) was obtained from Alfa Aesar (Ward Hill, MA, USA). 0.45 μm micropore membrane of polyvinylidene fluoride was supplied by Xingya Purifying Material Factory (Shanghai, China). Hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO_3) and hydrogen peroxide (H_2O_2, 30%, w/v) were obtained from Yantai Shuangshuang Chemicals Ltd (Shandong, China). Sodium chloride (NaCl) and potassium chloride (KCl) was obtained from Shanghai Hunter Fine Chemicals Ltd (Shanghai, China). Zirconium (IV) oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The HPLC-grade methanol was purchased from Yuwang Chemical Company (Shandong, China). Certified 2-hydroxy-4-methoxybenzophenone (BP-3, purity 100%, Lot No. 14971), 2-ethylhexyl-4-methoxycinnamate (EHMC, purity 98%, Lot No. 18565) and 2-ethylhexyl 4-(*N,N*-dimethylamino) benzoate (OD-PABA, purity 97%, Lot No. 23111) were purchased from AccuStandard (New Haven, USA). 2-Ethylhexyl salicylate (EHS, purity 99%, Lot No.

00902) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). The stock standard solution of 100 mg·L^{-1} of each compound was prepared in methanol and stored in amber bottles in the refrigerator at 4 ^{o}C, shielding from light. Working standard solutions were prepared by diluting the stock standard solution with ultrapure water to the required concentration to study extraction performance under different conditions. All other reagents were of analytical grade.

2.2 Instruments

A Waters 600E multi-solvent delivery system (Milford, MA, USA) equipped with Waters 2487 dual λ absorbance detector and a Waters Sunfire C_{18} chromatographic column (150 mm×4.6 mm, 5 μm) was used for all separations. Data collection was obtained with a N2000 workstation (Zhejiang University, China). The mobile phase was methanol/water (90/10, v/v) and the wavelength of UV detection was set at 310 nm. Desorption was performed in a commercially available SPME-HPLC interface (Supelco, PA, USA) and sealed by polyether ether ketone septum which is tight enough to withstand pressure as high as 29.7 MPa. Ultrapure water was obtained from a Sudreli water purifying system (Chongqing, China). Heating and stirring was carried out in a DF-101S water bath with magnetic stirrer (Zhengzhou, China). Electrodeposition of ZrO_2 nanoparticles coating onto the surface of the TiO_2-based wire was performed on a CHI832D analyzer (Shanghai, China). The morphology and composition of the fabricated fibers were characterized by an Ultra Plus microscope (Zeiss, Oberkochen, Germany) equipped with semi-quantitative microanalysis by energy dispersive X-ray spectroscopy (EDS).

2.3 Fabrication of Ti-TiO_2-ZrO_2 fibers

The fabrication of Ti-TiO_2-ZrO_2 fibers includes the following steps. A 10-mm tip segment of Ti wires was soaked in a mixture of concentrated HF, concentrated HNO_3 and water (1:3:6, v/v/v) at room temperature for 30 s, followed by ultrasonication in water.[24] Thereafter, the etching part was dipped in H_2O_2 (30%, w/v) solution held in a 15-mL plastic test tube sealed with a cap and then the plastic test tube was placed in an oil bath (200 $r \cdot min^{-1}$, 80 ^{o}C) for 24 h. Finally the Ti wires were rinsed gently with water and allowed to dry in air. Prior to electrodeposition of ZrO_2, the Ti-TiO_2 fibers were ultrasonically cleaned in ultrapure water for 1 min to remove surface debris and dipped in a 1.0 $mol \cdot L^{-1}$ sodium hydroxide for 60-min activation of the TiO_2-based surface and then in 0.1 $mol \cdot L^{-1}$ HCl for 30 min, and washed with ultrapure water for 5 min. Subsequently ZrO_2 nanoparticles were deposited onto the TiO_2-based surface in the electrolyte of 0.005 $mol \cdot L^{-1}$ $ZrOCl_2$ and 0.1 $mol \cdot L^{-1}$ KCl by CV between -2.0 and 0 V (versus Ag/AgCl) at a scanning rate of 20 $mV \cdot s^{-1}$ for 10 cycles.[36] The as-fabricated fibers were gently rinsed with ultrapure water and then dried in air.

2.4 Real water samples

Real environment water samples include 4 river water and 2 wastewater samples. River water samples were freshly collected from different sites in the Lanzhou section of the Yellow River. Wastewater samples were collected from local wastewater treatment plants. All real water samples were collected in amber glass and were filtered through 0.45 μm micropore membranes, then stored in the dark at 4 ^{o}C. The pH value of water samples was adjusted with 0.1 $mol \cdot L^{-1}$ HCl or ammonia prior to analysis.

2.5 SPME-HPLC procedure

15 mL of working standard solution or sample solution was transferred into a 20-mL glass

vial with 1-cm magnetic stirrer bar inside and a Teflon septum. The Ti-TiO_2-ZrO_2 fiber was immersed into the stirred solution for 30 min at 35 ^{o}C. Subsequently, the fiber was withdrawn from the sample solution and introduced into the SPME-HPLC interface for static desorption in mobile-phase. After desorption, six-port valve was switched from load to inject position, the mobile phase was passed through the interface and UV filters were introduced into the analytical column at a flow rate of 1 $mL\cdot min^{-1}$ for HPLC analysis. For next extraction, the fiber was immersed into methanol and ultrapure water to eliminate possible carry-over for 10 min and 5 min, respectively.

3. Results and discussion

3.1 Characterization of nanostructured Ti-TiO_2-ZrO_2 fibers

Nanostructured ZrO_2 can be deposited onto TiO_2-based surface through cathodic reactions.[37] The thickness of ZrO_2 coating can be controlled by the number of CV cycles. Fig. 1 shows the micrographs of scanning electron microscopy (SEM) obtained for a Ti wire fiber at different stage. The TiO_2-based surface (Fig. 1a and 1b) is rough and porous with pore size of 50-120 nm compared to that of the bare Ti wire (Fig. 1a_1) and can provide a desirable substrate for subsequent compact electrodeposition of ZrO_2. As shown in Fig. 1c-1f, some crackings of the electrodeposited ZrO_2 coatings were observed. These crackings result from a tension due to shrinking of the ZrO_2 coating layers.[38] Thicker ZrO_2 coatings electrodeposited by 20 CV cycles and 30 CV cycles lead to more significant crackings as shown in Fig. 1e and Fig. 1f. This phenomenon results in a significant decrease in effective surface area of ZrO_2 coatings and thereby a great decrease in peak area, and the best extraction capability was obtained for ZrO_2 coating with 10 CV cycles (See Fig. S1). Furthermore higher magnification of ZrO_2 coating in Fig. $1d_1$ clearly demonstrates that ZrO_2 nanoparticles were fabricated onto the nanostructured TiO_2 surface with a size distribution of 20-30 nm and a thickness of about 4.5 μm, and thereby greatly increase extraction efficiency of target UV filters. On the one hand, the electrodeposited ZrO_2 nanoparticles coating exhibits strong affinity for polar organic compounds due to the presence of Zr-OH at the surface of ZrO_2 coating. On the other hand, it is expected that strong Lewis acidic sites at the surface of ZrO_2 nanoparticles would show good affinity for target analytes with Lewis basic character. Thus 10 CV cycles were employed for the electrodeposition of ZrO_2 coating in this study.

Fig. 1

The chemical analysis of the TiO_2-based wire was also performed by EDS. The spectrum obtained for the TiO_2-based surface only shows peaks corresponding to the presence of titanium and oxygen (Fig. 2a). For the Ti-TiO_2-ZrO_2 fiber, a strong peak also appears at 2.1 keV (Fig. 2b). This can be attributed to the emission line of zirconium due to ZrO_2 nanoparticles electrodeposited onto the TiO_2-based surface. These phenomena provide additional evidence for the results obtained by SEM.

Fig. 2

3.2 Optimization of SPME conditions

The main parameters affecting the Ti-TiO_2-ZrO_2 fiber for SPME of four UV filters was examined in aqueous samples. Dependence of SPME on extraction and desorption time, temperature, ionic strength, stirring rate and pH was optimized to obtain excellent extraction efficiency.

3.2.1 Effect of extraction and desorption time

Extraction time is a crucial factor in SPME. Generally the longer extraction time results in the higher extraction efficiency and sensitivity prior to equilibrium. The extraction time profile of UV filters is shown in Fig. 3a. The chromatographic peak area nearly reaches its maximum within 30 min except OD-PABA. The equilibration time clearly indicates that ZrO_2 nanoparticles coating is favorable for mass transfer of UV filters from bulk solution to fiber coating. Taking account of a reasonable compromise between a good sensitivity and an acceptable time analysis, 30 min was chosen for SPME of UV filters in subsequent experiment. After extraction, solvent desorption of the extracted UV filters was performed in mobile phase. For all UV filters, the peak area reached the constant maximum within 4 min. Thus, 4 min was employed for the desorption of UV filters in mobile phase.

Fig. 3

3.2.2 Effect of extraction temperature

Temperature is a very important parameter for SPME because it can affect the extraction rate and equilibrium. Fig. 3b presents the effect of temperature on the extraction of UV filters from 15 to 65 ^{o}C. The highest extraction efficiencies were obtained at 35 ^{o}C. Thereafter, the extraction capability quickly decreased when the temperature continuously increased. This is most probably due to the decreased distribution coefficients of UV filters between the ZrO_2 coating and water along with increasing temperature. In addition, the dissolution of UV filters also decreases the extraction efficiency at higher temperature. Therefore extraction temperature of 35 ^oC was used.

3.2.3 Effect of ionic strength

Addition of the salt can decrease the solubility of less polar organic analytes and affect the surface properties of fiber coatings at the same time, and finally influence the adsorption behavior of the prepared fibers. Thus the effect of ionic strength was further examined by adding NaCl ranging from 0 to 30% (w/v) into the working solutions. A negative effect on extraction efficiencies of UV filters was observed in aqueous phase with more than NaCl of 5%. Therefore, no salt addition was recommended in this study.

3.2.4 Effect of stirring rate

Extraction efficiency enhances with increasing stirring rate because stirring accelerates the mass transfer of the analytes from the solution to fiber coating. In the experiment, the extraction efficiency maximum of UV filters was achieved at the stirring rate of 800 $r \cdot min^{-1}$. More vigorous stirring led to bubble formation which is unfavorable to adsorption process at the surface of fiber with $Ti\text{-}TiO_2\text{-}ZrO_2$ nanoparticles coating. Therefore the stirring rate was fixed at 800 $r \cdot min^{-1}$.

3.2.5 Effect of pH

Effect of pH on the SPME of UV filters was examined within the pH range of 2.0-9.0. Due to their protonation at pH<4, all UV filters are capable of existing in their cationic form and soluble in aqueous solutions. Thus extremely low extraction efficiencies for UV filters were obtained. At pH 7.0, their neutral forms are beneficial for their adsorption onto the

$Ti\text{-}TiO_2\text{-}ZrO_2$ coating and thereby the highest extraction efficiencies were achieved. In the case of pH>7.0, however, all UV filters exhibit rapidly decreased extraction efficiencies. Therefore, pH 7.0 was employed for SPME procedure.

3.3 Analytical figures of merit

The analytical performance of the fabricated $Ti\text{-}TiO_2\text{-}ZrO_2$ fibers was examined for targeted UV filters under optimized conditions. Table 1 summarizes their linear ranges with corresponding correlation coefficients (r^2), the recoveries and the limits of detection (LOD) (S/N = 3) of the proposed method. Good linearity and high sensitivity were achieved. The single fiber repeatability for five replicate extractions of UV filters at the spiking level of 50 $\mu g \cdot L^{-1}$ varied from 4.3% to 9.0% and from 9.4% to 12% for intraday and interday SPME-HPLC-UV of UV filters, respectively. The fiber-to-fiber reproducibility of five parallel fabricated fibers ranged from 4.3% to 11%. Furthermore the durable measurements for the single fiber in aqueous phase and mobile phase showed acceptable change in the extraction efficiency over 250 cycles of SPME.

Table 1 Analytical parameters of the proposed method (n=5)

UV filters	Linear range ($\mu g \cdot L^{-1}$)	r^2	Recovery (%)	Single fiber repeatability		Fiber-to-fiber reproducibility (%)	LOD ($\mu g \cdot L^{-1}$)
				Intraday (%)	Interday (%)		
BP-3	0.5-400	0.9994	82.24	5.0	12	11	0.032
OD-PABA	0.5-500	0.9984	97.42	4.3	11	4.3	0.044

EHMC	0.5-500	0.9970	103.7	9.0	9.4	10	0.075
EHS	0.5-500	0.9961	106.6	8.6	12	10	0.082

3.4 Real samples analysis

The proposed method was employed for the preconcentration and determination of the target UV filters in environmental water samples. Furthermore all water samples were fortified with the certified target analytes at two concentration levels (10 $\mu g \cdot L^{-1}$ and 50 $\mu g \cdot L^{-1}$ of each analyte) to identify the target UV filters based on their retention time and to study possible matrix effects. The proposed method was evaluated by means of relative recovery (defined as the ratio of detected concentration to that of spiked real water). The results were listed in Table 2. The mean recoveries ranged from 77.28% to 113.6% and RSD was between 4.9% and 12%. Furthermore Fig. 4 shows typical chromatograms of direct HPLC (Fig. 4a) and SPME-HPLC (Fig. 4b, 4c and 4d) for raw and spiked wastewater (No. 2) by the fabricated Ti-TiO_2-ZrO_2 fiber. As compared with commercial 100-μm PDMS (Fig. 4e) and 85-μm polyacrylate (Fig. 4f) fibers, the fabricated Ti-TiO_2-ZrO_2 fiber exhibits greatest extraction capability of UV filters for spiked wastewater at 50 $\mu g \cdot L^{-1}$ (Fig. 4d). These results clearly demonstrate that the fabricated Ti-TiO_2-ZrO_2 fiber is reliable and suitable for the preconcentration and determination of UV filters in environmental water samples.

Table 2 Analytical results of UV filters in different environmental water samples (n=3)

Samples	UV filters	Original	Spiked with 10 $\mu g \cdot L^{-1}$			Spiked with 50 $\mu g \cdot L^{-1}$		
		($\mu g \cdot L^{-1}$)	Detected	Recovery	RSD	Detected	Recovery	RSD

			(μg·L^{-1})	(%)	(%)	(μg·L^{-1})	(%)	(%)
River water under Bapanxia Bridge	BP-3	ND [a]	8.33	83.30	8.4	44.01	88.02	6.3
	OD-PABA	2.67	12.20	96.29	9.6	44.24	83.99	5.4
	EHMC	1.27	11.57	102.6	10	48.24	94.09	6.2
	EHS	0.72	9.55	89.08	8.5	43.23	85.23	7.4
River water under Yintan Bridge	BP-3	4.01	14.5	103.4	11	61.06	113.1	9.1
	OD-PABA	8.29	19.37	105.9	9.8	50.43	86.52	8.2
	EHMC	6.88	18.61	110.2	11	52.43	92.17	6.3
	EHS	7.84	15.70	88.00	10	55.37	95.72	5.5
River water under Donggang Bridge	BP-3	0.64	11.95	112.3	10	56.51	111.6	9.0
	OD-PABA	2.33	10.33	83.77	11	49.78	95.12	5.5
	EHMC	1.41	12.02	105.3	8.9	44.79	87.58	4.9
	EHS	0.83	8.37	77.28	7.9	43.11	84.81	6.4
River water under Shichuan Bridge	BP-3	ND	10.29	102.9	12	53.04	106.1	9.2
	OD-PABA	5.53	12.73	81.97	12	49.36	88.89	8.1
	EHMC	4.76	13.38	90.65	8.3	48.82	89.15	7.2
	EHS	1.24	10.27	91.37	9.2	42.87	83.67	6.5
Influent from wastewater treatment plant No.1	BP-3	ND	11.36	113.6	10	45.37	90.74	6.3
	OD-PABA	6.97	15.02	88.50	9.5	45.95	80.65	8.7
	EHMC	4.76	17.10	115.8	9.2	53.24	97.22	8.9
	EHS	ND	10.45	104.5	11	54.36	108.7	7.8

Influent from wastewater treatment plant No. 2	BP-3	ND	11.57	115.7	9.9	47.57	95.15	6.5
	OD-PABA	3.43	12.38	92.18	8.6	45.10	84.41	6.8
	EHMC	2.28	12.15	98.94	10	45.51	87.06	5.4
	EHS	ND	8.31	83.10	9.7	52.53	105.1	7.3

a) ND, Not detected or lower than LOD.

Fig. 4

3.4 Comparison of the proposed method with reported methods

The proposed method was compared with the reported methods with respect to sample volume, extraction time, linear range, LOD, RSD and recovery. As can be seen in Table 3, the extraction equilibrium was almost achieved within 30 min. Moreover, the LOD values also suggest that this proposed method exhibit high sensitivity for the determination of targeted UV filters. Simple operation procedure makes the sample preparation easy, rapid and suitable for the preconcentration and determination of trace UV filters in real environmental water. The experimental results for the proposed method are comparable or better than those in the reported literatures.[31,33,35,39-41]

Table 3 Comparison of the current method with other methods for extraction and determination of UV filters

Instrumentation[a]	Volume (mL)	Time (min)	Linear ranges ($\mu g \cdot L^{-1}$)	LOD ($\mu g \cdot L^{-1}$)	RSD (%)	Recovery (%)	Refs
SPME-GC-FID	5	45	10-500	0.87-2.47[b]	4.5-7.9	82-99	27
SPE-LC-DAD	500	~30	0.02-0.2	0.014[b]	2.8	95-97	29
SDME-LC-UV	20	37	1-150	0.07-0.19	2.8-7.9	96-110	30
HF-LPME-HPLC-UV	10	50	5-1000	0.2-0.5	1.1-8.4	95.2-104.9	31
MSA-DLLME-HPLC-DAD	20	>25	5-20000	0.2-0.8	1.4-4.8	91.3-97.1	33
DLLME-HPLC-UV	10	10	0.5-500	0.06-0.16	2.8-7.6	92.8-114	35
SPME-HPLC-UV	15	30	0.1-400	0.026-0.089	4.5-8.7	94-103	39
UDSA-IL-DLLME-UPLC-DAD	5	>6	2-1000	0.23-1.3	1.0-2.9	92-120	40
VA-DLLME-GC-MS	10	>4	0.05-10	0.02-0.1	6.1-12	71-120	41
SPME-HPLC-UV	15	30	0.5-500	0.032-0.082	4.2-8.9	82.2-106.6	This method

[a] DAD, photodiode array detection; FID, flame ionization detection; MSA, magnetic stirring-assisted; UDSA, Up-and-down shaker-assisted.

[b] Limit of quantitation.

4. Conclusions

In this study, ZrO_2 nanoparticles coating was fabricated on a nanostructured TiO_2-based substrate as a SPME fiber coating by previous chemical oxidation and subsequent elecrodeposition using CV technique. The ZrO_2 nanoparticles coatings were tightly attached onto the nanostructured TiO_2 substrate with larger surface area. This robust fiber was more effective than the commercially available PDMS and PA fibers for SPME of UV filters and used for more than 250 extraction and desorption cycles without the loss of the extraction capability. This novel Ti-TiO_2-ZrO_2 fiber was easily fabricated in a highly reproducible manner. It offered a simple, rapid, sensitive and inexpensive pretreatment way for the preconcentration and determination of targeted UV filters in real environmental water samples.

Acknowledgement

This research was financially supported by the National Natural Science Foundation of China (Grant no. 21265019).

References

1 C. L. Arthur and J. Pawliszyn, *Anal. Chem.*, 1990, **62**, 2145-2148.

2 B. Mokhtari, N. Dalali and K. Pourabdollah, *J, Sep. Sci.,* 2013, **36**,356-361.

3 H. T. Liu, L. Liu, Y. Q. Xiong, X. M. Yang and T. G. Luan, *J. Chromatogr. A*, 2010, **1217**, 6747-6753.

4 B. Mokhtari, N. Dalaali and K. Pourabdollah, *J. Chil. Chem. Soc.*, 2012, **57**, 1428-1431.

5 B. Mokhtari, N. Dalaali and K. Pourabdollah, *J. Chin. Chem. Soc.*, 2013, **60**, 625-631.

6 X. Zhang, J. B. Cai, K. D. Oakes, F. Breton, M. R. Servos and J. Pawliszyn, *Anal. Chem.*, 2009, **81**, 7349-7356.

7 B. Mokhtari and K. Pourabdollah, *Talanta*, 2011, **87**, 118-125.

8 N. Campillo, R. Peñalver, I. López-García and M. Hernández-Córdoba, *J. Chromatogr. A*, 2009, **1216**, 6735-6740.

9 Y. Liu, M. L. Lee, K. J. Hageman, Y. Yang and S. B. Hawthorne, *Anal. Chem.*, 1997, **69**, 5001-5005.

10 A. Mehdinia and M. O. Aziz-Zanjani, *Trends Anal. Chem.*, 2013, **42**, 205-215.

11 X. Z. Du, Y. R. Wang, X. J. Tao and H. L. Deng, *Anal. Chim. Acta*, 2005, **543**, 9-16.

12 L. Setkova, S. Risticevic, C. M. Linton, G. F. Ouyang, L. M. Bragg and J. Pawliszyn, *Anal. Chim. Acta*, 2007, **581**, 221-231.

13 H. Bagheri, E. Babanezhad and A. Es-Haghi, *J. Chromatogr. A*, 2007, **1152**, 168-174.

14 J. B. Zeng, B. B. Yu, W. F. Chen, Z. J. Lin, L. M. Zhang, X. Chen and X. R.Wang, *J. Chromatogr. A*, 2008, **1188**, 26-33.

15 P. Hashemi, M. Shamizadeh, A. Badiei, P. Z. Poor, A. R. Ghiasvand and A. Yarahmadi, *Anal. Chim. Acta*, 2009, **646**, 1-5.

16 Y. H. Wang, Y. Q. Li, J. Zhang, S. F. Xu, S. G.Yang and C. Sun, *Anal. Chim. Acta*, 2009, **646**, 78-84.

17 H. L. Xu, Y. Li, D. Q. Jiang and X. P. Yan, *Anal. Chem.*, 2009, **81**, 4971-4977.

18 X. Y. Cui, Z. Y. Gu, D. Q. Jiang, Y. Li, H. F. Wang and X. P. Yan, *Anal. Chem.*, 2009, **81**, 9771-9777.

19 N. Chang, Z. Y. Gu, H. F. Wang and X. P. Yan, *Anal. Chem.*, 2011, **83**, 7094-7101.

20 J. J. Ji, H. H. Liu, J. M. Chen, J. B. Zeng, J. L. Huang, L. H. Gao, Y. R. Wang and X. Chen, *J. Chromatogr. A*, 2012, **1246**, 22-27.

21 I. Zhitomirsky and A. Petric, *Mater. Lett.*, 2000, **46**, 1-6.

22 M. Grfin, A. A. Kurganov, S. Schacht, F. Schiith and K. K. Unger, *J. Chromatogr. A*, 1996, **740**, 1-9.

23 D. Budziak, E. Martendal and E. Carasek, *J. Chromatogr. A*, 2007, **1164**, 18-24.

24 D. D. Cao, J. X. Lü, J. F. Liu and G. B. Jiang, *Anal. Chim. Acta*, 2008, **611**, 56-61.

25 H. M. Liu, D. A. Wang, L. Ji, J. B. Li, S. J. Liu, X. Liu and S. X. Jiang, *J. Chromatogr. A*, 2010, **1217**, 1898-1903.

26 A. Salvador and A. Chisvert, *Anal. Chim. Acta*, 2005, **537**, 1-14.

27 D. A. Lambropoulou, D. L.Giokas, V. A.Sakkas, T. A. Albanis and M. I. Karayannis, *J. Chromatogr. A*, 2002, **967**, 243-253.

28 P. Y. Kunz and K. Fent, *Aquat. Toxicol.*, 2006, **79**, 305-325.

29 D. L. Giokas, V. A. Sakkas and T. A. Albanis, *J. Chromatogr. A*, 2004, **1026**, 289-293.

30 L. Vidal, A. Chisvert, A. Canals and A. Salvador, *Talanta*, 2010, **81**, 549-555.

31 D. D. Ge and H. K.Lee, *J. Chromatogr. A*, 2012, **1229**, 1-5.

32 B. Mokhtari and K. Pourabdollah, *J. Incl. Phenom. Macrocycl. Chem.*, 2012, **74**, 183-189.

33 P. P. Zhang, Z. G. Shi, Q. W. Yu and Y. Q. Feng, *Talanta*, 2011, **83**, 1711-1715.

34 B. Mokhtari and N. Dalali, *Chromatographia*, 2013, **76**, 565-570.

35 L. K. Xue, W. W. Ma, D. X. Zhang and X. Z. Du, *Anal. Methods*, 2013, **5**, 4213-4219.

36 G. D. Liu and Y. H. Lin, *Anal. Chem.*, 2005, **77**, 5894-5901.

37 F. C. Giacomelli, C. Giacomelli, A. G. De Oliveira and A. Spinelli, *Mater. Lett.*, 2005, **59**, 754-758.

38 S. K. Yen, *Mater. Chem. Phys.*, 2000, **63**, 256-262.

39 Y. Li, M. Zhang, Y. X. Yang, X. M. Wang and X. Z. Du, *J. Chromatogr. A,* 2014, ***1358,*** 60-67.

40 Y. C. Ku, M. L. Leong, W. T. Wang and S. D. Huang, *J. Sep. Sci.*, 2013, **36**, 1470-1477.

41 Y. F. Zhang and H. K. Lee, *J. Chromatogr. A*, 2012, **1249**, 25-31.

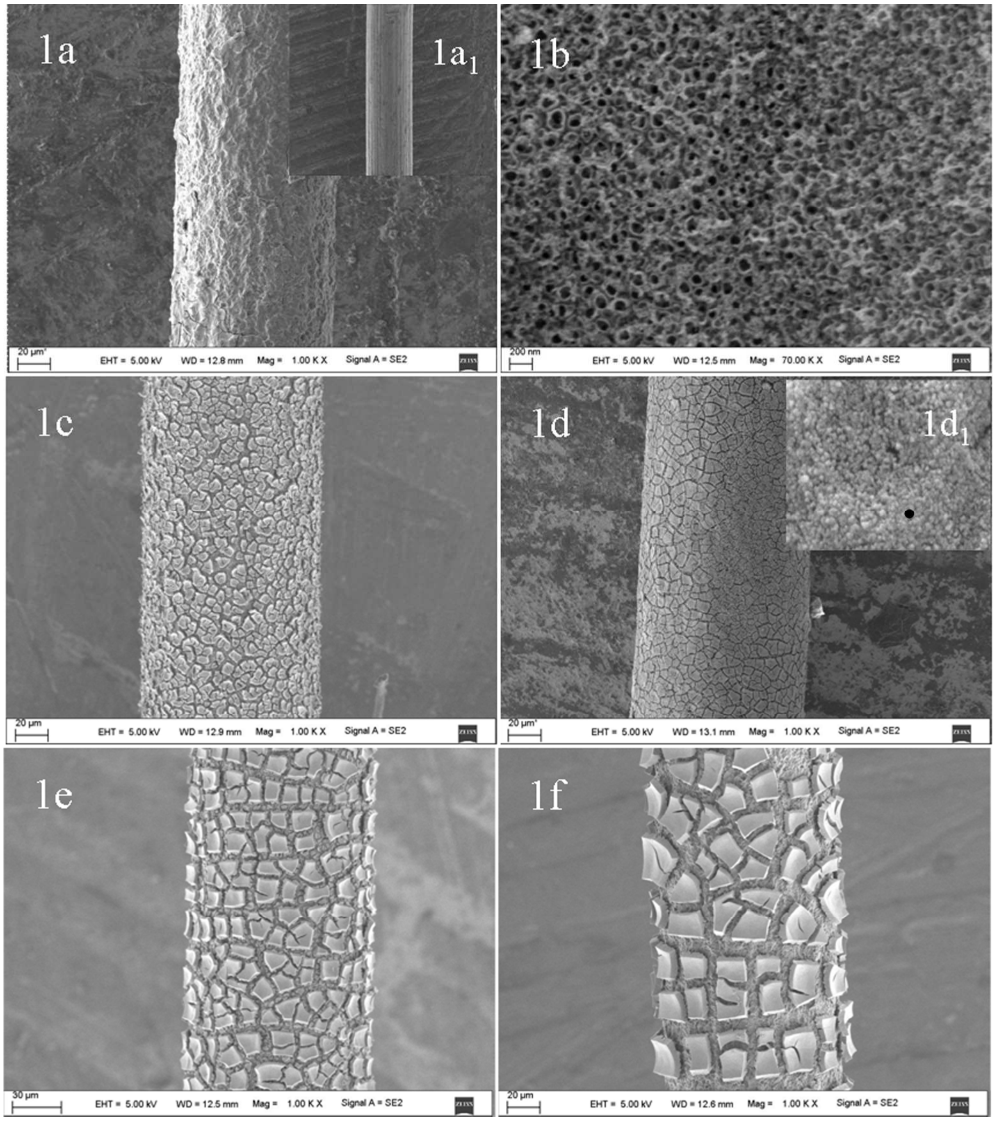


Fig. 1 SEM micrographs of TiO2-based wire surface (a×1000 and b×70000) and electrodeposited ZrO2 nanoparticles coatings (×1000) by CV after 5 (c), 10 (d), 20 (e) and 30 cycles (f).
254x283mm (300 x 300 DPI)

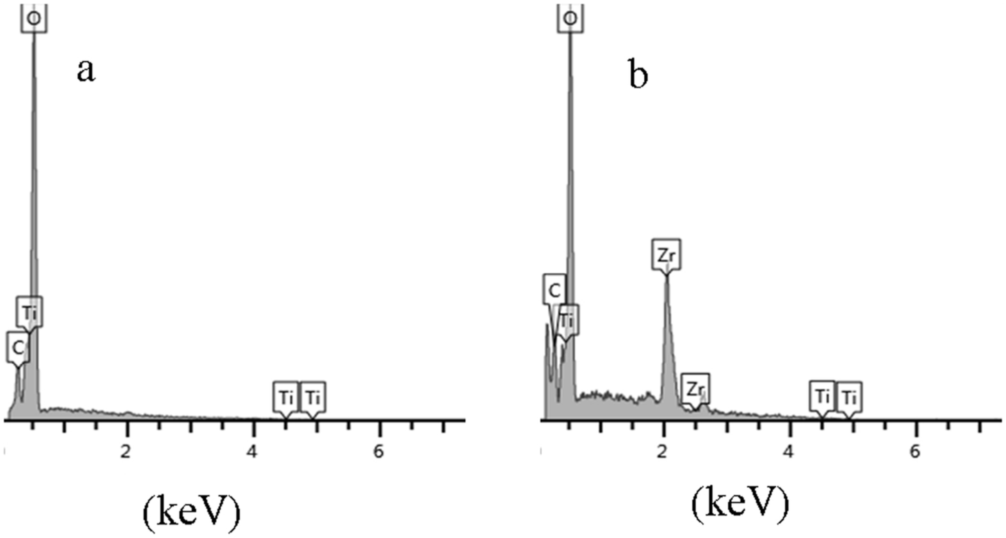


Fig. 2 EDS spectra of TiO2-based wire (a) and the Ti-TiO2-ZrO2 fiber (b).
128x69mm (300 x 300 DPI)

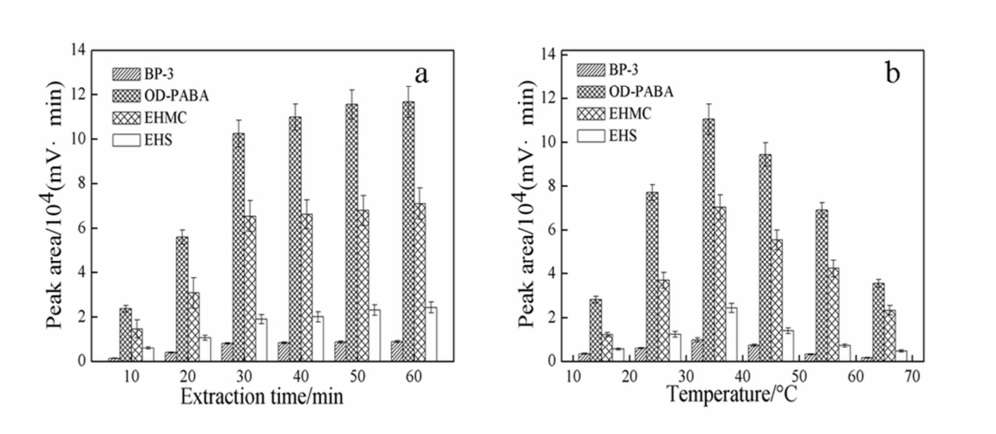


Fig. 3 Effect of extraction time and temperature on the extraction efficiency.
89x39mm (300 x 300 DPI)

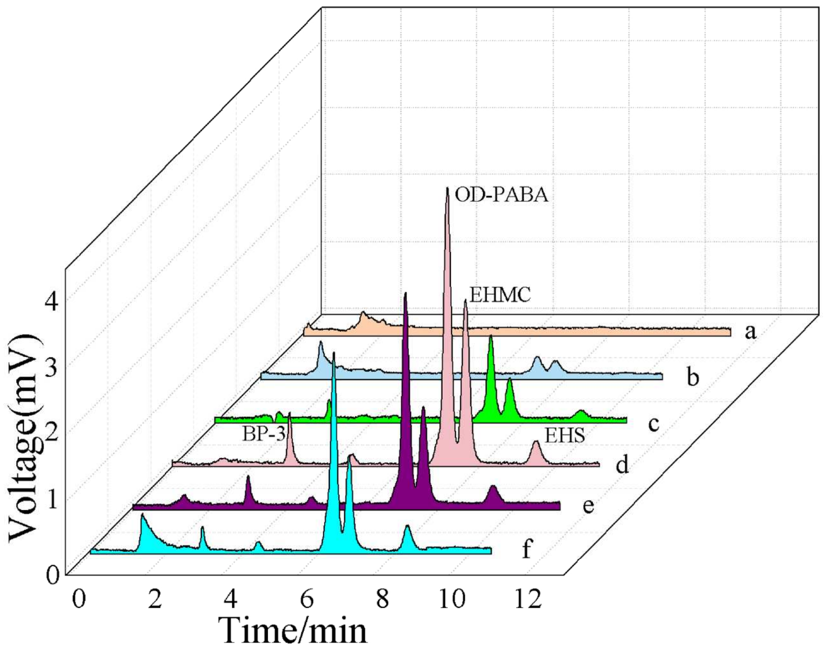


Fig. 4 Chromatograms of direct HPLC and SPME-HPLC for wastewater (No. 2).
Direct HPLC (a); SPME-HPLC with the Ti-TiO2-ZrO2 fiber for raw wastewater (b) and for spiked wastewater at 10 μg•L-1 (c) and 50 μg•L-1 (d); SPME-HPLC with 100 μm PDMS (e) and 85 μm PA (f) fibers for spiked wastewater at 50 μg•L-1.
BP-3: 2-hydroxy-4-methoxybenzophenone; EHMC: 2-ethylhexyl-4-methoxycinnamate; OD-PABA: 2-ethylhexyl 4-(N,N-dimethylamino) benzoate; EHS: 2-Ethylhexyl salicylate.

209x148mm (300 x 300 DPI)