

Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

1
2
3
4 **A new nitrogen-containing carbon nanoparticles coated stainless steel**
5
6
7 **fiber for selective solid-phase microextraction of ultraviolet filters**
8
9

10
11
12 **Tian-e Wang^a, Mei Guo^a, Wen-lan Song^a, Yi-da Zhang^a, Xin-zhen Du^{a,b*}**
13

14
15 ^a College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou
16
17 730070, P. R. China
18

19
20 ^b Key Lab of Bioelectrochemistry & Environmental Analysis of Gansu, Lanzhou 730070, P.
21
22 R. China
23

24
25 Tel: +86 931 7970796, Fax: +86 931 7970796, email: duxz@nwnu.edu.cn
26
27

28
29
30
31 **Abstract**
32

33
34 A new nitrogen-containing carbon nanoparticles (N-CNPs) coated fiber was developed for
35
36 solid phase microextraction (SPME) with direct electrodeposition of polyaniline coating on
37
38 etched stainless steel wire using potentiostatic technique followed by carbonization at 500 °C
39
40 under nitrogen atmosphere. The extraction performance of N-CNPs coating was investigated
41
42 towards polycyclic aromatic hydrocarbons (PAHs), ultraviolet (UV) filters and phthalate acid
43
44 esters (PAEs) in water samples coupled to high performance liquid chromatography with UV
45
46 detection (HPLC-UV). This N-CNPs coating shows excellent selectivity for UV filters
47
48 compared to that for PAHs and PAEs. Under optimized conditions, the linearity of UV filters
49
50 was in the range 0.02-200 µg L⁻¹ with corresponding correlation coefficient of 0.9921-0.9993.
51
52 The recoveries ranged from 89.2% to 119%. The relative standard deviations of single fiber
53
54 were between 4.83% and 7.82% (n=5) and fiber-to-fiber were between 7.94% and 10.14%
55
56
57
58
59
60

1
2
3
4 (S/N = 3). Their limits of detection and the limits of quantitation ranged from 0.006-0.203
5
6 $\mu\text{g L}^{-1}$ and 0.02-0.67 $\mu\text{g L}^{-1}$, respectively. The proposed SPME-HPLC-UV procedure was
7
8
9
10 successfully used for selective concentration and sensitive determination of UV filters in
11
12 environment water samples. Furthermore this new robust fiber was easily prepared in
13
14
15 reproducible manner.

16
17 **Keywords:** Nitrogen-containing carbon nanoparticles; Polyaniline; Carbonization; Solid
18
19 phase microextraction; Ultraviolet filters
20
21
22
23
24

25 26 1. Introduction

27
28 Solid phase microextraction (SPME) is a simple, solvent-free and efficient extraction
29
30 technique by integrating sampling, extraction, concentration with sample introduction
31
32 procedures easily coupled to analytical instrumentation [1]. Since its introduction, it has
33
34 gained tremendous attraction and found widespread applications [2-4]. This technique is
35
36 based on the distribution equilibrium of analytes between the matrix and a fiber coating.
37
38 Therefore the type, microstructure and properties of fiber coating play a crucial role in the
39
40 microextraction process. Currently, commercially available coatings include
41
42 polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene, carboxen, carbowax and
43
44 their composites. However, most of commercially available fibers are fragile and subject to
45
46 some drawbacks such as low thermal and chemical stability and easy swelling of polymeric
47
48 coatings in organic solvents, which limit their widespread applications [5]. For these reasons,
49
50 the development of fiber coatings for highly efficient extraction of the analytes has attracted
51
52 much attention [6]. In particular, great efforts have been devoted to the synthesis and/or
53
54
55
56
57
58
59
60

1
2
3
4 fabrication of novel nanomaterials coatings with improved durability and excellent extraction
5
6 performance for specified analytes using flexible metal wires as supporting substrates [7].
7
8

9 These metal-based fibers are physically strong and can be handled with great convenience in
10
11 a microextraction procedure. Due to their quite different physicochemical properties from
12
13 fused-silica fiber, however, there has been a great variety of preparation strategies for the
14
15 metal-wire supported SPME fibers.
16
17
18

19
20 Carbon-based materials have high adsorption capacity for organic compounds and have
21
22 already been used as new SPME coatings [8,9]. In recent years, considerable attention has
23
24 been paid to the SPME fibers coated with carbon nanomaterials (CNs) such as nanoporous
25
26 carbon [10,11], single-walled carbon nanotubes [2,12-14], multi-walled carbon nanotubes
27
28 [15-20] and graphene [21-26]. In particular, CNs coated metallic fibers exhibited better
29
30 extraction efficiency and longer life span due to their significantly greater surface-to-volume
31
32 ratio, higher chemical stability and special microstructures [10-12,16-19,21-24]. However, up
33
34 to now, there are no reports on nitrogen-containing CNs as SPME fiber coatings. Also it is
35
36 critical to find a proper way to firmly and uniformly immobilize CNs on metallic supports
37
38 with inert surface since CNs are difficult to dissolve or to disperse in common solvents.
39
40
41
42
43
44
45
46

47 It has been shown that polyaniline (PANI) has the advantages of hydrophilicity,
48
49 environmental stability and excellent extraction capability towards different polar organic
50
51 compounds [27]. In SPME, a stainless steel (SS) wire was frequently used as a supporting
52
53 substrate for the preparation of PANI coated fibers via electropolymerization due to its high
54
55 mechanical and chemical stability, moderate elasticity and low cost [4,29-32]. In this case,
56
57
58
59
60 firm and uniform nitrogen-containing CNs coatings will be obtained on the SS wire if PANI

1
2
3
4 coated SS (PANI/SS) fibers with special structures and unique surface properties are
5
6 carbonized by heating in inert atmosphere [27]. These nitrogen-containing CNs coatings offer
7
8 large surface area and high chemical stability which are ideal for a potential fiber coating
9
10 material for SPME. However, their applications have not been well explored in SPME.
11
12 Herein, we proposed a simple approach to the preparation of new nitrogen-containing carbon
13
14 nanoparticles (N-CNPs) coated an etched SS fiber (N-CNPs/SS) by
15
16 electropolymerization-carbonization method for the first time. Its extraction capability and
17
18 selectivity was evaluated for the concentration and separation of polycyclic aromatic
19
20 hydrocarbons (PAHs), ultraviolet (UV) filters and phthalate esters (PAEs) coupled to
21
22 high-performance liquid chromatography with UV detection (HPLC-UV). SPME conditions
23
24 were investigated and optimized for selective concentration and determination of UV filters.
25
26 The SPME-HPLC-UV procedure with N-CNPs/SS fiber was established to preconcentrate
27
28 and determine UV filters in the environmental water samples. Furthermore the SPME
29
30 performance of this new N-CNPs/SS fiber was compared with that of commercial
31
32 polyacrylate (PA) fiber under the optimized conditions.
33
34
35
36
37
38
39
40
41
42
43
44
45
46

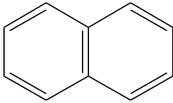
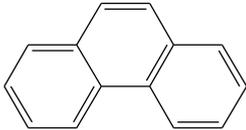
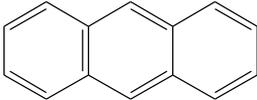
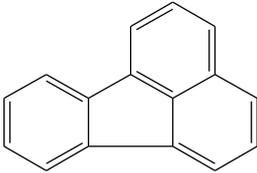
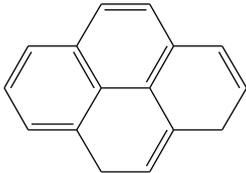
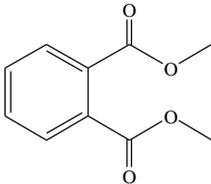
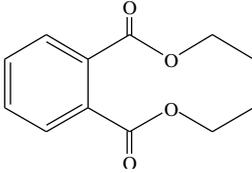
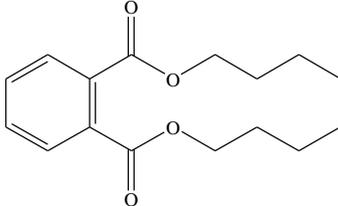
47 **2. Experimental**

48 **2.1 Reagents and materials**

49
50 HPLC-grade methanol was purchased from Shandong Yuwang Industry Co., Ltd. (Yucheng,
51
52 China). Hydrofluoric acid (40%) was obtained from Shuangshuang Chemical Company
53
54 (Yantai, China). Aniline (ANI) was purchased from Jianxin Chemical Reagent Co., Ltd
55
56 (Shanghai, China) and was further distilled under the vacuum before use. Sodium chloride
57
58
59
60

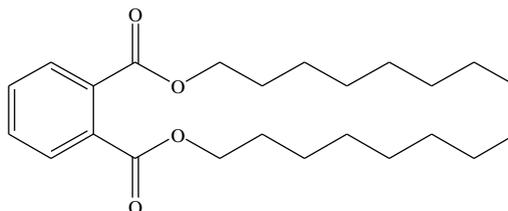
1
2
3
4 (NaCl), concentrated hydrochloric acid and sodium hydroxide were purchased from
5
6
7 Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Certified individual standards of
8
9
10 naphthalene (Nap), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu) and pyrene (Pyr)
11
12 were purchased from Aldrich (St. Louis, MO, USA). Certified individual standards of
13
14 dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), di-n-octyl
15
16 phthalate (DOP), di-(2-ethylhexyl) phthalate (DEHP), 2,4-dihydroxybenzophenone (BP),
17
18 2-hydroxy-4-methoxybenzophenone (BP-3), 2-ethylhexyl 4-methoxycinnamate (EHMC) and
19
20 2-ethylhexyl 4-(*N,N*-dimethylamino) benzoate (OD-PABA) were purchased from
21
22 AccuStandard (New Haven, CT, USA). Certified 2-ethylhexyl salicylate (EHS) was obtained
23
24 from Dr. Ehrenstorfer (Augsburg, Germany). Their chemical structures are listed in Table 1.
25
26
27
28
29
30
31
32 Stock solutions were prepared by dissolving individual standard in methanol with $100 \text{ mg}\cdot\text{L}^{-1}$,
33
34 and stored in the refrigerator at $4 \text{ }^{\circ}\text{C}$, shielding from light. Mixtures of standard working
35
36 solutions ($50 \text{ }\mu\text{g L}^{-1}$ each) were weekly prepared by diluting the stock standard solution with
37
38 ultrapure water to the required concentration to study extraction performance under different
39
40 conditions. All reagents were of analytical grade, unless otherwise stated. Stainless steel wire
41
42 (0.20 mm O.D.) was obtained from Gaoge (Shanghai, China). A polyacrylate (PA, 85 μm
43
44 thickness) SPME fiber was obtained from Supelco (Bellefonte, PA, USA). 0.45 μm
45
46 micropore membrane of polyvinylidene fluoride was supplied by Xingya Purifying Material
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Factory (Shanghai, China).

Table 1 Structure of PAHs, PAEs and UV filters.

| Chemical name | Chemical Structure |
|-------------------------------|--|
| Naphthalene (Nap) |  |
| Phenanthrene (Phe) |  |
| Anthracene (Ant) |  |
| Fluoranthene (Flu) |  |
| Pyrene (Pyr) |  |
| Dimethyl phthalate (DMP) |  |
| Diethyl phthalate (DEP) |  |
| Di-n-butyl phthalate (DBP) |  |

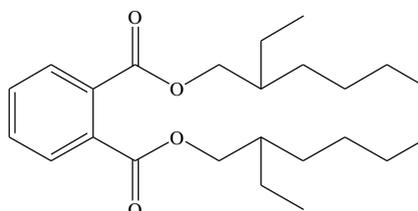
Di-n-octyl phthalate

(DOP)



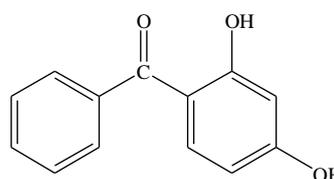
Di-(2-ethylhexyl) phthalate

(DEHP)



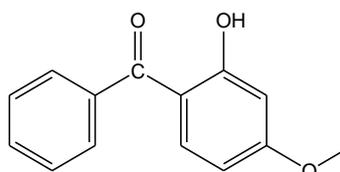
2,4-dihydroxybenzophenone

(BP)



Benzophenone-3

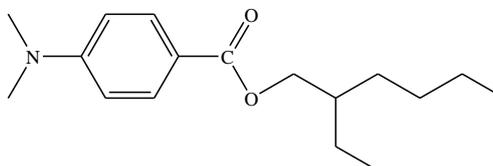
(BP-3)



Ethylhexyl dimethyl

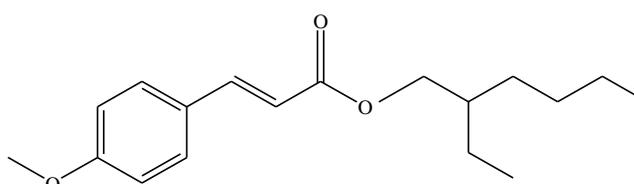
p-aminobenzoate

(OD-PABA)



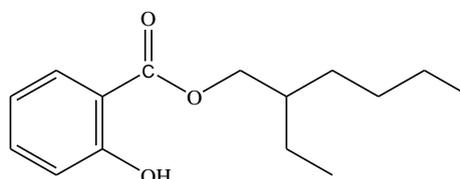
Ethylhexyl methoxycinnamate

(EHMC)



Ethylhexyl salicylate

(EHS)



2.2 Apparatus

A CHI832D electrochemical analyzer (Chenhua, China) was used for electrochemical

1
2
3
4 deposition of PANI. The PANI/SS fiber was carbonized under purging nitrogen gas at a flow
5
6 rate of $120 \text{ mL}\cdot\text{min}^{-1}$, using SRJK-2-13 tubular furnace (Guangming, China) with a
7
8 KSY-6D-16 Prog/Controller (Kewei, China). The fiber was characterized by an Ultra Plus
9
10 microscope (Zeiss, Oberkochen, Germany) equipped with semi-quantitative microanalysis by
11
12 energy dispersive X-ray spectroscopy (EDS). The pH values of sample were measured with a
13
14 PB-10 acidimeter (Beijing sartorius Instrument System Co., Ltd., China). In SPME, different
15
16 temperature and stirring rate were controlled by a DF101D thermostat with magnetic stirrer
17
18 (Zhengzhou, China). Ultrapure water was obtained from the Sudreli SDLA-B-X water
19
20 purification system (Chongqing, China). All separation was performed on Waters 600E
21
22 multi-solvent delivery system (Milford, MA, USA) equipped with Waters 2487 dual λ
23
24 absorbance detector and a zorbax Eclipse Plus C_{18} column (150 mm \times 4.6 mm, 5 μm , Agilent,
25
26 USA). A N2000 workstation (Zhejiang University, China) was used for the acquisition of data.
27
28 Desorption chamber was carried out in a commercially available Supelco SPME-HPLC
29
30 interface (Bellefonte, PA, USA). To remove background contamination, all glasswares were
31
32 immersed in chromosulfuric acid for 30 min and rinsed with ultrapure water, avoiding direct
33
34 contact with skin.
35
36
37
38
39
40
41
42
43
44
45

46 47 **2.3 Preparation of the N-CNPs/SS fiber**

48
49 Prior to coating, the SS wire was cleaned with methanol and ultrapure water in an ultrasonic
50
51 bath for 5 min to remove organic pollutants, respectively. The cleaned wire was immersed in
52
53 40% HF solution for 60 min at 40 $^{\circ}\text{C}$ consulting to Ref. [33]. Afterwards the etched fibers
54
55 were rinsed with ultrapure water in an ultrasonic bath for 5 min two times. The etched
56
57 segment of the SS wires was immediately immersed in an electrolyte solution of $0.5 \text{ mol}\cdot\text{L}^{-1}$
58
59
60

1
2
3
4 sulfuric acid and $0.05 \text{ mol}\cdot\text{L}^{-1}$ aniline. The PANI coating was directly electropolymerized
5
6 onto the surface of the etched segment of the SS wire for 40 min at 0.8V using potentiostatic
7
8 technique with a SS wire (15 mm long) as the working electrode, a platinum electrode (25
9
10 mm \times 100 μm O.D.) as the counter electrode and a saturated calomel electrode (SCE) as the
11
12 reference electrode. Subsequently the PANI/SS fiber was washed with acetone and ultrapure
13
14 water to remove the aniline monomer in the PANI coating and dried in vacuum for 3 h at 60
15
16 $^{\circ}\text{C}$. Finally, the PANI/SS fiber was carbonized in tubular furnace under nitrogen atmosphere
17
18 with a temperature programmed at a ramp rate of $3 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ until $500 \text{ }^{\circ}\text{C}$ and held for 2 h for
19
20 the pyrolysis of PANI coating. Prior to use, the prepared fiber was conditioned in the
21
22 SPME-HPLC interface until the baseline was achieved.

23 24 25 26 27 28 29 30 31 **2.4 Sample collection**

32
33 Real environmental water samples include 4 river water (pH, 7.43~7.91), 1 rainwater (pH,
34
35 7.89) and 2 wastewater samples (pH, 7.71 and 7.93). The water samples of the Yellow River
36
37 were collected at different sites of Lanzhou section of the Yellow River. Rain water sample
38
39 was collected inside school. Wastewater samples were collected from local wastewater
40
41 treatment plants. All real water samples were freshly collected in amber glass containers and
42
43 filtered through $0.45 \mu\text{m}$ micropore membranes, stored in the dark at $4 \text{ }^{\circ}\text{C}$.

44 45 46 47 48 49 50 51 **2.5 SPME-HPLC procedure**

52
53 The pH values of sample solutions were adjusted with hydrochloric acid and sodium
54
55 hydroxide. 15 mL of sample solutions was transferred into a 20 mL glass vial with 1 cm
56
57 magnetic stirrer bar inside and a Teflon septum. The N-CNPs/SS fiber was immersed into the
58
59 stirred solution for a period of time at elevated temperature. Subsequently, the fiber was
60

1
2
3
4 withdrawn from the sample solution and introduced into the SPME-HPLC interface for static
5
6 desorption in mobile phase. After solvent desorption, six-port valve was switched from load
7
8 to inject position, the mobile phase was passed through the interface and target compounds
9
10 were introduced into the analytical column. Methanol/water of 80/20 (v/v), 86/14 (v/v) and
11
12 75/25 (v/v) was employed as mobile phase at a flow rate of 1 mL·min⁻¹ for HPLC analysis of
13
14 PAHs, UV filters and PAEs, respectively. Corresponding absorption wavelength maxima of
15
16 UV detection were set at 254 nm, 300 nm and 280 nm for PAHs, UV filters and PAEs. Prior
17
18 to next extraction, the N-CNPs/SS fiber was immersed into methanol and ultrapure water to
19
20 eliminate possible carry-over for 15 min and 5 min, respectively.
21
22
23
24
25
26
27
28
29
30

31 **3. Results and discussion**

32 **3.1 Surface morphology of the N-CNPs/SS fiber**

33
34 Surface morphology of the prepared fibers was characterized by scanning electron
35
36 microscopy (SEM). As compared with the untreated SS wire (Fig. 1a), the etched SS wire
37
38 (Fig. 1b) shows rough and porous surface structure, providing the desired contact surface area
39
40 for subsequent strong adhesion of the PANI coating to the SS wire [4]. Fig. 1c exhibits PANI
41
42 nanoparticles (250 nm ~ 500 nm in diameter) coating electrodeposited onto the surface of the
43
44 etched SS wire. Such morphology could greatly increase the available surface area and
45
46 thereby improve the extraction capability of analytes. As can be seen in Fig. 1d, further
47
48 carbonization of PANI nanoparticles coating results in the formation of more uniform and
49
50 dense nanoparticles coating. These nanoparticles were interconnected and tightly attached
51
52 onto the etched SS wire substrate. This unique nanostructure possesses larger surface area,
53
54
55
56
57
58
59
60

more open access sites and better durability, which are most desirable for efficient SPME.

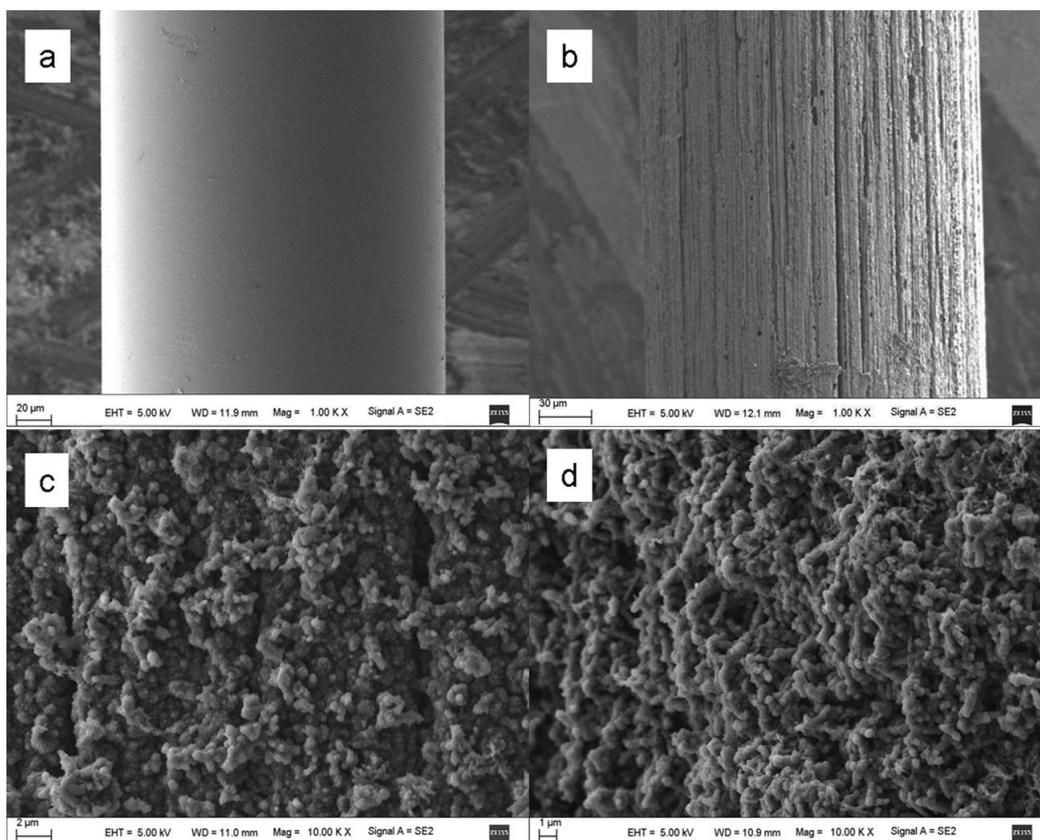


Fig. 1 SEM micrographs of the untreated SS wire (a), the etched wire (b), the PANI/SS fiber (c) and the N-CNPs/SS fiber (d).

3.2 Surface composition

Surface analysis of the PANI/SS fiber was further performed by EDS before and after carbonization. Compared with that of the naked SS fiber (Fig. 2a), the spectrum obtained for the PANI/SS fiber (Fig. 2b) shows peaks corresponding to the presence of C and N. The emission lines of Ni and Cr disappear but peaks corresponding to the presence of Fe still occur. Strong peak of C originates from the formation of PANI coating on the etched SS substrate. However weak peak of Fe suggests that the PANI nanoparticles coating should not be compact at the surface of the etched SS wire under the prescribed conditions. After

1
2
3
4 carbonization, the emission line of Fe almost disappears (Fig. 2c). This result clearly
5
6 indicates that more uniform and dense N-CNPs coating was achieved on the etched SS wire.
7
8
9 These phenomena also provide additional evidences for SEM images.
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

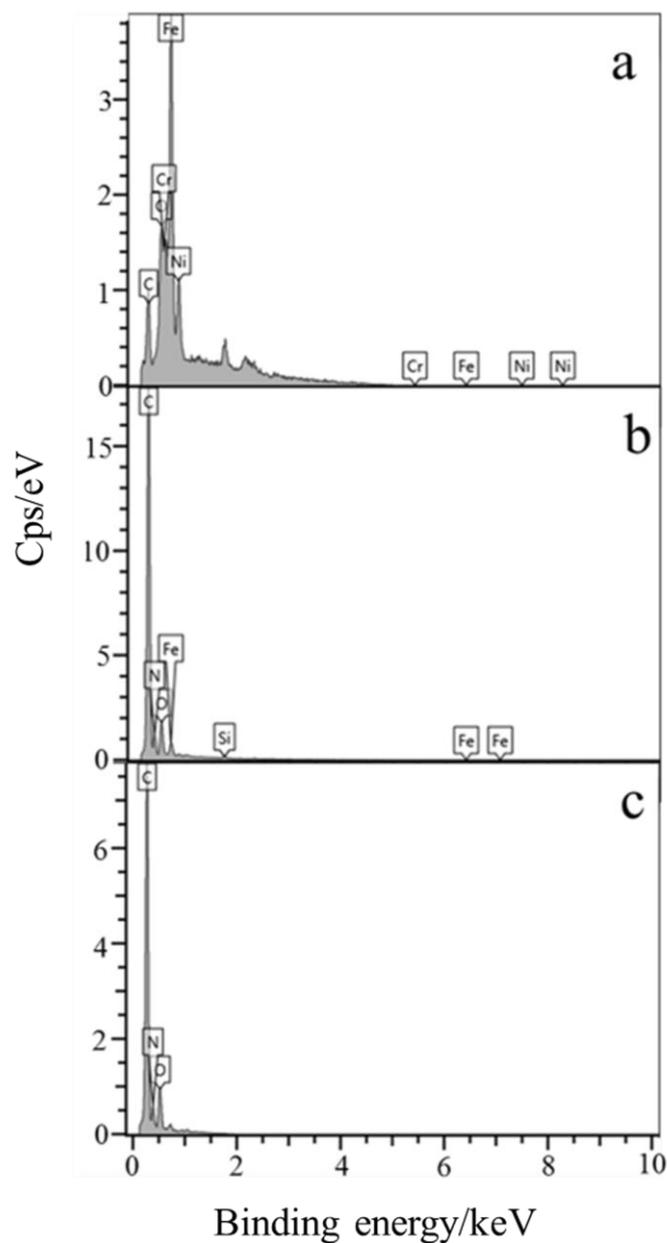


Fig. 2 EDS spectra of naked SS fiber (a), PANI/SS fiber (b) and N-CNPs/SS fiber (c).

3.3 Extraction performance

The extraction performance of the N-CNPs/SS fiber was evaluated by UV filters. As can be seen in Fig. 3, the N-CNPs/SS fiber shows excellent extraction capability for BP-3, OD-PABA and EHMC, but very low extraction capability for BP and EHS. As compared with the PANI/SS fiber (Fig. 3b), the N-CNPs/SS fiber exhibits excellent extraction efficiency for UV filters (Fig. 3c). This result should be attributed to the uniform N-CNPs coating with larger surface area and more open access sites.

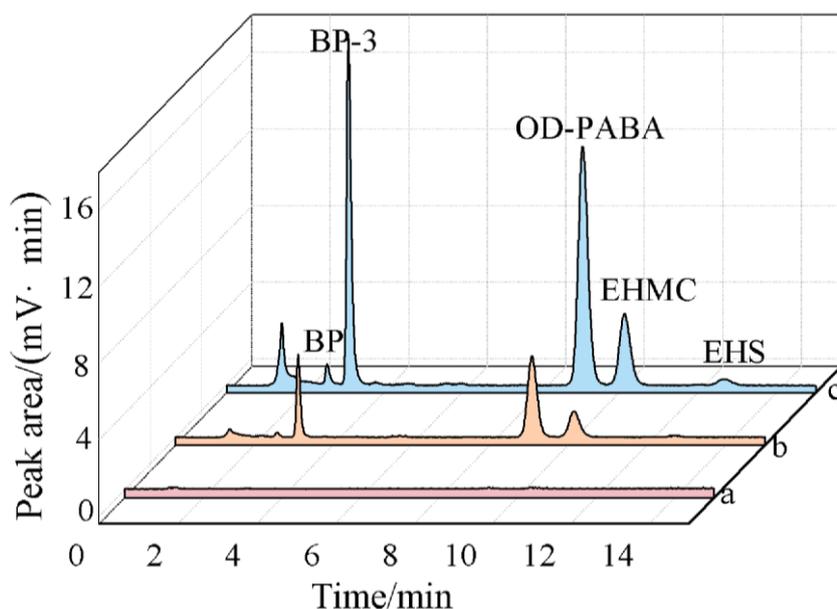


Fig. 3 Typical chromatograms of direct HPLC (a), corresponding SPME-HPLC with the PANI/SS fiber (b) and the N-CNPs/SS fiber (c) for UV filters spiked solution with $50 \mu\text{g L}^{-1}$.

PANI coating exhibits good extraction capability for various analytes such as phenolic compounds [4,28], aromatic amines [29], PAEs [30], polychlorinated biphenyls [32] and PAHs [34]. For this reason, the extraction efficiency and the selectivity of the N-CNPs

1
2
3
4 coating was further studied for SPME of PAHs, UV filters and PAEs (structures shown in
5
6
7 Table 1) from aqueous phase. As shown in Fig. 4, this fiber only exhibits excellent extraction
8
9
10 selectivity for some UV filters (Fig. 4d), while almost no or very poor extraction capability
11
12 toward PAHs (Fig. 4b) and PAEs (Fig. 4f). This result is very different from that obtained
13
14 with PANI coatings and that with CNs coatings as described above. N-doping should be
15
16 responsible for the selectivity of the N-CNPs coating. Such a less polar N-CNPs coating
17
18 provides a potential alternative for selective extraction of less polar UV filters from complex
19
20 environment water samples. Therefore this new fiber was employed for selective SPME of
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

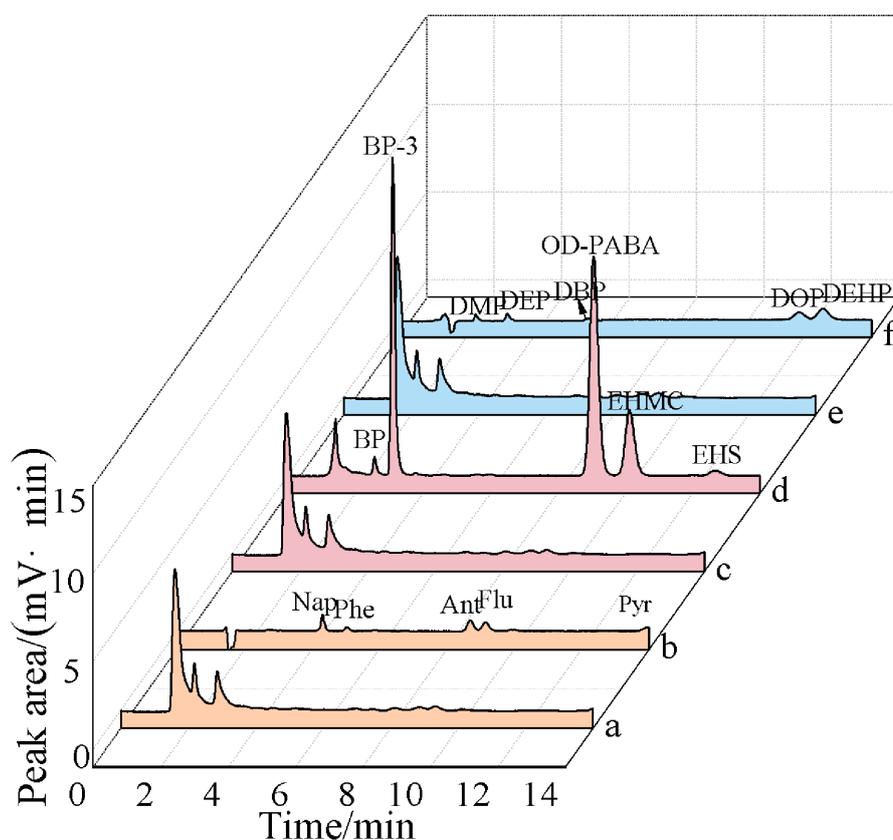


Fig. 4 Typical chromatograms of direct HPLC for PAHs (a), UV filters (c) and PAEs (e)

spiked water with $50 \mu\text{g L}^{-1}$ as well as corresponding SPME-HPLC with the N-CNPs/SS

1
2
3
4 fiber for PAHs (b), UV filters (d) and PAEs (f).
5
6
7
8

9 10 **3.4 Optimization of SPME conditions**

11
12 The adsorption and desorption of analytes on a SPME fiber is subjected to several main
13 parameters including extraction and desorption time, temperature, stirring rate, ionic strength
14 and pH. Thus the SPME conditions for BP, BP-3, OD-PABA, EHMC and EHS were studied
15 and optimized with working solutions at spiking level of $50 \mu\text{g L}^{-1}$.
16
17
18
19
20
21
22

23 **3.4.1 Effect of extraction and desorption time**

24
25 Extraction time is a significant factor in SPME. Fig. 5a shows the extraction time of UV
26 filters. 50 min was enough to nearly reach the equilibrium between the N-CNPs/SS fiber and
27 aqueous phase. Subsequently, solvent desorption of the extracted UV filters was performed in
28 mobile phase. For all UV filters, the peak area reached corresponding maximum within 6 min.
29
30
31
32
33
34
35
36 Thus, 50-min extraction and 6-min desorption were employed in subsequent experiment.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

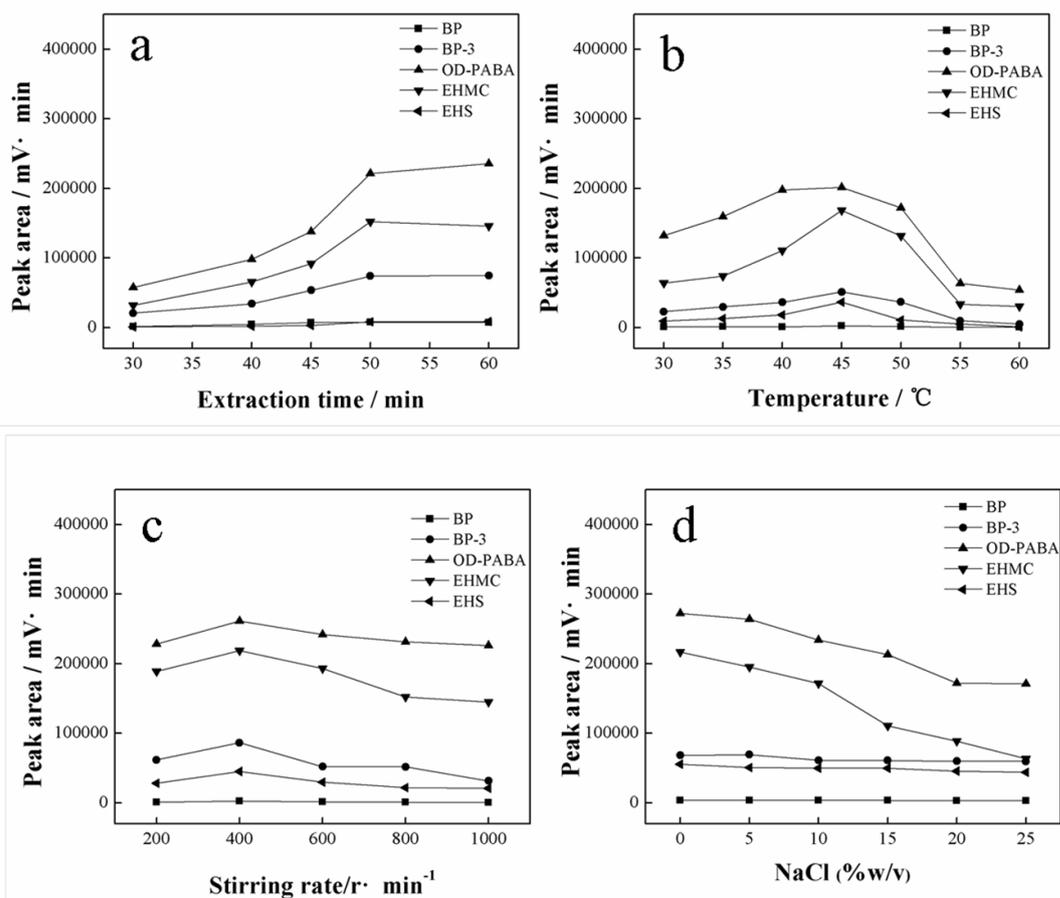


Fig. 5 Effect of extraction time (a), temperature (b), stirring rate (c) and ionic strength (d) on extraction efficiency.

3.4.2 Effect of extraction temperature

Temperature is very important for SPME because of its potential influence on the mass transfer and the partitioning of target analytes between fiber coating and sample solution. Fig. 5b presents the effect of temperature on the extraction of UV filters from 30 to 60 °C. The highest extraction efficiencies were obtained at 45 °C. Subsequently, the extraction capability rapidly decreased when the temperature continuously increased. This is most probably due to their decreased distribution coefficients between the N-CNPs coating and aqueous phase at temperature higher than 45 °C because adsorption is generally an exothermic process [35].

1
2
3
4 Furthermore, the dissolution of target UV filters also decreases the extraction efficiency at
5
6
7 higher temperature. Thus, 45 °C was used for extraction in further study.
8

9 10 **3.4.3 Effect of stirring rate**

11
12 Stirring promotes the diffusion of the analytes from aqueous solution to fiber coating and
13
14 thereby improves the extraction efficiency. As shown in Fig. 5c, the maximum extraction
15
16 efficiency of UV filters was achieved at the stirring rate of 400 r·min⁻¹. More vigorously
17
18 stirring might lead to form tiny bubble which is unfavorable to the adsorption of target
19
20 analyte molecules onto the surface of the N-CNPs coating. Therefore 400 r·min⁻¹ was
21
22 employed in the experiment.
23
24
25
26
27

28 29 **3.4.4 Effect of ionic strength**

30
31 Effect of ionic strength was examined by addition of NaCl into the working solutions. Fig. 5d
32
33 shows the dependence of SPME on the concentration of NaCl from 0 to 25% (w/v). Clearly
34
35 different negative effects on the extraction efficiency of UV filters were obtained. Apparently
36
37 more salt addition leads to an increase in sample viscosity, which decreases the diffusion
38
39 coefficients of the analytes in aqueous phase. Therefore, no salt addition was recommended
40
41
42 in this study.
43
44
45

46 47 **3.4.5 Effect of pH**

48
49 Effect of pH on SPME of UV filters was examined within the pH range of 2.0-9.0. In the case
50
51 of pH less than 4, extremely low extraction efficiencies for UV filters were obtained.
52
53
54 According to their molecular structures, these UV filters may be present in their protonated
55
56 forms due to the Bronsted acid-base equilibrium, resulting in their increased solubility in
57
58 aqueous solutions [36]. At pH 7.0, the neutral forms of UV filters are present due to their
59
60

deprotonation and beneficial for their adsorption onto the N-CNPs coating. Therefore, the highest extraction efficiencies were obtained. After pH more than 7.0, these UV filters exhibit rapidly decreased extraction efficiency. Thus, pH 7.0 was employed for SPME procedure.

3.5 Analytical performance

The analytical performance of the new N-CNPs/SS fiber was examined for target UV filters under the optimized conditions. Table 2 summarizes their linear ranges with corresponding correlation coefficients (r^2) and recoveries. Their limits of detection (LODs) and limits of quantitation (LOQs) were calculated based on signal-to-noise ratio of 3 and 10 of the proposed method, respectively. The repeatability of single fiber for five replicate extractions of UV filters at the spiking level of $50 \mu\text{g L}^{-1}$ varied from 4.83% to 7.82% for SPME-HPLC of UV filters. The fiber-to-fiber reproducibility for three parallel N-CNPs/SS fibers ranged from 8.56% to 10.14%.

Table 2 Analytical parameters of the proposed method

| UV filters | Linear equations * | Linear ranges ($\mu\text{g L}^{-1}$) | r^2 | Recovery (%) | RSD (%) | | LODs ($\mu\text{g L}^{-1}$) | LOQs ($\mu\text{g L}^{-1}$) |
|------------|--------------------|---|--------|--------------|-----------------------|-------------------------|----------------------------------|----------------------------------|
| | | | | | Single fiber (n=5) | Fiber-to-fiber (n=3) | | |
| BP | $Y=4.3x+270$ | 5-500 | 0.9991 | 89.2 | 7.82 | 10.14 | 0.203 | 0.67 |
| BP-3 | $Y=177.8x+3473$ | 0.5-200 | 0.9932 | 90.9 | 5.76 | 8.56 | 0.039 | 0.13 |
| OD-PABA | $Y=1212.4x+15504$ | 0.05-150 | 0.9921 | 108 | 4.83 | 9.28 | 0.006 | 0.02 |
| EHMC | $Y=544.3x+7802$ | 0.02-200 | 0.9983 | 119 | 5.14 | 7.94 | 0.008 | 0.03 |
| EHS | $Y=140.2x+1357$ | 0.1-200 | 0.9993 | 94.5 | 6.76 | 8.66 | 0.061 | 0.20 |

* Y, Peak area; x, Concentration of analytes

3.6 Real samples analysis

UV filters are synthetic chemical compounds and frequently used in sunscreen, cosmetics, personal care products and other pharmaceuticals in order to protect the skin from solar radiation [37]. However, excessive use of UV filters would lead to environmental pollution as well as accumulative negative effect on human health [38]. However, it is difficult to determine this kind of organic pollutants in real samples due to their low concentration and the co-existing interference. As a result, an appropriate sample pretreatment and enrichment procedure is necessary prior to analysis. The proposed method was applied to selective preconcentration and determination of UV filters in real environmental water samples. Furthermore addition of certified UV filters was employed to identify the target UV filters and examine possible matrix effects. The results of five replicate analyses were listed in Table 3 for real environmental water spiked with $5 \mu\text{g L}^{-1}$ or $10 \mu\text{g L}^{-1}$ of target UV filters. Fig. 6 shows typical chromatograms obtained for SPME-HPLC of target UV filters in raw influent with the N-CNPs/SS fiber. The matrix effect was minor. As compared with commercially available 85- μm PA fiber (Fig. 6c), the N-CNPs/SS fiber (Fig. 6d) exhibits much better extraction efficiency for target UV filters. The mean recoveries ranged from 83.6% to 119% with the RSD between 3.47% and 8.78%. These results clearly demonstrate that the new N-CNPs/SS fiber is reliable and suitable for selective preconcentration and sensitive determination of trace target UV filters in environmental water samples.

Table 3 Analytical results of UV filters in different environmental water samples (n = 5)

| Samples | UV filters | Original ($\mu\text{g L}^{-1}$) | Spiked ($\mu\text{g L}^{-1}$) | Detected ($\mu\text{g L}^{-1}$) | Recovery (%) | RSD (%) |
|---------------------|------------|--------------------------------------|------------------------------------|--------------------------------------|-----------------|------------|
| | BP | ND* | 10 | 8.36 | 83.6 | 8.78 |
| River water under | BP-3 | 0.87 | 5 | 6.96 | 119 | 4.39 |
| Bapanxia Suspension | OD-PABA | 1.02 | 5 | 6.72 | 112 | 7.30 |
| Bridge | EHMC | 1.06 | 5 | 5.45 | 89.9 | 5.18 |
| | EHS | ND | 5 | 4.34 | 86.8 | 6.84 |
| | BP | ND | 10 | 11.1 | 111 | 7.29 |
| | BP-3 | 2.28 | 5 | 6.82 | 93.7 | 6.66 |
| River water under | OD-PABA | 3.19 | 5 | 7.73 | 94.4 | 5.91 |
| Yintan Bridge | EHMC | 2.16 | 5 | 7.52 | 105 | 4.35 |
| | EHS | ND | 5 | 5.60 | 112 | 8.49 |
| | BP | ND | 10 | 10.82 | 108 | 6.44 |
| | BP-3 | 2.58 | 5 | 8.06 | 106 | 4.37 |
| River water under | OD-PABA | 3.06 | 5 | 7.44 | 92.3 | 5.61 |
| Donggang Bridge | EHMC | 2.64 | 5 | 6.82 | 89.3 | 8.60 |
| | EHS | 0.52 | 5 | 6.08 | 110 | 4.83 |
| River water under | BP | ND | 10 | 9.04 | 90.4 | 6.28 |
| Shichuan Bridge | BP-3 | 1.28 | 5 | 5.58 | 88.9 | 7.22 |

| | | | | | | | | |
|------------|-----------|--------|---------|------|----|-------|------|------|
| | | | OD-PABA | 3.74 | 5 | 7.78 | 89.0 | 3.60 |
| | | | EHMC | 1.16 | 5 | 5.94 | 96.4 | 5.82 |
| | | | EHS | ND | 5 | 4.62 | 92.4 | 8.76 |
| | | | BP | 1.14 | 10 | 10.72 | 96.2 | 3.47 |
| | | | BP-3 | 1.21 | 5 | 5.73 | 92.3 | 5.66 |
| Rainwater | inside | | OD-PABA | 2.27 | 5 | 6.26 | 86.1 | 8.18 |
| | | school | EHMC | 1.74 | 5 | 6.93 | 103 | 5.39 |
| | | | EHS | ND | 5 | 5.96 | 119 | 4.61 |
| | | | BP | 1.75 | 10 | 12.72 | 108 | 4.24 |
| Influent | from | | BP-3 | 2.62 | 5 | 6.87 | 90.2 | 3.85 |
| wastewater | treatment | | OD-PABA | 3.16 | 5 | 7.06 | 86.5 | 6.92 |
| plant | | | EHMC | 2.28 | 5 | 6.52 | 89.6 | 6.62 |
| | | | EHS | ND | 5 | 4.54 | 90.8 | 7.38 |
| | | | BP | ND | 10 | 11.06 | 111 | 8.43 |
| Effluent | from | | BP-3 | 1.38 | 5 | 5.82 | 91.2 | 4.94 |
| wastewater | treatment | | OD-PABA | 1.93 | 5 | 6.04 | 87.2 | 6.59 |
| plant | | | EHMC | 1.64 | 5 | 5.98 | 90.1 | 7.72 |
| | | | EHS | ND | 5 | 4.48 | 89.6 | 7.86 |

* ND, Not detected or lower than LOD.

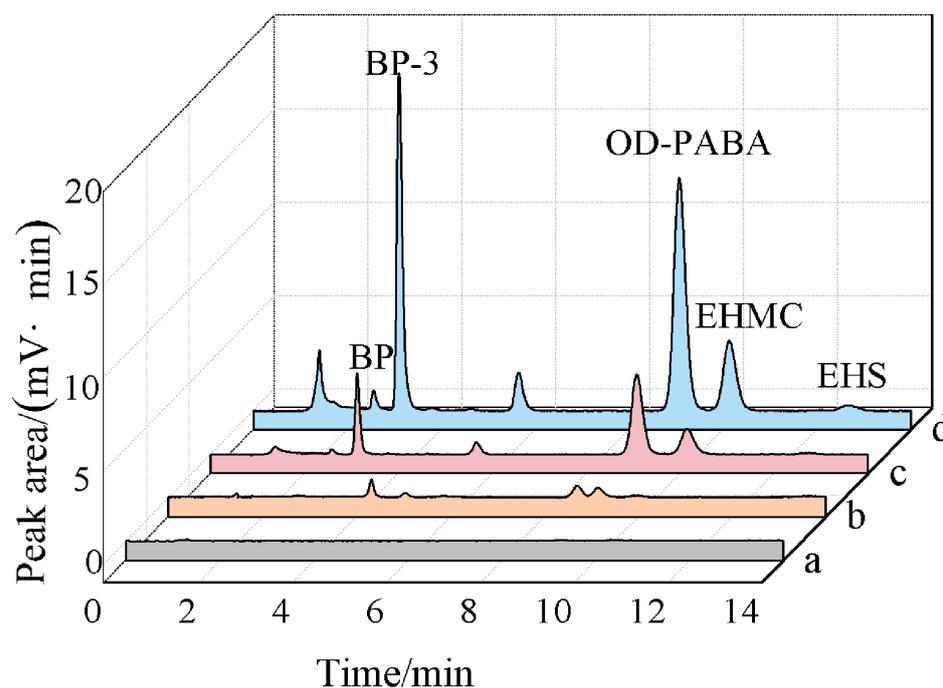


Fig. 6 Chromatograms of direct HPLC for raw influent (a) and raw influent spiked at $50 \mu\text{g L}^{-1}$ (b) as well as SPME-HPLC with $85 \mu\text{m}$ PA fiber (c) and the new N-CNPs/SS fiber (d) for UV filters spiked at $50 \mu\text{g L}^{-1}$.

3.7 Stability

Stability of the SPME fiber greatly depends on the physicochemical properties and the preparation strategies of the fiber coating, and are very important for its practical applications.

In order to examine its acid, alkali and solvent resistance, the new N-CNPs/SS fiber was allowed to be soaked in the solutions of $0.1 \text{ mol}\cdot\text{L}^{-1}$ HCl and $0.1 \text{ mol}\cdot\text{L}^{-1}$ NaOH as well as methanol, acetonitrile and tetrahydrofuran overnight. Negligible morphological changes were observed from its SEM image, indicating that the new N-CNPs coating was firmly immobilized to the etched SS wire substrate with rough surface structure and showed high

1
2
3
4 stability towards acid, alkali and common organic solvents. Furthermore the new N-CNPs/SS
5
6 fiber has withstood at least 200 times replicative extractions and desorptions according to the
7
8 prescribed experimental procedures. This new fiber is still reusable after eight week storage.
9
10 RSD from 8.56% to 10.14% was also obtained for three parallel N-CNPs/SS fibers under the
11
12 prescribed conditions. Moreover this new N-CNPs/SS fiber can be easily prepared in a
13
14 reproducible manner. The physical and chemical stability clearly demonstrates that the new
15
16 N-CNPs coating will find its practical applications in environmental water samples.
17
18
19
20
21
22

23 **3.8 Comparison of the proposed method with other methods**

24
25 The proposed method was compared with other SPME procedures for the analysis of UV
26
27 filters. Some experimental data are summarized in Table 4 with respect to extraction time,
28
29 linear ranges, RSD, LOD and recovery. It can be seen that LOD values of the proposed
30
31 method with the new N-CNPs/SS fiber were comparable or better than those reported in the
32
33 literatures. This might be due to the fact that this new N-CNPs coating possesses unique
34
35 surface properties and available larger surface area at the same time, and thereby provide the
36
37 enhanced adsorption efficiency for target analytes. Furthermore, the preparation of the
38
39 N-CNPs coating is simple, convenient and reproducible.
40
41
42
43
44
45
46
47
48
49

50 Table 4 Comparison of the current method with other methods for extraction and
51
52 determination of UV filters
53

| Instrumentation ^a | Time (min) | Linear ranges ($\mu\text{g L}^{-1}$) | LOD ($\mu\text{g L}^{-1}$) | RSD (%) | Recovery (%) | Refs |
|------------------------------|---------------|--|---------------------------------|------------|-----------------|------|
| | | | | | | |

| | | | | | | |
|--|----|----------|------------------------|----------|------------|--------|
| Graphene-SPME | 40 | 0.001-10 | 0.0005-0.007 | 5.7-11.3 | 102-114 | [23] |
| -GC-MS | | | | | | |
| PDMS-SPME | 45 | 10-500 | 0.87-2.47 ^b | 4.5-7.9 | 82-98 | [39] |
| -GC-FID | | | | | | |
| C ₁₂ -SPME | 60 | 5-200 | 0.69-1.37 | 0.6-1.9 | 69.7-102.4 | [40] |
| -HPLC-UV | | | | | | |
| TiO ₂ -SPME | 30 | 0.1-400 | 0.026-0.089 | 4.5-9.6 | 88.8-107 | [41] |
| -HPLC-UV | | | | | | |
| ZrO ₂ -TiO ₂ -SPME | 30 | 0.5-500 | 0.032-0.082 | 4.2-8.9 | 82.2-106.6 | [42] |
| -HPLC-UV | | | | | | |
| N-CNPs-SPME | | | | | | This |
| -HPLC-UV | 50 | 0.02-200 | 0.006-0.2 | 3.5-8.8 | 83.6-119 | method |

^a C₁₂, dodecyl; FID, flame ionization detection; MS, mass spectrometry; TiO₂, titanium oxide; ZrO₂, zirconium oxide.

^b Limit of quantification.

4. Conclusions

In this study, the new N-CNPs coating was prepared by the electropolymerization of PANI on etched SS wire substrate followed by the carbonization of PANI. It exhibits excellent extraction efficiency and good selectivity for SPME of UV filters due to its unique surface properties and available larger surface area. The N-CNPs/SS fiber offered a simple, sensitive and inexpensive pretreatment way for the selective concentration and determination of target

1
2
3
4 UV filters in real environmental water samples. Furthermore the N-CNPs coating was firmly
5
6 and homogeneously immobilized on the etched SS wire in a simple and reproducible manner.
7
8
9 This new robust fiber was allowed to withstand at least 200 times extraction cycles under the
10
11 prescribed conditions. It is expected that the carbonization of PANI with special
12
13 microstructures provides an alternative approach to the preparation of CNs coatings for
14
15 SPME fibers in the future.
16
17
18
19
20
21
22

23 **Acknowledgements**

24
25 This research was financially supported by the National Natural Science Foundation of China
26
27
28 (Grant no. 21265019).
29
30
31
32

33 **References**

- 34
35
36 [1] C. L. Arthur and J. Pawliszyn, *Anal. Chem.*, 1990, **62**, 2145-2148.
37
38 [2] J. X. Lu, J. F. Liu, Y. Wei, K. L. Jiang, S. S. Fan, J. Y. Liu and G. B. Jiang, *J. Sep. Sci.*,
39
40 2007, **30**, 2138-2143.
41
42
43 [3] C. Basheer, K. Narasimhan, M. Yin, C. Zhao, M. Choolani and H. K. Lee, *J. Chromatogr.*
44
45 *A*, 2008, **1186**, 358-364.
46
47
48 [4] L. Liu, H. X. Liu, Y. Li, X. M. Wang, and X. Z. Du, *Anal. Methods*, 2014, **6**, 3467-3473.
49
50
51 [5] M. D. F. Alpendurada, *J. Chromatogr. A*, 2000, **889**, 3-14.
52
53
54 [6] J. Q. Xu, J. Zheng, J. Y. Tian, F. Zhu, F. Zeng, C. Y. Su, G. F. Ouyang, *Trends Anal. Chem.*,
55
56 2013, **47**, 68-83.
57
58
59 [7] J. J. Feng, H. D. Qiu, X. Liu and S. X. Jiang, *Trends Anal. Chem.*, 2013, **46**, 44-58.
60

- 1
2
3
4 [8] M. Giardina and S. V. Olesik, *Anal. Chem.*, 2003, **75**, 1604-1614.
5
6
7 [9] T. Sun, J. Jia, N. Fang and Y. Wang, *Anal. Chim. Acta*, 2005, **530**, 33-40.
8
9
10 [10] A. Rahimi, P. Hashemi, A. Badiei, P. Arab and A. R. Ghiasvand, *Anal. Chim. Acta*, 2011,
11
12 **695**, 58-62.
13
14 [11] J. B. Zeng, C. Y. Zhao, J. J. Chen, F. Subhan, L. W. Luo, J. F. Yu, B. W. Cui, W. Xing, X.
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- [12] N. Rastkari, R. Ahmadkhaniha, N. Samadi, A. Shafiee and M. Yunesian, *Anal. Chim. Acta*, 2010, **662**, 90-96.
- [13] W. Y. Zhang, Y. Sun, C. Y. Wu, J. Xing and J. Y. Li, *Anal. Chem.*, 2009, **81**, 2912-2920.
- [14] F. Wu, W. P. Lu, J. H. Chen, W. Liu and L. Zhang, *Talanta*, 2010, **82**, 1038-1043.
- [15] J. X. Wang, D. Q. Jiang, Z. Y. Gu and X. P. Yan, *J. Chromatogr. A*, 2006, **1137**, 8-14.
- [16] J. B. Zeng, J. M. Chen, X. H. Song, Y. R. Wang, J. H. Ha, X. Chen and X. R. Wang, *J. Chromatogr. A*, 2010, **1217**, 1735-1741.
- [17] P. Kueseng and J. Pawliszyn, *J. Chromatogr. A*, 2013, **1317**, 199-202.
- [18] M. Sun, J. J. Feng, H. M. Qiu, L. L. Fan, X. J. Li and C. N. Luo, *Talanta*, 2013, **114**, 60-65.
- [19] M. Behzadi, E. Noroozian and M. Mirzaei, *Talanta*, 2013, **108**, 66-73.
- [20] A. Sarafraz-Yazdi, Z.R. Dizavandi and A. Amiri, *Anal. Methods*, 2012, **4**, 4316-4325.
- [21] J. M. Chen, J. Zou, J. B. Zeng, X. M. Song, J. J. Ji, Y. R. Wang, J. H. Ha and X. Chen, *Anal. Chim. Acta*, 2010, **678**, 44-49.
- [22] V. K. Ponnusamy and J. F. Jen, *J. Chromatogr. A*, 2011, **1218**, 6861-868.

- 1
2
3
4 [23] H. Zhang and H. K. Lee, *Anal. Chim. Acta*, 2012, **742**, 67-73.
5
6
7 [24] Y. Wang, X. Y. Wang, Z. P. Guo and Y. Chen, *Talanta*, 2014, **119**, 517-523.
8
9
10 [25] G. Y. Zhao, S. J. Song, C. Wang, Q. H. Wu and Z. Wang, *Anal. Methods*, 2011, **3**,
11
12 2929-2935.
13
14 [26] S. L. Zhang, Z. Du and G. K. Li, *J. Chromatogr. A*, 2012, **1260**, 1-8.
15
16
17 [27] G. Ćirić-Marjanović, *Synthetic Met.*, 2013, **177**, 1-47.
18
19
20 [28] Y. H. Wang, J. A. Zhang, D. Sheng and C. Sun, *J. Chromatogr. A*, 2010, **1217**,
21
22 4523-4528.
23
24
25 [29] M. J. Huang, C. Tai, Q. F. Zhou and G. B. Jiang, *J. Chromatogr. A*, 2004, **1048**,
26
27 257-262.
28
29
30 [30] X. Li, M. G. Zhong, S. F. Xu and C. Sun, *J. Chromatogr. A*, 2006, **1135**, 101-108.
31
32
33 [31] A. Mehdinia and M. F. Mousavi, *J. Sep. Sci.*, 2008, **31**, 3565-3572.
34
35
36 [32] Y. H. Wang, Y. Q. Li, J. Zhang, S. F. Xu, S. G. Yang and C. Sun, *Anal. Chim. Acta*,
37
38 2009, **646**, 78-84.
39
40
41 [33] H. L. Xu, Y. Li, D. Q. Jiang and X. P. Yan, *Anal. Chem.*, 2009, **81**, 4971-4977.
42
43
44 [34] H. Bagheri, E. Babanezhad and A. Es-Haghi, *J. Chromatogr. A*, 2007, **1152**, 168-174.
45
46
47 [35] C. L. Arthur, L. M. Killam, K. D. Buchholz and J. Pawliszyn, *Anal. Chem.*, 1992, **64**,
48
49 1960-1966.
50
51
52 [36] A. Salvador and A. Chisvert, *Anal. Chim. Acta*, 2005, **537**, 1-14.
53
54
55 [37] D. L. Giokas, A. Salvador and A. Chisvert, *Trends Anal. Chem.*, 2007, **26**, 360-374.
56
57
58 [38] M. Schlumpf, P. Schmid, S. Durrer, M. Conscience, K. Maerker, M. Henseler, M.
59
60 Gruetter, I. Herzog, S. Reolon, R. Ceccatelli, O. Faass, E. Stutz, H. Jarry, W. Wuttke and

1
2
3
4 W. Lichtensteiger, *Toxicology*, 2004, **205**, 113-122.
5

6
7 [39] D. A. Lambropoulou, D. L. Giokas, V. A. Sakkas, T. A. Albanis and M. I. Karayannis, *J.*
8
9 *Chromatogr. A*, 2002, **967**, 243-253.
10

11 [40] J. Li, L. Y. Ma, M. Q. Tang and L. Xu, *J. Chromatogr. A*, 2013, **1298**, 1-8.
12

13 [41] Y. Li, M. Zhang, Y. X. Yang, X. M. Wang and X. Z. Du, *J. Chromatogr. A*, 2014, **1358**,
14
15
16 60-67.
17

18 [42] Y. Li, Y. X. Yang, H. X. Liu, X. M. Wang, X. Z. Du, *Anal. Methods*, 2014, **6**,
19
20
21 8519-8525.
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60