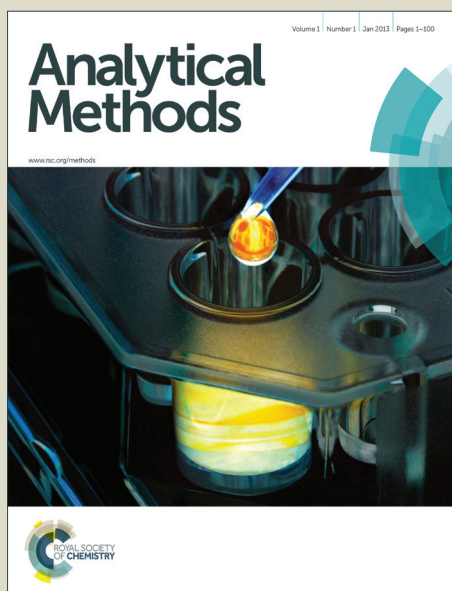


Analytical Methods

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.

Graphical abstract

The uniform porous polyaniline-coated fiber for solid-phase microextraction was prepared in the electrolyte solution of nitric acid using a chemically etched stainless steel wire as a metal substrate (Fig. 1). It has larger surface area and longer service time for the selective extraction and sensitive determination of bisphenol A in complex matrices.

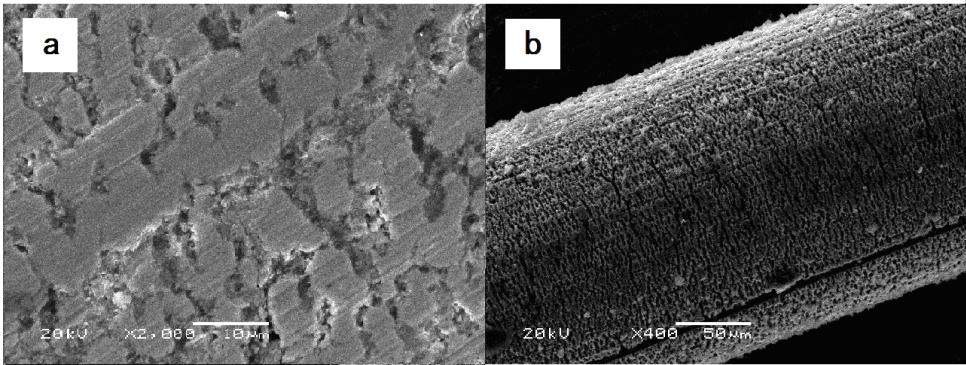


Fig. 1 SEM micrographs of chemically etched stainless steel wire (a) and porous polyaniline-coated fiber.

Rapid preparation of robust polyaniline coating on an etched stainless steel wire for solid-phase microextraction of dissolved bisphenol A in drinking water and beverages

Li Liu ^a, Hai-xia Liu ^a, Yi Li ^a, Xue-mei Wang ^{a,b} and Xin-zhen Du ^{*a,b}

A new approach for rapid preparation of porous polyaniline (PANI) coating on a stainless steel (SS) wire was developed in nitric acid containing aniline. The SS wire was firstly etched in hydrofluoric acid and then used as a working electrode for electrodeposition of PANI coating. The etching procedure on a SS wire provides porosity necessary for higher extraction capability of PANI coating and for the extraction phase to hold firmly onto the SS fiber. The porous structure of the PANI coating prepared in nitric acid (PANI-NO₃) was more uniform than that prepared in sulfuric acid (PANI-SO₄). These PANI coatings were applied to solid-phase microextraction (SPME) of bisphenol A (BPA) coupled to high performance liquid chromatography with ultraviolet detection (HPLC-UV). Their SPME performance was compared and SPME conditions based on the PANI-NO₃ coating was further optimized. The linear range was 0.01-100 ng·mL⁻¹ with correlation coefficient of 0.9996. Relative standard deviation was 2.36% for a spiked sample with BPA of 10 ng·mL⁻¹ (n=5) and limit of detection was 0.005 ng·mL⁻¹. The fiber-to-fiber reproducibility of 6.41% was achieved for three PANI-NO₃ coated fibers prepared under the same conditions. Finally, the porous

^a College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, P. R. China E-mail: duxz@nwnu.edu.cn; Fax: +86-0931-7970796; Tel: +86-0931-7970796

^b Key Lab of Bioelectrochemistry & Environmental Analysis of Gansu, Lanzhou 730070, P. R. China.

PANI-NO₃ coating was used for the selective and efficient preconcentration of dissolved BPA in drinking water and beverages. The recoveries of spiked BPA in the real samples ranged from 90.56% to 108.2%. The prepared PANI-NO₃ coated fibers have high mechanical strength and chemical stability, long lifetime, high extraction efficiency and good selectivity for the extraction of BPA in complex matrices.

Keywords: Polyaniline, metal-based fiber, electrodeposition, bisphenol A, solid-phase microextraction.

1. Introduction

In sample preparation, great efforts have been made to reduce the use of organic solvents and analysis time.¹ Microextraction techniques represent a step forward for the development of environmentally-friendly analytical techniques.^{2,3,4} In particular, liquid-phase microextraction (LPME) and solid-phase microextraction (SPME) minimize or eliminate the use of toxic organic solvents in performing rapid preconcentration and determination of target analytes.⁵⁻¹² As compared with LPME, SPME is a solvent-free alternative for sample preparation technique and has gained its popularity in the concentration and the separation of target analytes in different matrices because of its practical simplicity, rapidity, sensitivity and easy quantification.² It is based on the partitioning of the organic analytes between the sample matrix and thin extraction coating deposited onto a fiber. Currently, the general applications for SPME are mostly devoted to fused silica fibers coated with various polymeric coatings.² However, most of commercially available SPME fibers suffer from low

thermal, chemical and mechanical stabilities due to their coating materials onto the fragile fused silica fibers. Caution must be taken to prevent them from breakage during extraction and desorption. To overcome these drawbacks, the use of conductive polymers as SPME coatings on metal fibers has been demonstrated.¹⁰⁻¹⁸ Electrodeposition offers a simple and convenient way for the conductive polymeric coatings immobilized on metal substrates for SPME. Electrochemically coated fibers exhibit enhanced stability such as mechanical,¹⁶ thermal^{12,14,16} and chemical stability^{11,16} as well as solvent resistance^{11,16} compared to conventional polymer coated fibers. Especially, custom-made polyaniline (PANI)-coated fibers have been prepared on metal substrates for the extraction of aromatic amines,¹⁰ phthalates,¹¹ ionic analytes,¹³ phenols,¹⁴ polycyclic aromatic hydrocarbons,¹⁵ substituted benzenes¹⁶ and pesticides^{17,18} from water samples. The prepared PANI fibers showed equivalent/better extraction performance compared with the commercial polyacrylate fibers.¹¹ Generally a thicker PANI coating is needed on the metal fiber to achieve higher sensitivity. However more time is required to reach equilibrium for thicker PANI coating.¹⁷ Furthermore mass transfer in the coated polymers itself also influences extraction kinetics. Thus more porous PANI coating with larger specific surface area is an attractive and promising alternative for higher efficient extraction and also exhibits faster adsorption/desorption of the target analytes.^{11,17}

Bisphenol A (BPA) is widely used in the production of polycarbonate plastics and epoxy resins. There is extensive evidence that many consumer products contain and release BPA under normal conditions of use.¹⁹ In recent years, an increased interest has been raised for sensitive and accurate determination of BPA in aquatic environment,²⁰ food²¹ and biological

media²² in order to estimate the exposure to BPA and the associated health risk. However, the determination of BPA requires selective and sensitive methods because the matrices are very complex and BPA have been reported in the nanogram per milliliter range.²³ Generally, intensive preparation procedure was needed for the concentration and separation of BPA in complex matrices.^{21,22} To date, several researchers have reported successful concentration and determination of BPA.²⁴⁻³¹ However only one description was devoted to the SPME of BPA with the PANI-coated fiber prepared in sulfuric acid so far.³² In the present work, new porous PANI coating was prepared in the electrolyte solution of nitric acid by direct electrodeposition on an etched stainless steel (SS) wire and compared with conventional PANI coating in the electrolyte solution of sulfuric acid with respect to microextraction performance. Thereafter important factors affecting extraction capability of BPA were optimized coupled to high performance liquid chromatography with ultraviolet detection (HPLC-UV). A simple and sensitive method was established for the concentration and determination of dissolved BPA in aqueous samples. The new porous PANI-coated fiber was applied to the direct microextraction of dissolved BPA from drinking water and beverages.

2. Experimental

2.1 Chemicals and reagents

Certified standard of bisphenol A (purity 99+%, Lot No. 11118) was obtained from Dr. Ehrenstorfer (Augsburg, Germany). A stock standard solution of 500 mg·L⁻¹ BPA was prepared in methanol and stored at -4 °C in the refrigerator, shielding from light. Working standard solutions of BPA were prepared with doubly distilled water using stock standard

solution prior to analysis. Hydrofluoric acid (40%) was obtained from Shuangshuang Chemical Company (Yantai, China). HPLC-grade methanol was obtained from Yuwang Industrial Company (Yucheng, China). Acetone was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Chloroform was obtained from Beijing Chemical Works (Beijing, China). Tetrahydrofuran was purchased from Tianjing Kemiou Chemical Reagent Co. (Tianjing, China). Dimethylsulphoxide was purchased from Tianjing Chemical Reagent Co., Ltd (Tianjing, China). Aniline (ANI) was purchased from Jianxin Chemical Reagent Co., Ltd (Shanghai, China) and was further distilled under the vacuum before use. Sodium chloride (NaCl) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemical reagents were of analytical grade, otherwise stated. Doubly distilled water was used during the experiments. 0.45 μm micropore membrane of polyvinylidene fluoride was supplied by Xingya Purifying Material Factory (Shanghai, China).

2.2 Apparatus

All chromatographic measurements were performed on Waters 600E multi-solvent delivery system (Milford, MA, USA) equipped with Waters 2487 dual λ absorbance detector and a Waters Sunfire C₁₈ analytical column (150 mm \times 4.6 mm, 5 μm). Online data acquisition was performed on a N2000 workstation (Zhejiang University, China). The desorption chamber is a commercially available Supelco SPME-HPLC interface (Bellefonte, PA, USA). A commercially available 2- μL HPLC microsyringe (Gaoge, China) was modified for SPME. The modified microsyringe consists of a removable needle (30 mm \times 0.5 mm O.D. \times 0.35 mm I.D.) and a SS plunger wire (Grade 304, 75 mm \times 0.20 mm O.D.) inside. A CHI832D electrochemical analyzer (Chenhua, China) was used for eletrochemical deposition of PANI

with a SS plunger (15 mm long) as the working electrode, a platinum electrode (25 mm×100 μm O.D.) as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The PANI-coated fiber was characterized by a JSM-5600LV scanning electron microscope (JEOL, Japan). Different temperature and stirring rates were controlled by a DF101D thermostat with magnetic stirrer (Zhengzhou, China). The pH values of sample solution were adjusted by a PHS-3C meter (Shanghai, China). Doubly distilled water was produced with a Yarong SZ-93 distilled water device (Shanghai, China).

2.3 Sample collection and pretreatment

The samples measured include leaching water samples from commercially available polycarbonate baby feeding bottle and polypropylene cup, drinking water and beverages. The baby feeding bottle and the polypropylene (PP) cup were filled with tap water for 30 min at 80 °C, respectively.²⁶ Subsequently leaching water was immediately transferred to glass containers and cooled at room temperature. Drinking water and beverages in plastic bottles were purchased from a local supermarket. All samples were filtered with the micropore membrane of 0.45 μm and directly used for SPME without any pretreatment prior to analysis.

2.4 Preparation of porous PANI-coated fibers

Typical preparation process of the porous PANI-coated fiber consists of two discrete steps. The SS plunger wire was firstly rinsed with acetone to remove the organic pollutants, followed by distilled water. Afterwards, the 15-mm tip segment of the SS wire was immersed in hydrofluoric acid for 60 min at 40 °C with improved procedure.³³ The etched segment was rinsed with distilled water in an ultrasonic bath for 5 min two times. Thereafter, the etched segment of the SS wire was immediately immersed in acidic electrolytes. The PANI coatings

1
2
3
4 were directly electrodeposited onto the surface of the etched segment of the SS wire for 90
5
6 min under nitrogen atmosphere with a three-electrode system using potentiostatic technique
7
8 consulting the literature.¹⁷ Subsequently, the fibers were washed with distilled water two
9
10 times, followed by acetone to remove aniline monomer in the PANI coatings. Furthermore
11
12 the PANI-coated fibers were heated at 80 °C for 2 h under nitrogen atmosphere in order to
13
14 remove other volatiles from the fiber coatings. Finally the PANI-coated fibers were
15
16 introduced into SPME-HPLC interface and conditioned for 60 min in mobile phase at a flow
17
18 rate of 0.5 mL·min⁻¹ prior to use.
19
20
21
22

23 24 **2.5 SPME procedure**

25
26 An aliquot of BPA spiked solution or filtrate was transferred into a 15-mL sample vial with a
27
28 PTFE-laminated silicone septum and a 7-mm egg-shaped Teflon magnetic stir bar inside.
29
30 Thereafter NaCl was added to the sample solution at concentration level of 0.30 g·mL⁻¹. The
31
32 sample solutions was adjusted to pH 6.0 by 1 mol·L⁻¹ hydrochloric acid or sodium
33
34 hydroxide.²⁸ The total volume of sample solutions was 10 mL for each experiment.
35
36 Thereafter, the PANI-coated fiber was directly immersed into the sample solution for 30 min
37
38 at 40 °C with the stirring rate of 1000 rpm. After extraction, the piercing needle holding the
39
40 fiber with concentrated BPA was withdrawn from the vial and subsequently introduced into
41
42 the SPME-HPLC interface for static desorption in mobile phase (methanol/water, 80/20v/v)
43
44 within 7 min when the injection valve was in the load position. After desorption, the six-port
45
46 valve was switched from load to inject position, the mobile phase was passed through the
47
48 interface and BPA was introduced into the analytical column at a flow rate of 1 mL·min⁻¹.
49
50
51
52
53
54
55
56
57
58
59
60
UV wavelength was set at 278 nm. Chromatographic peak area was employed to examine

direct microextraction efficiency of porous PANI coating. To avoid carryover between extraction runs, the PANI-coated fiber was rinsed with methanol and distilled water, respectively.

2.6 Blank test

Some attention was needed to prevent contamination of BPA during sample preparation, which may interfere with quantification at low concentrations. Commercially available organic solvents and glass wares were used to avoid any BPA background contamination in the analysis. All glass wares were washed with methanol followed by distilled water before use. Throughout the experiment, BPA-free water was prepared using a quartz distilled device. In batch analysis, blank test was done to check no contamination.

3 Results and discussion

3.1 Morphology of porous PANI coating

The micrographs of the etched SS wire and the PANI-coated fiber were characterized by scanning electron microscopy (SEM). As shown in Fig. 1a and 1b, the etched SS wire exhibits rough surface compared to the bare one. It provides much larger contact surface area for further electrodeposition of PANI-NO₃ coating in the electrolytic solution of 0.05 mol·L⁻¹ ANI and 0.5 mol·L⁻¹ HNO₃ under nitrogen atmosphere using a three-electrode system. As shown in Fig. 1d, uniform porous PANI-NO₃ coating was observed on the etched SS wire compared to the smooth one on the bare SS wire shown in Fig. 1c. A porous PANI-NO₃ coating could greatly increase the available surface area and thereby improve the extraction capability of BPA. As shown in Fig. 2, SPME with porous PANI-NO₃ coating onto the

etched SS wire has more effective enrichment and leads to better sensitivity than that with smooth PANI coating on the bare SS wire for BPA of $10 \text{ ng}\cdot\text{mL}^{-1}$. Also the uniform and porous structure is very helpful for fast adsorption and desorption of BPA.

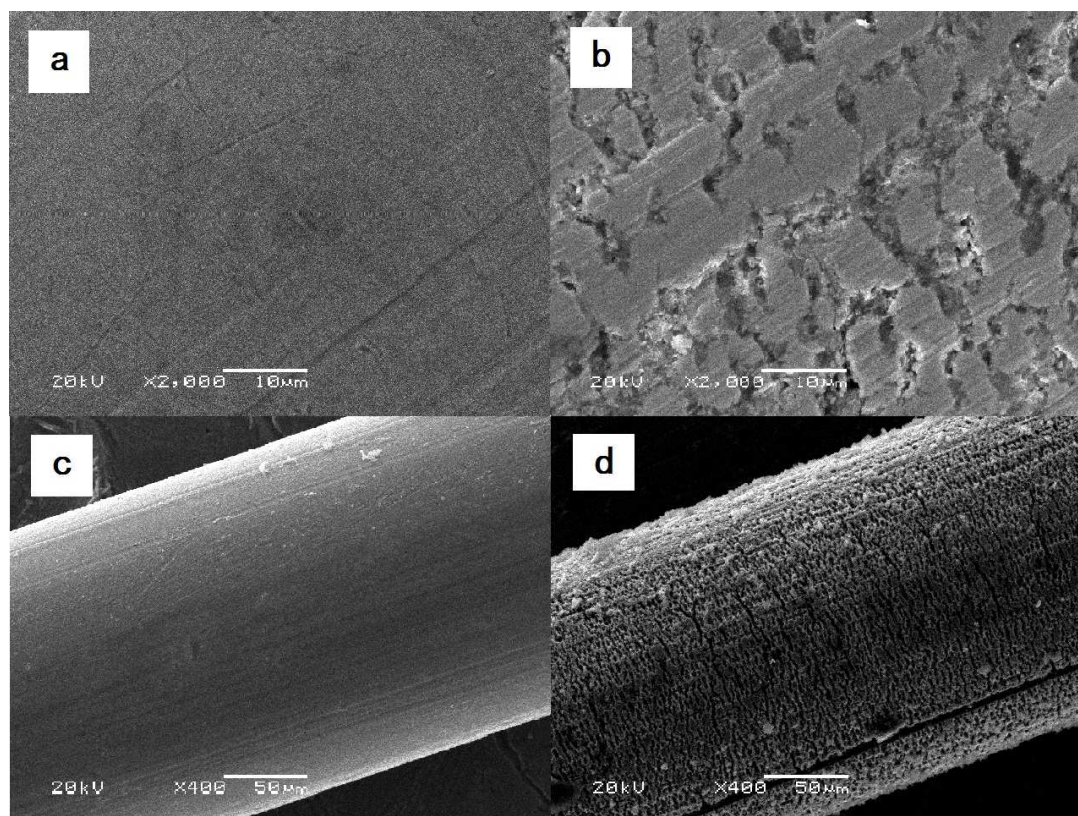


Fig. 1 SEM micrographs of SS wires before etching (a $\times 2000$) and after etching (b $\times 2000$), conventional PANI-NO₃ coating on the bare SS wire (c $\times 400$) and new PANI-NO₃ coating on the etched SS wire (d $\times 400$).

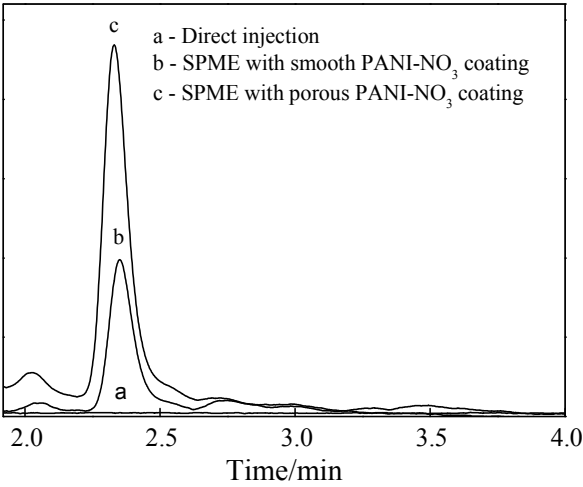


Fig. 2 Chromatograms of BPA for direct injection and SPME-HPLC.

3.2 Preparation of PANI coatings in different oxyacids

Generally the PANI-SO₄ coatings were directly electrodeposited on the smooth surface of the bare SS wire in the electrolytes of ANI and sulfuric acid.^{10,17} For this reason, the preparation of PANI-coated fibers was comparatively studied at deposition potential of 0.8 V and 0.9 V (vs SCE) in 0.5 mol·L⁻¹ sulfuric acid and nitric acid solutions containing 0.05 mol·L⁻¹ ANI using the etched SS wires as working electrodes, respectively. As shown in Fig. 3, the PANI-NO₃ coated fiber shows more uniform porous texture than the PANI-SO₄ coated fiber. In the following experiment, the extraction performance of the PANI-NO₃ and the PANI-SO₄ coatings was compared to examine their extraction capability.

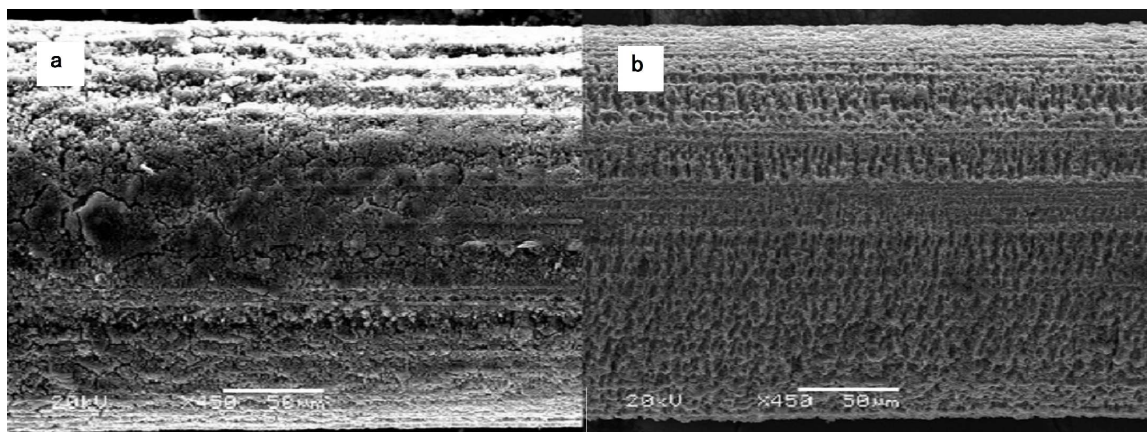


Fig. 3 SEM micrographs of electrodeposited PANI-SO₄ coating (a) and PANI-NO₃ coating (b) on the etched SS wires.

3.3 Extraction conditions

Working solution of 10 ng·mL⁻¹ BPA was employed to examine the effect of extraction and desorption time, temperature, stirring rate and ionic strength on the extraction efficiency of BPA with the PANI-coated fibers.

3.3.1 Effect of extraction time and desorption time

Extraction time is one of the key parameters affecting the extraction capability. Fig. 4 shows the effect of time on the extraction efficiency of BPA. The extraction efficiency of BPA quickly increased along with increasing time till it almost reached maximum within 30 min. It is obvious that both PANI-NO₃ and PANI-SO₄ coatings have short equilibration time.²⁶ This should be attributed to fast diffusion of BPA molecules into the porous PANI coating. Moreover uniform porous PANI-NO₃ coating provides much greater extraction capability than the PANI-SO₄ coating under the same conditions. Considering the analysis time, 30 min was selected in subsequent experiment.

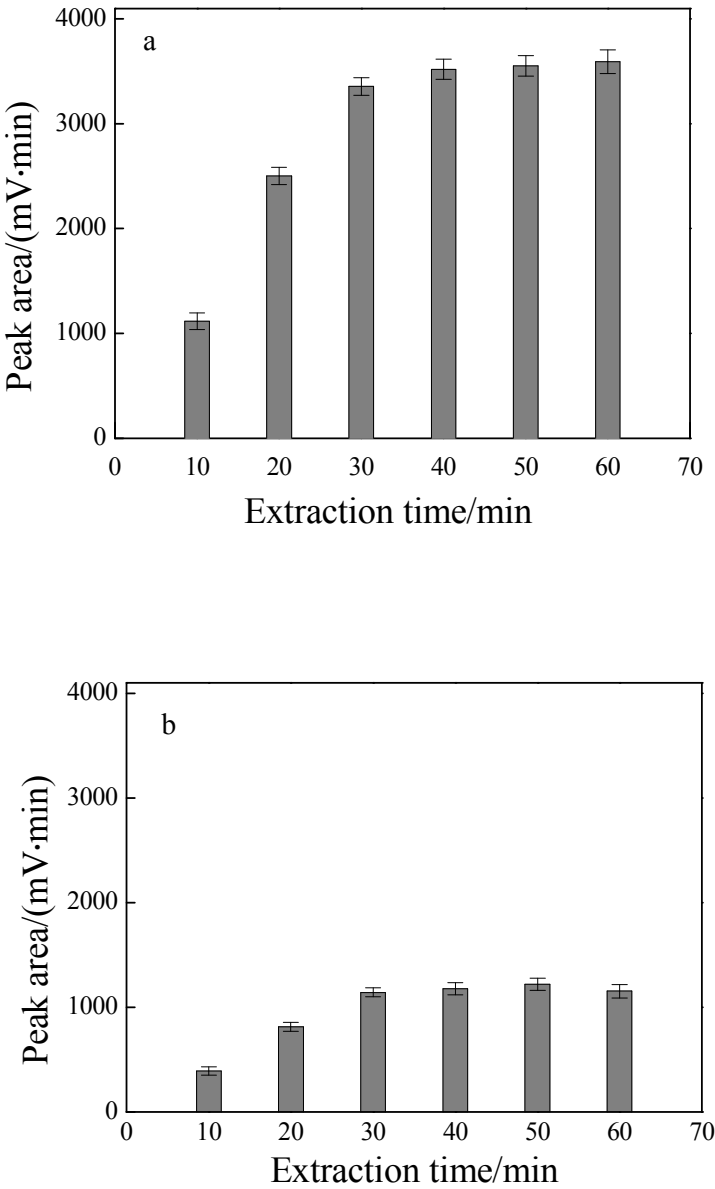


Fig. 4 Effect of extraction time on the extraction efficiency of BPA.

PANI-NO₃ coating (a) and PANI-SO₄ coating (b)

In SPME-HPLC procedure, desorption of analytes from a given fiber greatly depends on their solubility in the mobile phase.³⁴ The results showed that the peak area reached its constant maximum within 7 min. No detection of BPA occurred during the second desorption.

Thus 7 min was employed for static desorption in the experiment.

3.3.2 Effect of extraction temperature

In SPME, temperature generally plays an important role in adsorption process because of its potential influence on thermodynamic equilibrium and kinetic process of extraction.^{32,34} Fig. 5 shows the dependence of extraction on temperature of water matrix for SPME of BPA with the PANI-NO₃ and the PANI-SO₄ coatings. The extraction efficiency rapidly increases with rising temperature of water matrix from 10 to 40 °C. High temperature is favorable to mass transfer from aqueous phase to PANI coating, especially for the PANI-SO₄ coating. It clearly indicates that microextraction is a diffusion-controlled process for porous PANI coating. However, higher temperature than 40 °C also results in a rapid decrease in peak area which corresponds to decreased distribution coefficient from the thermodynamic point of view. Furthermore the temperature-dependence also provides additional evidence that the uniform porous PANI-NO₃ coating offer much better extraction capability than the PANI-SO₄ coating. Thus the PANI-NO₃ coated fiber was employed to optimize the experimental conditions in further study.

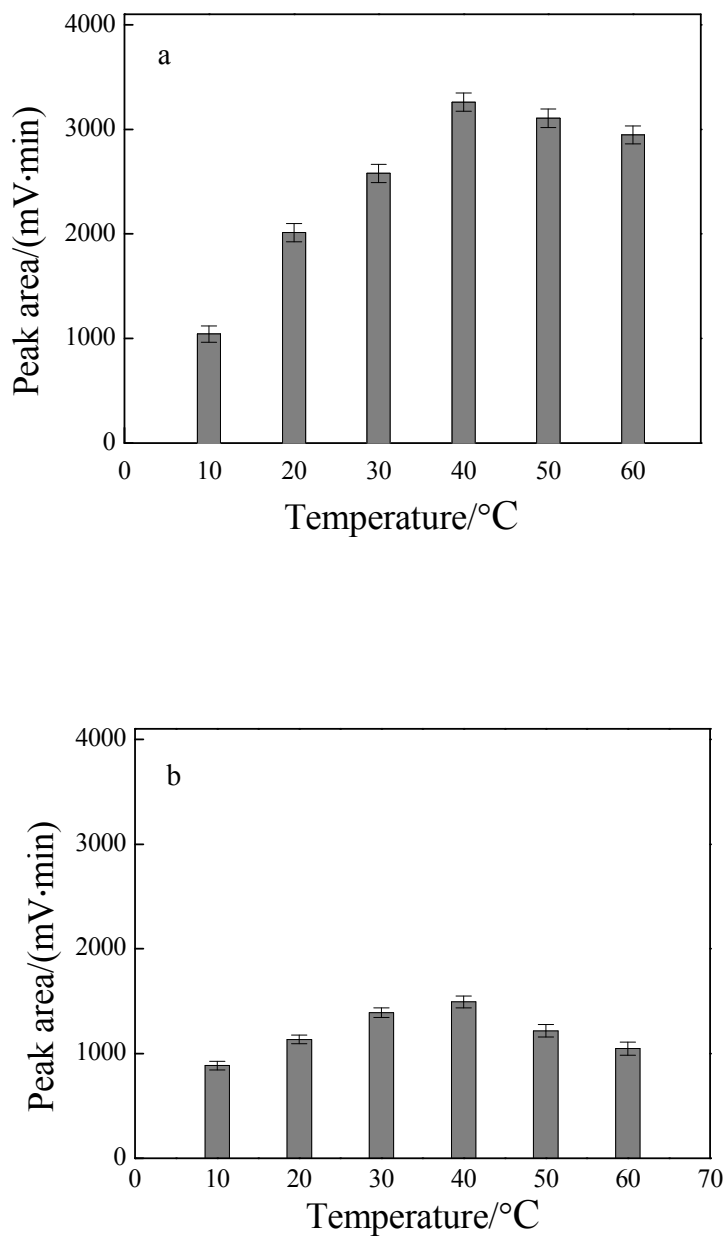


Fig. 5 Effect of temperature on the extraction efficiency of BPA.
PANI-NO₃ coating (a) and PANI-SO₄ coating (b)

3.3.3 Effect of stirring rate

Stirring is significantly important in immersion SPME because SPME is a dynamic diffusion-controlled process as described above. The extraction efficiency rapidly enhances

with increasing stirring rate because of the accelerated diffusion of BPA molecules to the porous PANI-NO₃ coating in aqueous solution. Maximum amount of adsorbed BPA was obtained at 1000 rpm (See Fig. S1 in Electronic Supplementary Information). Afterwards, the extraction efficiency reduced with the increasing stirring rate. Clearly more vigorously stirring is unfavorable to the extraction of BPA in porous PANI-NO₃ coating.

3.3.4 Effect of salt

Salt content of the sample affects the results from SPME because addition of salt into aqueous solution frequently causes a further decrease in solubility of less polar organic compounds in the water. The obtained result exhibits a positive effect of NaCl on the SPME of BPA with the porous PANI-NO₃ coated fiber. The extraction efficiency reached its maximum when the concentration of NaCl was greater than 0.30 g·mL⁻¹ (See Fig. S2 in Electronic Supplementary Information). Therefore 0.30 g·mL⁻¹ was employed for the SPME of BPA in the experiment.

3.4 Method evaluation

Under optimized conditions, quantification of BPA was performed with SPME-HPLC-UV procedure based on the external calibration method. The chromatographic peak area is a linear function of BPA concentration in the range of 0.01-100 ng·mL⁻¹ with correlation coefficient (r^2) of 0.9996. The recovery was 97.44% and the relative standard deviation (RSD) was 2.36% for a spiked sample with BPA of 10 ng·mL⁻¹ (n=5). The limit of detection (LOD) was 0.005 ng·mL⁻¹ (S/N=3). Furthermore three fibers were individually prepared under the same conditions. The fiber-to-fiber reproducibility of 6.41% was achieved. The satisfactory results reveal that the porous PANI-NO₃ coating is suitable for the preconcentration,

separation and determination of dissolved BPA in aqueous phase.

3.5 Stability of porous PANI-coated fiber

The robustness of the fiber coating is very important for practical applications. For this purpose, the prepared PANI-NO₃ coating was further immersed in 0.1 mol·L⁻¹ NaOH solution. It was found that the coating was still intact after 12 h. Also the porous PANI-NO₃ coated fiber was subjected to overnight exposure to methanol, dimethylsulphoxide, tetrahydrofuran and chloroform, respectively. A negative effect was found to be from 2.3% to 6.1% after exposure to these solvents for 12 h. The peculiar conjugate π -bond in the PANI coating should be responsible for its high hydrolytic stability in acidic and alkaline solutions and solvent resistance.¹⁶ According to the procedure described, the PANI-NO₃ coated fiber can at least withstand 150 times vigorous stirring extraction and desorption in mobile phase. In addition, the 95.41% response remained after four week storage for the spiked water with 10 ng·mL⁻¹, indicating that the porous PANI-NO₃ coated fiber has excellent long-term stability and is reusable after prolonged storage. The physical stability and the chemical inertness of the porous PANI-coated fiber clearly indicate that the etching procedure further enhances the immobilization of the PANI coating onto the SS wire and greatly improves the mechanical strength of the PANI fiber.

3.6 Applicability of SPME-HPLC-UV with porous PANI-NO₃ coated fiber

The porous PANI-NO₃ coated fiber was applied to the SPME of dissolved BPA in drinking water and beverages under the optimized conditions. As can be seen in Table 1, BPA of 6.28 ng·mL⁻¹ was detected in leaching water from baby feeding bottle. This result clearly indicates that BPA is released from new polycarbonate baby feeding bottle under normal conditions of

use. However no BPA was detected in leaching water from PP cup. In beverages except for black tea, dissolved BPA was found in concentrations ranging from 1.39 ng·mL⁻¹ to 91.62 ng·mL⁻¹. In particular, draft beer, orange juice and cola kept in plastic bottles contained high concentrations of BPA (67.20-91.62 ng·mL⁻¹). After the liquid samples were spiked with certified standard BPA, the matrix effect was further examined. As shown in Table 1, the matrix has a minor effect on the recoveries of dissolved BPA in orange juice, draft beer and tea. Good precision was also achieved. These data demonstrated that the porous PANI-NO₃ coated fiber can selectively separate and enrich BPA dissolved in complex matrices.

Table 1 Analytical results of SPME-HPLC-UV using porous PANI-coated fiber

Samples	Original (ng·mL ⁻¹)	Spiked (ng·mL ⁻¹)	Detected (ng·mL ⁻¹)	Recovery (%)	RSD (%)	Storage time
Leaching water from baby feeding bottle	6.28	5.00	12.20	108.2	1.64	1h
Leaching water from PP cup	ND ^a	10.00	10.00	100.0	1.44	1h
Barreled water	1.39	5.00	5.87	91.86	4.74	15d ^b
Bottled mineral water	5.91	5.00	10.55	96.70	4.43	17d
Bottled orange juice	91.62	10.00	97.16	95.61	1.31	121d
Draft beer ^c	76.02	10.00	86.89	101.0	1.49	4d
Bottled herb tea	14.78	10.00	22.44	90.56	2.28	117d
Bottled black tea	ND	10.00	10.44	104.4	4.56	99d
Bottled cola	67.20	10.00	75.40	97.67	4.32	61d

^a ND, Not detected or lower than limits of detection.

^b d, days.

^c Draft beer stored in plastic bottle of 1.5L.

3.7 Comparison of the proposed method with other methods

A comparison of the proposed method with other ones reported for BPA detection is summarized in Table 2. The present method showed a good linearity for BPA detection ($r^2 = 0.9996$). Moreover, much lower LOD indicates that this proposed method exhibited higher sensitivity for monitoring of BPA than those in the literatures except for SPME coupled to gas chromatography-mass spectrometry (GC-MS).²⁶ Also the data in Table 2 shows that the proposed method exhibited good recovery (90.56%-108.2%) and good precision (< 4.74%) for the concentration and determination of dissolved BPA in complex matrices. The satisfactory result suggests that SPME with the porous PANI-NO₃ coated fiber provide a better clean-up procedure for subsequent HPLC analysis. As a result, the proposed method was suitable for the analysis of dissolved BPA at trace levels in complex matrices.

Table 2 Comparison of the proposed method with other methods

Methods	Linearity (ng·mL ⁻¹)	r ²	LOD (ng·mL ⁻¹)	RSD (%)	Recovery (%)	Refs
CS/N-GS/GCE ^a	2.28-296.4	0.9996	1.14	4.5	95.8-106.5	23
AuNPs/SGNF/GCE ^b	18.2-57000	0.997	7.98	2.70-3.80	98.4-102.1	35
Graphene/GCE	11.4-228.0	0.9950	10.69	—	90.0	36
In tube-SPME-HPLC-DAD ^c	1.00-50.0	0.999	0.10	1.8-18.4	—	25
PA-SPME-GC-MS ^d	0.01-200	0.9963	0.002	5.2	103.7-111.6	26
HSD-PA-SPME-GC-MS ^e	0.001-100	0.9981	0.0004	9.0	102.6-110.3	26
MIP-SPME-HPLC-DAD ^f	5-200	0.995	2.4	4.9	92.5	28
CW/TPR-SPME-HPLC-FLD ^g	—	0.999	0.43	4.58	—	32
CPANI-SPME-HPLC-FLD ^h	—	0.994	0.014	2.00-8.10	84.9-110	32
PANI-SPME-HPLC-UV	0.01-100.0	0.9996	0.005	1.31-4.74	90.56-108.2	Present work

^a Chitosan/nitrogen-doped graphene sheets modified glassy carbon electrode^b Stacked graphene nanofibers/gold nanoparticles composite modified glassy carbon electrode^c In-tube SPME coupled to HPLC with diode array detector^d Polyacrylate coated fiber for SPME coupled to GC-MS^e Headspace derivatization PA coated fiber for SPME coupled to GC-MS^f Molecular imprinted polymer fiber for SPME coupled to HPLC with diode array detector.^g Carbowax/templated resin fiber for SPME coupled to HPLC with fluorescence detection^h Composite PANI-coated fiber for SPME coupled to HPLC with fluorescence detection

4. Conclusions

In this study, a new approach for rapid preparation of robust PANI-NO₃ coated fiber was developed in nitric acid. The etching procedure of the SS wire easily leads to subsequent electrodeposition of uniform porous PANI-NO₃ coating with large surface area and close contact of the PANI-NO₃ coating to the surface of SS wire. This approach was simple and could become a routine preparation procedure for porous PANI-coated fibers. The prepared PANI coating was homogeneous and showed good mechanical and chemical stability. As compared with the conventional PANI-SO₄ coated fiber, this new fiber has higher extraction capability of BPA and thereby higher sensitivity for BPA coupled to HPLC-UV. The sample pretreatment is simple and the selective extraction of BPA from complex matrices is feasible. The proposed method was applied to the concentration and determination of dissolved BPA in complex matrices with good recovery and precision. In addition, this work has found BPA contamination in consumer drinking products stored in plastic bottles. Therefore, we think that the monitoring of BPA is necessary for beverages such as beer, orange juice and cola.

Acknowledgments

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

References

- 1 M. Farré, S. Pérez, C. Goncalves, M. F. Alpendurada and D. Barcelo, *Trends Anal. Chem.*, 2010, **29**, 1347-1362.
- 2 M. F. Alpendurada, *J. Chromatogr., A*, 2000, **889**, 3-14.

- 3 M. Rezaee, Y. Assadi, M.-R. Milani Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, *J. Chromatogr. A*, 2006, **1116**, 1-9.
- 4 A. Sarafraz-Yazdi and A. Amiri, *Trends Anal. Chem.*, 2010, **29**, 1-14.
- 5 B. Mokhtari and K. Pourabdollah, *J. Incl. Phenom. Macrocycl. Chem.*, 2012, **74**, 183-189.
- 6 B. Mokhtari, N. Dalali and K. Pourabdollah, *J. Chil. Chem Soc.*, 2012, **57**, 1428-1431.
- 7 B. Mokhtari, N. Dalali and K. Pourabdollah, *J. Sep. Sci.*, 2013, **36**, 356-361.
- 8 B. Mokhtari, N. Dalali and K. Pourabdollah, *Chromatographia*, 2013, **76**, 565-570.
- 9 B. Mokhtari, N. Dalali and K. Pourabdollah, *J. Chin. Chem. Soc.*, 2013, 60, 625-631.
- 10 M. J. Huang, C. Tai, Q. F. Zhou and G. B. Jiang, *J. Chromatogr., A*, 2004, **1048**, 257-262.
- 11 X. Li, M. Zhong, S. F. Xu and C. Sun, *J. Chromatogr., A*, 2006, **1135**, 101-108.
- 12 Y. H. Wang, Y. Q. Li, J. Zhang, S. F. Xu, S. G. Yang and C. Sun, *Anal. Chim. Acta*, 2009, **646**, 78-84.
- 13 J. C. Wu, W. M. Mullett and J. Pawliszyn, *Anal. Chem.*, 2002, **74**, 4855-4859.
- 14 H. Bagheri, A. Mir and E. Babanezhad, *Anal. Chim. Acta*, 2005, **532**, 89-95.
- 15 H. Bagheri, E. Babanezhad and A. Es-Haghi, *J. Chromatogr., A*, 2007, **1152**, 168-174.
- 16 X. Li, J. M. Chen and L. C. Du, *J. Chromatogr., A*, 2007, **1140**, 21-28.
- 17 A. Mehdinia and M. F. Mousavi, *J. Sep. Sci.*, 2008, **31**, 3565-3572.
- 18 X. Li, C. M. Li, J. M. Chen, C. L. Li and C. Sun, *J. Chromatogr. A*, 2008, **1198-1199**, 7-13.
- 19 L. N. Vandenberg, R. Hauser, M. Marcus, N. Olea and W. V. Welshons, *Reprod. Toxicol.*,

- 2007, **24**, 139-177.
- 20 T. Suzuki, Y. Nakagawa, I. Takano, K. Yaguchi and K. Yasuda, *Environ. Sci. Technol.*, 2004, **38**, 2389-2396.
- 21 D. K. Alexiadou, N. C. Maragou, N. S. Thomaidis, G. A. Theodoridis and M. A. Koupparis, *J. Sep. Sci.*, 2008, **31**, 2272-2282.
- 22 M. Kawaguchi, K. Inoue, M. Yoshimura, R. Ito, N. Sakui, N. Okanouchi and H. Nakazawa, *J. Chromatogr., B*, 2004, **805**, 41-48.
- 23 H. X. Fan, Y. Li, D. Wu, H. M. Ma, K. X. Mao, D. W. Fan, B. Du, H. Li and Q. Wei, *Anal. Chim. Acta*, 2012, **711**, 24-28.
- 24 J. Salafranca, R. Batlle, C. Nerin, *J. Chromatogr., A*, 1999, **864**, 137-144
- 25 H. Kataoka, M. Ise and S. Narimatsu, *J. Sep. Sci.*, 2002, **25**, 77-85.
- 26 C. M. Chang, C. C. Chou and M. R. Lee, *Anal. Chim. Acta*, 2005, **539**, 41-47.
- 27 C. Basheer, A. Parthiban, A. Jayaraman, H. K. Lee and S. Valiyaveetil, *J. Chromatogr., A*, 2005, **1087**, 274-282.
- 28 F. Tan, H. Zhao, X. Li, X. Quan, J. Chen, X. Xiang and X. Zhang, *J. Chromatogr., A*, 2009, **1216**, 5647-5654.
- 29 P. Viñas, N. Campillo, N. Martínez-Castillo and M. Hernández-Córdoba, *Anal. Bioanal. Chem.*, 2010, **397**, 115-125.
- 30 J. L. Darias, V. Pino, J. L. Anderson, C. M. Graham and A. M. Afonso, *J. Chromatogr., A*, 2010, **1217**, 1236-1243.

- 31 J. J. Shu, P. F. Xie, D. N. Lin, R. F. Chen, J. Wang, B. B. Zhang, M. M. Liu, H. L. Liu and F. Liu, *Anal. Chim. Acta*, 2014, **806**, 152-164
- 32 M. J. Huang, G. B. Jiang and Y. Q. Cai, *J. Sep. Sci.*, 2005, **28**, 2218-2224.
- 33 H. L. Xu, Y. Li, D. Q. Jiang and X. P. Yan, *Anal. Chem.*, 2009, **81**, 4971-4977.
- 34 X. Z. Du, Y. R. Wang, X. J. Tao and H. L. Deng, *Anal. Chim. Acta*, 2005, **543**, 9-16.
- 35 X. L. Niu, W. Yang, G. Y. Wang, J. R., H. Guo and J. Z. Gao, *Electrochim. Acta*, 2013, **98**, 167-175.
- 36 B. Ntsewawana, B. B. Mamba, S. Sampath and O. A. Arotiba, *Inter. J. Electrochem. Sci.*, 2012, 3501-3512.