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# Sensitive monitoring of trace nitrophenols in water samples using multiple monolithic fiber solid phase microextraction and liquid chromatographic analysis

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ABSTRACT

In this work, a simple, efficient and environmentally friendly method—multiple monolithic fiber solid-phase microextraction (MMF-SPME) combining with high-performance liquid chromatography (HPLC) was first established for the determination of six trace nitrophenols in water samples. In order to prepare MMF-SPME, 1-allyl-3-methylimidazolium bis [(trifluoro methyl) sulfonyl] imide was co-polymerized with ethylene dimethacrylate to get single thin fiber (0.5 mm in diameter). Subsequently, four thin fibers were bound together to obtain the MMF-SPME. The effect of preparation conditions of MMF-SPME on the extraction performance was investigated in detail. In order to obtain the optimal extraction conditions of MMF-SPME for nitrophenols, several extractive parameters, including desorption solvent, extraction and desorption time, pH values and ionic strength in sample matrix were optimized. Under the optimum conditions, the linear ranges of 4-nitrophenol, 2,4-dinitrophenol, 5-methyl-2-nitrophenol, 5-methoxyl-2-nitrophenol were 0.5–200 μg/L and 1.0–200 μg/L for 2-nitrophenol and 4-tertbutyl-2-nitrophenol. The limits of detection ($S/N=3$) for the target analytes were 0.075–0.27 μg/L. At the same time, excellent method reproducibility was achieved in terms of intra- and inter-day precisions, indicated by the RSDs of both $<10.0\%$, respectively. Finally, the proposed method was successfully used to detect nitrophenols in different environmental water samples. Satisfactory recoveries ranged from 82.6% to 116% and the RSDs for reproducibility were less than 10% for target analytes in all real samples.



## 1. Introduction

Nitrophenols (NPs) are generated by a number of polluting processes, including those in industries such as dyestuffs, petroleum, pesticide, paper pharmaceutical [1,2]. NPs have become one of the most important contaminants present in the environment. Because of the toxicity and carcinogenicity, some of NPs are included in the list of priority pollutants in many countries. For instance, *p*-nitrophenol (*p*-NP) is one of the 129 organic pollutants listed by EPA [3]. At the same time, the maximum limits for *p*-NP in drinking water have been set by the European Commission, the Brazilian Environmental Council and EPA. The corresponding values are 0.1 μg/L, 100 μg/L and 60 μg/L, respectively [3,4]. Thereby, it is important to develop an efficient approach for the sensitive detection of NPs in environmental water samples.

So far, there are several analytical methods, including spectrophotometry [5], electrochemical method [6], HPLC [7], capillary electrophoresis [8] and gas chromatography [9], have been used to detect NPs compounds. Among them, chromatographic methods are used more frequently due to the high separation efficiency [7–9]. However, when GC is used to separate NPs, a derivatization step is required in order to improve the chromatographic performance and sensitivity. The derivatization of NPs is inconvenient and toxic derivatization reagents should be used. Compared with GC, HPLC is simple and convenient to separate NPs. Before HPLC analysis, enrichment step is necessary because the contents of NPs compounds in real samples are generally quite low. Because the contents of NPs compounds in real samples are generally quite low, prior to their determination an enrichment step is necessary. Up to now, various pretreatment techniques have been developed to extract NPs from aqueous samples, such as liquid-liquid extraction (LLE) [10], liquid-liquid microextraction (LLME) [11], solid-phase extraction (SPE) [12], solid-phase microextraction (SPME) [13,14], single-drop microextraction (SDME) [15] and stir bar sorptive extraction (SBSE) [16]. However, LLE is labor-intensive. Furthermore, it consumes much

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organic solvents. The extraction capacity of LLME is limited because low extraction solvent is used. SPE requires large volumes of toxic solvent, and the process is complicated and time consuming. The shortcomings of SDME include instability and volatility of the extraction solvent. For SBSE, long extraction times are needed.

Among above-mentioned extraction approaches for NPs, SPME has attracted much interest from researchers because there are several distinct advantages such as simplicity, rapidity, low sample consuming and environmental friendliness. The extraction medium plays an important role in SPME. It determines the extraction targets and performance. At the same time, the sensitivity and precision of the analysis are also affected strongly by the extraction medium of SPME. Up to now, there are a number of commercial and lab-made polymer-coated fibers for SPME such as polydimethylsiloxane (PDMS) [17], polyacrylate (PA) [18], polyaniline [19,20], nanomaterials [21,22], molecularly imprinted polymers (MIP) [23] and polymeric ionic liquids [24]. However, polymer-coated fibers suffer from insufficient chemical/thermal coating stability and limited extraction capacity. To overcome these advantages, coating-free fibers for SPME have been developed, such as graphene [25], pencil lead [26], carbon monolith [27], etcetera. Coating-free fibers eliminate the problems of coating stability and low extraction capacity associated with coated fibers. However, because of the thick sorbent in substrateless fibers, longer time should be spent in order to reach extraction equilibrium. Therefore, developing new extraction fibers with high extraction performance is highly desired.

Multiple monolithic fiber SPME (MMF-SPME) with monolithic material as extractive medium is a new extraction format which developed in our group [28]. The MMF-SPME is consisted of four independent thin monolithic fibers. In MMF-SPME, the aqueous samples can form convection during extraction because there are gaps between fibers. The formation of convection accelerates the extraction procedure. Therefore, the extraction speed of MMF-SPME is faster than that of coating-free fibers. At the same time, the total amount of sorbent in MMF-SPME is larger than that of coating-based fiber. Hereby, the MMF-SPME possesses higher extraction capacity. Furthermore, MMF-SPME is very flexible. According to the character of target analytes, the extraction medium-monolithic fiber can be easily designed and prepared to realize effective extraction of analytes. In present study, six nitrophenols were selected as target analytes. According to the structural characters of these NPs, there are hydrophobic aromatic rings and strongly polar hydroxyl and nitro groups (Table S1). A novel extractive medium based on poly (1-allyl-3-methylimidazolium bis [(trifluoro methyl) sulfonyl] imide-*co*-ethylene dimethacrylate) (AMED) monolith was designed and prepared. In the monolith, the aromatic ring can interact with the analytes through $\pi$-$\pi$ conjugation. The imidazole groups in the polymer can produce hydrogen-bond and dipole-dipole interactions with hydroxyl and nitro groups NPs. Therefore, the MMF/AMED-SPME is expected to extract NPs effectively. After the optimization of extraction conditions, a simple and sensitive methodology combining the MMF/AMED-SPME and liquid desorption (LD), followed by high performance liquid chromatography with diode array detection (MMF/AMED-SPME-LD-HPLC/DAD) for the direct analysis of trace NPs in water samples was developed.

## 2. Experimental

### 2.1. Chemicals

1-Allyl-3-methylimidazolium bis [(trifluoro methyl)sulfonyl]imide (AM) (98%) was purchased from Cheng Jie Chemical Co. LTD (Shanghai, China); Ethylene dimethacrylate (ED) (98%) were supplied by Alfa Aesar Ltd. (Tianjin, China); Azobisisobutyronitrile (AIBN) (97%, recrystallized before use) and N,N-dimethylformamide (DMF) (98%) were purchased from Shanghai Chemical Co. (China); HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia Company (Fairfield, USA); Water used throughout the study was purified using a Milli-Q water purification system (Millipore, USA).

2-Nitrophenol (2-NP) (98%), 4-nitrophenol (4-NP) (97%), 2,4-dinitrophenol (2,4-DNP) (98%), 5-methyl-2-nitrophenol (5-M-2-NP) (97%), 5-methoxy-2-nitrophenol (5-MO-2-NP) (97%) and 4-tertbutyl-2-nitrophenol (4-TB-2-NP) (98%) were supplied by Alfa Aesar Ltd. (Tianjin, China). The chemical properties of the above analytes are shown in Table S1. Water samples were collected from Xiamen city and filtrated through 0.45 μm membranes. All samples were stored at −4 °C before use. Individual stock solutions of NPs were prepared at a concentration of 10.0 mg/L by dissolving methanol and renewed monthly. The standard mixtures of NPs were prepared by dissolving 2.00 mg of each compound in methanol in 100 mL volumetric flask. The stock solutions were stored at 4 °C and diluted with ultrapure water to give the required concentration.

### 2.2. Instruments

HPLC analyses were carried out on a LC chromatographic system (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20A). Sample injection was carried out using a RE3725i manual sample injector with a 20 μL loop (Rheodyne, Cotati, CA, USA), all experiments were performed at room temperature.

The morphologies of monolithic materials were examined by a Model XL30 scanning electron microscopy (SEM) instrument (Philips, Eindhoven, The Netherlands). The pore size distribution of the monolith was measured on mercury intrusion porosimeter Model PoreMaster-60 (Quantachrome Instruments, Florida, USA). Elemental analysis (EA) was carried out on PerkinElmer (Shelton, CT, USA) Model PE 2400. FT-IR was performed on an Avatar-360 FT-IR instrument (Thermo Nicolet, Madison, WI, USA).

### 2.3. Chromatographic conditions

The separation of NPs was performed on a Phenomenex C18 column (5 μm particle size, 250 mm × 4.6 mm i.d.). Optimum separation was obtained with a binary mobile phase composed of ultrapure water (solvent A) and ACN (solvent B). The gradient elution program was as follows: 0–10.0 min = 50% B, 10.0–12.0 min = 50%B-20% B and kept to 15 min, 15.0–19.0 min = 20%B-90% B and kept to 25.0 min, 25.0–27.0 min = 90%B-50% B and kept to 30 min. The detector wavelength was set at 270 nm for 2-NP and 4-TB-2-NP, 300 nm for 4-NP and 5-MO-2-NP, 342 nm for other NPs. The flow rate was 1.0 mL/min, and injection volume was 20 μL.

### 2.4. Preparation of MMF/AMED-SPME

The preparation procedure of MMF/AMED-SPME is quite convenient. It includes two steps. The first step is the synthesis of single thin poly (AM-*co*-ED) monolithic fiber (AEMF). AIBN was used as polymerization initiator (1% (w/w) of the total monomer amount) and DMF was used as porogen in the all polymerization reaction. Different concentrations of monomer and porogen were used for different AEMF (Table 1). The monomer mixtures, porogen and AIBN were mixed ultrasonically into a homogenous solution, and then the reactant solution was purged with nitrogen for 5 min. Subsequently, the reactant mixture was introduced into a glass capillary (0.5 mm in diameter and 10 cm in length) with the aid of a syringe. After that, both ends of capillary were sealed with two small pieces of rubber. The filled glass capillary was placed in an oven and heated at 75 °C for 12 h. After the polymerization, 2 cm length of glass capillary was cut off carefully with grindstone. Firm, integrated and elastic AEMF (2 cm in length and 0.5 mm in diameter) (Fig. 1a) was obtained. For

comparison, thick AEMF (1.0 mm in diameter) was synthesized as the same procedure described as above. In the second step, several thin AEMFs were carefully tied up with parafilm at the glass part of AEMF to form fiber bunch. Then, the fiber bunch was dipped in methanol for 24 h to remove the residual monomers, porogen and uncross-linked polymers. Finally, the fiber bunch was dried in air for 1 h to obtain the final MMF/AMED-SPME. The Fig. 1a and b show the photos of single thin AEMF and MMF/AMED-SPME with four AEMFs, respectively. The polymerization equation is depicted in Fig. S1.

### 2.5. MMF/AMED-SPME procedure

Stirring extraction and LD modes were used in this work. The MMF/AMED-SPME was activated with methanol and ultrapure water in sequence. A volume of 20 mL of sample solution was added into a 25 mL vial containing an $8 \times 2$ mm stirring bar. MMF/AMED-SPME was performed by direct immersion of the fiber bunch in the sample solution for some time under low stirring (a vortex just appeared) using a magnetic stirrer. After extraction, the MMF/AMED-SPME was

**Table 1**
Extraction performance of different MMF/AMED-SPMEs for NPs.

| NO. | Monomer mixture | | Polymerization mixture | | Enrichment factor | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | AMM (%, w/w) | ED (%, w/w) | Monomer mixture (%, w/w) | Porogen solvent (%, w/w) | 4-NP | 2,4-DNP | 2-NP | 5-M-2-NP | 5-MO-2-NP | 4-TB-2-NP |
| 1 | 5 | 95 | 65 | 35 | 14 | 12 | 10 | 13 | 14 | 18 |
| 2 | 10 | 90 | 65 | 35 | 14 | 12 | 10 | 13 | 14 | 18 |
| 3 | 15 | 85 | 65 | 35 | 17 | 14 | 12 | 15 | 16 | 23 |
| 4 | 20 | 80 | 65 | 35 | 19 | 15 | 14 | 17 | 18 | 24 |
| 5 | 25 | 75 | 65 | 35 | 16 | 12 | 13 | 15 | 16 | 18 |
| 6 | 20 | 80 | 55 | 45 | 11 | 9 | 9 | 10 | 11 | 14 |
| 7 | 20 | 80 | 60 | 40 | 10 | 8 | 8 | 9 | 10 | 13 |
| 8 | 20 | 80 | 70 | 30 | 15 | 13 | 11 | 14 | 15 | 21 |
| 9 | 20 | 80 | 75 | 25 | 13 | 11 | 9 | 13 | 14 | 18 |

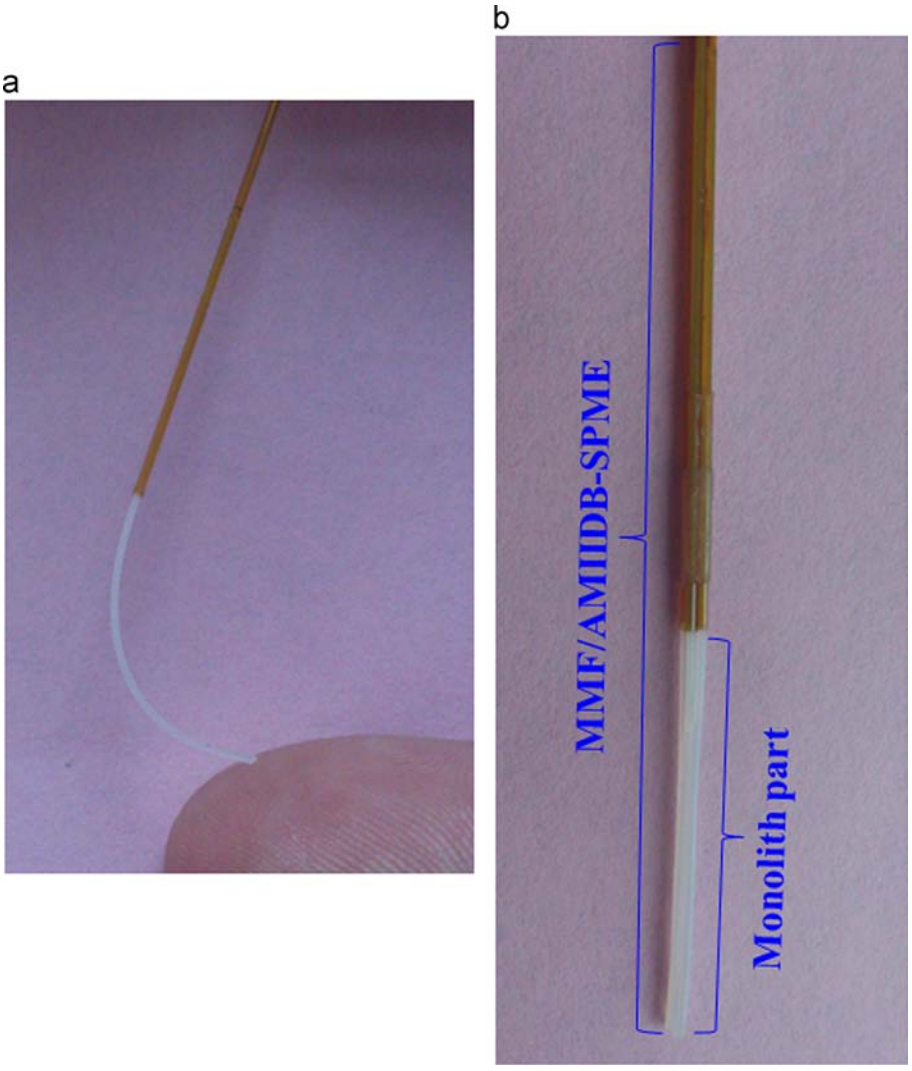


**Fig. 1.** The photos of single thin AEMF (a) and MMF/AMED-SPME with four AEMFs (b).

removed and desorbed with 400 μL desorption solvent (methanol) in a 0.4 mL vial insert. The stripping solvent was used directly for HPLC analysis. Between samples, fiber bunch was reconditioned in two consecutive steps of 15 min by immersion in methanol and ultrapure water, respectively.

### 2.6. Preparation of environmental water samples

Tap, lake and river water samples were collected in 2.5 L amber glass bottles and stored in the dark at 4 °C until analysis. All the samples were vacuum-filtered through a 0.45 μm nylon filter to remove suspended matter. The pH values of sample solutions were adjusted to 4.0 by 0.1 mol/L HCl, and ionic strength was adjusted to 15% (w/v) by addition of NaCl. After that, MMF/AMED-SPME procedure was used to extract NPs from the above-mentioned water samples.

### 2.7. Method validation

The LOD and LOQ values of each analyte were considered as the concentration giving a signal to noise ratio of 3 and 10, respectively. The calibration curves were made by fortified with the analytes at each of eight concentrations from 0.5 to 200 μg/L. The spiked samples were performed with complete SPME procedure. The calibration curves were calculated using the linear least squares regression analyses of the peak area to concentration ratios. To evaluate the intra-day precision of proposed method, four replicates samples with 100 μg/L spiking concentration were extracted and analyzed within one day. The inter-day precision of the method was assessed at a l00 μg/L spiking concentration during a period of four consecutive days.

## 3. Results and discussion

### 3.1. Preparation and characterization of MMF/AMED-SPME

To obtain the expected extraction performance and useful life span of MMF/AMED-SPME, preparation parameters including the content of monomer, cross-linker and porogen were investigated in detail (Table 1). It can be seen from the data that the extraction performance of MMF/AMED-SPME for the target analytes is affected strongly by the content of AMII, ED and DMF in polymerization. Appropriate content of monomer favors the increase of extraction performance. Comprehensively considering extraction capacity, extraction speed and useful longevity of MMF/AMED-SPME, the optimal conditions for the preparation of MMF/AMED-SPME were the proportion of AMII kept 20% in the monomer mixture, the ratio of monomer mixture to porogen was 65/35 (%, w/w) (MMF/AMED-SPME-4). Therefore, the MMF/AMED-SPME-4 was used in the following studies.

The monolith prepared under the optimal polymerization conditions (MMF/AMED-SPME-4) was characterized by EA, FTIR, SEM and MIP. EA results demonstrated that its carbon, nitrogen and sulfur contents were 35.6%, 7.82% and 10.9 (w/w), respectively, indicating that AM and ED were polymerized successfully. The FT-IR spectrum (Fig. S2) also confirms the success polymerization of AM and ED. As can be seen from the spectrum, the strong absorption peak around 2980 $cm^{-1}$ belongs to $CH_3$ and $CH_2$ groups. Strong adsorption at the 1731 $cm^{-1}$ belongs to C═O stretching band of ED. The adsorption observed at 1629 $cm^{-1}$ contributes to C═N stretching band of imidazole groups. The two strong bands at 1388 and 1178 $cm^{-1}$ indicate the existence of sulfonyl groups. Fig. 2a and b show the SEM images of the AEMF at 100× and 20 000× magnification, respectively. It can be seen from Fig. 2a that the AEMF is integrated and homogeneous. At the same time, the even pore size and microglobules of the monolithic material can be clearly observed (Fig. 2b). Fig. 2C shows the pore size distribution plot. It was found that pore size distribution is uniform, most of the pore sizes are around 250 nm. The existence of uniform pore size distribution ensures that the monolith possesses good permeability and favorable mass transfer during the extraction procedure. Furthermore, the total surface area was 25.2 $m^2/g$ for the porous monolith calculated from a Brunauer-Emmett-Teller (BET) plot. The relatively large surface area ensures that there are more adsorptive sites for analytes. Therefore, it can be expected that the new MMF/AMED-SPME possesses high extraction capacity.

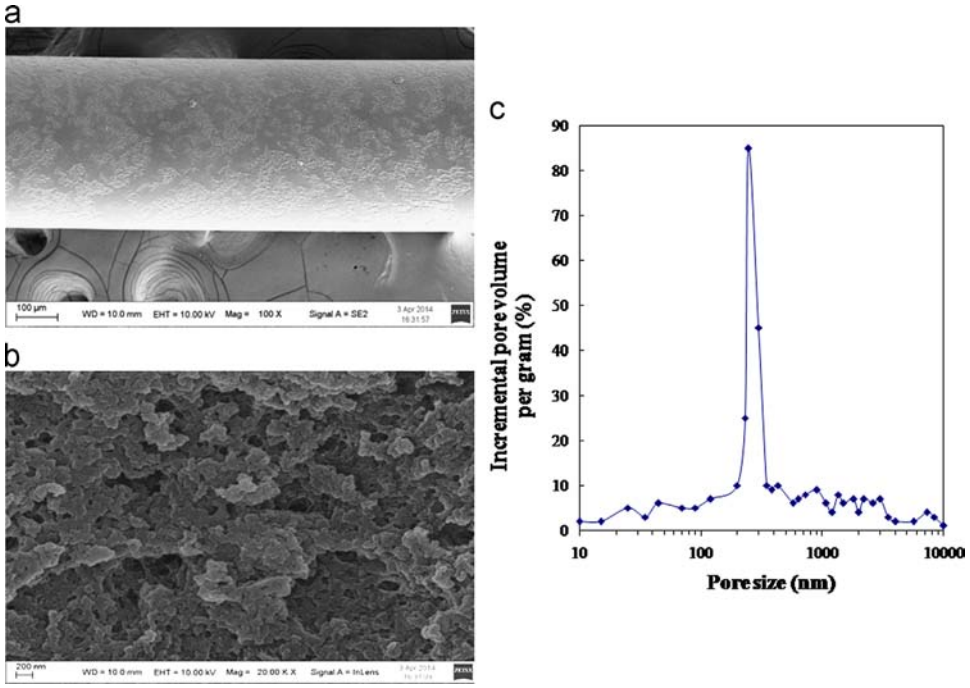


**Fig. 2.** The SEM images of the AEMF at 100× magnification (a), 20000× magnification (b) and pore size distribution plot of poly (AMII-*co*-ED) monolith (c).

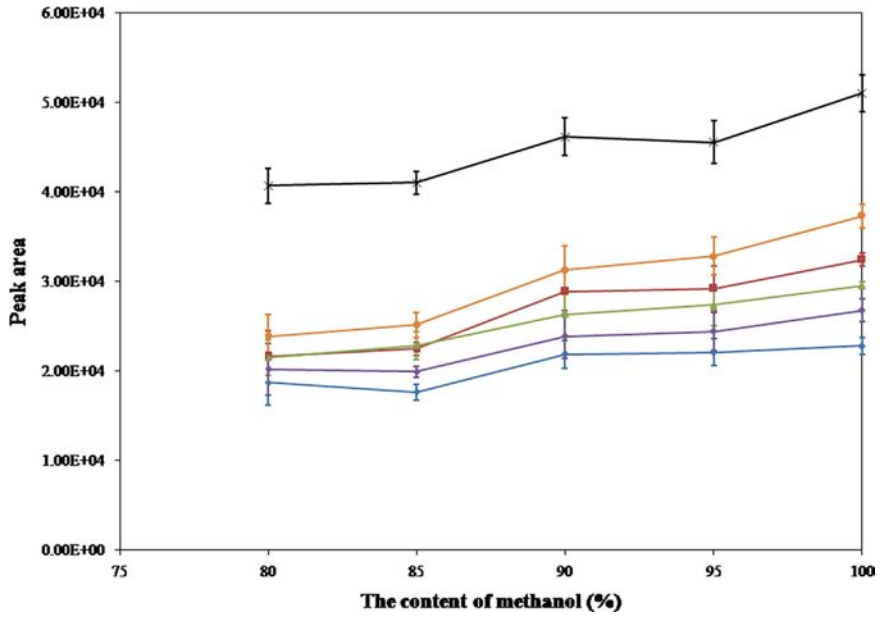


**Fig. 3.** The effect of desorption solvent on extraction efficiency. Conditions: extraction and desorption time were both 0.5 h; no salt was added in the sample and the pH values of sample matrix were not adjusted. The spiked concentration was 100 μg/L for each NP. Symbols: ∗2,4-DNP; ● 5-M-2-NP; ■ 4-TB-2-NP; ▲ 4-NP; ◆ 5-MO-2-NP; ◆ 2-NP.

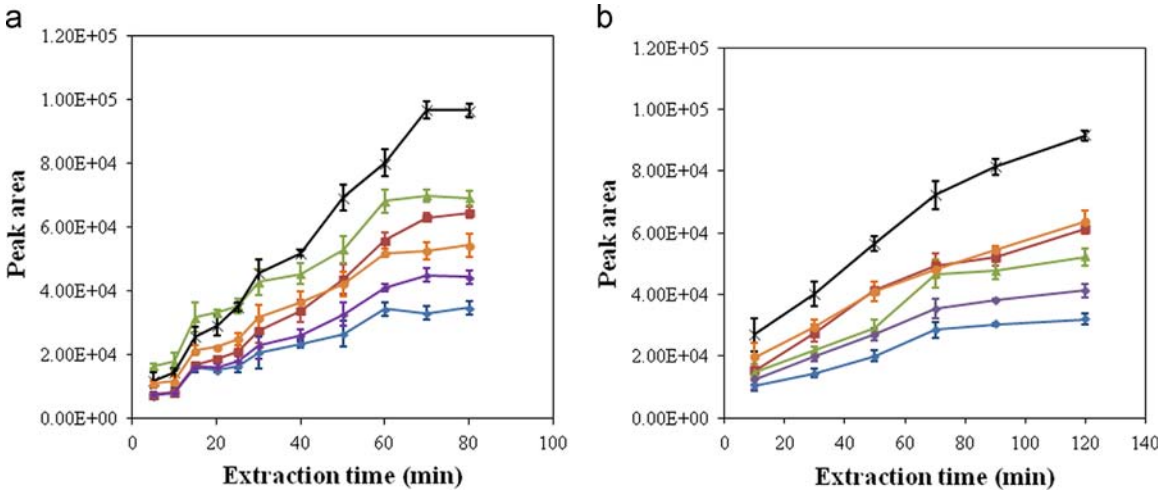


**Fig. 4.** The effect of extraction time on extraction efficiency. (a) MMF/AMED-SPME; (b) thick fiber Conditions: methanol was selected as desorption solvent; desorption time was 0.5 h. The other extraction parameters and symbols were the same as in Fig. 3.

### 3.2. Optimization of MMF/AMED-SPME method

Before the proposed MMF/AMED-SPME was applied to analyze NPs in water samples, several parameters, such as desorption solvent, extraction and desorption time, pH values and salt concentration, which related to the extraction efficiency, were optimized.

#### 3.2.1. Desorption solvent

In this study, methanol/water binary solvent was selected as desorption solvent. The content of methanol in desorption solvent varied from 80% to 100% (v/v). Fig. 3 shows that the extraction efficiencies reach maximum for all studied NPs when methanol content is 100%. Therefore, methanol was chosen as the desorption solvent.

#### 3.2.2. Extraction and desorption time

The SPME procedure is a time dependant process. Fig. 4a depicts the extraction time profile of the studied analytes on MMF/AMED-SPME. For each analyte, 70 min is enough for them to achieve equilibrium on the fiber bunch. To further evaluate the extraction speed of MMF/AMED-SPME, the extraction time profile of thick fiber (1.0 mm in diameter and 20 mm in length; at the same time, the weight of the monoliths was equal to the weight of the monoliths in MMF/AMED-SPME) was also studied for comparison (Fig. 4b). The extraction efficiency enhanced with the increase of extraction time, but the equilibrium did not be reached even the extraction time was prolonged to 120 min. At the same time, the extraction performance of thick fiber was far lower than that obtained with MMF/AMED-SPME when the extraction time was 70 min, which indicated that most part of sorbents in the thick fiber had not contacted with analytes. The

comparison well indicates that MMF/AMED-SPME possesses satisfactory extraction speed. The reason is that there are gaps between thin fibers of MMF/AMED-SPME, convection can be formed between the thin fibers during extraction. Therefore, the analytes can reach the sorptive sites quickly [28]. The investigation of desorption time showed that the NPs could be eluted from the sorbent completely in 10 min when the extraction time was 70 min (Fig. S3). Consequently, 70 min and 10 min were adopted for extraction and desorption procedure, respectively, in the following research.

### 3.2.3. Sample pH value

Sample pH value will influence the existing form of NPs. The ionic forms of the analytes largely weaken the interactions between analytes and sorbent. Therefore, it is important to control the pH value to enhance the affinity of the analytes toward the monolith and to improve extraction efficiency. At present study, the effect of pH on the extraction efficiency was investigated by adjusting the pH value of sample solution ranging from 2.0 to 11.0. As shown in Fig. 5, the extraction efficiencies improve with the increase of pH values from 2.0 to 4.0, and the extraction efficiencies decrease when pH values increase continuously. The interesting variation trend may be explained as follows: at low sample pH values, the protonation procedure happened on nitrogen atoms of sorbent and NPs. Therefore, there were electrostatic repulsions between sorbent and NPs. At the same time, only π-π interaction contributed to the extraction because the molecules of NPs were ionic forms. The above-mentioned reasons leaded to poor extraction performance at low sample pH values. With the increase of pH values, the electrostatic repulsions between sorbent and NPs disappeared gradually because of deprotonation procedure. At the same time, hydrophobic interaction increased between sorbent and analytes. Furthermore, hydrogen-bonding and dipole-dipole interactions produced by the polar groups between the sorbent

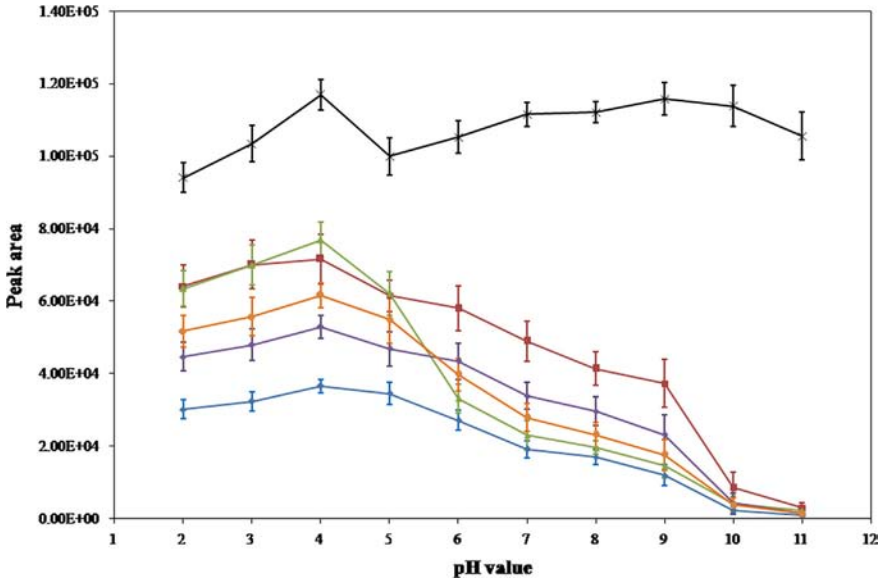


**Fig. 5.** The effect of pH value of sample matrix on extraction efficiency. Conditions: extraction and desorption time were 70 and 10 min, respectively; the sample pH values were adjusted by 0.1 mol/L HCl or 0.1 mol/L NaOH. The other conditions and symbols are the same as in Fig. 4.

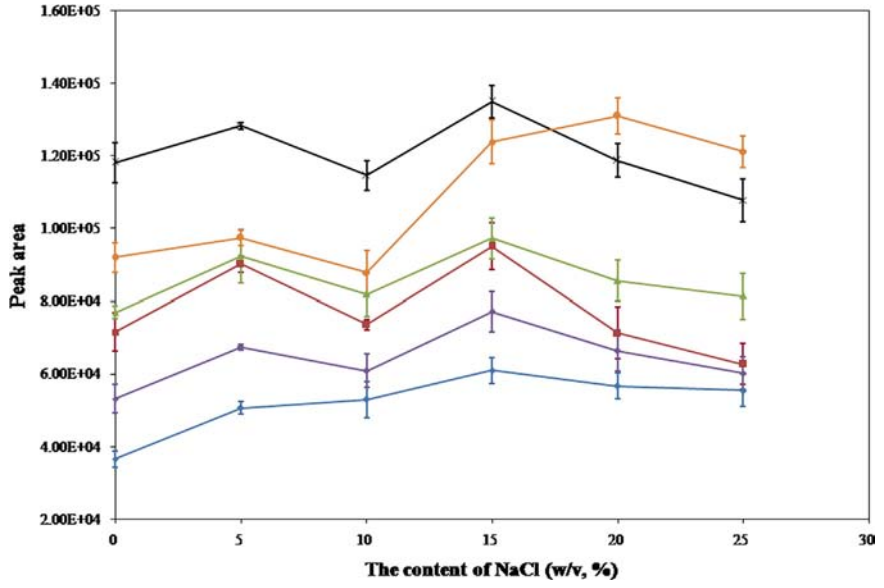


**Fig. 6.** The effect of salt concentration in sample matrix on extraction efficiency. Conditions: pH value of sample matrix was adjusted to 4.0. The other conditions and symbols are the same as in Fig. 4.

and the analytes also contributed to the extraction. Therefore, higher extraction performance could be obtained with the increase of pH values. However, when the pH values increased continuously, the favorable hydrogen-bonding and dipole-dipole interactions were weakened by overmuch hydroxyl groups in solution. At the same time, molecules of NPs became ionic forms again because of dissociation of phenolic hydroxyl groups. Therefore, the extraction performance decreased when sample pH values increased continuously. The above results well demonstrate that multi-interaction such as hydrophobic, $\pi$-$\pi$, hydrogen-bonding and dipole-dipole interactions co-contribute to the extraction of MMF/AMED-SPME for NPs. According to the results and in order to obtain stable extraction efficiencies, pH 4.0 was selected for subsequent experiments.

### 3.2.4. Salt concentration

Typically, there are salting-out and salting-in effects when salt is added into sample solution [29]. Salting-out effect can increase the extraction efficiency, however, the salting-in effect will decrease the extraction efficiency. Hereby, the effect of salt concentration in matrix was investigated by addition of NaCl from 0 to 25% (w/v). As shown in Fig. 6, salt concentration affected the extraction efficiencies strongly. The optimal salt concentration was 15% for 2-NP, 4-NP, 2,4-DNP, 5-MO-2-NP and 4-TB-2-NP. For 5-M-2-NP, the maximum extraction efficiency could be obtained when salt concentration was 20%. However, there was no obvious difference in extraction efficiency between 15% and 20% salt concentration. Therefore, for experimental convenience, 15% (w/v) salt addition was chosen in the following studies.

Based on the experimental results, the optimal MMF/AMED-SPME conditions for NPs are as follows: using methanol as desorption solvent; extraction and desorption time were 70 min and 10 min, respectively; the pH value of sample matrix was 4.0; 15% (w/v) salt was added in sample matrix. Under the optimized extraction conditions, the MMF/AMED-SPME exhibited satisfactory extraction performance to NPs. Fig. 7b shows the chromatograms of NPs after extraction. Compared with Fig. 7a (direct injection of spiked sample without extraction), it can be seen that all the analytes are obviously enriched after treatment with MMF/AMED-SPME. The good results may contribute to the multiply interactions such as hydrophobic, π-π, hydrogen-bonding and dipole-dipole interactions between the new MMF/AMED-SPME and NPs. Furthermore, it is important to stress that the MMF/AMED-SPME possessed excellent longevity. It could be reused more than 250 times without decreasing the extraction efficiency.

## 3.3. Method validation

A series of experiments with regard to the linearity, limits of detection (LODs), limits of quantification (LOQs), method reproducibility

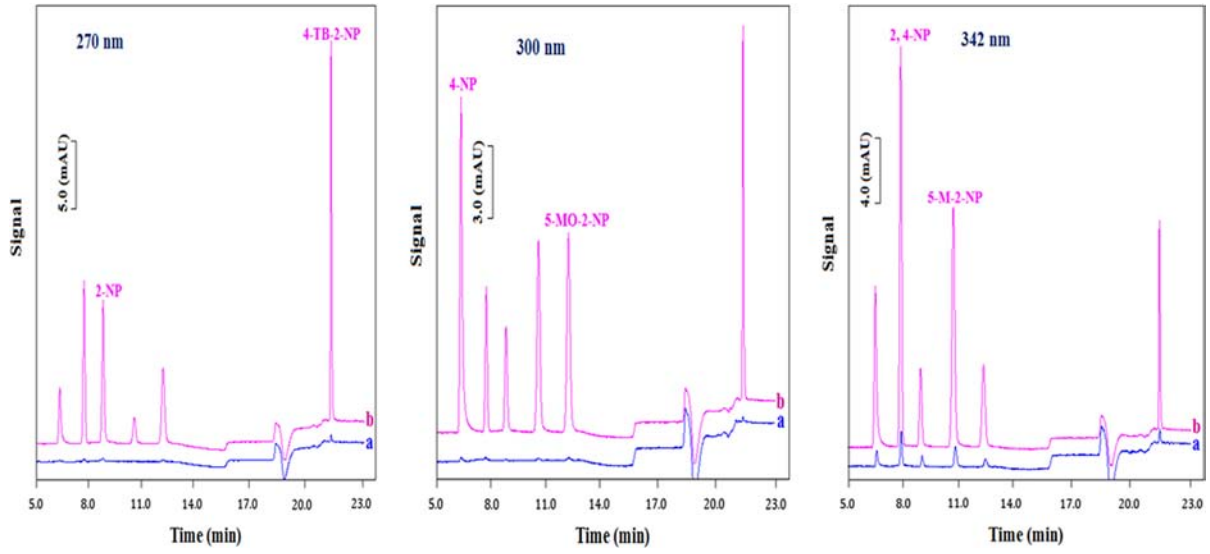


**Fig. 7.** HPLC chromatograms of six NPs. (a) Direct injection of spiked water sample; (b) Spiked water sample with each analyte at 100.0 μg/L and treated with MMF/AMED-SPME. Conditions: methanol was used as desorption solvent; extraction and desorption time were 70 and 10 min, respectively; the pH value of sample matrix was 4.0; 15% (w/v) salt was added in sample matrix. The spiked concentration was 10 μg/L for each NP.

**Table 2**
Linear dynamic range, correlation coefficients, LODs and LOQs, precisions and bunch-to-bunch reproducibility achieved for NPs.

| Compound | Linear range[a] (μg/L) | $R^2$ | LOD[b] (μg/L) | LOQ[c] (μg/L) | Intra-day assay variability[d] (RSD, %, $n=4$) | Inter-day assay variability[d] (RSD, %, $n=4$) | Bunch-to-bunch reproducibility[d] (RSD, %, $n=4$) |
|---|---|---|---|---|---|---|---|
| 4-NP | 0.5–200 | 0.9993 | 0.13 | 0.43 | 4.4 | 6.7 | 7.7 |
| 2,4-DNP | 0.5–200 | 0.9988 | 0.096 | 0.32 | 5.6 | 6.8 | 8.7 |
| 2-NP | 1.0–200 | 0.9987 | 0.25 | 0.82 | 4.5 | 4.7 | 6.8 |
| 5-M-2-NP | 0.5–200 | 0.9989 | 0.14 | 0.46 | 6.9 | 6.9 | 7.4 |
| 5-MO-2-NP | 0.5–200 | 0.9992 | 0.075 | 0.25 | 6.1 | 7.0 | 5.0 |
| 4-TB-2-NP | 1.0–200 | 0.9997 | 0.27 | 0.88 | 8.2 | 9.3 | 8.8 |

[a] :Spiked level includes 0.5, 1.0, 5.0, 10.0, 20.0, 50.0, 100.0, and 200.0 μg/L, respectively.
[b] :$S/N=3$.
[c] :$S/N=10$.
[d] :assay at 100 μg/L level.

**Table 3**
Comparison of the limits of detection (μg/L) and recoveries of present method with other methods for NPs detection.

| Methods | 2-NP | 4-NP | 2,4-DNP | Recoveries (%) | Ref. |
|---|---|---|---|---|---|
| SBSE-HPLC/DAD | / | 1.50 | / | / | [16] |
| SBSE-HPLC/DAD | / | 0.87 | / | / | [30] |
| SBSE-HPLC/UV | 0.14 | 1.18 | 30 | 90.7–115.6 | [31] |
| MSPE[a]-HPLC-UV | 0.4 | 0.3 | 0.4 | 84–109 | [32] |
| UAEM[b]-HPLC-UV | 1 | 0.25 | 0.5 | 92.0–115 | [33] |
| MS-USAEME[c]-UHPLC/UV | / | 0.6 | 3.0 | 88–101 | [34] |
| SPME-HPLC/UV | 0.67 | 0.25 | 0.65 | 23.5–65.6 | [35] |
| MIP-SPME-HPLC/UV | / | 0.33 | / | 98–103 | [36] |
| SPME-HPLC/UV | 1.6 | 3.6 | 4.1 | / | [37] |
| HS-SPME-GC/FID | 7.5 | / | / | / | [38] |
| HS-SPME-GC/MS | 0.38 | 0.75 | 1.6 | 111–118 | [39] |
| SPME-GC/MS | / | 10 | / | 86.4–89.2 | [40] |
| SDME[d]-GC/MS | 0.029 | 0.038 | / | / | [41] |
| SPE-GC/MS | 0.30 | 1.00 | / | 60–110% | [42] |
| MMF/AMIIED-SPME | 0.25 | 0.16 | 0.096 | 82.6–116 | proposed method |

[a] :MSPE-magnetic solid phase extraction;
[b] :UAEM-Ultrasound-assisted emulsification microextraction;
[c] :MS-USAEME-manual shaking-enhanced, ultrasound-assisted emulsification microextraction;
[d] :SDME-single-drop microextraction.

**Table 4**
Results of determination and recoveries of real water samples spiked with six NPs.

| Samples | Spiked(μg/L) | Detected (μg/L)/recovery (%RSD, $n=3$) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 4-NP | | 2,4-DNP | | 2-NP | | 5-M-2-NP | | 5-MO-2-NP | | 4-TB-2-NP | |
| Tap water | 0 | ND | | ND | | ND | | ND | | ND | | ND | |
| | 10 | 9.02 | 90.2 (8.2) | 9.35 | 93.5 (9.4) | 8.54 | 85.4 (6.2) | 9.28 | 92.8 (9.7) | 9.39 | 93.9 (7.9) | 9.46 | 94.6 (9.3) |
| | 100 | 97.1 | 97.1 (3.9) | 98.9 | 98.9 (3.3) | 99.6 | 99.7 (6.6) | 95.6 | 95.6 (4.5) | 98.1 | 98.1 (5.7) | 91.9 | 92.0 (5.6) |
| Lake water | 0 | 0.44 | | ND | | ND | | ND | | ND | | ND | |
| | 10 | 9.54 | 91.0 (8.3) | 9.42 | 94.2 (9.4) | 8.26 | 82.6 (6.9) | 10.8 | 108 (9.7) | 8.85 | 88.5 (9.5) | 9.26 | 92.6 (9.1) |
| | 100 | 114 | 113 (9.6) | 116 | 116 (9.8) | 111 | 111 (6.3) | 110 | 110 (8.9) | 111 | 111 (7.7) | 107 | 107 (9.4) |
| River water | 0 | ND | | ND | | ND | | ND | | ND | | ND | |
| | 10 | 8.86 | 88.6 (1.1) | 10.5 | 105 (1.0) | 9.06 | 90.6 (4.8) | 9.58 | 95.8 (3.6) | 9.93 | 99.3 (2.9) | 10.5 | 105 (2.2) |
| | 100 | 92.2 | 92.2 (5.4) | 105 | 105 (6.1) | 99.0 | 99.0 (4.6) | 99.2 | 99.2 (6.1) | 102 | 102 (6.6) | 99.2 | 99.2 (8.2) |

ND: not detected.

was performed to validate the proposed method at the optimized working conditions. Results obtained are listed in Table 2.

The linear dynamic ranges for 4-NP, 2,4-DNP, 5-M-2-NP and 5-MO-2-NP were 0.5–200 μg/L, and 1.0–200 μg/L for 2-NP and 4-TB-2-NP. All the linear dynamic ranges possess good linearity ($R^2 > 0.99$). The LOD and LOQ were in the range of 0.075–0.27 and 0.25–0.88 μg/L, respectively. At the same time, excellent method reproducibility was achieved in terms of intra- and inter-day precisions, bunch-to-bunch reproducibility indicated by relative standard deviations less than 9%, 10% and 9%, respectively. These results demonstrate that the proposed method has good reproducibility and high sensitivity for the monitoring of NPs.

### 3.4. Comparison with other methods

So far, a few of analytical methodologies have been proposed for the determination of 2-NP, 4-NP and 2,4-DNP. However, to the best of our knowledge, there is no report about the monitoring of 5-M-2-NP, 5-MO-2-NP and 4-TB-2-NP. Table 3 shows the comparison of present method with other reported analytical methodologies for 2-NP, 4-NP and 2,4-DNP in environmental water samples.

It can be seen from the comparison, lower LOD could be obtained in the present method than other methods with the same kind of detector [16,30–37].Typically, higher sensitivity can be achieved when high sensitivity detectors such as flame ionization detection (FID) and mass spectrum (MS) are used. However, the LODs for 2-NP, 4-NP and 2,4-DNP achieved in proposed method are lower than that obtained with HS-SPME-GC/FID [38], HS-SPME-GC/MS [39], SPME-GC/MS [40] and SPE-GC/MS [42]. At the same time, the spiked recoveries achieved in the present method is far better than that obtained in SPME-HPLC/UV [35], and at the same level as that got in other works [31–34,36,39–42].

### 3.5. Application in real water sample analysis

The practical applicability of the proposed method was evaluated by extracting NPs from water samples of different sources including tap, lake and river water. The results in Table 4 show that only low concentration of 4-NP was detected in lake water sample. To further evaluate the feasibility of the proposed method, extraction recoveries were assessed by spiking different standard solutions (10.0 μg/L and 100.0 μg/L, respectively). The results show that the recoveries of the all target analytes from the all samples are in the range from 82.6% to 116% with the RSDs less than 10%, indicating that the proposed method is feasible for the monitoring of trace nitrophenols in water samples.

## 4. Conclusions

In present work, a new SPME based on multiple monolithic fiber was successfully prepared using 1-allyl-3-methylimidazolium bis [(trifluoro methyl)sulfonyl]imide and ethylene dimethacrylate as precursors. The MMF/AMED-SPME can effectively extract nitrophenols with multiply interactions such as hydrophobic, $\pi$-$\pi$, hydrogen-bonding and dipole-dipole interactions. Under optimized conditions,

the developed method of MMF/AMED-SPME-HPLC/DAD can be used to determine trace NPs in water samples effectively. In comparison with the existing extraction methods for the monitoring of NPs, the proposed method was simple, sensitive, cost-effective, fast and environmentally friendly. Taken together, the proposed method may serve as a promising alternative to the monitoring of NPs in environmental water samples.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.10.059.

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