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Amine functionalized polyacrylonitrile fibers for the selective preconcentration of trace metals prior to their on-line determination by ICP-MS†

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Amine functionalized polyacrylonitrile fibers (PANFs) were prepared and applied for the simultaneous separation and preconcentration of V(v), As(III), Sn(IV), Sb(III) and Bi(III) from environmental water samples in this paper. The functional PANFs were first prepared by nucleophilic substitution reaction between hydroxylamine hydrochloride and polyacrylonitrile fibers, and then the reactant obtained in the first step was subjected to a ring opening reaction with epichlorohydrin, followed by modification with triethylenetetramine (TETA). The structure of the final polymer fibers was analyzed by Fourier transform infrared spectroscopy (FT-IR), and the morphology was characterized by scanning electron microscopy (SEM). A home-made solid phase extraction (SPE) pretreatment column was filled with PANFs, and then online connected with inductively coupled plasma mass spectrometry (ICP-MS) for quantitative determination of metal ions. Under the optimized experimental conditions, the target metal ions were eluted rapidly and quantitatively using 0.3 mol L⁻¹ HNO₃ solution. Only with 30 mL sample solution, high enrichment factors of 120 were obtained for V(v), As(III), Sn(IV) and Sb(III), and 115 for Bi(III), respectively. The detection limits achieved were low: 1.2, 0.9, 1.7, 1.5 and 2.3 ng L⁻¹ for V(v), As(III), Sn(IV), Sb(III) and Bi(III), respectively, and the relative standard deviations (RSDs) were below 3.0%. The advanced fiber materials prepared in this work have the advantages of low cost, environmental friendliness and high adsorption efficiency, and the on-line preconcentration method has greatly improved the analysis efficiency. Finally, the feasibility and accuracy of the method were validated by successfully analyzing Certified Reference Materials (CRMs) as well as lake, river and sea water samples.

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1. Introduction

Heavy metal pollution is becoming more and more serious with the development of industrialization and urbanization. For example, the compounds of vanadium have moderate and high toxicity to humans and animals. The toxicity is related to the valence state, solubility and uptake pathway of vanadium. Poisoning can occur if more than 10 mg of vanadium is ingested per day; vanadium pollution in water is a global problem and has been reported in the USA, Japan and China.¹ Inorganic arsenic is released into the environment from mining and ore dissolution, which are the main sources of soil and water pollution. In China, the maximum allowable concentration of

arsenic in drinking water is 0.01 mg L⁻¹, and that in surface water including fishery water is 0.04 mg L⁻¹. The increase of antimony content in water is caused by the erosion of antimony-bearing rocks by running water, the discharge of industrial waste water, and the fall of atmospheric antimony dust. Antimony exists in the form of Sb(v) in fresh water, and in the form of complex ions in seawater. The average content of antimony in river is about 0.2 μg L⁻¹, and 0.24 μg L⁻¹ in seawater. Tin content in fresh water is between 0.004 and 0.09 μg L⁻¹, and that in seawater is 0.002–0.81 μg L⁻¹. Phytoplankton and brown algae can highly enrich tin from seawater, which will bring harm to the whole marine system. Some organo-tin compounds are very toxic and can destroy sulfur-containing proteins, and the maximum allowable concentration of tin in surface water is 0.1 mg L⁻¹. Bismuth (Bi) is used to treat gastric ulcer diseases, and if a large amount of bismuth is deposited in the brain and kidney, it will cause uremia, poor memory and other symptoms. More importantly, the damage to the brain and kidney caused by bismuth is silent. Hence, there is an ever-increasing need for effective and selective separation and determination techniques for metal ions due to the increasing prominence of environmental concerns.²

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For the detection of metal ions, a variety of spectral and mass spectrometry analysis methods have been well developed. Among them, ICP-MS is usually preferred due to the merits of multielement sequential determination, high sensitivity and easy to couple with other analytical techniques. Although satisfactory results and high sensitivity have been achieved using diversified instrument assisted analytic methods for a unique metal, the direct determination of trace metals either with complicated matrices or at extremely low levels is still problematic. Accordingly, various separation and enrichment methods have been introduced for the determination of heavy metals.³ For instance, diversified liquid phase micro-extraction (LPME) pretreatment methods including dispersive liquid-liquid micro-extraction (DLLME),^{4,5} hollow fiber LPME^{6,7} and stirring-assisted LPME⁸ have been applied in the field of heavy metal analysis. Moreover, other sample pretreatment processes such as cloud point extraction⁹ and solid phase extraction (SPE)^{10–12} have also been invented for this purpose. As we know, the conventional liquid-liquid extraction method usually needs a large number of expensive organic toxic reagents, which makes the method not only cumbersome, but also slightly harmful to humans. Instead, solid phase extraction is a relatively mature technique. It is based on the reversible interactions between the target and an adsorbent in a column through physical or chemical adsorption, followed by an elution process.¹³

The adsorption efficiency of metal ions depends on the core filler used for solid phase extraction. So far, many adsorption materials have been developed and applied in the area of metal ion separation and analysis. In many previous reports, multiple advanced materials including magnetite nano-composites,^{14–16} nano-magnetic graphene oxides,^{17–19} and metal-organic frameworks (MOFs)^{20,21} have been extensively employed for metal ion preconcentration. Porous polymer materials have been used in the extraction of trace organic compounds as early as 1979, and are composed of low cost pure organic groups. Porous organic polymers have been widely used in environmental pollutant removal, chromatographic separation, catalysis, and energy storage and conversion due to their high specific surface area, controllable pore structure, good chemical and thermal stability and easy surface functionalization.²² For example, magnetic porous organic polymers (MOPs) were adopted as novel adsorbents for Bi preconcentration.²³ Besides, ionic imprinted polymers (IIPs) have been used for the isolation and preconcentration of inorganic arsenic.^{24,25} Furthermore, diversified composite porous polymer materials have also been successfully developed for metal ion preconcentration.^{26–28} Among these porous polymer materials, polyacrylonitrile fibers have been well applied in the field of water treatment.²⁹ For instance, a colorimetric Hg²⁺ sensor based on porphyrin functionalized polyacrylonitrile fibers was prepared.³⁰ In addition, a polyacrylonitrile/aluminum oxide nanofiber adsorbent was synthesized and evaluated as an adsorbent for removing thorium(IV) ions from aqueous solution.³¹ Furthermore, amino-functionalized polyacrylonitrile fibers were utilized for adsorption of Hg(II) ions from aquatic media.³² It can be seen from previous reports that due to the unique merits such as

environmental friendliness, large surface area and feasibility of further modification, the potential application of polyacrylonitrile fibers in the metal ion separation and enrichment field needs to be further explored. Design and preparation of advanced polyacrylonitrile fibers with the advantages of simplicity, low cost and versatile enrichment capability is highly desirable and challenging.

In this study, triethylenetetramine (TETA) modified polyacrylonitrile fibers (PANFs) were designed attentively, prepared and used to adsorb V(V), As(III), Sn(IV), Sb(III) and Bi(III) from real environmental water samples through solid phase extraction. Usually, the SPE procedures were coupled off-line with detection steps. However, these interrupted procedures followed by manual transfer to a final analyzer may be prone to sample contamination or losing an aliquot of the sorbent retaining target analytes.³³ In order to improve the repeatability and reliability of experimental data, as well as improve analysis efficiency, the online combination of SPE quantitative technology was implemented. For this purpose, an external high-pressure infusion pump was introduced to load water samples. All of the trace metal ions can be selectively and quickly retained on the amine functionalized PANFs, then quantitatively eluted and determined by the on line SPE-ICP-MS technique.

The key factors affecting adsorption efficiencies of V(V), As(III), Sn(IV), Sb(III) and Bi(III), including pH, sample volume, flow rate, wash time, eluent type and matrix effects, were optimized with standard solutions. The proposed method was also extended for the determination of the target metal elements in real environmental water samples, and blank control experiments and parallel spike tests were performed for each sample at the same time. The on-line solid phase extraction coupled with inductively coupled plasma mass spectrometry (ICP-MS) method established in this work integrates separation, enrichment and detection, which greatly improves the analysis efficiency. The prepared fiber material not only is low cost and highly reusable, but also has a good adsorption effect, and is expected to be commercialized. Finally, the accuracy and feasibility of the established method have been verified using a series of Certified Reference Materials (CRMs) with the respective numbers of GSB07-3175-2014-1 (V), GSB07-3171-2014-5 (As), BWZ6705-2016 (Sn) and GSB07-1376-2001-1 (Sb) for water quality monitoring.

2. Experimental

2.1 Instrumentation

In this work, preconcentration of the trace metals was performed using an STI PT501 high pressure pump (Surwit Technology Inc., Hangzhou, China, <http://www.surwit.com>). After the on-line SPE procedure, the trace metals were extracted quickly *via* a U3000 pump (Thermo Fisher, USA, <http://www.thermofisher.com>) and analyzed using an iCAP Q ICP-MS (Thermo Fisher, USA, <http://www.thermofisher.com>). In order to obtain the best signal to background (S/N) ratio and analysis results, the important parameters of ICP-MS were optimized to ensure that the double charged ions (⁶⁹Ba²⁺/¹³⁸Ba⁺

ratio) and oxide ions ($^{156}\text{CeO}^+ / ^{140}\text{Ce}^+$) are less than 3%. The optimized ICP-MS operating conditions are summarized in Table S1.†

In order to compare the adsorption material before and after modification, an X-ray fluorescence spectrometer (XRF) (Axios mAX, Netherlands, <http://www.panalytical.cn>) was used for N observation. The fibers and the initial raw materials were characterized using a Nicolet iS50 FT-IR (Thermo Fisher, USA, <http://www.thermofisher.com>). Field emission scanning electron microscopy (SEM) (S-4800, Hitachi, <https://www.hitachi-hightech.com>) was adopted for morphology observation. A mercury porosimeter (AutoPore IV 9510, USA, <http://www.micromeritics.com.cn>) was used to measure the specific surface area of fibers. The pH values were measured with an FE20 pH-meter (Mettler Toledo, Shanghai, China, <https://www.mt.com>). The hollow stainless steel column used in this experiment was supplied by Ningbo Yinzhou Baishun Experimental Instrument Co., Ltd. (Ningbo, Zhejiang, China, <http://www.nbbaishun.com>).

2.2 Standard solutions and reagents

Ultrapure water with a conductivity of 18.2 MΩ cm (Millipore, <http://www.merckmillipore.com>) was utilized in the experiment. Standard solutions of V(v), As(III), Sn(IV), Sb(III) and Bi(III) were purchased from the National Standard Material Center of China (Beijing, China, <http://www.bzwz.com>). A mixed standard stock solution of 1.0 μg L⁻¹ was prepared in 2.0% nitric acid medium. All the stock solutions were kept in plastic bottles and stored at 4 °C in the dark. Nitric acid 65% extra pure (Merck, <http://www.merck-china.com>) was used for preparing standard solutions and in other experimental processes. Ammonium hydroxide and ammonium nitrate were both purchased from Sinopharm Chemical Reagent Co., Ltd (<http://www.sinoreagent.com>). Certified reference materials (CRMs) with the numbers GSBZ3175-94 (V), GSB07-3171-2014 (As), BWZ6705-2016 (Sn), GSB07-1376-2001 (Sb) and GSB07-3382-2017 (Bi) were purchased from the National Standard Materials Center of China in Beijing (Beijing, China, <http://www.bzwz.com>).

Polyacrylonitrile fibers were obtained from Bairui Building Materials (Shenzhen, China, <http://www.szhybr.com>). Sodium carbonate, hydroxylamine hydrochloride, epichlorohydrin and triethylenetetramine (TETA) were purchased from Energy Chemical (Shanghai, China, <https://www.energy-chemical.com>). Isopropanol, acetone and ethanol used as cleaning reagents were purchased from Sigma-Aldrich (Shanghai, China, <https://www.sigmaaldrich.com>).

2.3 Synthesis of amine functionalized polyacrylonitrile fibers

The amine functionalized PANFs were prepared following a general experimental procedure already reported in the literature. First, hydroxylamine hydrochloride (3.8 g, 54 mmol) was stirred in 100 mL water solution, in order to neutralize its acidity, and sodium carbonate (3.0 g, 28 mmol) was added and kept for 10 min. Then the initial raw polyacrylonitrile fibers (5.0

g) were added and the reaction was carried out at 70 °C for 24 h. After filtration, the yellow fibers (PAN-1) were washed with water and dried at 55 °C to a constant weight (6.85 g) under vacuum.

To an isopropanol mixture of PAN-1 (6.0 g), a solution of epichlorohydrin–acetone (4.8 g epichlorohydrin and 100 mL acetone aqueous solution with a volume ratio of 1 : 1) was added. The mixture was stirred at 60 °C for 24 h. After filtration, the fibers were washed with ethanol and water successively. As before, PAN-2 was dried at 55 °C to a constant weight (6.82 g) under vacuum.

A solution of triethylenetetramine (TETA 3.0 g, 21 mmol) in 150 mL of ethanol was slowly added to the PAN-2 fibers (6.0 g), and the mixture was stirred at 60 °C for 24 h to carry out the critical modification reaction. Finally, the amine-functionalized polyacrylonitrile fibers were washed with ethanol and water successively, and dried in a vacuum at 55 °C. After solvent removal, the amine functionalized PANFs with a constant weight of 7.05 g were obtained. The synthesis of the PANFs is summarized in Fig. 1.

2.4 Preparation of the home-made column

The dry filling method was used in this study to fill 100 mg amine functionalized fibers into a customized stainless steel hollow mini-column (30 mm × 4.6 mm), with a wrench to tighten both ends. Before the performance test, certain volumes of ethanol and ultrapure water were sequentially passed through the home-made column to remove possible impurities. Finally, the stability of the extraction column was tested under high pressure and high flow rate, and the pressure was stable and no leakage was found.

2.5 The solid phase extraction (SPE) procedure

For metal ion adsorption, 16 kinds of trace metals were used for separation and enrichment verification. Among these elements, V(v), As(III), Sn(IV), Sb(III) and Bi(III) can be adsorbed rapidly on the home-made SPE column without any additional reagent. At the same time, more than 95% adsorption efficiency was obtained, and since the above elements usually exist in environmental water and may bring harm to human health, they were selected as target analytes in this study.

The on line SPE-ICP-MS system for the preconcentration and analysis of these elements in environmental water samples is shown as a schematic diagram (Fig. S1†). The prepared mini-column was fixed on a rotary injection valve (6 channels) instead of the sample loop of HPLC, as shown in Fig. S1(a).† First, all the water samples were loaded onto an SPE column using an STI PT501 pump, and subsequently, the target metal ions were extracted quantitatively using 0.3 mol L⁻¹ HNO₃ solution *via* a U3000 pump, as shown in Fig. S1(b).† Three replicates of 30 mL sample solution containing the analytes were delivered and loaded onto the mini-column, and then the adsorption of metal ions on the amine functionalized polyacrylonitrile fibers was equilibrated quickly due to strong chelation treatment and some possible specific affinity. The online hyphenated system was then washed with ultra-pure water to remove possible residues in the pipeline and

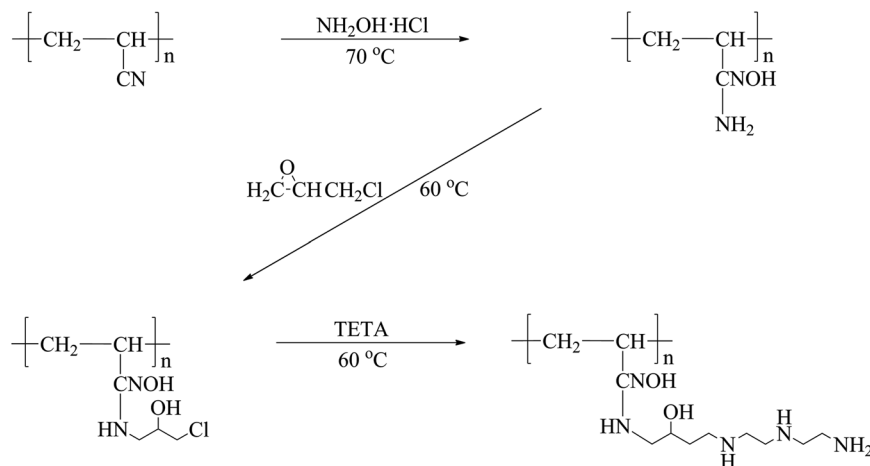


Fig. 1 The synthetic route to amine functionalized polyacrylonitrile fibers.

interface. With a low concentration nitric acid solution, all the five trace metal ions were eluted completely and delivered into ICP-MS for the following determination. Three replicates of blank were also tested during the experiment process.

2.6 Sample collection and preparation

The representative lake, river and seawater samples were collected from the Zhejiang province. All the samples were delivered to the laboratory for immediate analysis, or they were stored at 4 °C in a refrigerator until analysis. Before the on-line procedure, the water samples were filtered through a cellulose acetate filter with 0.22 μm pore size and transferred to a clean polyethylene plastic container. For the certified reference materials, due to the high sensitivity of the established method, appropriate dilution was required before analysis. For spike-recovery tests, all the trace metal ions were added before dilution and filtration.

3. Results and discussion

3.1 Choice of materials

Amine functionalized polyacrylonitrile fibers have the characteristics of chelate fibers, and present excellent chemical stability, acid and alkali resistance and high mechanical strength. In particular, they are equipped with plenty of chelate groups. Herein, polyacrylonitrile fibers were chosen to react with hydroxylamine hydrochloride and transformed into an amidoxime group, and then epichlorohydrin was selected for easily performing a ring opening reaction. Finally, it is significant to anchor diamine ligands into the surface of fibers by amination with triethylenetetramine in ethanol. The amino groups in the molecular structure of PANFs can provide electron pairs to form the coordination bond, and thus, the obtained modified fibers have the ability to adsorb metal ions through chelation.

The extraction feasibility of the prepared amine-functionalized polyacrylonitrile fibers towards the transition metal ions V(v), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II),

and Cd(II), and the main group elements As(III), Sn(IV), Sb(III), Pb(II), Tl(II) and Bi(III) was investigated. The results showed that, under a neutral environment, V(v), As(III), Sn(IV), Sb(III) and Bi(III) can be selectively and quantitatively adsorbed on the modified fibers (adsorption efficiency >93%) without any additional conditions.

3.2 Characterization of the amine-functionalized polyacrylonitrile fibers

The morphology and structure of the amine functionalized PANF material were characterized by various advanced technologies. According to the results of X-ray fluorescence spectrometer analysis, at a certain binding energy, the N peak can be observed to be enhanced evidently after TETA modification, as shown in Fig. S2.† From the energy spectrum results, the percentage of nitrogen in the starting material is about 9.97%, while the percentage of N in the modified fiber is up to 21.03%.

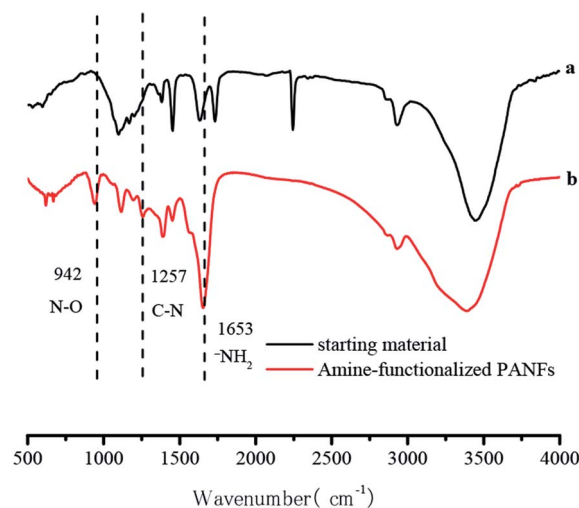


Fig. 2 FT-IR spectrum of the PANFs and the starting material used to synthesize PANFs.

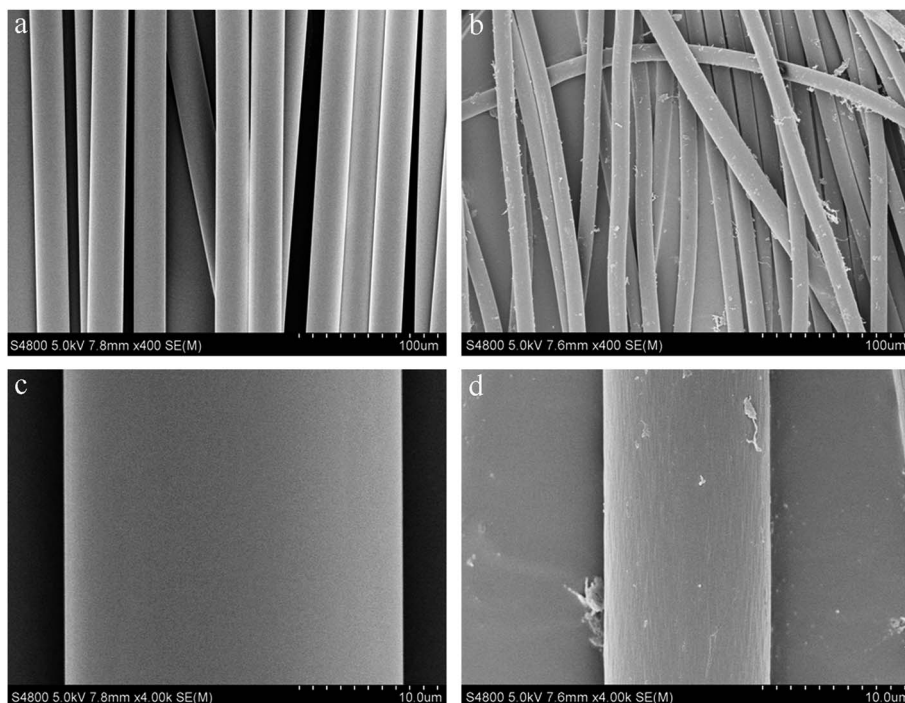


Fig. 3 SEM characterization of the PANFs with different magnifications and resolutions. Under a magnification of 400 (a) initial material (b) modified PANFs, under a magnification of 4000 (c) initial material (d) modified PANFs.

The BET surface area of the PANFs measured using a mercury porosimeter was $218.6 \text{ m}^2 \text{ g}^{-1}$.

The resultant amine functionalized PANFs and the starting material used to synthesize functionalized fibers were compared by FT-IR. As shown in Fig. 2 (black line is the starting material, red line is the PANFs), the wave numbers 942 cm^{-1} , 1257 cm^{-1} and 1653 cm^{-1} are assigned to the characteristic absorption peaks of $-\text{OH}$, $-\text{C}-\text{O}-$ and $-\text{NH}_2$ groups, respectively. In contrast, these characteristic absorption peaks were not observed for the internal structure of the original material. Also, the surface morphology of the polyacrylonitrile fibers before and after functionalization was observed by SEM, and the pictures are shown in Fig. 3. Under $400\times$ magnification, it can be observed that the surface of the initial material is very smooth (Fig. 3a), while obvious morphological changes and some binding phases appear on the surface of the modified PANFs (Fig. 3b). With the magnification increased to $4000\times$ (Fig. 3c and d), the morphology changes before and after modification can be seen more clearly.

3.3 Optimization of the method

The important parameters affecting the analysis results were optimized: (a) sample pH value; (b) sample flow rate; (c) sample volume; (d) wash time; (e) eluent type and (f) eluent flow rate. The adsorption behavior of $\text{V}(\text{v})$, $\text{As}(\text{iii})$, $\text{Sn}(\text{iv})$, $\text{Sb}(\text{iii})$ and $\text{Bi}(\text{ii})$ in the pH range of 2–9 was investigated in detail, and the results are presented in Fig. 4. Therefore, solutions containing suitable amounts of dilute nitric/acetic acid–ammonium acetate buffer with pH 2–6, and ammonia–ammonium chloride with pH 8–9

were prepared in ultrapure water. It can be seen that the adsorption percentage of the targets increased with the increase of pH in the range of 2–7, and then decreased slowly with further increases of pH. The reason might be that the $-\text{NH}_2$ group was stable in a neutral environment, and it has the best chelating ability towards most metal ions under these conditions. Thus, in order to obtain better adsorption efficiency and avoid hydrolysis of metal ions at higher pH, pH 7 was adopted in the subsequent experiments. Respective data and figures of other experimental conditions (Fig. S3 and S4†) are given in the ESI.† It was found that the following experimental conditions can give best results: (a) a sample pH value of 7; (b) sample flow

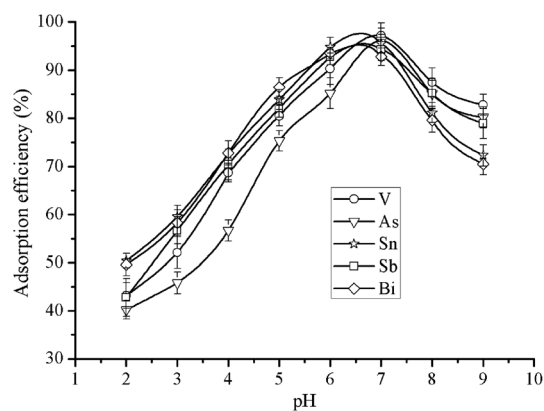


Fig. 4 Effect of pH on the adsorption percentage of trace metals. Concentration: $0.1 \mu\text{g L}^{-1}$, flow rate: 3 mL min^{-1} , sample volume: 30 mL.

rate of 3 mL min⁻¹; (c) sample volume of 30 mL; (d) wash time of 1 min; (e) 0.3 mol L⁻¹ HNO₃ solution; (f) eluent flow rate of 1 mL min⁻¹.

3.4 Effect of coexisting ions in real water samples

The possible effects of coexisting interfering ions in environmental water samples on the recoveries of V(v), As(III), Sn(IV), Sb(III) and Bi(III) were also studied. In the absence of interfering ions, the lowest adsorption efficiency of the target analyte is 93%; therefore, the tolerance limit of coexisting ions is defined as the largest amount which causes recovery of the targets to be less than 93%. For this purpose, 30 mL of the solution containing 0.1 µg L⁻¹ each of the five metal ions and various amounts of interfering ions (as indicated in Table 1) were treated with the on-line solid phase extraction procedure. According to the recovery results, it can be seen that all the trace metal ions could be quantitatively recovered in the presence of these potential major interfering ions, indicating that the competitive adsorption and desorption of coexisting interfering ions are minimal. In conclusion, the synthesized PANFs have a good selectivity towards these metal ions under the optimal conditions.

3.5 Adsorption capacity study

In order to examine the adsorption capacity of the PANFs, a standard mixed solution containing 1.0 mg L⁻¹ V(v), As(III), Sn(IV), Sb(III) and Bi(III) was prepared, and the adsorption

equilibrium time of the mixed solution and amine functionalized polyacrylonitrile fibers was 12 hours. For this purpose, the initial and equilibrium amounts of these metal ions were determined by ICP-MS (dilution is required before testing). The breakthrough volume is defined as the total amount of metal ions sorbed per gram of the functional fibers. The obtained capacities of the PANFs were found to be 593 ± 10, 571 ± 8, 468 ± 6, 463 ± 6 and 435 ± 8 mg g⁻¹ (n = 3) for the above five metal ions, respectively.

3.6 Reuse of the home-made column

A good separation and enrichment mini-column should have good reusability and regeneration performance. Naturally, successive adsorption and desorption cycles by passing 30 mL of sample solution including all the five metal ions through the home-made SPE column were inevitably performed to test its endurance. The stability and potential regeneration of the mini-column were assessed by monitoring the changes of the relevant recoveries. The column can be reused after regeneration, neutralization with a certain concentration of ammonia solution, and washing to neutral with ultrapure water, and thus up to 150 adsorption–elution cycles without an obvious decrease in the recoveries for the analytes were achieved.

3.7 Analytical features and environmental water sample analysis

The analytical characteristics of the optimized method are summarized in Table 2. Calibration curves were made by correlating the intensity (cps) of ions after preconcentration and their concentration in the original spiked standard solution (c, ng mL⁻¹). A calibration curve point with high concentration can be omitted benefitting from the high sensitivity of ICP-MS. Thus, a series of standard solutions with different concentration gradients (0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 µg L⁻¹) were prepared, and the initial concentrations were determined by ICP-MS without passing through the SPE column. The enrichment factors (EFs) were calculated as the levels of metal ions after the on-line SPE procedure *versus* before preconcentration. For instance, if the targets in the sample were enriched by 100 times, the minimum concentration of 0.005 µg L⁻¹ will be increased to 0.5 µg L⁻¹, and the intensity signals of

Table 1 Tolerance limits of the potentially interfering ions

Potentially interfering ions	Tolerable limit of ions (mg L ⁻¹)
K ⁺ , Na ⁺ , Li ⁺	10 000
Ca ²⁺ , Mg ²⁺ , Ba ²⁺	5000
Fe ³⁺ , Al ³⁺	30
Mn ²⁺ , Ni ²⁺ , Zn ²⁺ , Cu ²⁺	20
Cl ⁻	8000
Br ⁻	6000
SO ₄ ²⁻	5000
NO ₃ ⁻	2000
PO ₄ ³⁻	1000

Table 2 Analytical characteristics of on-line SPE-ICP-MS for the determination of trace elements

Elements	Analytical feature				
	V	As	Sn	Sb	Bi
Linear range (µg L ⁻¹)	0.005–5	0.005–5	0.005–5	0.005–5	0.005–5
Correlation coefficient (R ²)	0.9991	0.9996	0.9992	0.9993	0.9986
LODs (ng L ⁻¹) (3σ, n = 7)	1.2	0.9	1.7	1.5	2.3
LOQs (ng L ⁻¹) (3σ, n = 7)	4.1	3.0	5.6	5.1	7.7
Linear equation (y = ax + b)	25.33x + 115.7	5.669x + 24.09	37.52x + 172.5	28.99x + 169.3	50.43x + 198.7
RSDs (%; n = 10)	2.3	1.2	2.9	1.8	3.5
Enrichment factors (EFs)	120	120	120	120	115
Sample volume (mL)	30	30	30	30	30
Extraction time (min)	10	10	10	10	10

Table 3 Determination of V, Cr, As, Sn and Sb in Certified Reference Materials

CRMs	Found ^a ($\mu\text{g L}^{-1}$)	Certified value ^c ($\mu\text{g L}^{-1}$), mean \pm S.D. ^b
GSB07-3175-2014-1 (V)	0.588 \pm 0.003	0.586 \pm 0.002
GSB07-3171-2014-5 (As)	0.244 \pm 0.002	0.245 \pm 0.001
BWZ6705-2016 (Sn)	0.660 \pm 0.003	0.657 \pm 0.003
GSB07-1376-2001-1 (Sb)	0.101 \pm 0.001	0.103 \pm 0.001

^a After 500 times dilution for V, while 100 times for the remaining. ^b Standard deviation ($n = 3$). ^c Uncertainties expressed as 95% confidence interval with $n = 3$.

Table 4 Comparison of the analytical performance with that of other adsorbents and methods

Adsorbent	Detection method	LODs (ng L^{-1})	EFs	Sample volume (mL)	Pretreatment time (min)	Ref.
Maghemite	MSPE-ETAAS	30 (Sb)	242 (Sb)	75	18	15
Magnetic graphene oxide	ICP-OES	1500 (Sb)	9 (Sb)	16.8	3	16
FTGCNCs	ICP-MS	1.2 (As)	120 (As)	120	11	19
MOFs	ETAAS	3.0 (V)	400 (V)	400	21.5	21
MOPs	ICP-MS	3.4 (Bi)	15 (Bi)	0.5	30	23
Sintered materials	ICP-AES	43 (V)	—	300	10	27
Amine functionalized PANFs	ICP-MS	1.2 (V)	120 (V)	30	10	This work
		0.9 (As)	120 (As)			
		1.7 (Sn)	120 (Sn)			
		1.5 (Sb)	120 (Sb)			
		2.3 (Bi)	115 (Bi)			

V(v), As(III), Sn(IV), Sb(III) and Bi(III) ions were used as the Y-axis in the calibration curves. The limits of detection (LODs) and limits of quantification (LOQs) were based on the $3\sigma/10\sigma$ criteria (σ is the standard deviation of the measurement of eleven blank samples after applying the on-line SPE procedure). The LODs for V(v), As(III), Sn(IV), Sb(III) were a little lower than that of Bi(III), and the reasons might be that the background equivalent concentrations of the former were relatively low than that of the latter. The relative standard deviations (RSDs) for ten replicate measurements of $0.1 \mu\text{g L}^{-1}$ metals were calculated to be in the range of 1.2–3.5%.

For practical application, the method was applied for determination of the five trace metals in lake, river and seawater samples. Three replicates of sample and blank solutions were tested throughout the entire analytical procedure, and the spike tests were also performed to validate the accuracy of the method. The results for real water samples are exhibited in Table S2,† and almost all the trace metals can be detected in environmental water samples. In addition, satisfactory repeatability was achieved, and the RSDs for parallel experiments were below 4%, and also, the recoveries of the spiking test varied from 98% to 102%. Finally, Certified Reference Materials for water quality monitoring were selected to verify the feasibility and accuracy of the on-line SPE-ICP-MS method. Since the initial concentrations of the target ions in the CRMs are relatively high, suitable dilutions were needed according to the linear range of the present method ($0.005\text{--}5.0 \mu\text{g L}^{-1}$). The Certified Reference Materials of water quality standard samples were used to validate the accuracy of the on-line SPE-ICP-MS method. From the results provided in Table 3, the analytical

results for V(v), As(III), Sn(IV) and Sb(III) were in good agreement with the certified values, which illustrated that the on-line method developed in this study is suitable for practical environmental water analysis.

3.8 Comparison with other adsorbents and methods

Table 4 shows the comparison of the amine functionalized PANFs and the SPE-ICP-MS method with other known materials and methods for the determination of V(v), As(III), Sn(IV), Sb(III) and Bi(III) [15, 16, 19, 21, 23, 27]. As can be seen, the detection limit (0.9 ng L^{-1}) of the established method is very low compared with those of other established methods. In addition, the amine functionalized polyacrylonitrile fibers have relatively high enrichment factors and good adsorption efficiency for several trace elements. Moreover, the advantages of the established on-line SPE-MS analysis technology are less sample volume consumption (30 mL) and shorter analysis time (10 min), which can greatly improve the analysis efficiency.

4. Conclusion

Amine functionalized polyacrylonitrile fibers were prepared and packed into a home-made SPE mini-column for adsorption of trace metals in this study. The prepared functional polymer fibers have the merits of low cost, reusability and high adsorption capacity. By the employment of a high pressure pump for sample loading, a simple and rapid on-line SPE-ICP-MS method has been established for the selective recognition and high sensitivity determination of V(v), As(III), Sn(IV), Sb(III) and Bi(III) in environmental water samples. In addition, the

mini-column features a high sample flow rate, high adsorption efficiency and relatively long lifetime for the analysis of surface water and seawater samples. The on-line preconcentration procedure has good stability and reliability, and relatively high enrichment factors were obtained. These characteristics are of great interest for laboratories performing routine analysis of trace metal ions. Therefore, the coupling of SPE with the ICP-MS technique is simple and sensitive for the preconcentration and determination of trace metals. The challenges for this process are exploration of advanced materials with high adsorption capacity and screening standardized extraction conditions for most elements. One of the top highlights of the amine functionalized polyacrylonitrile fibers is their ability to rapidly separate and enrich a variety of trace metals from real environmental water samples simultaneously.

Author contribution

Xiaoyu Jia carried out experiments and supervised the whole project and manuscript preparation; Junyi Zhao carried out synthetic experiments and wrote the original draft of the experiment part; Jiani Wang and Hongyun Ren characterized starting materials and amine functionalized polyacrylonitrile fibers; Zixiao Hong and Kun Wu supervised the characterization.

Conflicts of interest

The authors declare that they have no financial interests or personal relationships that could have influenced the work reported in this document.

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