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Arsenic sorption and speciation with branch-polyethyleneimine modified carbon nanotubes with detection by atomic fluorescence spectrometry

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ABSTRACT

Multi-wall carbon nanotubes (MWNTs) are modified with branched cationic polyethyleneimine (BPEI). The MWNTs–BPEI nanocomposites serve as a novel adsorbent and exhibit favorable selectivity toward adsorption of As(V). Appropriate amount of MWNTs–BPEI suspension containing ca. 5 mg of the composites is used to pack a mini-column for on-line solid phase extraction preconcentration of inorganic arsenic in a sequential injection system, following detection by hydride generation atomic fluorescence spectrometry. At pH 5.8, an sorption efficiency of 80% is achieved for As(V) at 10 $\mu g\ L^{-1}$, resulting in a sorption capacity of 26.18 $mg\ g^{-1}$. Meanwhile, the sorption efficiency for As(III) is $<5\%$. The retained As(V) is readily recovered by 100 μL NH_4HCO_3 (0.6%, m/v). With a sample volume of 2.0 mL, an enrichment factor of 16.3 for As(V) is obtained along with a detection limit of 14 $ng\ L^{-1}$ within a linear range of 0.05–1.50 $\mu g\ L^{-1}$. A RSD of 3.6% is derived at 0.5 $\mu g\ L^{-1}$. Total amount of arsenic is obtained by converting As(III) to As(V) and following the same procedure. The speciation of inorganic arsenic is realized by difference. This procedure is validated by analyzing a certified reference material of human hair (GBW09101), achieving satisfactory agreements between the certified and the obtained values. Speciation of As(V) and As(III) is also performed in snow water and rain water samples.

1. Introduction

Arsenic is a ubiquitous element existing widely in air, soils, rocks, natural waters and organisms [1]. Arsenic is a toxic element to human health and its toxicity is associated closely to the existing forms, inorganic arsenic species are more toxic than organic counterparts [2,3]. Nowadays, the quantification of total arsenic in various sample matrixes is no longer sufficient to reflect the risks of arsenic to the environment and human health [4]. In this respect, it is highly important to perform arsenic speciation in complex sample matrixes.

For the speciation of inorganic As (III) and As (V), the methodologies for separation and preconcentration reported in the literatures are usually based on liquid chromatography [5], capillary electrophoresis [6] or in combination with hydride generation (HG) [7]. Generally, the concentrations of arsenic species in environmental samples are found at trace levels, thus high sensitive detection techniques are necessary for this purpose, including inductively coupled plasma-mass spectrometry (ICP-MS), electrothermal atomic absorption spectroscopy (ETAAS), atomic emission spectroscopy (AES) and atomic fluorescence spectroscopy (AFS) [8–11]. ICP-MS is most widely employed for the detection of arsenic species because of its very high sensitivity. AFS has comparable sensitivity with respect to ICP-MS for the detection of hydride and/or vapor generation elements. In addition, the running cost of AFS is much lower than that by ICP-MS. Therefore, AFS has been an alternative to ICP-MS [12–14]. Some recent advances on hydride/vapor generation have been reviewed [15,16]. It demonstrated that in the field of arsenic speciation, hydride generation atomic fluorescence spectrometry is one of the most powerful strategies. However, when handling ultra-trace amount of arsenic in complex sample matrix, the direct determination of arsenic species is difficult and therefore preliminary sample pretreatment with separation and preconcentration is highly desired. Solid phase extraction (SPE) is widely applied for the adsorption and preconcentration of ultra-trace arsenic from complex sample matrixes [17]. SPE can readily provide favorable enrichment factor with low sample and reagent consumption, at the same time it tends to avoid the risk of sample contamination and analyte loss. This feature is particularly useful when pursuing on-line automatic operation by coupling with a sequential injection system [18–20]. Among various sorbent materials, e.g., biological cells, PTFE particles or turnings, nanometer-sized TiO_2, activated carbon, yeast and activated alumina, carbon nanomaterials have been employed for the sorption of targets of interest [21–27]. Recently, carbon nanotubes (CNTs) have been exploited as sorbent due to high surface area, the ability of establishing π–π interactions as well as mechanical, chemical, and thermal stability [28]. The analytical capabilities

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of CNTs can be further improved or manipulated by surface modification to meet the demand for retaining different type of analytes attributed to its orientation and specificity [29,30]. We have previously reported the functionalization of multi-wall carbon nanotubes with positively charged hydrophilic branched architecture polymer. The introduction of basic functional groups on the carbon nanotubes well facilitated the isolation of acidic protein [31].

In the present work, multi-wall carbon nanotubes were functionalized with branched cationic polyethyleneimine (BPEI), and the BPEI–MWNTs composites were for the first time employed as adsorbent for the selective retention of As (V) in the presence of As(III) which are usually existing as anionic species in natural waters. The adsorption was realized in a flow system and the retained As (V) was stripped off by using dilute NH_4HCO_3 solution as eluent. The quantification of arsenic was performed by hydride generation-atomic fluorescence spectrometry, and arsenic speciation was done by difference.

2. Experimental

2.1. Instrumentation

A AFS-9130 atomic fluorescence spectrometer (Titan Instruments Co., Beijing, China) is employed, with arsenic hollow cathode lamp (Beijing General Research Institute for Nonferrous Metals, China) as radiation source. The operating parameters of the AFS instrument, including the atomizer height, negative high voltage of the photomultiplier, lamp current, carrier and shield argon flow rate, are investigated in terms of sensitivity and reproducibility. The optimized experimental parameters are summarized in Table 1.

The measurement of pH values is performed with an Orion Model 868 pH meter (Thermo Electron). A KQ5200 DB ultrasonic system (Kunshan Ultrasonic Instruments Co., Ltd., China) is used for the dispersion of carbon nanotubes and functionalized composites in aqueous medium.

A FIAlab-3000 sequential injection system (FIA lab Instruments, Bellevue, USA) with a 2.5 mL syringe pump and an 8-port selection valve is employed for fluidic delivery. All the external channels were made of polytetrafluoroethylene (PTFE) tubing (0.8 mm i.d.). The entire system is controlled with a computer running the FIA lab for Windows software.

Surface charge analysis is investigated by measuring the zeta potential of the material with a Zetasizer Nano ZS90 (Malvern, England). Thermogravimetric analysis (TGA) is performed on a HCT-2 thermogravimetric analyzer (Beijing Heng-Jiu Instruments) under nitrogen protection. FTIR spectra are obtained using a Nicolet-6700 FTIR spectrophotometer (Thermo Instruments Inc., USA) within the range of 500 cm^{-1} to 4000 cm^{-1}.

2.2. Reagents and solutions

All the reagents used are at least of analytical reagent grade, and deionized (DI) water of 18 $M\Omega\ cm^{-1}$ is used throughout.

Table 1
Operating parameters of the AFS instrument.

Parameter	Setting
Hollow cathode lamp	Arsenic 197.2 nm
Negative high voltage of PMT	350 V
Lamp current	65 mA
Carried argon flow	350 mL min^{-1}
Shield argon flow	800 mL min^{-1}
Atomizer height	8 mm

Multi-wall carbon nanotubes are obtained from Shenzhen Nanotech Port Co. Ltd., with diameter of 60–100 nm, length of 5–5 mm and specific surface area of 40–30 $m^2\ g^{-1}$ (L.MWNTs-60100).

Branched polyethyleneimine (Mw ~ 25 kDa) is received from Aldrich Milwaukee, MI, USA. It is used without further pretreatment.

Working standard solutions of As(III) and As(V) are prepared by stepwise dilution of stock solutions of 100 mg L^{-1}.

A 1.0% (m/v) $NaBH_4$ solution is prepared by dissolving $NaBH_4$ in 0.5% (m/v) NaOH. This solution is prepared daily.

Other chemicals used are: nitric acid, sodium chloride, ammonium bicarbonate, sulfuric acid and potassium permanganate.

2.3. Preparation of the BPEI–MWNTs composites [31]

Commercial MWNTs are pretreated to remove the residual surface impurities by immersing in 50% ethanol (v/v) and sonicating for 20 min to achieve sufficient dispersion. The MWNTs were collected by centrifugation and washed with DI water repeatedly to ensure the complete removal of the residuals. The MWNTs were then washed with 1% HCl to eliminate any metal residues on the surface and finally rinsed with DI water until neutral washout was obtained. The oxidized MWNTs were prepared by suspending the treated MWNTs in a sulfuric acid/nitric acid mixture (3:1, v/v) and sonicating for 3 h to generate carboxylic acid groups. After washed with DI water, the oxidized MWNTs were collected and mixed with 10 mg mL^{-1} branched polyethyleneimine (BPEI) and 1.0 mol L^{-1} NaCl aqueous solution. The BPEI modification was achieved by electrostatic attraction between the positively charged protonated amines in the polymer and the carboxyl groups on the oxidized MWNTs surface. The BPEI–MWNTs were thoroughly washed with 0.1 mol L^{-1} NaCl and DI water, and then dispersed in water prior to storage for use in the separation and preconcentration of arsenic.

2.4. Column preparation

Appropriate amount of the BPEI–MWNTs composites suspension is injected into a piece of PTFE tubing (1.6 mm i.d.) blocked at both ends with a small amount of glass wool to avoid leakage of the composites during the adsorption process. About 5 mg of the BPEI–MWNTs composites are used to pack a mini-column with an effective length of ca. 10-mm. Before use, the mini-column is flushed alternatively forward and backward with DI water at a flow rate of 15 $\mu L\ s^{-1}$. The mini-column is finally evacuated with air for the ensuing use.

2.5. Sample pretreatment

Snow water and rain water: fresh snow is collected from the campus of Northeastern University and stored in an air-tight flask at 4 °C following melting. Rain water is collected in the same campus. Before starting the preconcentration process, the water samples are filtered through a 0.22 μm mixed cellulose ester membrane (Shanghai Xinya Company, China) and adjusted to pH 5.8 with dilute HCl and/or NaOH solution.

Certified reference material CBW 09101 (human hair): 0.0500 g of the sample is taken into a PTFE digestion vessel along with 5 mL of concentrated HNO_3. After soaking for 2 h at room temperature, the mixture is digested on a microwave oven by using the following program: 140 °C/10 atm for 2 min, 170 °C/18 atm for 2 min, 190 °C/25 atm for 2 min, 220 °C/30 atm for 8 min. Afterwards the mixture is evaporated to ca. 1 mL on a hot plate at 150 °C. An appropriate amount of hydrogen peroxide (30%, v/v) is added into the PTFE digestion vessel, and the mixture is then heated to near dryness. The residue is cooled to room temperature and then dissolved with DI water and transferred to

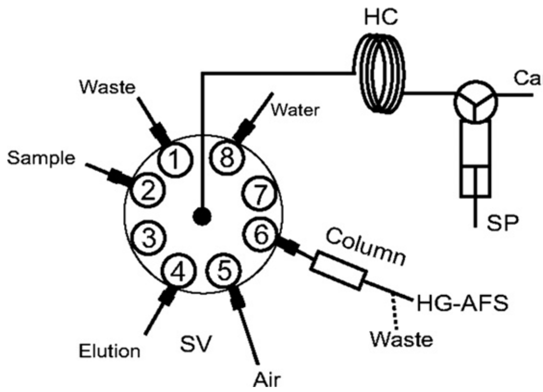

Fig. 1. The flow manifold for arsenic on-line separation and preconcentration with BPEI–MWNTs packed mini-column coupled with hydride generation-atomic fluorescence spectrometry (HG-AFS). SP: syringe pump; SV: selection valve; HC: holding coil.

a 50-mL volumetric flask. A blank is processed by following the same procedure.

2.6. Operating procedure

Fig. 1 illustrates the on-line arsenic separation and preconcentration set-up by integrating a BPEI–MWNTs composites packed mini-column in a sequential injection system. DI water is adopted as carrier solution.

The syringe pump is first set to aspirate 150 μL carrier at 100 μL s^{-1}, 200 μL air and 2000 μL sample solution via port 5 and port 2 respectively at 50 μL s^{-1}. The stacked zones are subsequently dispensed at 15 μL s^{-1} to flow through port 6 to facilitate the sorption of arsenic on the BPEI–MWNTs mini-column. Thereafter, 300 μL of carrier, 200 μL of air, 100 μL of the eluent (0.6% NH_4HCO_3, m/v) are sequentially aspirated into the holding coil at 100 μL s^{-1}, 50 μL s^{-1} and 40 μL s^{-1} respectively. By dispensing the zones to flow through the mini-column at 10 μL s^{-1}, the retained arsenic is recovered by the NH_4HCO_3 solution. The eluate is collected and used to facilitate hydride generation and atomic fluorescence spectrometric determination of arsenic. The hydride generation is realized by adopting the two ancillary syringe pumps of the AFS instrument as detailed in the following section.

After the adsorption/desorption process, 500 μL of carrier, 50 μL of air, 300 μL of NH_4HCO_3 solution (0.6%, m/v) are sequentially aspirated into the holding coil, which are afterwards directed to flow through the mini-column at 15 μL s^{-1} for eliminating any potential residues on the BPEI–MWNTs mini-column.

3. Results and discussion

3.1. Characterization of the BPEI–MWNTs nanocomposites

Surface charge analysis indicated that the BPEI–MWNTs composites are positively charged within a wide range of pH 2–11 attributed to the presence of amide groups, while the oxidized MWNTs are negatively charged due to the formation of carboxylic groups at the ends and tips of the carbon nanotubes. It is documented that in TGA analysis MWNTs-COOH exhibits a weight loss at 600 °C, while decomposition of BPEI happens at 500 °C. In the present case an obvious weight loss was recorded at ca. 500 °C, corresponding to the decomposition of BPEI. This clearly demonstrated the noncovalent immobilization of BPEI on MWNTs and resulted in a coating amount of BPEI of ca. 5.8%. FT-IR spectra indicated the presence of carboxylic groups for the oxidized MWNTs, as illustrated by the characteristic absorptions at 3430 cm^{-1} and 1720 cm^{-1} for stretching vibrations of O–H and C$=$O. The characteristic absorptions of BPEI are clearly identified for the BPEI–MWNTs composites. The absorptions at 3300–3600 cm^{-1}, 2971 cm^{-1} and 2919 cm^{-1} are assigned to the stretching vibrations of N–H, asymmetric and symmetric stretching vibration of CH_2 in the surface of BPEI–MWNTs. The above results well demonstrated the non-covalent immobilization of BPEI onto the sidewalls of the MWNTs.

3.2. pH-dependent adsorption behavior of As(V) and As(III)

pH value of the sample solution plays an important role for the adsorption of inorganic arsenic species, because it determines the ionic characteristics of both As (III) and As (V) as well as the surface properties of the sorption material, i.e., the BPEI–MWNTs composites. BPEI contains primary and secondary amines in its structure and thus the surface of the BPEI–MWNTs composite is positively charged. The dissociation constants (pKa) of H_3AsO_4 are 2.2, 6.9 and 11.5, and it exists mainly as anionic species within a wide pH range. On the other hand, however, the pKa values for H_3AsO_3 are 9.2, 12.2 and 13.4, that means it is neutral at $pH < 9.2$. Under such a condition, As (V) is readily retained by the BPEI–MWNTs via electrostatic interaction, whereas the adsorption of As (III) is negligible or marginal.

The effect of pH value on the adsorption of both inorganic arsenic species is examined within a range of pH 2–9, and the results are shown in Fig. 2. It is clearly seen that at $pH < 2$, the adsorption of either As(V) or As(III) is negligible, because in this case both inorganic arsenic species are existing as neutral molecules while the surface of the BPEI–MWNTs nanocomposite is positively charged. With the increase of pH value, the adsorption of As(V) improves and maximum adsorption is achieved at pH 4.0–5.8, i.e., the adsorption efficiency is ca. 80%. Within the same range, i.e., pH 2–9, As(III) exists in the form of neutral molecule, thus its adsorption is minimum, i.e., an sorption efficiency of $< 5\%$ is obtained. For practical applications, the pH value of the sample solution is adjusted to 5.8.

3.3. The sample loading process

In a flow system for the adsorption of analyte species, the sample loading flow rate is an important parameter for governing

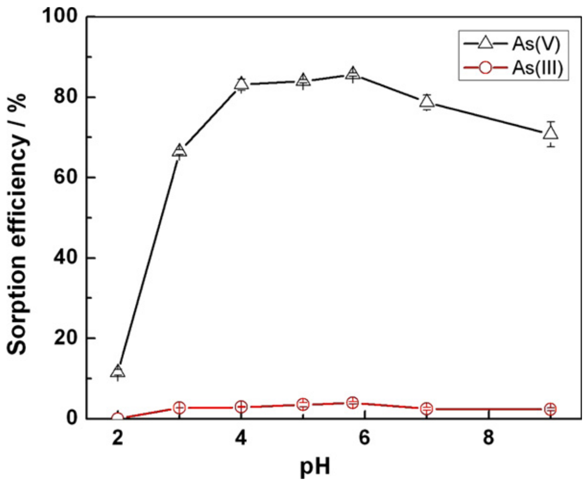

Fig. 2. The pH dependent adsorption efficiencies of the two inorganic arsenic species. The concentration of As(V) and As(III): 10 μg L^{-1}; sample volume: 100 μL; sample loading flow rate: 15 μL s^{-1}; eluent: 100 μL of 0.6% (m/v) NH_4HCO_3; elution flow rate: 10 μL s^{-1}.

the sorption efficiency as well as the analysis frequency. In the present case, the effect of the loading flow rate is investigated within a range of 5–25 $\mu L\,s^{-1}$ by using a small sample volume of 100 μL with a higher arsenic concentration of 10 $\mu g\,L^{-1}$. The experimental results demonstrated that the sorption of As(V) onto the BPEI–MWNTs composites is a fairly fast process, that is a sorption efficiency of $>80\%$ for As (V) is achieved at a sample loading flow rate of $<20\,\mu L\,s^{-1}$, whereas at the same experimental conditions the sorption of As (III) is virtually not observed, i.e., the sorption efficiency is $<5\%$. For further experiments a sample loading flow rate of 15 $\mu L\,s^{-1}$ is adopted.

3.4. *The elution process*

An appropriate eluent is required for effective recovery of the As (V) adsorbed on the surface of the BPEI–MWNTs nanocomposites. Although hydrochloric acid is generally a favorable medium for the ensuing hydride generation reaction, its strong acidity is harmful to the basic functional groups on the BPEI–MWNTs nanocomposites and thus tends to deteriorate the composites which might exclude the repetitive use of the mini-column. In an alkali medium deprotonation of the sorbent is facilitated so that the electrostatic interaction between the BPEI–MWNTs composites and As (V) become weak. Further practice indicated that a strong alkali medium, i.e., NaOH solution, can readily recover majority of the retained As(V), however, it caused loss of part of the adsorption capacity toward As(V) for the ensuing operations, due to partial strip of the amide groups on the BPEI–MWNTs nanocomposites. After careful evaluations, a weak alkali medium, i.e., NH_4HCO_3 solution, is used as eluent for the recovery of the retained As(V) which provides a favorable recovery while in the meantime results in minimum effect on the surface property of the BPEI–MWNTs composites.

Fig. 3 illustrated that the recovery of As(V) improves with the increase of NH_4HCO_3 concentration from 0.4% to 0.6% (m/v), and afterwards the recovery rate remains high up to 1.0% (m/v). Considering that a lower concentration of NH_4HCO_3 is preferential for the ensuing hydride generation process, and a 100% recovery of As(V) has been achieved at 0.6% (m/v) NH_4HCO_3, this solution is practical as eluent. The elution flow rate within the range of 2–15 $\mu L\,s^{-1}$ is investigated. The experimental results demonstrated that favorable recovery rate of $>95\%$ could be achieved when the elution flow rate is set within 2–10 $\mu L\,s^{-1}$, while an even higher flow rate results in gradually decline of the recovery rate. For further practice, an elution flow rate of 10 $\mu L\,s^{-1}$ is employed.

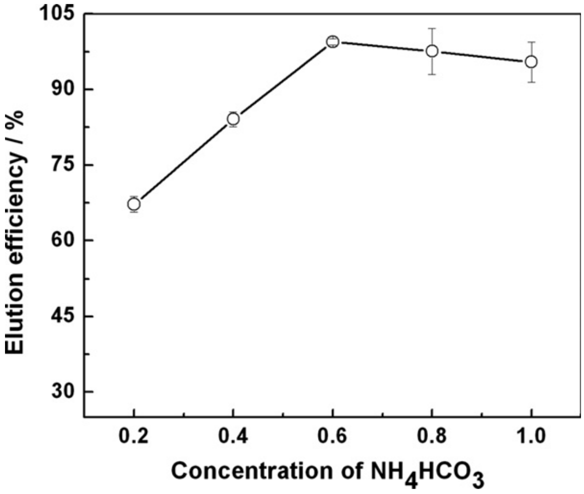

Fig. 3. Effect of the eluent concentration on the elution efficiency. Arsenic concentration: 0.5 $\mu g\,L^{-1}$; sample volume: 2 mL; sample loading flow rate: 15 $\mu L\,s^{-1}$; eluent: 100 μL of 0.6% (m/v) NH_4HCO_3; elution flow rate: 10 $\mu L\,s^{-1}$; pH 5.8.

It is demonstrated that the mini-column packed with BPEI–MWNTs nanocomposites is suitable for repetitive operations. Our experimental results have shown that the sorption efficiency of the mini-column for As(V) remains virtually unchanged after 30 successive adsorption/desorption cycles when processing 10 $\mu g\,L^{-1}$ of arsenic. For treating low concentration of arsenic samples, an even longer life-time of the mini-column should be achieved.

After recovery of the retained As(V) from the BPEI–MWNTs mini-column, one of the ancillary syringe pumps of the AFS instrument was set to aspirate 500 μL DI water and the 100 μL eluate in 10% HCl sandwiched by 100 μL air at both ends, another syringe pump aspirates 500 μL of $NaBH_4$ solution (1.0%, in 0.5% NaOH). Both pumps were set to direct the fluidic zones at a flow rate of 100 $\mu L\,s^{-1}$. The confluence of the fluids at downstream facilitates hydride generation. The hydride was separated in the gas–liquid separator and transported into the AFS atomizer by an air flow of 350 $mL\,min^{-1}$ for atomization and quantification.

3.5. *Interferences*

To evaluate the selectivity of the BPEI–MWNTs composites toward As(V), the potential interfering effects of some commonly encountered foreign ions in environmental sample matrixes are investigated with the proposed procedure. When treating 0.5 $\mu g\,L^{-1}$ As(V) within an error range of $\leq \pm 5\%$, the tolerant ratios of various coexisting species are10,000-fold for K^+, Na^+, Cl^-, NO_3^-, 4000-fold for Mg^{2+}, 2000-fold for Cu^{2+}, 500-fold for MnO_4^-, 200-fold for Pb^{2+}, Cd^{2+} and Ni^{2+}, 100-fold for Co^{2+}, Hg^{2+} and $Cr_2O_7^{2-}$. In practice for handling real world environmental water samples, the contents of the above ionic species cannot exceed the tolerant concentration or after appropriate dilution, thus the BPEI–MWNTs composites can be directly used for the processing of water samples without further treatment.

3.6. *Analytical performance and validation*

Under the above discussed optimal conditions, the performance data obtained for the on-line solid phase extraction preconcentration of As (V) with BPEI–MWNTs nanocomposites as adsorbent hyphenated to hydride generation-atomic fluorescence spectrometry are given in Table 2. With a sample volume of 2.0 mL, an enrichment factor of 16.3 is obtained. A detection limit of 14 $ng\,L^{-1}$ is achieved within a linear range of 0.05–1.50 $\mu g\,L^{-1}$. In addition, a precision of 3.6% RSD is obtained at the level of 0.5 $\mu g\,L^{-1}$ As (V).

A comparison of the characteristic performance data of the present system with some of the reported procedures based on separation and preconcentration with detection by HG-AFS, GF-AAS and HG-ICPMS has been summarized in Table 3. The sensitivity of

Table 2
The performance data for on-line solid phase extraction preconcentration of As(V) with BPEI–MWNTs composites as adsorbent coupled to hydride generation-atomic fluorescence spectrometry.

Item	Value
Sample volume	2000 μL
Eluent volume	100 μL
Detection limit (3σ, $n=7$)	14 $ng\,L^{-1}$
RSD (0.5 $\mu g\,L^{-1}$, $n=9$)	3.6%
Linear range	50–1500 $ng\,L^{-1}$
Enrichment factor	16.3

Table 3
A comparison of the detection limit and precision of the present procedure with some of the reported data based on separation and preconcentration protocols.

Method/sample	Sample consumption (mL)	LOD (ng L^{-1})	RSD (%)	Ref.
SI-cellulose fiber-GFAAS/water and Hijiki	2	19/As(III)	2.7% at 2 μg L^{-1}	[5]
FI-KR-ICPMS/river water	5	21/As(III)	2.8% at 1 μg L^{-1}	[32]
FI-KR-HG-AFS/seawater and river water	6	23/As(III)	1.3% at 1 μg L^{-1}	[33]
SI-BPEI–MWNTs-SPE-HG-AFS/hair and water	2	14/As(V)	3.6% at 0.5 μg L^{-1}	This method

Table 4
Analytical results of arsenic in certified reference material GBW 09101 and inorganic arsenic speciation in snow water ($n=3$, 95% confidence level).

Sample	Certified value (μg g^{-1})		Found value (μg g^{-1})	
GBW09101	0.59 ± 0.07		0.56 ± 0.01	
Sample	Found As(V) (μg L^{-1})	Found total As (μg L^{-1})	Spiked As(V) (μg L^{-1})	Recovery (%)
Snow water	1.52 ± 0.08	5.16 ± 0.12	3.2	108
Rain water	2.04 ± 0.39	3.60 ± 0.14	4.0	92.5

the present method is comparable with those of the procedure with detection by ICPMS. In addition, it is much improved with respect to that by HG-AFS and GF-AAS procedures. The use of very small sample volume by this procedure is further advantageous, i.e., the improvement on enrichment factor can be readily performed by increasing the sample volume within a certain range.

The present procedure is afterwards validated by analyzing a certified reference material of human hair (GBW09101), and the analytical results in Table 4 illustrated a fair agreement between the certified and the found values of the total arsenic content. The procedure is further demonstrated by speciation of inorganic arsenic in snow and rain water. The amount of As(V) is obtained by following the present procedure, while for the quantification of total inorganic arsenic, As(III) is converted to As(V) with oxidation by hydrogen peroxide as detailed elsewhere [34]. The results were summarized in Table 4. Further, spiking recovery of As(V) in the snow and rain water samples is performed giving rise to favorable results.

4. Conclusions

The present work describes the functionalization of multi-wall carbon nanotubes (MWNTs) with branched cationic polyethyleneimine (BPEI), which creates a novel adsorbent for the selective retention of As(V) in the presence of As(III). This investigation provides a useful approach for the development of new sorbent materials for various target analytes. The BPEI–MWNTs nanocomposites exhibit a favorable adsorption efficiency for As(V) in real samples, demonstrating the practical usefulness of the material in processing environmental samples, and thus providing a potential approach for the speciation of inorganic arsenic.

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