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Separation and preconcentration of Arsenic(III) ions from aqueous media by adsorption on MWCNTs

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Abstract A simple and sensitive method using mini-column packed with multi-walled carbon nanotubes (MWCNTs) combined with graphite furnace atomic absorption spectrometry (GFAAS) for preconcentration and determination of ultra trace amounts of As(III) in an aqueous medium is proposed. The procedure is based on the solid phase extraction of the As(III)-sodium diethyldithiocarbamate (As-NaDDTC) chelate on MWCNTs. Various parameters such as the effect of pH, eluent type and volume, amount of sorbent, and matrix effects on the quantitative recoveries of analyte ions were evaluated. It was found that sorption is quantitative and desorption occurs with 4.0 mL of 3.0 mol L⁻¹ HNO₃ in acetone. The limit of detection of the method was 0.008 ng mL⁻¹ for GFAAS with enrichment factor of 125 and the relative standard deviation (RSD) 0.97% (*n* = 8, *C* = 10 ng mL⁻¹). This method has been applied to the determination of ultra trace As(III) in water and rice plant and its ash successfully.

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1. Introduction

Nowadays, much attention has been paid to pollution by arsenic due to its toxicity and ubiquitous nature. Arsenic is a worldwide recurring pollutant and is well known as a source of serious health effects by prolonged intake even at low concentrations. Long term exposures or intake of arsenic can

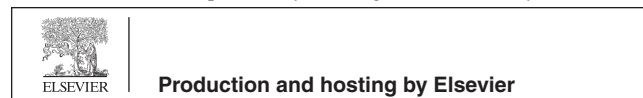
result in permanent and severe damage to human health such as skin lesions, rhagades and damage to mucous membranes, digestive, respiratory, circulatory and nervous system. Moreover, it is associated with skin, liver and lung cancers (Watson and Yager, 2007). Due to arsenic's health and toxicological effects, many regulatory agencies, such as the WHO and the U.S.EPA, have lowered the maximum contaminant level to 10 µg L⁻¹ (WHO, 1996; EPA, 2001).

The determination of arsenic and other poisonous elements at trace level is very important in the content of environmental protection, food and agricultural chemistry as well as high purity materials. However, the direct determination of arsenic in complex matrices is limited due to their usually low concentrations and matrix interferences. In trace analysis, therefore, a preconcentration and/or separation are necessary to improve sensitivity and selectivity of determination (Cai et al., 2003).

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Solid phase extraction (SPE) is one of the most popular techniques used for this purpose. In both of two kinds of SPE (batch and column techniques) analytes are sorbed on different water-insoluble materials and eluted with acids or other reagents have been widely used (Camel, 2003).

SPE offers a number of important benefits in comparison with laborious classical liquid–liquid extraction, such as simple and fast extractor system, reduced solvent usage and exposure, low disposal costs, high concentration factor and ability of treating large volume samples free from contamination (Arpa and Bectas, 2006; Rekha et al., 2007).

Several specific sorbents have been proposed for SPE, such as C_{18} bonded silica (Xiong et al., 2008; Chen et al., 2009; Jal et al., 2004; Chron et al., 2005), polymeric sorbents (Huck and Bonn, 2000; Rao et al., 2004), zeolites (Vassileva and Furuta, 2001; Elizalde-Gonzalez et al., 2001) and activated carbon (Tavakkoli et al., 2012). These have been successfully applied for various metal ions or arsenic in different kinds of samples.

Carbon nanotubes (CNTs) have also great analytical potential as a solid phase extraction adsorbent for metal ions (Liang et al., 2005a,b; Lu et al., 2006; Luan and Chiu, 2006; Li et al., 2005; Valcarcel et al., 2005). CNTs are novel carbon materials that possess many unique electronic, mechanical and chemical properties, high surface and excellent strength (Trojanowicz, 2006).

The chemistry of CNTs has been already the subject of several reviews (Liu et al., 2004; Biesaga and Pyszynska, 2006; Li et al., 2004). Although CNTs are typically inert, they can adsorb molecules via non-covalent force, such as hydrogen bonding, π - π stacking, electrostatic force, van der Waals forces and hydrophobic interactions. These interactions as well as hollow and layered nanosized structures make them a good candidate for use as adsorbents (Li et al., 2009). The surface, made up of hexagonal arrays of carbon atom in graphene sheets, interacts strongly with other molecules or atoms (Zhou et al., 2006; Yang et al., 2006).

The application of Multi Walled Carbon Nanotubes (MWCNTs) for the preconcentration of heavy metal ions, rare earth elements and organometallic compounds has been reported in the literatures (Tuzen et al., 2008; Tuzen and Soyak, 2007; Liang et al., 2005a,b; Liang and Han, 2006).

In this work, the adsorption behavior of As(III) on MWCNTs was studied. The aim of the present work is to establish new separation and preconcentration procedures based on adsorption of As(III)-NaDDTC chelates on mini column packed with MWCNTs and determination by graphite furnace atomic absorption spectrometry (GFAAS). Experimental parameters affecting the preconcentration of arsenic were studied and optimized. This method was applied to separation and determination of As(III) in rice straw and its ash, drinking water, mineral water and well water samples and was obtained an interesting result.

2. Materials and methods

2.1. Reagents

All chemicals used in this work, were of analytical grade. Deionized water was used for all dilutions. All the plastic and glass ware were cleaned by soaking in dilute HNO_3 (1:9) and were rinsed with distilled water prior to use. Arsenic(III)

stock standard solution (1 g L^{-1}) was prepared by dissolving 1.320 g As_2O_3 in about 20 mL 1.0 mol L^{-1} NaOH. To this solution 50 mL of 0.5 mol L^{-1} HCl was added and the volume was completed to 1 L with deionized water. Working solution of As(III) was prepared daily by appropriate dilution of stock solution. Multiwalled carbon Nanotubes (Aldrich, Milwaukee, WI, USA, no: 636614) was purchased from Aldrich, USA. The BET surface area and density of nanotubes were $300\text{ m}^2\text{g}^{-1}$ and 2.1 g mL^{-1} , respectively. Sodium diethyldithiocarbamate (NaDDTC) (Merck, Germany) was used as the chelating agent to form the hydrophobic arsenic complexes. A 1% (W/V) NaDDTC solution was prepared by dissolving suitable amount of NaDDTC in doubly distilled water. The solutions were discharged after 1 day.

2.2. Instruments

A sense AA-GBC atomic absorption spectrometry with deuterium background corrector and GBC hollow cathode lamp was used. The operating conditions were as follows: wave length, 193.7 nm; slit width, 1 nm; lamp current, 8 mA.

The pH values were controlled with a Metrohm pH meter with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. All instrumental parameters are used as recommended by the manufactures. The temperature program and chemical matrix modifier were optimized for As(III) determination with GFAAS. At first chemical matrix modifier (Pd, Ni/Pd or $Ni(NO_3)_2$) was injected into a pre-heated tube at $90\text{ }^\circ\text{C}$. The injected volume was $10\text{ }\mu\text{L}$. Then $10\text{ }\mu\text{L}$ of the sample was injected. The best results were obtained with 0.08 mol L^{-1} $Ni(NO_3)_2$ solution and selected temperatures and other parameters are shown in Table 1.

2.3. Preparation of sorbent and column

Raw MWCNTs were heated at $350\text{ }^\circ\text{C}$ for 30 min to remove amorphous carbon. Then raw MWCNTs were oxidized with concentrated HNO_3 according to the literature with minor modification before being used. In order to create binding sites onto the surface, 1 g of MWCNTs was first soaked in 10 mL of concentrated HNO_3 for 6 h at room temperature while being stirred. Then the solution was filtered and washed with distilled water until the pH was neutral. Then MWCNTs were dried prior to storage for use in preconcentration of arsenic.

One hundred milligrams of MWCNTs was added into a $10\text{ mm} \times 80\text{ mm}$ polypropylene column with a glass wool

Table 1 Optimized furnace program for the analysis of As in liquid solution.

Step	Temperature ($^\circ\text{C}$)	Ramp (s)	Hold (s)
Drying 1	50	1	2
Drying 2	90	10	10
Drying 3	120	15	3
Pyrolysis 1	800	10	5
Pyrolysis 2	800	0	1
Atomization	2350	0.8	2
Cleaning	2400	1	2

support at the both ends of it. The column was preconditioned by the blank solution at the desired pH values prior to each use.

2.4. Test procedure

An aliquot of As(III) was adjusted to desired pH values and NaDDTC solution was added to it to form the As-NaDDTC chelates. After 15 min, the solution was loaded to the column at a flow rate of 2.0 mL min^{-1} . Afterward, the retained As-NaDDTC was eluted with the desired volume and concentration eluent. The eluent was analyzed for the determination of As(III) concentration by GFAAS.

3. Results and discussions

First experiments showed that MWCNTs were not modified sufficiently with NaDDTC, as a result the preconcentration was not done. Thus, before the passing sample solution through the column, chelating factor (NaDDTC) was added to form the As-NaDDTC chelate.

3.1. Effect of pH

The pH value plays an important role with respect to the adsorption of different ions on MWCNTs. In order to evaluate the effect of pH, the pH values of sample solutions were adjusted to a range of 1.0–6.0 and processed according to the recommended procedure. The recovery of As(III) ion was calculated. The results are shown in Fig. 1. As(III) was recovered quantitatively in the pH of 2.0. Hence, pH 2.0 was selected as the optimum pH value in this study.

3.2. Eluent type and volume

Different kinds of eluent solution such as HCl, HNO_3 , acetone, ethanol and $\text{Na}_2\text{S}_2\text{O}_3$ with various concentrations were used for desorption of As-NaDDTC chelates from MWCNTs. The results are given in Table 2. Quantitative recoveries for analyte ions were obtained only with 3.0 mol L^{-1} HNO_3 in acetone.

The effect of eluent volume on the recoveries of the analytes was also studied by using 2–8 mL of 3.0 mol L^{-1} HNO_3 in ace-

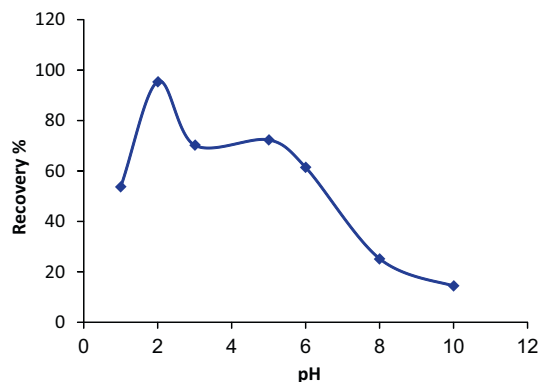


Figure 1 Effect of pH of a sample solution on recovery of arsenic. (Arsenic concentration in sample solution: 20 ng mL^{-1} ; volume of sample solution: 20 mL ; sample flow rate: 2.0 mL min^{-1} ; eluent: 4 mL of 3.0 mol L^{-1} HNO_3 in acetone).

Table 2 Effect of various eluents on the recoveries of As(III). (Eluent volume: 4 mL , $N = 3$).

Eluents	Recovery (%)
Ethanol	12 ± 2^a
Acetone	78 ± 2
3 mol L^{-1} HCl	23 ± 1
3 mol L^{-1} HNO_3	10 ± 2
0.1 mol L^{-1} $\text{Na}_2\text{S}_2\text{O}_3$	47 ± 2
3 mol L^{-1} HNO_3 in acetone	96 ± 1

^a Mean \pm standard deviations.

tone. (For this proposed, 20 mL sample solution $20.0 \text{ } \mu\text{g L}^{-1}$ As(III) was used). It was found that quantitative recoveries could be obtained with 4.0 – 8.0 mL of 3.0 mol L^{-1} HNO_3 in acetone. Therefore, the volume of 4 mL of 3.0 mol L^{-1} HNO_3 in acetone was used in the following experiments.

3.3. Effect of flow rates of sample and eluent solution

The flow rate of the sample and elution solutions is a measure of the contact time between the sample solution and the sorbent (Mester and Sturgeon, 2003). Thus the flow rate was adjusted simply by connecting the adsorbing column to a flask, which had a controllable vacuum. Aliquots of 20.0 mL of $20.0 \text{ } \mu\text{g L}^{-1}$ As(III) solutions at pH 2.0 were introduced into a packed column containing 100 mg of the sorbent. It was found that retention and recovery of the ions were independent of flow rate in a range of 0.5 – 4 mL min^{-1} . In order to achieve good precision, a flow rate of 2.0 mL min^{-1} was chosen for sample and elution solutions in all experiments.

3.4. Effect of the amount of NaDDTC

Sodium diethyldithiocarbamate is a ligand for metal ions; it was used in the literature for this purpose (Rathore et al., 2006). The amount of ligand is also an important factor for the quantitative recoveries of analytes in solid phase extraction processes. In order to investigate the optimum amounts of sodium diethyldithiocarbamate on quantitative recoveries of the arsenic ion, the study was examined by varying the amounts of NaDDTC from 0 to 5.0 mg . The results showed that As(III) could not be adsorbed at all by the MWCNTs without NaDDTC. The recovery values increased with the increasing amounts of NaDDTC. After the addition of 1.0 mg of NaDDTC, the recovery values were quantitative. On this basis, all the studies were carried out with 1.0 mg of NaDDTC.

3.5. Effect of the amount of MWCNTs

The effect of the amount of MWCNTs on the recovery of arsenic was investigated under mentioned optimal experimental conditions. As can be seen from Fig. 2, the recovery was found quantitative in amounts of 100 – 300 mg . Therefore, in further studies, the short column was filled with 100 mg of MWCNTs.

3.6. Breaking through volume

Breakthrough volumes and optimal sample volume were investigated in order to obtain an enrichment factor as high

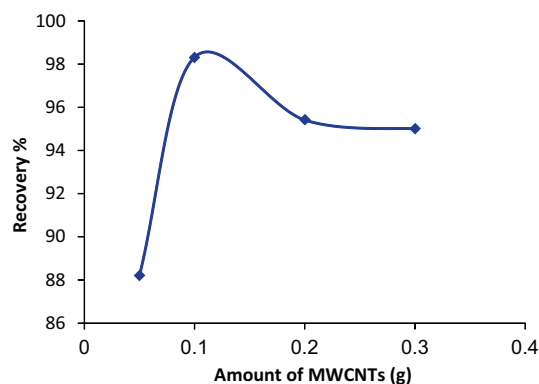


Figure 2 Effect of amount of MWCNTs on recovery of As(III). (Arsenic concentration in sample solution: 20 ng mL^{-1} ; volume of sample solution: 20 mL; sample flow rate: 2.0 mL min^{-1} ; eluent: 4 mL of $3.0 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone).

as possible. Experiment was done by using different sample volumes (20–600 mL) with the same arsenic concentration of 10.0 ng mL^{-1} . Breakthrough was considered to occur when the recovery was below 95%. The stable recoveries above 95% were observed when the sample volumes ranged from 20 to about 500 mL. However, the recoveries were lower than 90% when the sample volume increased to 600 mL, so the breakthrough volume for arsenic on MWCNTs was about 500 mL. Considering the packed amount of MWCNTs in cartridge (about 100 mg) used in this study, finally, sample volume of 500 mL was used as the optimal sample volume. Thus the enrichment factor was calculated by the ratio of the highest sample volume (500 mL) and the lowest eluent volume (4 mL). The enrichment factor was 125.

3.7. Adsorption capacity

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analyte from a given solution. 0.1 g sorbent was added to 50 mL of solution containing 10.0 mg of As(III) and 0.1 g NaDDTC at pH 2.0. The adsorption amount of As(III) was measured in different times (20, 30, 40, 50 min) and the adsorption amount was reached to constant value in 40 min. After shaking for 40 min, the mixture was filtered to study the adsorption capacity of sorbent. Ten milliliters of the supernatant solution was diluted to 1000 mL and determined by GFAAS. The experimental results demonstrated that the adsorption capacity of MWCNTs for As(III) was 79.8 mg g^{-1} .

3.8. Column reuse

The MWCNTs' sorbent was subjected to several loadings with the sample solution and subsequent elution. The stability and potential regeneration of the column were investigated. The column can be reused after being regenerated with 10 mL of $3.0 \text{ mol L}^{-1} \text{ HNO}_3$ in acetone and 20 mL of doubly distilled waters respectively and stable up to at least 20 adsorption-elution cycles without decrease in the recovery of As(III).

3.9. Effects of diverse ions

The influences of possible matrix ions in the environmental samples and some transition metals on the recoveries of As(III) on MWCNTs were also examined. A 20 mL portion of sample solution containing analytes and a given amounts of foreign ions were concentrated. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of the analyte less than 90%, are given in Table 3. It was observed that the proposed method is selective and can be used in various samples.

3.10. Analytical performance

The limit of detection (LOD) of the presented solid phase extraction study was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The limit of detection for As(III) based on three times the standard deviation of the blank ($n = 8$) was 0.008 ng mL^{-1} . The reproducibility of the procedure was evaluated under the optimum conditions with 20 ng mL^{-1} of As(III) ion. The relative standard deviation (RSD) was founded to be $\pm 0.97\%$ for 8 times determination.

The calibration curves for determination of As(III) according to the general procedure under the optimized conditions are shown in Fig. 3. Linearity in the final solution was

Table 3 Effect of foreign ions on the recovery of As(III) ($N = 3$).

Diverse ion	At concentration	Recovery (%)
Na^+	300 mg L^{-1}	96.61 ± 1.47^a
Ca^{2+}	300 mg L^{-1}	97.23 ± 1.72
Mg^{2+}	300 mg L^{-1}	98.14 ± 2.17
K^+	250 mg L^{-1}	97.84 ± 1.27
Ba^{2+}	$500 \text{ }\mu\text{g L}^{-1}$	98.62 ± 2.27
Zn^{2+}	$500 \text{ }\mu\text{g L}^{-1}$	96.96 ± 1.02
Ni^+	$1000 \text{ }\mu\text{g L}^{-1}$	99.17 ± 3.56
Pb^{2+}	$1000 \text{ }\mu\text{g L}^{-1}$	96.86 ± 1.04
Cu^{2+}	$400 \text{ }\mu\text{g L}^{-1}$	98.18 ± 1.50
Al^{3+}	$300 \text{ }\mu\text{g L}^{-1}$	99.02 ± 1.14
Fe^{2+}	$300 \text{ }\mu\text{g L}^{-1}$	96.46 ± 1.08
NO_3^-	300 mg L^{-1}	97.16 ± 1.44
SO_4^{2-}	300 mg L^{-1}	98.35 ± 2.31

^a Mean \pm standard deviations.

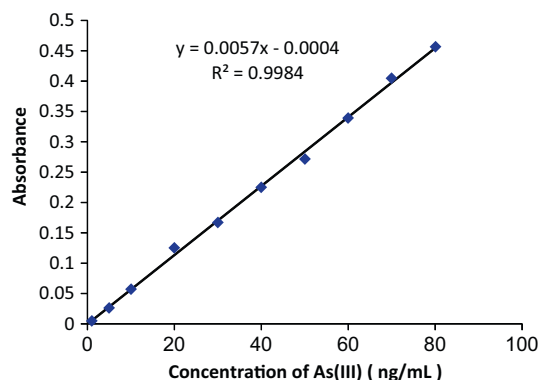


Figure 3 Calibration curves for arsenic.

Table 4 Determination of As(III) in some real samples (N = 3).

Samples	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water	0	0.34 ± 0.03^a	–
	5	5.31 ± 0.01	99.4
	10	10.22 ± 0.05	98.5
Well water	0	2.01 ± 0.02	–
	5	6.90 ± 0.02	98.4
	10	11.98 ± 0.03	99.8
Mineral water	0	3.26 ± 0.03	–
	5	7.85 ± 0.04	95.0
	10	13.05 ± 0.01	98.4
Rice plant	0	1.70 ± 0.01	–
	5	6.62 ± 0.03	98.8
	10	11.68 ± 0.02	99.8
Ash of rice straw	0	0.51 ± 0.03	–
	5	5.31 ± 0.07	96.4
	10	10.44 ± 0.03	99.3

^a Mean \pm standard deviations.

maintained between 1.0 and 80.0 ng mL⁻¹ with a correlation factor of 0.998 for As(III).

3.11. Analytical application

Rice is a bioaccumulative plant for the more toxic arsenic species arsenate and arsenite (Abedin et al., 2001). High arsenic concentrations in irrigated soils and water may lead to evaluated concentrations of arsenic in rice grain or in rice straw (Pizarro et al., 2003). This method was applied to separation and determination of As(III) in rice straw and its ash, drinking water, mineral water and well water samples. Before analysis, all the water samples were filtered through 0.45 μm membrane filters to remove suspended solids and stored in acid-cleaned polyethylene bottles at 4 °C in refrigerator. A little of rice straw and leaf was washed, dried and torn to pieces. Then 1 g was weighed and turned into ashes in an electric oven at 500 °C. For other sample was used 1 g dried rice straw and leaf. Then both samples were prepared based on the procedure recommended by Pizarro et al. (2003) and the proposed method was applied to the determination of As(III) in rice samples. The recoveries of spikes of the analytes were also studied. The analytical results and the recoveries are given in Table 4.

4. Conclusion

It can be concluded from the results that MWCNTs are an effective sorbent for ultra trace amounts of arsenic and can be used for its preconcentration from aqueous solution. The proposed method based on preconcentration with MWCNTs mini column and determination by GFAAS showed enough sensitivity for trace arsenic determinations and the precision and accuracy were satisfactory. The method could be applied

to the separation, preconcentration and determination of arsenic in real sample. The experiment results in this work demonstrate that amount of As(III) in rice straw and leaf is different with ash of rice plant. Therefore we can conclude that after burning residue of rice plant in rice paddy, a portion of arsenic is released and the air will be much polluted.

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