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DEVELOPMENT OF MULTIWALLED CARBON NANOTUBES BASED SOLID PHASE EXTRACTION FOR THE DETERMINATION OF TRACE LEVEL OF Mn(II) AND Sn(IV) IN RIVER WATER SAMPLES

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ABSTRACT. This paper reports a multiwalled carbon nanotubes (MWCNTs) modified with 3-amino-7-dimethylamino-2-methylphenazine (Neutral Red, NR) as a new solid phase extractor for determination of ultra trace amounts of Mn(II) and Sn(IV). The metal ions were retained on -column filled with the solid phase at a flow rate of 3.0 mL/min. The retained metal ions were eluted with 3 mol L^{-1} solution of HCl and measured by flame atomic absorption spectroscopy (FAAS). The effect of different variables such as, sample pH, concentration of 3-amino-7-dimethylamino-2-methylphenazine (Neutral Red, NR), sample flow rate, eluting solution and the effect of interfering ions have been investigated systematically. The calibration graph was linear in the range of 0.4-100 µg L^{-1} and 0.6-150 for Mn(II) and Sn(IV), respectively. Under optimized conditions, the limit of detections (LOD) were 0.12 and 0.16 µg L^{-1} for Mn(II) and Sn(IV), respectively. The method was used for determination of target metal ions in some water samples from rivers located in industrial and nonindustrial areas.

Keywords: *Solid phase extraction; 3-amino-7-dimethylamino-2-methylphenazine (Neutral Red, NR); Multiwalled carbon nanotubes; river water samples; Flame atomic absorption spectrometry, Mn(II) AND Sn(IV)*

INTRODUCTION

Natural processes as well as antropogenic activities are both sources of metals and their compounds into the environment. Since exposure to heavy metals is potentially harmful their monitoring in environmental, biological and clinical samples even at trace levels is nowadays required by law and other regulations in many cases [1]. Mining operations and heavy industry in the developing world is leading to the accumulation of high concentrations of

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toxic heavy metals in natural waters. Today, it is understood that exposure to heavy metals may seriously affect human health. [2]

Manganese is an essential element for human life, however, excessive levels of manganese are detrimental to the organism. Humans exposed to very high levels of manganese over a long time can develop mental and emotional disturbances and slow, clumsy body movements. Therefore, the determination of trace amounts of manganese in samples from various matrices is very important for certain areas of study. [3]

Tin is widely used in industry due to features such as low melting point, affinity to form alloys, and corrosion resistance. Exposure to Sn and its compounds can produce several effects such as neurological, hematological and immunological. Inhalation of inorganic compounds of Sn can induce to pneumoconiosis and ingestion may lead to gastrointestinal effects. Exposure to organic compounds of Sn inhibits the synthesis of hemeoxygenase and may be genotoxic, while its skin contact may cause severe irritation and burning. Other effects include kidney and liver damage [4].

Solid-phase extraction (SPE) is one of the most employed preconcentration methods that can be applied in off-line or online systems, with the advantage of possible automatization. SPE consists of the retention of metal species (or its derivatives) on the appropriate solid sorbent packed in a column or microcolumn and the later desorption with the adequate solvent. Thus, the concentration and separation of the analyte from the rest of sample matrix is achieved. [5] Solid-phase extraction (SPE), owing to its flexibility, absence of emulsion, simplicity, sampling in the field, safety, and ease of automation, is a preferred method for separation and enrichment of the target. SPE requires that the adsorbent possess a stronger selective adsorption ability. [6]

Carbon nanotubes (CNTs) are one of the most commonly used building blocks of nanotechnology. With one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they seem to be a very interesting material. Carbon nanotubes (CNTs) have been proposed as a novel solid phase extractor for various inorganic and organic materials at trace levels. [7]

Carbon nanotubes (CNTs) have become attractive materials, since its discovery in 1991, because of their novel structure characteristics. [8-18] Recently, Carbon nanotubes as an adsorbent for the preconcentration of traces heavy metals have become very popular. [19-29]

In this article, we have modified MWCNTs using NR and applied this functionalized material to SPE coupled with FAAS for simultaneously determination of Mn(II) and Sn(IV) in the water samples from rivers located in industrial and nonindustrial areas. Also for the validity of the method the Mn(II) and Sn(IV) levels in the final solutions were determined by ICP-AES using the general procedures.

RESULTS AND DISCUSSION

To obtain a sufficiently high efficiency of a SPE procedure, the study was focused on optimization of the extraction parameters containing, pH, amounts of NR and adsorbent, sample volume, elution conditions such as volume and concentration of eluent, flow rate of solution and matrix ions.

Effect of pH

The pH value plays an important role with respect to the adsorption of different ions on CNTs.[25] To evaluate the effect of pH on the extraction efficiency of Mn(II) and Sn(IV) as NR chelates adsorb on multiwalled carbon nanotubes, the pH of the sample solutions, were adjusted to fit in the range of 2–10. It is observable in Fig. 1, quantitative recoveries (>95%) were obtained for all studied ions at the pH range of 6–8. So, the pH 7 was selected for all subsequent studies.

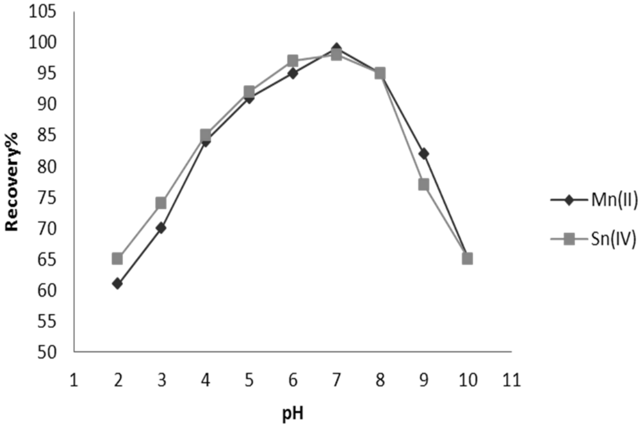

Figure 1. The effect of pH on the recoveries of the metal ions (N= 3.0.)

Effect of eluent type

The elution of the absorbed analytes could be achieved by using an appropriate eluent solution capable of effectively striping them from the MWCNTs and bring them into the solution [26]. Thus, the effects of various eluents (nitric acid, hydrochloric acid and acetic acid) on the recoveries of Mn(II) and Sn(IV) ions from multiwalled carbon nanotubes modified with NR were also investigated. The results are shown in Table 1. The results indicated that 3 mol L^{-1} HCl was sufficient for quantitative elution (>95%). Furthermore, the influence of eluent volume (1–5 mL) on the recoveries was studied by using 3 mol L^{-1} HCl. By adding 2 mL of 3 mol L^{-1} HCl, quantitative recoveries were obtained for all analyte ions. The recoveries were not quantitative for the other eluents listed in Table 1. Therefore, 2 mL of 3 mol L^{-1} HCl was used as eluent for further work.

Table 1. The effect of various eluents on the analyte ion recoveries.

Eluent Recovery %		
	Mn(II)	**Sn(IV)**
1 mol L^{-1} HCl	92±0.4	91±1.3
2 mol L^{-1} HCl	95±3.0	95±2.4
3 mol L^{-1} HCl	99±2.2	98±1.6
1 mol L^{-1} HNO_3	85±2.8	88±1.2
2 mol L^{-1} HNO_3	89±1.1	91±1.1
3 mol L^{-1} HNO_3	91±3.0	90±2.0
1 mol L^{-1} CH_3COOH	67±2.6	73±3.1
2 mol L^{-1} CH_3COOH	73±1.2	78±2.5
3 mol L^{-1} CH_3COOH	77±1.3	68±2.5

Effect of amount of chelating agent

To evaluate the effect of ligand on the recovery of metal ions, different amounts of NR solution (3×10^{-4} mol L^{-1}) in the range of 0-5 mL was investigated. As presented in Fig. 2, the recoveries of analyte ions increased with increasing amounts of NR added and reached a constant value over 95% with at least 3 mL. The recovery values of analytes were quantitative at the amounts of ligand range of 3-5 mL. Hence, 3 mL of ligand was selected for subsequent studies. At lower concentrations, the amount of ligand is insufficient to extract all the analyte in the solution. But at higher concentrations, all the analyte species were used, thus, process of complex formation was stop and the percentage of recoveries remained nearly constant, in other words, the limiting factor is analyte concentration.

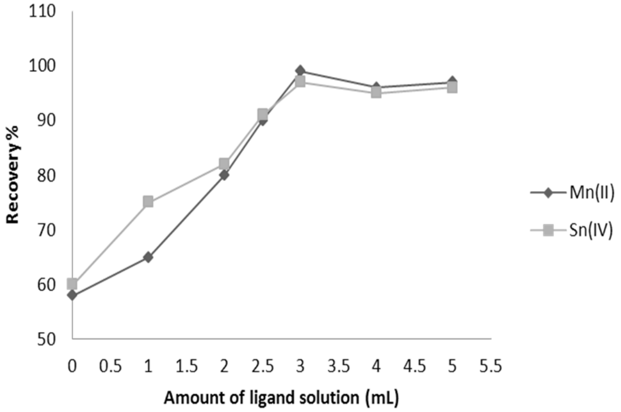

Figure 2. Effect of amount of ligand solution on the recoveries of analytes.

Effect of amounts of adsorbent (MWCNTs)

The amount of solid phase extraction material is another important factor on the column studies to obtain quantitative recoveries. On the other hand, an excess amount of the adsorbent can also prevent the quantitative elution of the retained metals by a small volume of the eluent. To estimate the impact of adsorbent mass on the recovery of metal ions, different amounts of adsorbent (50-400 mg), packed into an SPE column, were investigated, following the preconcentration procedure. The recoveries of metal ions increased with increasing amounts of adsorbent. For less than 200 mg of adsorbent, the recoveries amounts are not quantitative and it is due to by-passing of the liquid in the SPE column [19]. Thus absorbent weight of 200 mg was found to be suitable for this purpose.

Effect of the sample volume

The preconcentration and separation of the analytes are usually performed at a lower concentration. In order to improve the relative sensitivity of the procedure when determining very low concentration of analytes, a relative large sample volume is usually suggested. Therefore, the maximum volume of sample solution was investigated by increasing the volume of metal ion solution by passing 100–600 mL of sample solutions. The effects of sample volumes on the recoveries of the two analytes are shown in Figure 3. The results showed that the maximum sample volume could be up to 500 mL with the recovery >95%. Therefore, 500 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. The preconcentration factor (PF) is calculated by the ratio of the highest sample volume (500 mL) and the lowest eluent volume (2 mL). The preconcentration factor was calculated as 250.

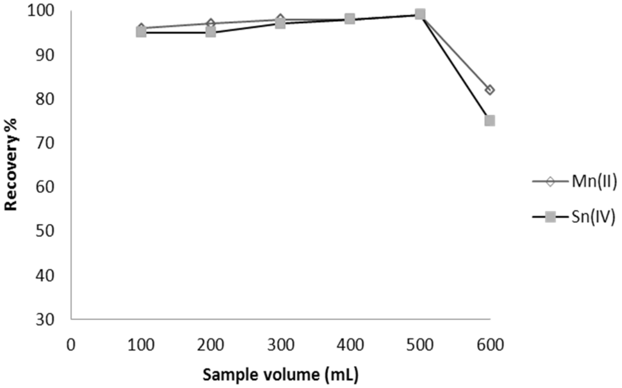

Figure 3. Effect of sample volume on the recoveries of analytes (N= 3.0)

Flow rates of sample and eluent solutions

The influences of the flow rates of sample and eluent solutions on the retentions of Mn(II) and Sn(IV) were also investigated keeping other conditions constant. Low flow rates can be time consuming. The flow rates were investigated in the range of 1–5 mL min−1 and under the optimum conditions (pH and eluent type). It was found when the flow rates of the sample and eluent solutions were at the range of 1.0-3.0 and 1.0-4.0 mL min^{-1}, The recoveries of analytes were quantitative. At higher flow rates, there was a decrease in the recovery in that there was not sufficient contact time between MWCNTs and sample solution. Therefore, all the studies were carried out for flow rates of sample and eluent solutions at a flow rate of 3.0 mL/min.

Effect of foreign ions

The influences of possible matrix ions in the environmental samples and some transition metals on the recoveries of analytes on multiwalled carbon nanotubes were also examined.

The obtained results were presented in Table 2. The tolerance limit is defined as ions had no significant interferences in the preconcentration and determination of the analyses. This is due to the low adsorbing capacity or rates for interfering ions. These results demonstrate that the method has a good tolerance to interference and is suitable for Mn(II) and Sn(IV) detection.

Table 2. Effect of interfering ions on the recoveries of the analytes (N= 3).

Ion	**Concentration (mg L^{-1})**	**Recovery (%)^a**	
		Mn(II)	**Sn(IV)**
Ag^+, K^+, Na^+, Cl^-, Li^+, I^-	10000	98±1	95±1
SO_4^{-2}, Ca^{2+}, CO_3^{-2}, Br^-, $C_2O_4^{-2}$	8000	98±1	97±2
Mg^{2+}, F^-	6000	96±2	98±1
HCO_3^{-2}, NO_3,	3000	99±1	97±2
PO_4^{-3}, CH_3COO^-	1500	95±2	96±3
Ni^{2+}, Pb^{2+}	500	96±3	95±1
Cd^{2+} , Mo^{5+}	250	98±2	98±2
Pd^{2+}	100	95±1	98±3
Hg^{2+}, Al^{3+}, Cr^{3+}	10	97±2	99±2

^{a} Mean ± standard deviations.

Adsorption capacity

For investigation of the adsorption capacity of multiwalled carbon nanotubes, 0.1 g MWCNTs was added to 50 ml of solution containing 1.0 mg of metal ion at pH 7.0. After shaking for 30 min, the mixture was filtered. Ten milliliters of the supernatant solution was diluted to 100 ml and determined by flame atomic absorption spectrometry. This procedure was repeated for each analyte ions separately. The capacity of modified MWCNTs for Mn(II) and Sn(IV) was found to be 86.6 and 77.8 mg g^{-1}, respectively.

Analytical performance

Using the optimized experimental conditions, calibration curves of enrichment process were linear in the range of 0.4-100 μg L^{-1} and 0.6-150 μg L^{-1} for Mn(II) and Sn(IV), respectively. The detection limits, based on three times the standard deviation of 10 runs of blank solution, were found to be 0.12 and 0.16 μg L^{-1} for Mn(II) and Sn(IV), respectively. The relative standard deviation (RSD), nine determinations of 1.0 μg L^{-1} of Mn(II) and Sn(IV) were 4.0 and 2.6%, respectively (N=9). The correlation coefficients for Mn(II) and Sn(IV) were 0.9997, 0.9995, respectively. The preconcentration factor for the proposed method was 250.

Analytical applications

A solid phase extraction method was applied to determination of trace Mn(II) and Sn(IV) in water samples from river located in industrial and nonindustrial areas. Various amounts of analytes were also spiked to these water samples. The results are given in Table 3 and Table 4. A good agreement was obtained between the added and measured Mn(II) and Sn(IV) amounts. The accuracy of the method was verified by the analysis of samples spiked with known amounts of the analytes. These results indicated the suitability of NR-MWCNT for selective SPE and determination of trace Mn(II) and Sn(IV) in environmental samples. The river water samples were also analysed by (ICP-AES). As Table 3 and Table 4. shows there is a good agreement between the results obtained by the proposed method with those obtained by the ICP-AES. This reveals the capability of the method for determination of Mn(II) and Sn(IV) in all real samples without considerable error. In Table 5, the relative comparison of analytical performance with those reported in the literature [26-29].

Table 3. The results for determination of Pd(II) and Cd(II) in various river water samples by FAAS

Sample	Added (μg L^{-1})		Found [a] (μg L^{-1})		Recovery (%)		RSD(%)	
	Mn(II)	Sn(IV)	Mn(II)	Sn(IV)	Mn(II)	Sn(IV)	Mn(II)	Sn(IV)
River Water[b]	-	-	71.48±0.06	84.28±0.02	-	-	1.1	2.3
	100	100	173.93±0.02	182.52±0.03	101.43	99.04	1.1	1.4
	200	200	275.12±0.04	285.65±0.05	101.34	100.48	1.3	1.3
River Water[c]	-	-	65.25±0.05	50.65±0.04	-	-	3.0	2.1
	100	100	164.79±0.07	153.56 ±0.09	99.72	101.93	2.9	2.7
	200	200	265.61±0.05	241.41±0.09	100.51	96.31	3.1	2.5
River Water[d]	-	-	61.14±0.01	67.19±0.02	-	-	1.9	2.6
	100	100	162.22±0.02	164.74±0.01	100.67	98.53	1.5	2.2
	200	200	263.16±0.04	260.11±0.03	100.77	97.35	2.8	1.5
River water[e]	-	-	5.31±0.05	12.61±0.05	-	-	1.8	2.1
	100	100	103.31±0.03	109.64 ±0.07	98.10	97.36	2.6	1.5
	200	200	205.16±0.09	211.51±0.09	99.92	99.48	1.5	2.3

[a] $\bar{x} \pm ts\sqrt{n}$ at 95% confidence (N = 5)
[b] From karoon river, located in a industrial area
[c] From zayande rood river, located in a industrial area
[d] From khour musa, located in a industrial area
[e] From pole zohre located in a nonindustrial area

Table 4. The results for determination of Pd(II) and Cd(II) in various river water samples by ICP-AES.

Sample	Added (μg L^{-1})		Found [a] (μg L^{-1})		Recovery (%)		RSD(%)	
	Mn(II)	Sn(IV)	Mn(II)	Sn(IV)	Mn(II)	Sn(IV)	Mn(II)	Sn(IV)
River Water[b]	-	-	71.35 ±0.01	84.15±0.01	-	-	2.1	2.1
	100	100	173.62±0.05	181.85±0.03	101..32	98.75	1.1	1.9
	200	200	275.12±0.04	285.65±0.05	101.51	100.79	1.2	2.1
River Water[c]	-	-	65.25±0.05	50.65±0.04	-	-	1.2	2.1
	100	100	164.79±0.07	153.56 ±0.09	99.56	100.89	2.4	2.7
	200	200	265.61±0.05	241.41±0.09	100.04	99.18	1.2	1.7
River Water[d]	-	-	61.14±0.01	67.19±0.02	-	-	1.8	2.1
	100	100	162.22±0.02	164.74±0.01	102.47	99.14	1.5	2.2
	200	200	263.16±0.04	260.11±0.03	101.99	97.17	1.2	2.9
River water[e]	-	-	5.31±0.05	12.61±0.05	-	-	1.0	2.0
	100	100	103.31±0.03	109.64 ±0.07	97.66	101.03	2.2	2.9
	200	200	205.16±0.09	211.51±0.09	99.89	100.27	1.6	3.1

[a] $\bar{x} \pm ts\sqrt{n}$ at 95% confidence (N = 5)
[b] From karoon river, located in a industrial area
[c] From zayande rood river, located in a industrial area
[d] From khour musa, located in a industrial area
[e] From pole zohre located in a nonindustrial area

Table 5. Comparison of the proposed method with recent studies reported in literature using solid phase extraction

Analytes	Medium	Eluent (mol L^{-1})	PF[a]	LOD[b] (μg L^{-1})	Reference
Cu^{2+} , Cd^{2+} , Mn^{2+}	pH=9	1 (HNO_3)	28.9	0.13–0.58	26
Mn^{2+}	pH=10	0.5 (HCl)	17	0.7	27
Sn^{2+}, Sn^{4+}	pH=2	1.0 (HNO_3)	100	0.7-1.1	28
Mn^{2+}, Pb^{2+}	pH=9	2.0 (HNO_3)	-	0.6-1	29
Mn^{2+}, Sn^{4+}	pH=7	3 (HCl)	250	0.12-0.16	This work

[a] PF: Preconcentration factor
[b] LOD: Limit of detection

EXPERIMENTAL

Apparatus

A Metrohm pH-meter (model 691, Switzerland) was used in order to adjust the pH at desirable values. A Chemtech Analytical Instrument model CTA-3000 atomic absorption spectrometer (Bedford, England) equipped with a flame burner was used for analysis of the understudy metals, including lamp currents and wavelength were those recommended by the manufacturer. All metals were measured under optimized operating conditions by FAAS with an air–acetylene flame. Inductively coupled plasma (ICP) model Varian Liberty 150AX Turbo was used for the validity of concentration determination of the analyte.

Standard solutions and reagents

Analytical reagent-grade chemicals were used in this work. All the plastic and glassware were cleaned by soaking in 10% HNO_3 solution and then rinsed with distilled water prior to use. Standard solutions (1000 mg L^{-1}) of Mn(II) and Sn(IV) ions were prepared from high purity compounds, supplied by E. Merck (Darmstadt, Germany). The working standard solutions were prepared by diluting stock standard solution. A 3×10^{-4} mol L^{-1} solution of (NR) reagent was prepared by dissolving 0.008 gr of it it in 100 mL water. McIlvaine's buffer solution in the pH range of 2-10 was used to adjust pH values by adding 16.47 mL of Na_2HPO_4 and 3.53 mL of acid citric. Multiwalled carbon nanotube was purchased from Aldrich, (Milwaukee, WI, USA). The BET (Brunauer–Emmett-Teller) surface area and density of nanotubes were 300 m^2 g^{-1} and 2.1 g mL^{-1}, respectively.

Preparation of the column

Two-hundred milligrams of multiwalled carbon nanotubes was loaded into an SPE column (10 mm × 150 mm). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before use, 3 mol L^{-1} HCl were passed through the column to clean it.

Recommended procedure

A standard solution containing 0.4-100 μg L^{-1} of Mn (II) and 0.6-150 μg L^{-1} of Sn(IV) and the pH value was adjusted to 7 with McIlvaine's buffer solution. then NR was added to form the [metal-(NR)] chelates. After that, the solutions passed through the column gravitationally. Subsequently, metal ions retained on the MWCNT, were eluted with the desired volume and concentration of eluent. The eluent was analyzed for the determination of metal concentrations by flame atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry (ICP-AES).

Sample preparations

The river water samples were collected from the rivers located in industrial and non industrial areas. The water samples were filtered through a 0.45 μm PTFE Millipore filter. After adjusting to the desired pH values, the solutions were passed through the column gravitationally.

CONCLUSION

The proposed method offers a simple, inexpensive, selective and sensitive method for the enrichment of Mn(II) and Sn(IV) using MWCNTs modified by NR as a solid-phase extractant for SPE coupled with FAAS. The proposed method was proved to be simple, rapid and reliable and could be used for studied metal ions determination in environmental samples. The high accuracy of the proposed method was confirmed by recovery test with standard addition method. The possible interference of some important ions was investigated and no important interference was encountered. The MWCNTs has great potential as an adsorbent for the preconcentration and determination of trace metal ions in complex samples. The accuracy and validity of the method is provable by the comparison among the resultant results of the proposed method and those obtained by ICP-AES method (Table 3 and Table 4). High sensitivity and selectivity, and also the good detection limits and high preconcentration factor (PF=250.0) which is comparable or higher than the other solid-phase extraction methods in literature (mentioned at section 2.10)

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