

# Preconcentration and determination of trace amounts of $\text{Cd}^{2+}$ using multiwalled carbon nanotubes by solid phase extraction-flame atomic absorption spectrometry

Hossein Tavallali<sup>1\*</sup>, Vahid Fakhraee<sup>2</sup>

<sup>1</sup>Department of Chemistry, Payame Noor University 19395-4697, Tehran , I.R. of IRAN.

<sup>2</sup>Department of Chemistry, Faculty of science, Islamic Azad University, Omidyeh branch, Omidyeh, IRAN.

\*Corres.author: [tavallali@yahoo.com](mailto:tavallali@yahoo.com)

**Abstract:** Multiwalled carbon nanotubes (MWNTs) were used as absorbent for extraction of  $\text{Cd}^{2+}$  ions in the presence of 1-(2-pyridylazo)-2-naphthol (PAN) as a chelate by solid phase extraction method. The complexes were eluted with  $1 \text{ mol L}^{-1} \text{ HNO}_3$  in acetone and determined the analyte by flame atomic absorption spectrometry. The influences of the experimental parameters including pH of the solutions, amounts of MWNTs, amounts of PAN, eluent type and volume and sample volume on the quantitative recoveries of analyte ion were investigated. Calibration curve was linear in the range of  $5\text{--}120 \mu\text{g L}^{-1}$ , relative standard deviation and detection limit were % 1.42 for  $60 \mu\text{g L}^{-1}$  of  $\text{Cd}^{2+}$  and  $0.43 \mu\text{g L}^{-1}$  respectively. The Preconcentration factor obtained 40. The presented method has been applied to the determination of analyte in Iranian and foreign rice sample which gave satisfactory results.

**Keywords:** Solid Phase Extraction, Cadmium, Multiwalled Carbon Nanotubes, PAN.

## 1. Introduction

Some of heavy metals like copper, cobalt are necessary for human life, while some heavy metals like lead, cadmium are problematic for human. Main sources of heavy metals in the environmental samples are industrial facilities and traffic [1, 2]. Accurate and sensitive determinations of them are the important part of analytical chemistry studies. Due to its cheap cost, simplicity, atomic absorption spectrometry is the main instrument for the determination of heavy metals in many laboratories. However, the determination of metals at  $\mu\text{g L}^{-1}$  level by especially flame atomic absorption spectrometry is impossible due to their lower levels and interferic effects of 1A

and 2A group elements in the determinations [3-5]. In order to solve these problems in flame atomic absorption spectrometric determinations, separation enrichment procedures including cloud point extraction, membrane filtration, liquid-liquid extraction, coprecipitation, solid phase extraction have been used [6-11]. Among these preconcentration techniques, solid phase extraction is preferred a lots of researchers due to its advantages including as simple and fast extractor system, easily adaptable to the preconcentration and to the determination of trace metal ions by flow injection analysis technique. Solid phase extraction has a relatively high concentration factor and the ability of treating large volume samples

free from contamination [12, 13]. Solid phase extraction technique has been widely used in the preconcentration/separation of trace and ultra trace amounts of inorganic and organic species, in order to enhance sensitivity and to separate analytical matrix. Nowadays, in the solid phase extraction studies transition metals at trace level, investigation of the usage of new materials as solid phase extractor is an important ratio. At this point, carbon nanotubes (CNTs) have been proposed as a novel solid phase extractor for various inorganic and organic materials at trace levels [14-17]. CNTs are one of the most commonly used building blocks of nanotechnology. CNTs can be visualized as a sheet of graphite that has been rolled into a tube, and divided into multiwalled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) according to the carbon atom layers in the wall of the nanotubes [18-23]. Liang et al. have proposed a preconcentration system based on the adsorption of copper ions at trace levels on multiwalled carbon nanotubes [17]. A solid phase extraction procedure for trace rare earth elements in various samples on multiwalled carbon nanotubes prior to their inductively coupled plasma atomic emission spectrometric determinations has been presented [24]. The potential usage of multiwalled carbon nanotubes as a solid phase extraction adsorbent for the preconcentration of trace Cd, Mn and Ni has been investigated by Liang et al. [25]. Li et al. have studied on the adsorption of lead [26] and cadmium [27] ions on carbon nanotubes. In this article, a preconcentration-separation procedure for traces amounts of cadmium ions in the presence of PAN as a chelates on multiwalled carbon nanotubes was described. The conditions for quantitative and reproducible preconcentration, elution and subsequent flame atomic absorption spectrometric determination of cadmium were established.

## **2. Experimental**

### **2.1. Reagents and solutions**

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionized water (Milli-Q Millipore 18.2 M,  $\text{cm}^{-1}$  conductivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute  $\text{HNO}_3$  (1+9) and were rinsed with distilled water prior to use. The element standard solutions used for calibration were produced by diluting a stock solution of 1000  $\text{mg l}^{-1}$  of the given element supplied by Sigma and Merck. Stock solutions of diverse elements were prepared from high purity compounds.

The calibration standards were not submitted to the preconcentration procedure.

Multiwalled carbon nanotube (Plasma Chem GmbH) was purchased from Plasma, Rudower Chaussee 29, and D- 12489 Berlin. The Purity of nanotubes was more than 95%. An 1-(2-pyridylazo)-2-naphthol (PAN) solution (0.1%, w/v) was prepared by dissolving the requisite amounts of PAN in water/ethanol (75/25%, v/v). The solution was discharged one day.

Buffer solutions (pH 2-3) were prepared by appropriate amounts of 1  $\text{mol l}^{-1}$  HCl and  $\text{NaBO}_3$ . Acetate buffer solutions ( $\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$ ) were prepared by mixing of appropriate volumes of 0.1  $\text{mol l}^{-1}$  acetic acid and 0.1  $\text{mol l}^{-1}$  sodium acetate solutions for pH 4 and 6. Buffer pH 7,8 were prepared by mixing of appropriate volumes of 1 $\text{mol l}^{-1}$  sodium dihydrogene phosphate and phosphoric acid solutions. Ammonium buffer solution ( $\text{NH}_4^+/\text{NH}_3$ ) was prepared by mixing of appropriate amounts of 0.1  $\text{mol l}^{-1}$  ammonia and 0.1  $\text{mol l}^{-1}$  ammonium chloride solutions for pH 9.

### **2.2. Instruments**

A Perkin-Elmer AAnalyst 300 atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and air-acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. Milestone Ethos D closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 C) was used [28].

### **2.3. Column preparation**

150 mg of multiwalled carbon nanotubes was loaded after washing acetone, 1 $\text{mol l}^{-1}$   $\text{HNO}_3$  solution and water, respectively, into a 10 mm  $\times$  100 mm glass column with a glass frit resin support. The resin bed was approximately 1 cm. The column was preconditioned by the blank solution prior to each use. After the elution, the resin in the column was washed with a 10-15 mL of the eluting solution and of water, subsequently.

### **2.4. Test procedure**

Test solutions containing 5-120  $\mu\text{g}$  of each analytes were adjusted to desired pH. Then PAN was added to form the metal-PAN chelates. After 10 min, the solution was loaded to the column. The flow of sample solution through the column was gravitationally performed. After passage of the

solution finished, the column was washed with 2 ml PAN solution adjusted to the working pH. The metals were recovered with the aid of 5 ml of 1 mol l<sup>-1</sup> HNO<sub>3</sub> in acetone at 5.0 ml min<sup>-1</sup> of flow rate. The analyte concentrations in the final solution were determined by flame atomic absorption spectrometry.

### 3. Results and discussion

In order to obtain quantitative recoveries of the metal ions on multiwalled carbon nanotubes, the enrichment/separation procedure was optimized for various analytical parameters such as pH. Sample volume, amounts of multiwalled carbon nanotubes, matrix effects etc. The percent of metal adsorbed on nanotubes was calculated from the amounts of metal in the starting sample and the amounts of metal in the final solution.

#### 3.1. Influences of pH

Because the pH of the aqueous samples is the very important factor for the quantitative recoveries of the metal ions in the solid phase extraction studies [29], the influences of pH of the analyte solutions on the recoveries of Cd (II), as PAN chelates on multiwalled carbon nanotubes were investigated in the pH range 6.0-11. The quantitative recoveries (>95%) for Cadmium were found at the pH 9. The recovery values were decreased after pH 9. At the acidic pH values, the recoveries were not quantitative. This value is supported to our quantitative recovery values at the basic pHs. All subsequent studies were carried out at pH 9 by using an Ammonium buffer solution. Effects of pH on the absorption of the analyte were given in Fig. 1. The volume of buffer solution had no effect in the range of 2-10 ml.

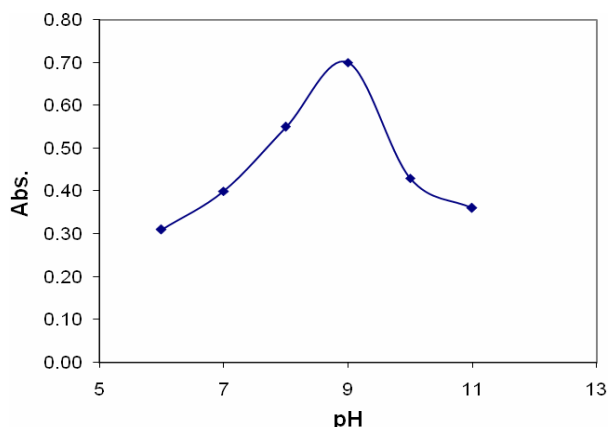


Fig.1. Effects of pH on the absorption of Cd<sup>2+</sup> on multiwalled carbon nanotubes

#### 3.2. Effects of amounts of PAN

The amounts of the ligand are also an important factor for the quantitative retentions of metal ions in solid phase extraction techniques. In order to investigate the optimum amounts of PAN on the quantitative recoveries of the analyte ions on multiwalled carbon nanotubes, the study was examined by varying the amounts of PAN from 0.5 to 2.5 mg. The results are given in Fig. 2. The recoveries of analyte ions increased with increasing amounts of PAN added and reached a constant value over 95 % with at least 1.5 mg. The recovery values of analytes were quantitative at the amounts of ligand of 1.5 mg. On this basis, all the studies were carried out at a PAN amount of 1.5 mg.

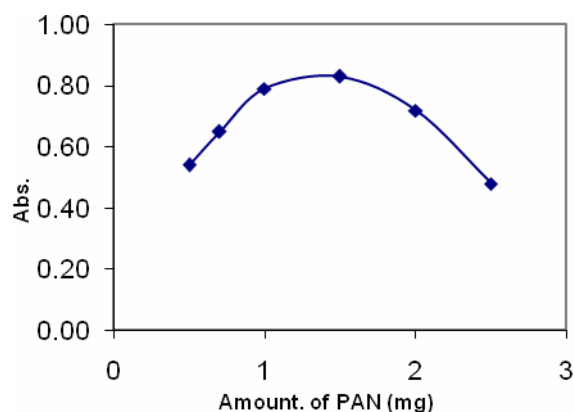


Fig.2. Effects of amount of PAN on the absorption of Cd<sup>2+</sup> on multiwalled carbon nanotubes

#### 3.3. Eluent type and volume

Various eluent solutions were used for desorption of metal PAN chelates from multiwalled carbon nanotubes. The results were given in Table 1. Quantitative recoveries for analyte ions were obtained only with 1 mol l<sup>-1</sup> HNO<sub>3</sub> in acetone. HNO<sub>3</sub> in acetone was found to be the most satisfactory combination in experiments using both PAN. Recoveries were not generally quantitative other eluents used present study with some exceptions shown in Table 1.

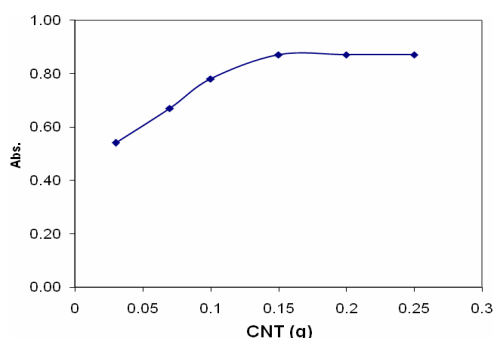
The effect of eluent volume on the recoveries of the analytes was also studied by using 1 mol l<sup>-1</sup> HNO<sub>3</sub> in acetone; it was found that quantitative recoveries could be obtained with 4.0-6.0 ml of 1 mol l<sup>-1</sup> HNO<sub>3</sub> in acetone. Therefore, the volume of 5.0 ml of 1 mol l<sup>-1</sup> HNO<sub>3</sub> in acetone was used in the following experiments.

**Table 1. Effects of eluent type on the recoveries of the Cd<sup>2+</sup>**

Eluent type	HCl 0.5 mol l <sup>-1</sup>	HCl 1.0 mol l <sup>-1</sup>	HNO <sub>3</sub> 0.5 mol l <sup>-1</sup>	HNO <sub>3</sub> 1.0 mol l <sup>-1</sup>	HNO <sub>3</sub> 1.0 mol l <sup>-1</sup> in acetone
Recovery (%)	30	35	47	64	98

**3.4. Effects of amounts of multiwalled carbon nanotubes (MWNTs)**

The effects of the amounts of multiwalled carbon nanotubes on the adsorption of analyte were investigated at 5.0 ml min<sup>-1</sup> flow rates of sample and eluent solutions. The recovery values for analyte ions were found quantitative in the resin amounts of 150-250 mg. In all further studies, the short glass column was filled with 150 mg of MWNTs. The results were given in Fig.3



**Fig.3. Effects of amount of multiwalled carbon nanotubes on the absorption of the Cd<sup>2+</sup>**

**3.5. Flow rates of sample and eluent solutions**

It is expected that sample solutions can be passed through the multiwalled carbon nanotubes column at a higher flow rate without sacrificing the recoveries because a large volume of sample solution is needed in the preconcentration step. The effect of the flow rate of the sample and eluent solutions on the recoveries of Cd (II) on MWNTs was examined in the range of 1.0-10.0 ml min<sup>-1</sup>. Five milliliters per minute was chosen as the flow rate of the sample and eluent solutions in subsequent experiments.

**3.6. Effect of the sample volume**

In order to obtain high preconcentration factor, the effect of sample volume on the sorption behavior of analyte on MWNTs was investigated by passing 25-

300 ml of solutions. Amount of cadmium in supernatant solution determined by flame atomic absorption spectrometry. The sorption of cadmium ions were quantitatively recovered at the range of 50-200 ml. At the higher volumes than 200 ml, the recoveries for analytes were not quantitative. The preconcentration factor for preconcentration of analyte is calculated by the ratio of the highest sample volume for analyte (200 ml) and the lowest eluent volume (5 ml). The preconcentration factor was 40.

**3.7. Effect of divers 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. A 5 ml portion of sample solution containing analyte and a given amounts of foreign ions were concentrated. The experimental results are shown in Table 2. The ions normally present in natural waters do not interfere under the experimental conditions used until the proportion of foreign ions to analyte is equal 1000 and for transition metals be equal 500. The results show that the proposed preconcentration /separation method could be applied to the highly saline samples that contains some transition metals at mg l<sup>-1</sup> Levels.

**Table 2: Effect of divers ions on the absorption of the analyte**

Ion	Foreign ions Analyte
Cu <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Fe <sup>3+</sup> , Al <sup>3+</sup>	1000
NO <sub>3</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , HCO <sub>3</sub> <sup>-</sup> , F <sup>-</sup> , Cl <sup>-</sup>	1000
Ag <sup>+</sup> , Zn <sup>2+</sup> , Pb <sup>2+</sup> , Mn <sup>2+</sup>	500

**3.8. Adsorption capacity**

In order to study the adsorption capacity of multiwalled carbon nanotubes, 0.1g MWNTs was added to 50 ml of solution containing 0.1 mg of metal ion at pH 9.0. After shaking for 30 min, the mixture was filtered. 10 milliliters of the supernatant solution was diluted to 50 ml and determined by flame atomic absorption spectrometry. The capacity of MWNTs for analyte was found as 8.6 mg g<sup>-1</sup>. The stability of multiwalled carbon nanotubes was excellent. The adsorption of metal-PAN chelate is related with the physical interaction of the surface of the nanotubes and the metal-PAN chelate.

**3.9. Figures of merit**

The detection limit (LOD) of the presented solid phase extraction study was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The detection limits, defined as the concentration

equivalent to three the standard deviation (N=10) of the reagent blank were found as 0.43 µg l<sup>-1</sup>. Calibration curve was linear in the range of 5-120 µg l<sup>-1</sup> in optimum conditions. Precision of the method was obtained at various concentrations of Cd<sup>2+</sup> and the results shown in table 3.

**3.10. Applications of the presented procedure**

The presented procedure was applied to the determination of analyte in Iranian and foreign rice sample after microwave digestion. The results are in good agreement with the certified values for the analyte.

The results are shown in Table 4. A good agreement was obtained between the added and measured analyte amounts. These results confirm the validity of the proposed method. The presented method could be applied successfully for the separation, preconcentration and determination of trace amounts of cadmium ions in real samples.

**Table 3. Amount of RSD in different concentration of Cd<sup>2+</sup> (N=5)**

Conc. of Cd <sup>2+</sup> (µg l <sup>-1</sup> )	Results	$\bar{X}$	S	RSD%
15	15(2), 16(3)	15.6	0.547	3.51%
60	58(2), 59(2), 60(1)	58.8	0.836	1.42%
110	107(2), 109(2), 11(1)	108.6	1.670	1.54%

**Table 4: Determination of analyte in rice sample by perposed method**

	Sample	Add Cd <sup>2+</sup> µg l <sup>-1</sup>	Found Cd <sup>2+</sup> µg l <sup>-1</sup>	Recovery %
foreign rice	Khatere rice	0.0	0.0	0.0
		20	21.0	105.0
		50	52.0	104.0
	Mohsen rice	0.0	0.0	0.0
		20.0	22.0	110.0
		50.0	49.0	98.0
Iranian rice	Anbarbo rice	0.0	0.0	0.0
		20.0	21.0	105.0
		50.0	51.0	102.0
	Lenjan rice	0.0	0.0	0.0
		20.0	19.0	95.0
		50.0	51.0	102.0

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