



## Separation and Preconcentration Trace Amounts of Nickel Ion Using Modified Multiwalled Carbon Nanotubes Sorbent Prior to Flame Atomic Absorption Spectrometry Determination

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### ABSTRACT

In this work, a selective method for separation and preconcentration of nickel ions at trace level on modified multiwalled carbon nanotubes columns and determination by flame atomic absorption spectrometry (FAAS) has been developed. Multiwalled carbon nanotubes were oxidized with concentrated HNO<sub>3</sub> and then modified with loading 1-(2-pyridylazo)-2-naphthol. The sorption of Ni(II) ions was quantitative in the pH =9. Elution of the adsorbed nickel was carried out with 5.0 mL of 0.1 mol L<sup>-1</sup> HNO<sub>3</sub>. The amount of eluted nickel was measured using flame atomic absorption spectrometry. Factors influencing sorption and desorption of Ni(II) ions were investigated, including the sample pH, flow rates of sample and eluent solution, eluent type, breakthrough volume and interference ions. The relative standard deviation of the method was ±0.57% (n=8) and the limit of detection was 2.04 × 10<sup>-2</sup> μg mL<sup>-1</sup> (3σ<sub>m</sub>/m, n=8). The method was applied to the determination of Ni(II) in water samples and standard alloy (NKK. NO. 920, Aluminum Alloy).

**KEYWORDS:** Modified multiwalled carbon nanotubes; Preconcentration; Nickel determination; Water sample; NKK. NO. 920, Aluminum Alloy.

### 1. INTRODUCTION

The monitoring of the levels of heavy metal ions in environmental samples is an important part of analytical chemistry due to their positive or negative influences on the human body [1-3]. Removal of heavy metal ions in wastewaters has been an extensive industrial research subject, as these are highly toxic at low concentrations [4]. Nickel is one such known heavy metal pollutant, found mainly in effluents discharged from industries such as nickel-cadmium battery manufacturing [5], electroplating [6], mineral processing, metal finishing [7], etc. Among separation/preconcentration methods, solid phase extraction (SPE) due to faster operation, easier manipulation and reduction of the use of organic solvents, less stringent requirements for separation, higher preconcentration factor and easier compatibility with analytical instruments have been widely studied. At present, nano-sized materials and carbon nanotubes are more important in SPE [8-9]. Carbon nanotubes (CNTs) are an allotrope of carbon. A carbon nanotube is a one atom thick sheet of graphite rolled up into a seamless cylinder with diameter of the order of a nanometer [10]. CNTs have high surface area, mechanical strength, thermal and chemical stability. Due to their unique characteristic and strong adsorption ability [11], they have been successfully used to remove many

kinds of pollutants such as dioxin from air [6], lead [12], cadmium [13], zinc [14], fluoride [15], 1,2-dichlorobenzene [16] and trihalomethanes [17] from different matrices. Atomic absorption spectrometer (AAS) is generally main instrument of analytical chemistry laboratories for the determination of traces heavy metal ions, due to its relatively low cost [18-19]. The goal of this study is to modify MWCNTs by 1-(2-pyridylazo)-2-naphthol (PAN). Moreover, the performances of modified multiwalled carbon nanotubes (MMWCNTs) are tested as a new sorbent for the preconcentration of trace Ni(II). Separation and preconcentration of Ni(II) were carried out in a glass column filled with MMWCNTs and the Ni(II) is determined by AAS.

### 2. EXPERIMENTAL

#### 2.1. Reagents

All chemical materials were of analytical reagent grade. Nickel (II) nitrate hexa hydrate 99% from Merck (Merck, Darmstadt, Germany) was dissolved in double distilled water. Buffer solution with pH=9 was prepared by mixing an appropriate ratio 0.1 mol L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O and NaOH. A 0.1% solution of 1-(2-pyridylazo)-2-naphthol (Merck) was prepared by dis-

solving it in ethanol. MWCNTs with an average outer diameter of 3–20 nm, length of 1–10  $\mu\text{m}$ , number of walls 3–15 and surface area of  $350 \text{ m}^2\text{g}^{-1}$  were obtained from PlasmaChem. GmbH (Berlin, Germany).

### 2.2. Instruments

The Nickel measurements were performed with a Varian SpectrAA 220 atomic absorption spectrometer (Australia, <http://www.varianinc.com>). A nickel hollow cathode lamp operating at 4.0 mA, resulting in an analytical wavelength of 232.0 nm was used as the radiation source. A deuterium background correction was applied and the slit width was set at 0.2 nm. Acetylene flow,  $1.0 \text{ L min}^{-1}$ ; air flow as oxidant,  $4.0 \text{ L min}^{-1}$ . All measurements were carried out in the integrated absorbance (peak area) mode. The pH values were adjusted with a metrohm 827 pH meter (model 827, Switzerland, [www.metrohm.com](http://www.metrohm.com)) supplied with a combined glass electrode; calibrated against two standard buffer solutions at pH 4.0 and 7.0. The column dimensions were 4–60 mm with a sintered glass plate located at the bottom of the column.

### 2.3. Preparation of MMWCNTs

Raw MWCNTs were heated at  $300^\circ\text{C}$  for 40 min to remove amorphous carbon. Prior to use, MWCNTs were oxidized with concentrated  $\text{HNO}_3$  according to the literature, in order to create binding sites onto the surface of MWCNTs [20]. The treatment was carried out by the dispersion of 5 mL of  $6 \text{ mol L}^{-1} \text{ HNO}_3$  to 1.0 g of MWCNTs and then refluxing for 6 h at  $100^\circ\text{C}$ . Afterward, the oxidized MWCNTs were washed with distilled water until the removal of any excess nitric acid (neutral pH of solution), then a 0.1% solution of 1-(2-pyridylazo)-2-naphthol was added to MWCNTs and refluxed for 3 h at  $75^\circ\text{C}$  that produced MMWCNTs which were dried at  $100^\circ\text{C}$  and stored for use.

### 2.4. Preparation of column

MMWCNTs (50 mg) were dispersed in water and then poured into a funnel-tipped glass tube plugged with a small piece of glass wool at the ends. A glass column packed with 0.05 g of MMWCNTs sorbent (height of packing being about 15 mm) were used as the operational column. The column could be used repeatedly 50 times after washing with distilled water.

### 2.5. Recommended procedure

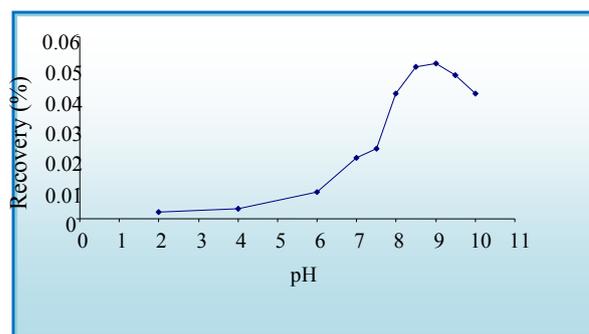
An aliquot of the solution containing 5  $\mu\text{g}$  of nickel was taken in a 100 mL beaker and it was added to 5 mL of buffer solution with pH=9, then diluted to 20 mL with distilled water. This solution was passed through the column at a flow rate of  $2 \text{ mL min}^{-1}$ . After passing this solution, the column was washed with 5 mL of distilled water. The adsorbed nickel on the column was eluted with 5.0 mL of  $0.1 \text{ mol L}^{-1}$  nitric acid, at a flow rate  $1 \text{ mL min}^{-1}$ . The eluents was collected in a 5.0 mL volumetric flask and nickel was determined by flame atomic absorption spectrometry.

## 3. RESULT AND DISCUSSION

MWCNTs have a low tendency for the retention of Ni(II) (less than 58%) but were not selective. The MWCNTs can adsorb organic material, so 1-(2-pyridylazo)-2-naphthol was added to MWCNTs [21], since 1-(2-pyridylazo)-2-naphthol is a good reagent complexing with Ni(II). The results showed that the recovery of nickel ions by using oxidized MWCNTs is higher than 97%. Moreover, oxidized MWCNTs are selective for the separation of Ni-PAN complex. In order to obtain highly sensitive, accurate and reproducible results, analytical parameters including pH, type and volume of eluent solution, breakthrough volume and flow rates of sample and eluent were optimized for the preconcentration of nickel.

### 3.1. Effect of the sample pH

The pH of the solution plays a unique role on metal-chelate formation and subsequent extraction. The extraction yield depends on the pH at which the complex formation occurs. In the present work, the effect of pH upon the complex formation of target ions was studied within the pH range of 2.0–10. The percentage of sorption of Ni(II) on the sorbent surface as a function of the pH of the sample solution is shown in (Fig. 1). The optimum pH range was around 8.5–9.0. In subsequent studies, the pH was maintained at approximately 9.0.



**Fig. 1.** The effect of sample solution pH on the percent sorption of  $\text{Ni}^{2+}$ . Conditions: Ni, 5.0  $\mu\text{g}$ ; sample flow rate,  $2 \text{ mL min}^{-1}$ ; eluent solution, 5.0 mL  $\text{HNO}_3$  with a flow rate  $1 \text{ mL min}^{-1}$ . Instrumental settings: wavelength, 232.0 nm; lamp current, 4.0 mA; slit width, 0.2 nm; acetylene flow,  $1.0 \text{ L min}^{-1}$ ; air (as oxidant) flow,  $4.0 \text{ L min}^{-1}$ .

### 3.2. Effect of flow rate of sample

Flow rate of the sample solution is a measure of the contact time between the sample solution and the sorbent. The flow rate of the sample solution was studied within the range  $0.5\text{--}5.0 \text{ mL min}^{-1}$ . Results showed that the flow rate variation in the range of  $0.5\text{--}3.5 \text{ mL min}^{-1}$  did not have a significant effect on the sorption of the Ni(II). It was found that the adsorption of Ni(II) on MMWCNTs is relatively rapid. In order to achieve better precision, a flow rate of  $2.0 \text{ mL min}^{-1}$  was chosen for further studies.

### 3.3. Selection of eluent

Selection of the eluent is a key step in the optimization of SPE conditions. Four solvents, such as, HCl,  $\text{HNO}_3$ ,

H<sub>2</sub>SO<sub>4</sub> and EDTA were used in order to find the best eluents for desorption of nickel ion from the sorbent surface. The results showed that the best recovery was achieved when HNO<sub>3</sub> was used as eluent. It was found that 5.0 mL of HNO<sub>3</sub> 0.1 M was sufficient to elute the complex from oxidized MWCNTs.

### 3.4. Effect of eluent flow rate

The effect of eluent flow rate on desorption of Ni-PAN complex from the sorbent surface was studied in the range of 0.1–3.0 mL min<sup>-1</sup>. Flow rate of 1.0 mL min<sup>-1</sup> was chosen in subsequent work.

### 3.5. Breakthrough volume

When solutions containing 1.0 µg of Ni(II) in 100, 200, 300, 400 and 500 mL water were passed through the columns, the Ni(II) was quantitatively retained in all cases. Therefore we conclude that the breakthrough volume of the method under optimum conditions should be greater than 500 mL. Consequently, by considering the final elution volume of 5.0 mL of 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and a breakthrough volume of 500 mL, a pre-concentration factor of 100 was easily achievable.

### 3.6. Evaluation of sorbent capacity

The sorption capacity of MMWCNTs was determined by passing different volumes of 60.0 µg mL<sup>-1</sup> Ni(II), followed by the determination of retained Ni(II) using FAAS. The maximum capacity of the sorbent was 1416 µg of Ni(II) per gram of sorbent. The MMWCNTs sorbent was subject to several loadings with the sample solution and the subsequent elution. It was found that adsorption properties of the adsorbent remained constant after 55 cycles of sorption and desorption.

### 3.7. Interferences

The potential interferences of some ions on the pre-concentration and determination of metal ions were examined. In these experiments, solutions of 0.5 µg mL<sup>-1</sup> of the analytes containing the interfering ions were treated according to the optimized procedures. Table 1 shows tolerance limits of the interfering ions. In the interferences of coexisting ions in binary mixtures of Ni(II) with foreign ions were studied on the percentage of recovery of nickel. After introducing the binary solution into a column, the adsorbed nickel ion was eluted by 5.0 mL of 0.1 mol L<sup>-1</sup> nitric acid. The content of nickel in effluents was determined by using FAAS and the recoveries were calculated. Considering the selectivity provided by the solid phase extraction and flame atomic absorption spectrometry, many anions and cations were evaluated. An ion was considered to interfere when its presence produced a variation of 4% error.

### 3.8. Analytical curve and sensitivity

The calibration line exhibited a good linearity over the ranges of 0.01–10.0 µg mL<sup>-1</sup> with equation  $A=0.0594C+0.0007$  and correlation coefficients better than 0.9991. The limit of detection (LOD) of the method for determination of nickel was studied under the

optimal experimental conditions. The LOD was 0.024 µg mL<sup>-1</sup>. ( $3S_b/m$ ,  $S_b$  is the standard deviation of eight replicates of the blank measurement). The relative standard deviation (RSD) was  $\pm 0.57\%$  ( $n=8$ ,  $C=0.05$  µg mL<sup>-1</sup>) and the sensitivity for 1% absorbance was 62.3 ng mL<sup>-1</sup>.

**Table 1.** Effect of interfering ions

Coexisting ion	Recovery (%)	Coexisting ion/Ni (II)
I <sup>-</sup>	100.0	7500
NO <sub>3</sub> <sup>-</sup>	102.7	4000
SCN <sup>-</sup>	103.0	12000
PO <sub>4</sub> <sup>3-</sup>	101.0	3500
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	102.1	200
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	101.2	5000
EDTA	97.3	50
NH <sub>4</sub> <sup>+</sup>	99.6	6000
Ca <sup>2+</sup>	100.0	1000
Pb <sup>2+</sup>	102.1	400
Zn <sup>2+</sup>	97.5	400
Mn <sup>2+</sup>	101.1	150
Mg <sup>2+</sup>	103.0	800
Hg <sup>2+</sup>	96.0	50
K <sup>+</sup>	100.1	2500
Co <sup>2+</sup>	99.0	250

### 3.9. Analysis of nickel in standard alloys

The method was applied to determination of nickel in Nippon Keikinzo Kogyo (NKK) CRM No. 920 Aluminum alloy. A 100.0 mg sample of the standard alloy was decomposed with 10 mL of a mixture which contained concentrated HNO<sub>3</sub> and HCl (1:1 ratio) and the solution was evaporated to dryness by heating in a water-bath. The solution was filtered and diluted to 100.0 mL with distilled water in a standard flask. An aliquot of this sample was taken and the procedure was applied. The results obtained are given in Table 2. These results are in agreement with the certified values.

### 3.10. Analysis of nickel in waste water and waste water samples

The procedure was applied to the determination of nickel in waste water from Shiraz and Kerman in Iran. Reliability was checked by analysis spiking experiments. The samples were spiked at different concentration level ng mL<sup>-1</sup>. The results of this investigation are given in Table 3. It can be seen that the recovery of spiked samples are good and these results also, demonstrate the applicability of the method to the determination of nickel in sample type examined.

**Table 2.** Analysis of nickel in standard alloy.

Sample	Composition (%)	Found <sup>a</sup>	Recovery (%)
NKK.No. 920 Aluminum Alloy	Si, 0.78;	0.279±0.06	96.2%
	Fe, 0.729;		
	Mg, 0.46;		
	Cr, 0.27;		
	Zn, 0.80;		
	Ti, 0.15;		
	Bi, 0.06;		
	Ga, 0.05;		
	Ca, 0.03;		
	Co, 0.10;		
	Ni, 0.29;		
V, 0.15;			
Cu, 0.71;			
Mn, 0.20;			

<sup>a</sup> Mean±SD, n=3.**Table 3.** Analysis of Ni(II) in wastewater samples

Sample	Spiked (ng mL <sup>-1</sup> )	Found <sup>a</sup> (ng mL <sup>-1</sup> )	Recovery (%)
Wastewater (Shiraz) <sup>b</sup>	-	B.L.R <sup>c</sup>	-
	5.0	5.1±0.2	102.0
Wastewater (Shiraz) <sup>d</sup>	-	N.D <sup>e</sup>	-
	5.0	4.8±0.4	96.0
Wastewater (Kerman) <sup>f</sup>	-	0.97	-
	5.0	6.14 ±0.3	103.4

<sup>a</sup> Mean ±SD, n=3, <sup>b</sup> Cement factory, <sup>c</sup> B.L.R.: Below the linear range<sup>d</sup> Narges oil factory, <sup>e</sup> N.D: Not detectable, <sup>f</sup> Copper factory

#### 4. CONCLUSIONS

This paper demonstrates the use of a sorbent based on the MMWCNTs as a sorbent for the separation and preconcentration of low levels of nickel ions in different samples. By using this sorbent, a simple, rapid, precise, accurate and reliable method is developed for the preconcentration of trace amounts of nickel. The method is economical due to the possibility of multiple uses of the sorbent. The procedure used for the measurement of nickel in standard alloy shows a good accuracy. The proposed procedure was applied for the determination of nickel in complex samples.

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