

Flame atomic absorption spectrometric determination of trace amounts of lead, cadmium and nickel in different matrixes after solid phase extraction on modified multiwalled carbon nanotubes

Research Article

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Abstract: The potential of modified multiwalled carbon nanotubes (a solid-phase extraction sorbent), for the simultaneous separation and preconcentration of lead, cadmium and nickel; has been investigated. Lead, cadmium and nickel, were adsorbed quantitatively; on modified multiwalled carbon nanotubes (in the pH range of 2–4). Parameters influencing, the simultaneous preconcentration of Pb(II), Ni(II) and Cd(II) ions (such as pH of the sample, sample and eluent flow rate, type and volume of elution solution and interfering ions), have been examined and optimized. Under the optimum experimental conditions, the detection limits of this method. for Pb(II), Ni(II) and Cd(II) ions, were 0.32, 0.17 and 0.04 ng mL⁻¹ in original solution, respectively. Seven replicate determinations, of a mixture of 2.0 µg mL⁻¹ lead and nickel, and 1.0 µg mL⁻¹ cadmium; gave a mean absorbance of 0.074, 0.151 and 0.310, with relative standard deviation 1.7%, 1.5% and 1.2%, respectively. The method has been applied, to the determination of trace amounts of lead, cadmium and nickel; in biological and water samples, with satisfactory results.

Keywords: Carbon nanotubes • Lead determination • Nickel determination • Cadmium determination • Preconcentration

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1. Introduction

Heavy metals are considered to be serious inorganic pollutants; which cannot be destroyed. They can form compounds that are toxic (even in very low concentrations [1–5]), to humans, animals, plants and aquatic life [6–8]. The heavy metal may be found in several sources, including air, soil and water; and mainly originate from industrialization and its consequences. The accurate determination, of trace quantities of heavy metal ions, in the environment; is a potential area of study, for analytical chemistry [9–12].

Currently, the most common analytical methods for trace determination, of heavy metals are; flame atomic absorption spectrometry (FAAS) [13,14]; electrothermal atomic absorption spectrometry (ET-AAS) [15,16]; inductively coupled plasma emission spectrometry (ICP-AES) [17]; and inductively coupled plasma-mass spectrometry (ICP-MS) [18]. However, all aforementioned methods (except FAAS) require relatively high-cost apparatus, and high instrumentation complexity; limiting their widespread application to routine analytical works. FAAS is widely employed, in the determination of heavy metals, because of its low cost, friendly operation, high sample throughput and good selectivity

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[19]. However, this method often suffers from its low sensitivity; this limitation can be overcome, by applying a preconcentration step, prior to the determination step [20]. The most widely used techniques, for the separation and preconcentration of trace metals, include solid phase extraction, coprecipitation, liquid–liquid extraction, membrane filtration, floatation and cloud point extraction [21–28]. Recently, the solid phase extraction technique, has been preferred by researchers, because of its advantages to enrichment; high recovery; simplicity; rapid and low organic solvent consumption. The main requirements, for substances to be used as solid-phase extraction sorbents, are as follows [29]: the ability to extract a large number of elements, over a wide pH range; fast quantitative sorption and elution; high capacity; regenerability and accessibility. Numerous substances have been proposed, and applied as solid-phase extraction sorbents, such as chelating resins, modified silica, activated carbon, polyurethane foam, cellulose and biological substances.

Since their discovery in 1991, carbon nanotubes (CNTs) have attracted great attention, because of their unique properties. CNTs can be visualized, as sheets of graphite rolled into a tube, and divided into; multiwalled carbon nanotubes (MWNTs) [30], and single-walled carbon nanotubes (SWNTs) [31] (according to the carbon atom layers in the wall of the nanotubes). The hexagonal arrays of carbon atoms, in graphene sheets of the CNTs surface, have a strong interaction with other molecules or atoms; this interaction makes CNTs, a promising adsorbent material, to replace activated carbon in many applications. Recently, Li *et al.* [32–34] suggested that CNTs, show high efficiency for Pb^{2+} , Cd^{2+} and F^- removal; from aqueous solutions, after oxidation treatment with nitric acid.

In this work, the analytical potential of MWNTs, modified with 1-(2-pyridylazo)- 2-naphthol (PAN) as an adsorbent (for the preconcentration of traces of the heavy metals lead, cadmium and nickel ions); was investigated. This method is described in detail, in the experimental section, and was applied to measure lead, cadmium and nickel in water samples.

2. Experimental Procedure

2.1 Apparatus and reagents

A Varian model SensAA GBC (Dandenong, Australia) atomic absorption spectrometer, equipped with deuterium background correction; was used for measuring the three analyte ions, in an air-acetylene flame. GBC hollow cathode lamps for lead, cadmium and nickel; were used as light sources. The selected

wavelengths for the determination of lead, cadmium and nickel were 283.2, 228.8 and 232 nm, respectively. The other operating parameters, were set according to the manufacturer recommendation. The acetylene flow rate, and the burner height; were adjusted in order to obtain the maximum absorbance signal (while aspirating the analyte solution). A Metrohm pH meter (Herisau, Switzerland); was employed for pH measurements. A funnel-tipped glass tube (80×10 mm); was used as a column for preconcentration. All glass ware and columns, were washed with a mixture of concentrated hydrochloric acid, and concentrated nitric acid (1:1) before use. Double de-ionized water (DDW), was used for all dilutions. High purity reagents from Sigma (St. Louis, MO, USA), and Merck (Darmstadt, Germany); were used for all preparations of the standard and sample solutions. The stock solutions of lead, cadmium and nickel (at a concentration of 1000.0 $\mu\text{g mL}^{-1}$), were prepared from high purity reagents. The working solutions, were prepared by appropriate dilution, of the stock solutions. Multiwalled carbon nanotubes (95% purity and 1–10 μm in length, 3–15 walls), were purchased from Plasma Chem GmbH (Berlin, Germany). A 0.5% solution of 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol, was prepared. Buffer solutions were prepared, from 0.1 mol L^{-1} acetic acid, and 0.1 mol L^{-1} sodium acetate; for pH 3–6, from 0.1 mol L^{-1} potassium dihydrogen phosphate, and 0.1 mol L^{-1} disodium hydrogen phosphate, for pH 6–8; and from 0.5 mol L^{-1} ammonia, and 0.5 mol L^{-1} ammonium acetate, for pH 8–11. Solutions of alkali metal salts (1%), and various metal salts (0.1%); were used for studying the interference of anions and cations, respectively.

2.2. Preparation of modified MWCNTs

Before use, the MWCNTs materials, were oxidized with concentrated HNO_3 (according to literature with minor modifications) before being used. 2.0 g of MWCNTs, were first soaked in 20 mL of concentrated HNO_3 , for 10 h at room temperature (while being stirred) [35]; to create binding sites onto the surface. The oxidized MWCNTs, were washed repeatedly with DDW; until the residual acid was completely removed; the MWCNTs were then dried at 80°C. 2.0 g of oxidized MWCNTs, were suspended in 20 mL 0.5% (w/v) solution of PAN in ethanol (because it was reported in the literature, that the PAN reagent would form a stable complex with the mentioned cations [36]), and stirred for 5 h. The solid was filtered, washed with de-ionized water and dried at 80°C. The amount of PAN adsorbed on the MWCNTs, was estimated by spectrometric measurements from the residual amount of PAN in solution.

Table 1. Effect of type and concentration of eluent on the recovery of the investigated ions

Eluent	Recovery (%)		
	Pb	Cd	Ni
0.5 mol L ⁻¹ H ₂ SO ₄	61	82	69
1.0 mol L ⁻¹ H ₂ SO ₄	75	98	84
0.1 mol L ⁻¹ KSCN	32	53	61
0.1 mol L ⁻¹ Na ₂ S ₂ O ₃	48	41	53
0.5 mol L ⁻¹ HCl	86	91	88
1.0 mol L ⁻¹ HCl	99	100	99

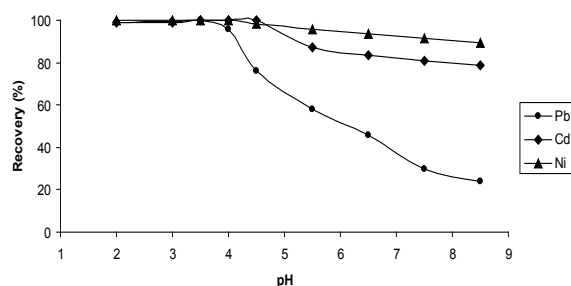


Figure 1. The influence of the pH of aqueous solution on the recovery of analyte ions. Conditions: lead and nickel, 10.0 µg; cadmium, 5.0 µg; Buffer, 2 mL; flow rate of sample, 1 mL min⁻¹; final solution, 5.0 mL of 1.0 mol L⁻¹ HCl solution; flow rate of eluent, 1 mL min⁻¹; reference, reagent blank.

2.3. Sample preparation

Two certified reference materials (CRMs) (furnished by the National Institute for Environment Studies (NIES)); No. 1 Pepperbush, and NIES No. 7 Tea Leaves, were analyzed. Approximately 0.50 g of this material, were weighed accurately into a Teflon cup, and dissolved in concentrated nitric acid (~10 mL), with heating in a water bath. The solution was cooled, diluted and filtered. The filtrate was made to 100.0 mL, with deionized water in a calibrated flask. An aliquot of the sample solution was taken, and lead, cadmium and nickel ions were determined by the general procedure.

River and well water samples, were collected in acid-leached polyethylene bottles. The river water samples, were collected from Rayen, Shahdad and Kohpayeh, in Kerman, Iran. The well water sample, was collected from Payame Noor University, Kerman, Iran. The only pretreatment, was acidification to pH 2 with nitric acid; which was performed immediately after collection, in order to prevent adsorption of the metal ions, on the flask walls. The samples were filtered, before analysis, through a cellulose membrane (Millipore) of 0.45 µm pore size.

2.4. Preparation of column

50 mg of modified MWNTs, were introduced into a funnel-tipped glass tube (80×10 mm); plugged with a small portion of glass wool, at both ends. Before use, 5 mL of 2.0 mol L⁻¹ HCl solution, and 10 mL of DDW; were passed through the column, to clean and condition it. Then, the column was conditioned to the described pH, with 10 mL of buffer solution.

2.5. General preconcentration procedure

30 mL of an aqueous solution containing 10.0 µg of lead and nickel, and 5.0 µg of cadmium ions; were taken, and the pH was adjusted to about 3. The resulting solution was passed through the column; at flow rate of about 1 mL min⁻¹. Then, the column was rinsed; with 5 mL of DDW, and the adsorbed ions were eluted with 5.0 mL of 1.0 mol L⁻¹ HCl, at flow rate of about 1 mL min⁻¹. The analyte ions in the eluent, were determined by FAAS.

3. Results and Discussion

In this study, a combination of SPE with FAAS was developed; for determination of trace amounts of lead, cadmium and nickel. Several factors, that may affect the preconcentration and extraction process (including pH, type and volume of elution solution, flow rate of sample and eluent, sample volume and matrix effect), were optimized. The optimizations were carried out, in an aqueous solution, containing 10.0 µg of lead and nickel, and 5.0 µg of cadmium ions.

3.1. Effect of pH on preconcentration

Since the pH of the aqueous sample solutions, is an important analytical factor, in the solid phase extraction studies of metal ions [37,38]; the influence of pH on the preconcentration of cadmium, nickel and lead ions was examined, in the pH range of 2–8.5 (keeping the other parameters constant). The pH of the metal sample solutions, was adjusted by using buffer solution (given in Chapter 2), before passing through column. The recovery percent of analytes are shown in Fig. 1, and, as can be seen at pH less than 4; the three analyte ions were quantitatively (>95) retained on the sorbent. When pH > 4, the formation of Pb(OH)₂, Cd(OH)₂ and Ni(OH)₂ could possibly be occurring; and the recoveries percent were decreased. A pH of 3 in the middle of the pH range, was considered as being the optimum value; to avoid an abrupt change in adsorption (which may occur due

to minor changes in the pH). Further studies were done at pH 3, by using acetic acid/acetate buffer solution. The volume of the relevant buffer added (5 mL), had no effect on the recoveries. Therefore, 2 mL of the buffer, were used in all subsequent experiments.

3.2. Elution of the adsorbed ions

Other important factors, that affect the preconcentration procedure, is the type, volume and concentration of the eluent, used for the removal of analyte ions; from the sorbent [39]. Optimization of the elution conditions, were performed in order to obtain the maximum recovery; with the minimal concentration and volume, of the elution solution. Various eluents (5 mL) were studied, according to the general procedure; with the results shown in Table 1. As can be seen, the three analyte ions were quantitatively eluted from the sorbent, with only 1 mol L⁻¹ HCl. Therefore, 5 mL of 1 mol L⁻¹ HCl, was used in all subsequent experiments.

3.3. Flow rate

The retention of an element on an adsorbent, also depends on the flow rate of the sample solution. The effect of flow rates of sample, and eluent solutions, on the retention and recovery, of the three analyte ions on modified MWNTs; were investigated in the range 0.5-3 mL min⁻¹. The flow rate was adjusted, by connecting the adsorbing column to a flask; which had a controllable vacuum. It was found that retention and recovery of the ions, was independent of flow rate in a range 0.5-2 mL min⁻¹; and the adsorption of the analyte ions on MMWCNTs, are relatively rapid. Therefore, a flow rate of 1 mL min⁻¹, was applied for sample and elution solutions; in all subsequent experiments.

3.4. Effect of the sample volume

In order to explore, the possibility of enriching low concentrations of analyte from large volumes; the effect of sample volume, on the recovery of analyte ions was investigated. For this purpose, 25, 100, 250, 500, 600, 700 and 800 mL of aqueous solution, containing 10.0 µg of lead and nickel, and 5.0 µg of cadmium ions; were processed according to the general procedure. The results are given in Table 2. The recovery of cadmium ion, throughout the working range; was acceptable, but lead and nickel ions, were recovered quantitatively in the range 25-600 mL. With respect to eluent volume (5 mL), preconcentration factors (the ratio of the highest sample volume, to the lowest eluent volume) for lead, cadmium and nickel 120 were obtained.

Table 2. Influence of the sample volume on the recovery of analyte ions

Sample volume (mL)	Recovery (%)		
	Pb(II)	Ni(II)	Cd(II)
25	99	99	99
100	99	98	99
250	98	98	98
500	98	97	98
600	97	97	97
700	91	89	97
800	84	82	95

Table 3. Tolerance limit of foreign ions

Foreign ions	Added as	Interference/Analyte ions(II) ratio ^a		
		Pb(II)	Ni(II)	Cd(II)
CH ₃ COO ⁻	CH ₃ COONa.3H ₂ O	10000	8000	6000
NH ₄ ⁺	NH ₄ Cl	5000	4000	4000
H ₂ PO ₄ ⁻	KH ₂ PO ₄	5000	5000	5000
HPO ₄ ²⁻	Na ₂ HPO ₄	5000	5000	5000
Ca ²⁺ , Mg ²⁺	CaCl ₂ , MgCl ₂	1000	1200	1000
Al ³⁺	AlCl ₃	200	100	100
Cu ²⁺	Cu(NO ₃) ₂	200	200	200
Ba ²⁺	BaCl ₂	300	200	200
Fe ³⁺	Fe(NO ₃) ₃	150	100	200
Mn ²⁺	MnSO ₄	200	200	100
Zn ²⁺	ZnCl ₂	200	400	100
Co ²⁺	Co(NO ₃) ₂	200	100	100

Conditions were the same as Fig. 1.

^a The ratio interference/analyte ions is w/w.

3.5. Adsorption capacity

To determine adsorption capacity of modified MWNTs, a batch method was selected. 50 mL of aqueous solution containing 2.0 mg of lead, 1.0 mg nickel, and cadmium, at pH 3; was added to 0.1 g of modified MWNTs. After shaking for 10 min, the mixture was filtered, and 10 mL of supernatant solution was diluted to 100.0 mL, and was determined by FAAS. The capacity of modified MWNTs for lead, nickel and cadmium ions; was found to be 9.3, 1.5 and 1.0 mg g⁻¹, respectively.

Table 4. Analytical parameters of the method

Statistical parameters	Pb	Ni	Cd
Linear ranges (ng mL ⁻¹ - µg mL ⁻¹)	0.83-15.0	0.83-10.0	0.17-3.0
Regression equations	A=0.0354X+0.0071	A=0.0765X+0.005	A=0.3091X+0.0046
Correlation coefficients (R)	0.9983	0.9993	0.9986
RSD%	1.7	1.5	1.2
Detection limits (ng mL ⁻¹)	0.32	0.17	0.04

Table 5. Comparison the detection limits of proposed methods with other methods.

Method	Enrichment factor	Detection limit (ng mL ⁻¹)	References
SPE-FAAS	Pb:120	Pb:0.32	This work
	Ni:120	Ni:0.17	
SPE-FAAS	Cd:120	Cd:0.04	40
	Pb:75	Pb:16	
SPE-FAAS	Cd:100	Cd:4.2	41
	Ni:100	Ni:25	
SPE-FAAS	Cd:50	Cd:10	42
	Pb:42	Pb:12.01	
SPE-FAAS	Ni:63	Ni:28.73	43
	Cd:52	Cd:1.34	
SPE-FAAS	Pb:300	Pb:13.88	44
	Ni:250	Ni:8.72	
SPE-FAAS	Cd:200	Cd:4.71	44
	Pb:400	Pb:2.5	
SPE-FAAS	Ni:150	Ni:6.5	44
	Cd:400	Cd:2.5	

3.6. Effect of foreign ions

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference; may be attributed to the preconcentration step. To perform this study, various salts and metal ions were added individually; to a solution containing 10.0 µg of lead and nickel, and 5.0 µg of cadmium ions, and the general procedure was applied. The tolerance limit was set; as the concentration of the foreign ion required to cause ±5% error. Table 3 shows the tolerance limits of the interference ions. The results demonstrate, that the presence of large amounts of species commonly present in water samples; have no significant effect on the SPE of lead, nickel and cadmium.

Table 6. Determination of Pb(II), Ni(II) and Cd(II) ions in certified reference materials

Sample	Certified value (µg g ⁻¹)	Found ^a (µg g ⁻¹)
NIES, No. 1	Pb: 5.5±0.8	Pb: 5.6±0.2
Pepperbush	Ni: 8.7±0.6	Ni: 8.6±0.4
	Cd: 6.7±0.5;	Cd: 6.9±0.3
NIES, No. 7	Pb: 0.80	Pb: 0.82±0.03
Tea Leaves	Ni: 6.5	Ni: 6.6±0.3
	Cd: 0.030	Cd: 0.029±0.001

^a Average of four determination±standard deviation

3.7. Calibration, precision and detection limit

Under the optimized conditions, calibration curves were constructed; for the determination of lead, nickel and cadmium, according to the general procedure. Linearity was maintained between 0.83 ng mL⁻¹ to 15.0 µg mL⁻¹ for lead; 0.83 ng mL⁻¹ to 10.0 µg mL⁻¹ for nickel; and 0.17 ng mL⁻¹ to 3.0 µg mL⁻¹ for cadmium, in initial solution. The detection limit, was determined as three times the standard deviation (10 replicate measurements); of the absorbance of a blank sample. The detection limits of this method, in the original solution, for Pb(II), Ni(II), and Cd(II) ions were 0.32, 0.17 and 0.04 ng mL⁻¹, respectively. Seven replicate determinations, of a mixture of 2.0 µg mL⁻¹ lead and nickel, and 1.0 µg mL⁻¹ cadmium gave a mean absorbance of 0.074, 0.151 and 0.310, with relative standard deviation 1.7%, 1.5% and 1.2%, respectively. The analytical parameters, are given in Table 4.

Table 7. Analysis of Pb(II), Ni(II) and Cd(II) ions in water samples

Sample	Found ^a (ng mL ⁻¹)	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	Recovery (%)
River Water (Rayen, Kerman)	Pb: 8.7±0.4	Pb: 10.0	Pb: 18.9±0.7	102
	Ni: 7.4±0.4	Ni: 10.0	Ni: 17.7±0.6	103
	Cd: 1.43±0.07	Cd: 5.0	Cd: 6.37±0.4	98.8
River Water (Shahdad, Kerman)	Pb: 7.3±0.3	Pb: 10.0	Pb: 17.7±0.6	104
	Ni: 9.1±0.5	Ni: 10.0	Ni: 19.3±0.7	102
	Cd: 1.11±0.06	Cd: 5.0	Cd: 6.13±0.4	100.4
Well Water (Payame Noor University of Kerman)	Pb: 9.5±0.5	Pb: 10.0	Pb: 19.2±0.7	97
	Ni: 8.6±0.5	Ni: 10.0	Ni: 18.9±0.7	103
	Cd: 2.49±0.11	Cd: 5.0	Cd: 7.44±0.6	99
River Water (Kohpayeh, Kerman)	Pb: 8.1±0.4	Pb: 10.0	Pb: 18.2±0.6	101
	Ni: 7.9±0.4	Ni: 10.0	Ni: 17.6±0.6	97
	Cd: 1.35±0.06	Cd: 5.0	Cd: 6.45±0.6	102

^a Average of four determination, ±standard deviation

A comparison of the proposed method, with the other reported preconcentration methods [40–44], for the lead and nickel and cadmium extraction from water samples; are given in Table 5. The obtained detection limits, by the proposed method; are comparable to most of those reported in the literature.

added Pb(II), Ni(II) and Cd(II) ions, were quantitatively recovered from the water samples; by the proposed procedure. These results demonstrate, the applicability of the procedure for lead, nickel and cadmium determination; in water samples.

3.8. Analysis of Certified Reference Material

The accuracy and applicability of the proposed method, has been applied to the determination of Pb(II), Ni(II) and Cd(II) ions, in the National Institute for Environment Studies (NIES) No. 1 pepperbush, and NIES No. 7 Tea Leaves. Results are given in Table 6. It was found, that there is no significant difference, between results obtained by the proposed method, and the certified results. These results indicate, the applicability of the developed procedure; for simultaneous preconcentration of lead and nickel, and cadmium; and that it is free of interference.

3.9. Applicability of proposed procedure for analysis of water samples

The proposed procedure, has been applied to the determination of lead, nickel and cadmium content; in different water samples. The results are given in Table 7. As can be seen from the results in Table 7, the

4. Conclusions

It can be concluded from the results, that modified MWNTs are an effective sorbent; for separation and preconcentration of trace amounts of lead and nickel, and cadmium from various samples. The proposed method has the following advantage: it is simple, rapid, reproducible, and has a high enrichment factor (120) and low analysis cost. The reusability of the sorbent was greater than 50 cycles; without any loss in its sorption behavior. The accuracy of the proposed method, is shown by analysis of certified reference materials.

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