Preconcentration of some trace elements via using multiwalled carbon nanotubes as solid phase extraction adsorbent

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ABSTRACT

In present study preconcentration followed by solid phase extraction of heavy metal ions, Cu(II), Co(II), Ni(II) and Pb(II) using a multiwalled carbon nanotubes (MWNTs) and complexing reagent *o*-cresolphthalein complexone were investigated. The effects of parameters, including pH of the solutions, amounts of complexing reagent, eluent type, sample volume, flow rates of solution, and matrix ions, were examined for the optimum recoveries of the analyte ions. The preconcentration factor was 40. Detection limit (3 s) obtained for the investigated metals in the optimal conditions were observed in the range of 1.64–5.68 $\mu g\,l^{-1}$. The validation of the presented method was obtained by the analysis of certified reference material HR 1 (Humber river sediment), the obtained results were agreed with certified values. The optimum experimental conditions that ensure the efficiency of the procedure have been investigated and have been successfully applied to the determination of trace elements in environmental samples with satisfactory results.

1. Introduction

Heavy metals (HMs) are considered as serious inorganic pollutants which cannot be destroyed. Heavy metals are persistent environmental contaminants, and having a high enrichment factor and slow removal rate. They have toxic effects on human health, animals, plants and life in aquatic system [1–3]. The heavy metal may originate from several sources including air, soil and water, and that is mainly caused by industrialization and its consequences. To determine the trace quantity of heavy metal ions accurately in the environment is a potential study area for analytical chemistry [3–6]. Determination of trace quantities of heavy metals requires the use of sensitive and selective techniques such as flame atomic absorption spectrometry (FAAS) is an important instrument for these determinations due to its simplicity and lower cost compared with atomic neutron activation analysis or inductively coupled plasma mass spectrometry. Generally, in trace metal determination, a preconcentration and separation procedure is necessary to improve sensitivity and selectivity of determination. 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 [7–12]. Recently lots of researchers prefer solid phase extraction technique because of its advantages to enrichment, high recovery, simple, rapid, low organic solvent consumption and the ability to combine with different detection techniques in on-line or off-line mode [13]. In solid phase extraction studies, the suitable adsorbent usage is a critical factor to get high enrichment efficiency [14]. Since its discovery in 1991, carbon nanotubes (CNTs) have become attractive materials due to their novel structure characteristics [15–19]. The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface are having strong interactions with molecules or ions. The large surface areas make them a promising solid sorbent for preconcentration procedures [20–22]. They can be visualized as a graphite sheet rolled up into a cylinder, with either a singlewalled or a multiwalled structure [16]. Tarley et al. [23] reported that the use of multiwalled carbon nanotubes (MWNTs) loaded simple flow injection mini column preconcentration system for determination of cadmium. Liang et al. [24,25] have used MWNTs for preconcentration of cadmium, copper, and rare earth elements [26]. The effects of dimensions of MWNTs on its enrichment efficiency of lead, cadmium, copper and zinc ions have been investigated by El-Sheikh et al. [27]. Pseudomonas aeruginosa immobilized MWNTs have been used as biosorbent for cobalt, cadmium, lead, manganese, chromium and nickel ions by Tuzen et al. [28]. Tuzen et al. [29] have used MWNTs as solid phase extractor for copper, cadmium, lead, zinc, nickel and cobalt ions as ammonium pyrrolidine dithiocarbamate chelates. Study of a speciation procedure based on adsorption of Cr(VI)-APDC chelates on MWNTs for environmental samples was achieved by Tuzen et al. [30].

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In the presented work, the analytical potential of MWNTs as an adsorbent for the preconcentration of traces heavy metals copper, cobalt, nickel and lead ions as their o-cresolphthalein complexone chelates was investigated. The procedure, using a solid phase extraction column loaded with MWNTs as sorbent, for the preconcentration of traces of understudy metals in water samples prior to their determination by FAAS.

2. Experimental

2.1. Instrumentation

The analysis was carried out using a PerkinElmer Model 3110 (Norwalk, CT, USA), equipped with a flame burner. Operational parameters for metals understudy, including lamp currents and wavelength were those recommended by the manufacturer. All metals were measured under optimised operating conditions by FAAS with an air–acetylene flame. The pH values in the aqueous phase were measured with a Sartorius PT-10 model (Göttingen, Germany) pH meter.

2.2. Reagents

Ultrapure water was used throughout the work. All chemicals were of analytical reagent grade unless otherwise stated. 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 Cu(II), Co(II), Ni(II) and Pb(II) ions were prepared from high purity compounds, supplied by E. Merck (Darmstadt, Germany). The working standard solutions were prepared by diluting stock standard solution.

The following buffers were used to control the pH of the solutions: o-H_3PO_4–$NaH_2PO_4 \cdot 2H_2O$ (pH 2–3), CH_3COONH_4–CH_3COOH (pH 4–6), CH_3COONH_4 (pH 7), NH_4Cl–NH_3 (pH 8–10).

Multiwalled carbon nanotube (Aldrich Milwaukee, WI, USA, no.: 636614) was purchased from Aldrich, 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. Certified Standard reference material (NWRI, HR 1 (Humber river sediment)) was used in the experiments. A solution of o-cresolphthalein complexone (Aldrich Milwaukee, WI, USA, no: P5631) (0.05%, w/v) was prepared by dissolving the sufficient amounts of o-cresolphthalein complexone in 40% ethanol.

2.3. Preparation of the column

Two hundred milligrams of MWNT was loaded into a $10 \, mm \times 150 \, mm$ glass column with a glass frit resin support after washing with $2 \, mol \, l^{-1}$ HNO_3 and water successively. The thickness of resin bed was approximately 1.5 cm. Before each use, $2 \, mol \, l^{-1}$ HNO_3 solution and water were passed through the column in order to clean it. Then, the column was conditioned to the desired pH values with buffer solutions. The column was conditioned with distilled water during the passing time for the next experiment.

2.4. General preconcentration procedure

The desired mass of MWNT was loaded into the column and preconditioned as described in Section 2.3. A portion of aqueous sample solution containing Cu, Co, Ni and Pb was prepared, and then o-cresolphthalein complexone was added to form the metal-o-cresolphthalein complexone chelates. After that, the solutions were adjusted to the desired pH values and passed through the column gravitationally. Subsequently, metal ions retained on the MWNT, were eluted with the desired volume and concentration
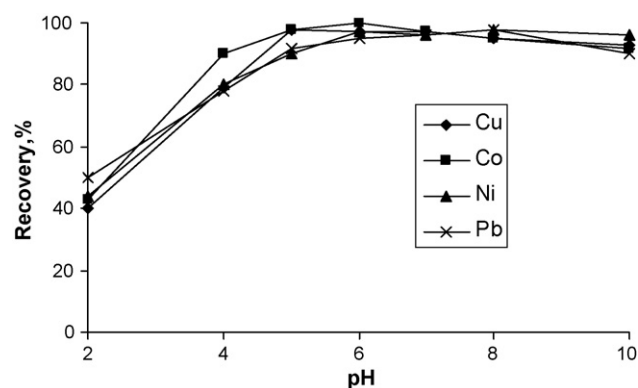

Fig. 1. Effect of pH on the recoveries of the metal ions on multiwalled carbon nanotubes ($N = 3$, eluent: $2.0 \, mol \, l^{-1}$ HNO_3, amount of adsorbent: 200 mg).
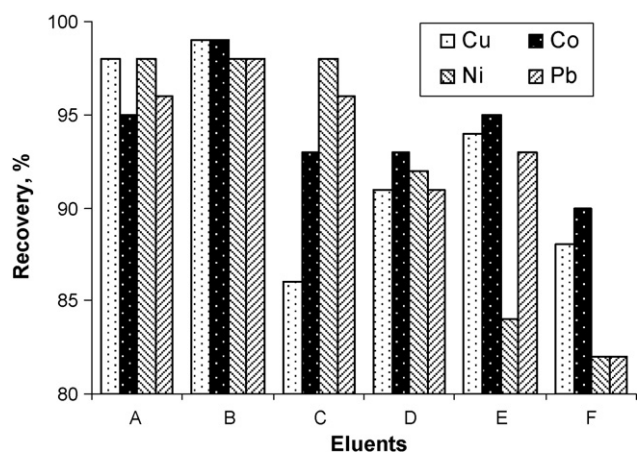

Fig. 2. Influences of some eluents on the recoveries of analyte ions (A: $1 \, mol \, l^{-1}$ HNO_3, B: $2 \, mol \, l^{-1}$ HNO_3, C: $3 \, mol \, l^{-1}$ HNO_3, D: $1 \, mol \, l^{-1}$ HCl, E: $2 \, mol \, l^{-1}$ HCl, F: $3 \, mol \, l^{-1}$ HCl).

of eluent. The eluent was analyzed for the determination of metal concentrations by flame atomic absorption spectrometry.

2.5. Application to real samples

The proposed method was applied to different water samples including tap, sea, spring and mineral water samples. The samples collected in polyethylene bottles were filtered through a cellulose membrane filter (Millipore) of $0.45 \, \mu m$ pore size. The pH of the samples was adjusted to 7.0 with buffer solution. Then
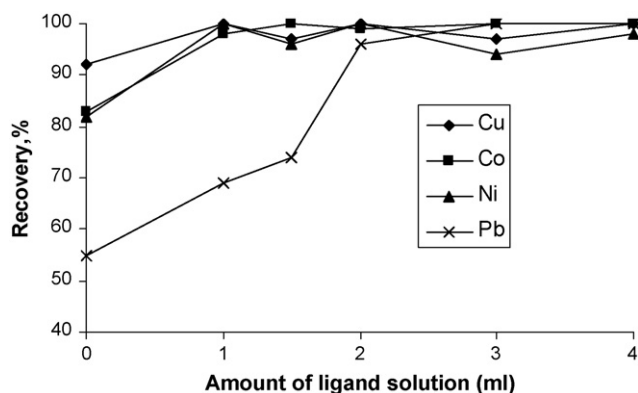

Fig. 3. Effect of amount of ligand solution on the recoveries of analytes on multiwalled carbon nanotubes (0.05%, w/v, $N = 3$, pH 7.0).
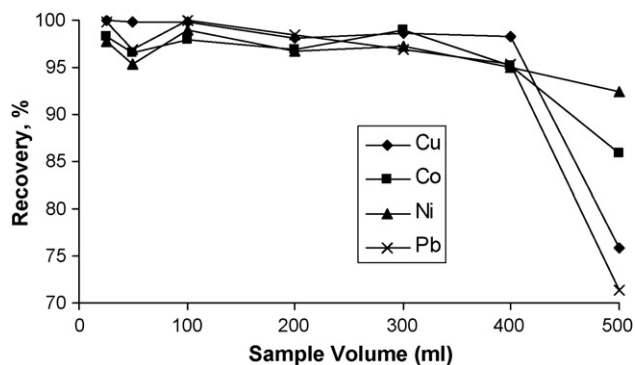
Fig. 4. Effect of sample volume on the recoveries of analytes ($N = 3$, pH 7.0).

the preconcentration procedure as given above was applied to understudy water samples. The analyte concentrations in the samples were determined by flame atomic absorption spectrometry.

To validate the presented method, another application was performed to a standard reference material of HR 1. In order to digest CRM, triplicate sample of (250 mg) were weighed and placed into an Erlenmeyer flask, 15 ml of HNO_3 (65%) and 5 ml of HCl (37 %) were added and heated for 1 h at 150 °C. This process was repeated twice. After the solubilization was completed, the extra acid was evaporated to dryness. The digested sample was dissolved in distil water and were filtered through a blue band filter paper, then diluted up to 50.0 ml with distilled water in volumetric flask. Then the procedure given above was applied. A blank digest was carried out in the same way.

3. Results and discussion

3.1. Effect of pH on sorption

The pH value plays an important role for the quantitative recoveries of the metal ions during the solid phase extraction procedure [28–34]. In order to evaluate the effect of pH values on the recoveries of Cu(II), Co(II), Ni(II) and Pb(II) as o-cresolphthalein complexone

Table 2
The results for NWRI reference material of HR 1 (Humber river sediment) (sample quantity (g): 0.25, $N = 3$).

Analytes	Certified value ($\mu g\,g^{-1}$)	Found value ($\mu g\,g^{-1}$)	Recovery (%)
Cu	78.5	77.2 ± 1.2[a]	98.3
Co	13.0	12.9 ± 1.6	99.2
Ni	38.5	36.9 ± 2.3	95.8
Pb	144.0	136.3 ± 8.2	94.7

[a] Mean ± standard deviation.

Table 3
The results for the addition-recovery tests for the analyte ions in some real samples ($N = 6$).

Element	Added (μg)	Tap water		Mineral water	
		Found (μg)	Recovery (%)	Found (μg)	Recovery (%)
Cu	0	ND	–	ND	–
	5	5.1 ± 0.1	102	4.8 ± 0.2	96
	10	9.8 ± 0.2	98	10.2 ± 0.4	102
	20	20.0 ± 0.1	100	19.8 ± 0.2	99
Co	0	ND	–	ND	–
	5	4.8 ± 0.3	96	4.8 ± 0.4	96
	10	9.8 ± 0.3	98	9.5 ± 0.8	95
	20	19.2 ± 0.3	96	19.1 ± 0.4	95
Ni	0	ND	–	ND	–
	5	4.9 ± 0.3	98	4.8 ± 0.4	96
	10	9.7 ± 0.3	97	9.7 ± 0.6	97
	20	19.4 ± 0.6	97	19.2 ± 0.4	96
Pb	0	ND	–	ND	–
	5	4.8 ± 0.5	96	5.2 ± 0.6	104
	10	9.6 ± 0.7	96	9.7 ± 0.7	97
	20	19.2 ± 0.7	96	19.2 ± 0.9	96

ND: not detected.

chelates adsorb on multiwalled carbon nanotubes, from sample solutions, were adjusted to a pH range of 2.0–10.0. As shown in Fig. 1, quantitative recoveries (>95%) were obtained for all studied ions at the pH range of 6.0–8.0. All subsequent studies were carried out at pH 7.0 by using CH_3COONH_4 buffer solution.

Table 1
Influences of the matrix ions on the recoveries of the analytes ($N = 3$).

Ion	Concentration ($mg\,l^{-1}$)	Added as	Recovery (%)			
			Cu	Co	Ni	Pb
Na^+	20000	NaCl	98 ± 1	97 ± 2	96 ± 2	95 ± 2
K^+	5000	KCl	95 ± 1	95 ± 2	99 ± 2	97 ± 2
Ca^{2+}	5000	$CaCl_2$	95 ± 1	98 ± 2	95 ± 2	95 ± 2
Mg^{2+}	5000	$Mg(NO_3)_2$	96 ± 1	97 ± 2	95 ± 2	95 ± 2
Cl^-	20000	NaCl	97 ± 1	95 ± 2	96 ± 2	95 ± 2
F^-	1000	NaF	96 ± 3	95 ± 3	95 ± 2	95 ± 2
NO_3^-	3000	KNO_3	96 ± 1	97 ± 2	95 ± 2	95 ± 2
SO_4^{2-}	3000	Na_2SO_4	96 ± 1	95 ± 2	99 ± 2	95 ± 2
PO_4^{3-}	3000	$Na_3PO_4 \cdot 12H_2O$	96 ± 1	98 ± 2	99 ± 2	97 ± 2
CH_3COO^-	1000	CH_3COONa	95 ± 1	97 ± 2	99 ± 2	95 ± 2
HCO_3^-	1000	$KHCO_3$	96 ± 1	97 ± 3	96 ± 2	97 ± 2
HPO_4^{2-}	2500	$Na_2HPO_4 \cdot 12H_2O$	95 ± 1	96 ± 3	96 ± 2	97 ± 2
CO_3^{2-}	2500	Na_2CO_3	96 ± 2	95 ± 2	95 ± 2	97 ± 2
Al^{3+}	50	$Al(NO_3)_3 \cdot 9H_2O$	98 ± 1	95 ± 3	99 ± 2	99 ± 2
Fe^{3+}	2	$FeCl_3$	98 ± 1	99 ± 3	95 ± 2	97 ± 2
Mn^{2+}	50	$MnSO_4 \cdot H_2O$	96 ± 1	100 ± 2	95 ± 2	97 ± 2
Zn^{2+}	5	Zn in powder form	95 ± 1	95 ± 2	95 ± 2	95 ± 2
Cd^{2+}	50	$Cd(NO_3)_2 \cdot 4H_2O$	95 ± 1	98 ± 2	99 ± 2	99 ± 2
Cr^{3+}	2	$Cr(NO_3)_3 \cdot 9H_2O$	95 ± 1	100 ± 2	99 ± 2	95 ± 2
Ni^{2+}	20	$Ni(NO_3)_2 \cdot 6H_2O$	95 ± 1	95 ± 2	–	95 ± 2
Pb^{2+}	20	$Pb(NO_3)_2$	97 ± 1	95 ± 2	99 ± 2	–
Co^{2+}	20	$Co(NO_3)_2 \cdot 6H_2O$	95 ± 1	–	95 ± 2	95 ± 2
Cu^{2+}	20	$Cu(NO_3)_2 \cdot 3H_2O$	–	95 ± 2	96 ± 2	97 ± 2

Table 4
The application of presented method in environmental samples ($N=6$, sample volume: 400.0 ml, final volume: 10.0 ml).

Analytes	Tap water ($\mu g\,l^{-1}$)				Sea water ($\mu g\,l^{-1}$)	Yahyali spring water ($\mu g\,l^{-1}$)	Mineral water ($\mu g\,l^{-1}$)
	Home	Office	Resort	Public garden			
Cu	BDL	3.7 ± 0.3	6.7 ± 0.5	BDL	2.7 ± 0.4	12.9 ± 0.4	3.7 ± 0.6
Co	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Ni	BDL	BDL	BDL	BDL	7.0 ± 1.3	6.0 ± 1.3	BDL
Pb	BDL	BDL	BDL	BDL	4.1 ± 1.7	BDL	BDL

BDL: below the detection limit.

3.2. Effect of eluent type

Various concentrations of HCl and HNO_3 were performed for the eluation of metal-*o*-cresolphthalein complexone chelates from multiwalled carbon nanotubes. The results obtained are given in Fig. 2. It was found that $2\,mol\,l^{-1}$ HNO_3 was sufficient for quantitative elution (>95%). The effect of eluent volume (2–10 ml) on the recoveries was studied by using $2\,mol\,l^{-1}$ HNO_3. Quantitative recoveries were obtained for all analyte ions with 10.0 ml of $2\,mol\,l^{-1}$ HNO_3. Therefore, 10.0 ml of $2\,mol\,l^{-1}$ HNO_3 was used as eluent in the following experiments.

3.3. Effect of amount of ligand solution

o-Cresolphthalein complexone is a ligand for metal ions, it was used in literature for this purpose [35,36]. The amount of ligand is also an important factor for the quantitative recoveries of analyes in solid phase extraction processes [37–42]. Different amounts of *o*-cresolphthalein complexone solution (0.05%, w/v), ranging 0.0–4.0 ml, were examined to investigate the optimum amount of ligand solution on the quantitative recoveries of analytes on multiwalled carbon nanotubes. The results are given in Fig. 3. The recoveries were quantitative for all analytes in the range of 2.0–4.0 ml. Due to this data, all the studies were carried out at a ligand amount of 2.0 ml.

3.4. Effect of the sample volume

In order to investigate the possibility of enrichment of trace quantities of understudy analytes, the effect of sample volume on the recovery of metal ions was also studied by passing 25.0–500.0 ml of sample solutions. The results are shown in Fig. 4. At the higher volumes then 400 ml, the recoveries for analytes were not quantitative. The preconcentration factor for simultaneous preconcentration and extraction is calculated by the ratio of the highest sample volume for each analytes (400 ml) and the lowest final eluent volume (10 ml). In present study the possible preconcentration factor was 40.

3.5. Effect of divers ions

The effect of common coexisting ions on the recoveries of the analyte ions on multiwalled carbon nanotubes was also investigated. The experimental results are summarized in Table 1. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and

Table 5
Comparative data from some recent studies using multiwalled carbon nanotubes as solid phase extractor.

Analytes	System	Medium	Eluent	PF	LOD	Reference
Cd^{2+}	On-line coupling of a flow preconcentration system using multiwalled carbon nanotubes	pH 4.9	$0.5\,mol\,l^{-1}$ HCl	51	$11.4–38.1\,ng\,l^{-1}$	[23]
Cu^{2+}	Multiwalled carbon nanotubes/microcolumn	pH 6.0	$0.5\,mol\,l^{-1}$ HCl	150	$0.42\,ng\,ml^{-1}$	[24]
Cd^{2+}, Cu^{2+}	Multiwalled carbon nanotubes/flow injection on-line microcolumn coupled with flame atomic absorption spectrometry	pH 6.0	$0.5\,mol\,l^{-1}$ HCl	24–25	$0.11–0.30\,\mu g\,l^{-1}$	[25]
Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}	Multiwalled carbon nanotubes with different dimensions/cartridge	pH 9.0	$1.0\,mol\,l^{-1}$ HNO_3	20	$0.278–0.867\,ng\,ml^{-1}$	[27]
Co^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Cr^{3+}, Ni^{2+}	Pseudomonas aeruginosa immobilized multiwalled carbon nanotubes as biosorbent/column	pH 9.0	$1.0\,mol\,l^{-1}$ HNO_3	50	$0.24–2.60\,\mu g\,l^{-1}$	[28]
Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}	Multiwalled carbon nanotubes/ammonium pyrrolidine dithiocarbamate (APDC)/column	pH 2.0	$1.0\,mol\,l^{-1}$ HNO_3 in acetone	80	$0.30–0.60\,\mu g\,l^{-1}$	[29]
Cr^{6+}	Multiwalled carbon nanotubes/speciation/ammonium pyrrolidine dithiocarbamate (APDC) and oxidation of Cr^{3+}/column	pH 2.0	$1.0\,mol\,l^{-1}$ HNO_3	100	$0.90\,\mu g\,l^{-1}$	[30]
Cd^{2+}, Mn^{2+}, Ni^{2+}	Multiwalled carbon nanotubes/self made polytetrafluoroethylene (PTFE) microcolumn	pH 8.0	$0.5\,mol\,l^{-1}$ HNO_3	25	$21.0–48.0\,ng\,l^{-1}$	[33]
Co^{2+}	Multiwalled carbon nanotubes oxidized with concentrated HNO_3/1-(2-pyridylazo)-2-naphtol (PAN)/column	pH 7.0	$0.5\,mol\,l^{-1}$ HNO_3	300	$0.55\,ng\,ml^{-1}$	[34]
Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}	Multiwalled carbon nanotubes/*o*-cresolphthalein complexone/column	pH 7.0	$2.0\,mol\,l^{-1}$ HNO_3	40	$1.64–5.68\,\mu g\,l^{-1}$	Present work

LOD: limit of detection, PF: preconcentration factor.

determination of analytes. It was observe that the presence of ions normally present in natural water do not interfere under the experimental conditions applied.

3.6. Flow rates of sample and eluent solutions

The flow rate of the sample play role in adsorbing on the adsorbent while the flow of eluent solutions affects the recoveries of the analyte ions and duration of complete analysis. Therefore, the effect of the flow rates of sample and eluent solutions were examined under the optimum conditions (pH and eluent type). The flow rate of the sample and eluent solutions had no significant influence on the quantitative recoveries of the analytes at the range of 1.0–4.0 and 1.0–3.0 ml min^{-1}, respectively.

3.7. Detection limits

The detection limits, defined as the concentration equivalent to three times the standard deviation ($N = 10$) of the blank solutions of the presented preconcentration study for Cu, Co, Ni and Pb with a preconcentration factor 40 were 1.64, 5.31, 5.68 and 3.52 μg l^{-1}, respectively.

3.8. Analytical applications

In order to establish the validity of the proposed method, the method was applied to the determination of studied analytes in a standard reference material of HR 1. The results, based on the average of three replicates, are presented in Table 2. As can be seen, the results are in good agreement with reference values.

The proposed method was applied to the determination of analytes in tap water and mineral water samples. The recoveries of spikes of the analytes were also studied. The results are given in Table 3. These good results confirm the validity of the presented method. Also, the real environmental water sample applications were carried out by the proposed solid phase extraction procedure and the results are shown in Table 4.

4. Conclusion

This work has demonstrated the feasibility of the developed solid phase extraction method based on adsorption of copper, cobalt, nickel and lead ions as their *o*-cresolphthalein complexone chelates on multiwalled carbon nanotubes prior to their atomic absorption spectrometric determinations. The method was simple, easy and also rapidly applied for environmental samples including natural water. The validity of the proposed method using certified reference material of river sediment, proved its application. The comparison of the results found in the present study and some recent studies using multiwalled carbon nanotubes as solid phase extractor [29–33] was given in Table 5. Our method is simple, fast and preconcentration factor is relatively higher then the methods in literature. The system was used for 50 subsequent preconcentration cycles without any loss on the adsorption properties of multiwalled carbon nanotubes all throughout of the work.

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