

Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes

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Abstract

Multiwalled carbon nanotubes (MWNTs) were used as solid phase extractor for Cu(II), Cd(II), Pb(II), Zn(II), Ni(II) and Co(II) ions as ammonium pyrrolidine dithiocarbamate (APDC) chelates, in the present study. The influences of the experimental parameters including pH of the solutions, amounts of MWNTs, amounts of APDC, eluent type and volume, sample volume etc. on the quantitative recoveries of analyte ions were investigated. The effects of matrix ions of natural waters and some transition metals on the recoveries of the analyte ions were also examined in the model solutions. Tests of addition/recovery for analyte ions in real samples were performed with satisfactory results. The detection limits (3 s) for the analyte ions were in the range of 0.30–0.60 $\mu\text{g l}^{-1}$. The concentrations of analytes in standard reference materials (NIST RM 8418 Wheat gluten, LGC 6010 Hard drinking water and NIST SRM 1515 Apple leaves) pretreated by the presented method were measured with FAAS and the analytical values were well agreed with the certified values and the reference values without the interference of major components. The presented method has been applied to the determination of analytes in food and environmental samples with satisfactory results.

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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 interferences 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

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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 the presented paper, a preconcentration–separation procedure for traces heavy metal ions as their ammonium pyrrolidine dithiocarbamate chelates on multiwalled carbon nanotubes. The conditions for quantitative and reproducible preconcentration, elution and subsequent flame atomic absorption spectrometric determination of copper, cadmium, lead, zinc, nickel and cobalt 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 $18.2 \text{ M}\Omega \text{ cm}^{-1}$ conductivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute 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 mg l^{-1} of the given element supplied by Sigma and Aldrich. Stock solutions of diverse elements were prepared from high purity compounds. The calibration standards were not submitted to the preconcentration procedure.

Multiwalled carbon nanotube (Aldrich no.: 636630) was purchased from Aldrich, Milwaukee, WI, USA. The BET surface area and density of nanotubes were $600 \text{ m}^2 \text{ g}^{-1}$ and 2.1 g ml^{-1} , respectively. It has high purity. SEM photograph of multiwalled carbon nanotube is given in Fig. 1.

An ammonium pyrrolidine dithiocarbamate (APDC) solution (0.1%, w/v) was prepared by dissolving the requisite amounts of APDC in water/ethanol (75/25%, v/v). The solution was discharged one day. NIST RM 8418 Wheat gluten, LGC 6010 Hard drinking water and NIST SRM 1515 Apple leaves standard reference materials were used in the experiment.

Phosphate buffer solutions ($\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$) were prepared by mixing of appropriate volumes of 1 mol l^{-1} sodium dihydrogen phosphate and phosphoric acid solutions for pH 2–3. Acetate buffer solutions ($\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$) were prepared by mixing of appropriate volumes of 0.1 mol l^{-1} acetic acid and 0.1 mol l^{-1} sodium acetate solutions for pH 4 and 6. For pH 7, a 250 ml of borate buffer was prepared by use of 2.5 ml of 1 mol l^{-1} HCl and 0.445 g NaBO_2 . Ammonium buffer

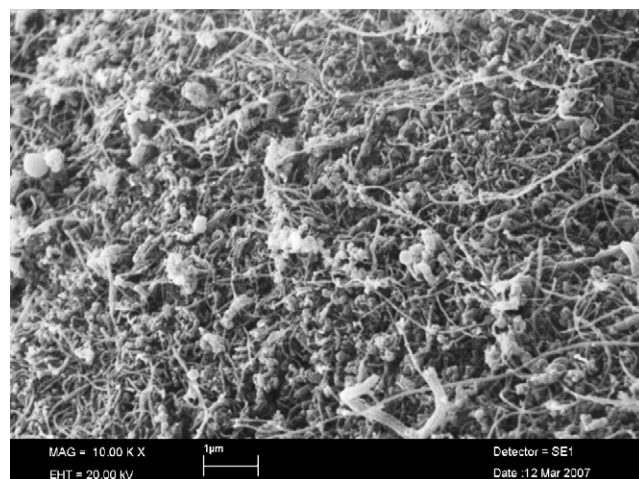


Fig. 1. SEM photograph of multiwalled carbon nanotube.

solution ($\text{NH}_4^+/\text{NH}_3$) was prepared by mixing of appropriate amounts of 0.1 mol l^{-1} ammonia and 0.1 mol l^{-1} ammonium chloride solutions for pH 8.

2.2. Instruments

A Perkin-Elmer AAnalyst 700 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 an air-acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer. SEM image was obtained on a LEO 440 scanning electron microscope (SEM).

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. Digestion conditions for microwave system for standard reference materials, tomato sauce, canned fish, tobacco and chickpea samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min [28–30].

2.3. Column preparation

Three-hundred milligrams of multiwalled carbon nanotubes was loaded after washing acetone, 1 mol l^{-1} HNO_3 solution and water, respectively, into a $10 \text{ mm} \times 100 \text{ mm}$ glass column with a glass frit resin support. The resin bed was approximately 1.5 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 of the eluting solution and of water, subsequently.

2.4. Test procedure

Test solutions containing 5–20 μg of each analytes were adjusted to desired pH. Then APDC was added to form the metal-APDC 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 fin-

ished, the column was washed with 2 ml APDC solution adjusted to the working pH. The metals were recovered with the aid of 10 ml of 1 mol l^{-1} HNO_3 in acetone at 5.0 ml min^{-1} of flow rate. The analyte concentrations in the final solution were determined by flame atomic absorption spectrometry.

2.5. Application to natural water samples

Tap water, spring water, seawater were collected in pre-washed (with detergent, doubly deionized distilled water, dilute HNO_3 and doubly deionized distilled water, respectively) polyethylene bottles.

The water samples including LGC 6010 Hard drinking water were filtered through a cellulose membrane filter (Millipore) of $0.45 \mu\text{m}$ pore size. The pH of the samples was adjusted to 2.0 with buffer solution. Then the preconcentration procedure given above was applied to the samples. The levels of analytes in the samples were determined by flame atomic absorption spectrometry.

2.6. Application to microwave digested samples

NIST SRM 1515 Apple leaves (250 mg) and NIST RM 8418 Wheat gluten standard reference materials (250 mg) were digested with 6 ml of HNO_3 (65%), 2 ml of H_2O_2 (30%) in microwave digestion system and diluted to 50.0 ml with deionized water. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solutions.

In order to digest tomato sauce, canned fish, tobacco and chickpea samples, 1.0 g of sample was digested with 6 ml of concentrated HNO_3 and 2 ml of H_2O_2 in microwave system. After digestion of the samples, the volume of the digested sample was made up to 50.0 ml with distilled water. The blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration procedure given above was applied to the samples.

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 [31–36], the influences of pH of the analyte solutions on the recoveries of Cu(II), Cd(II), Pb(II), Zn(II), Ni(II) and Co(II) as APDC chelates on multiwalled carbon nanotubes were investigated in the pH range 2.0–8.0. The quantitative recoveries (>95%) for copper, cadmium, lead, zinc,

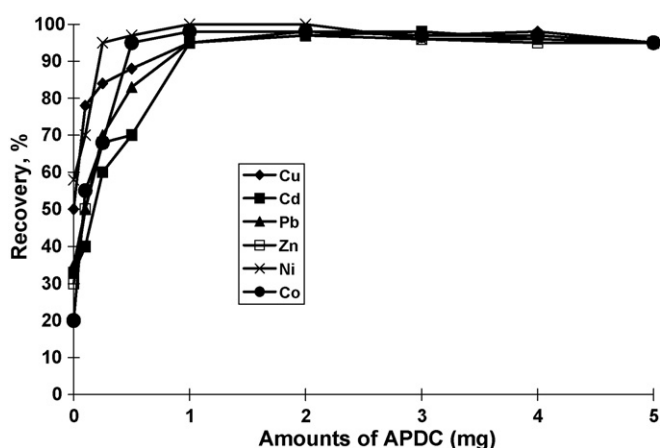


Fig. 2. Effects of amounts of APDC on the recoveries of analytes on multiwalled carbon nanotubes (MWNTs) (pH 2, $N=3$).

nickel and cobalt ions were found at the pH range of 2.0–6.0. The recovery values were decreased after pH 7. At the basic pH values, the recoveries were not quantitative. $\text{p}K_a$ value for ammonium pyrrolidine dithiocarbamate is 3.29 [37]. This value is supported to our quantitative recovery values at the acidic pHs. All subsequent studies were carried out at pH 2.0 by using a phosphate buffer solution. The volume of buffer solution had no effect in the range of 2–10 ml.

3.2. Effects of amounts of APDC

The amounts of the ligand are also an important factor for the quantitative retentions of metal ions in solid phase extraction techniques [38,39]. In order to investigate the optimum amounts of ammonium pyrrolidine dithiocarbamate on the quantitative recoveries of the analyte ions on multiwalled carbon nanotubes, the study was examined by varying the amounts of APDC from 0 to 5.0 mg. The results are given in Fig. 2. The recoveries of analyte ions increased with increasing amounts of APDC added and reached a constant value over 95% with at least 1.0 mg. The recovery values of analytes were quantitative at the amounts of ligand range of 1.0–5.0 mg. On this basis, all the studies were carried out at an APDC amount of 1.0 mg.

3.3. Eluent type and volume

Various eluent solutions were used for desorption of metal-APDC chelates from multiwalled carbon nanotubes. The results were given in Table 1. Quantitative recoveries for analyte ions were obtained only with 1 mol l^{-1} HNO_3 in acetone. As explained by Yang and Jackwerth [40,41], HNO_3 in acetone was found to be the most satisfactory combination in experiments using both APDC. Recoveries were not generally quantitative other eluents used present study with some exceptions shown in Table 1. Our results found in the present work agree with the data given in Yang and Jackwerth [40,41] and in our articles [42,43].

The effect of eluent volume on the recoveries of the analytes was also studied by using 1 mol l^{-1} HNO_3 in acetone; it

Table 1
Effects of eluent type on the recoveries of the analytes (Eluent volume: 10 ml, $N=3$)

Eluent type	Recovery (%)					
	Cu	Cd	Pb	Zn	Ni	Co
0.5 mol l ⁻¹ HCl	20 ± 2 ^a	30 ± 2	25 ± 2	80 ± 2	55 ± 2	15 ± 1
1 mol l ⁻¹ HCl	25 ± 2	37 ± 1	30 ± 3	83 ± 3	62 ± 2	20 ± 1
0.5 mol l ⁻¹ HNO ₃	50 ± 1	45 ± 2	85 ± 3	84 ± 3	80 ± 2	30 ± 2
1 mol l ⁻¹ HNO ₃	60 ± 2	50 ± 3	97 ± 2	92 ± 3	98 ± 3	40 ± 2
1 mol l ⁻¹ HNO ₃ in acetone	98 ± 2	98 ± 3	98 ± 3	100 ± 3	99 ± 3	98 ± 3

^a Mean ± standard deviations.

was found that quantitative recoveries could be obtained with 8.0–10.0 ml of 1 mol l⁻¹ HNO₃ in acetone. Therefore, the volume of 10.0 ml of 1 mol l⁻¹ HNO₃ in acetone was used in the following experiments.

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

The effects of the amounts of multiwalled carbon nanotubes on the adsorption of analytes were investigated at 5.0 ml min⁻¹ flow rates of sample and eluent solutions. The recovery values for analyte ions were found quantitative in the resin amounts of 200–400 mg. In all further studies, the short glass column was filled with 300 mg of MWNTs.

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. The effect of the flow rate of the sample and eluent solutions on the recoveries of Cu(II), Cd(II), Pb(II), Zn(II), Ni(II) and Co(II) on MWNTs was examined in the range of 1.0–10.0 ml min⁻¹. The flow rate of the sample and eluent solutions had no obvious influence on the quantitative recoveries of analytes at the range of 1.0–6.0

and 1.0–7.0 ml min⁻¹, respectively. 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 analytes on MWNTs was investigated by passing 25–500 ml of solutions. The sorption of copper and nickel ions were not affected by sample volume between 25 and 500 ml, while cadmium, lead, zinc and cobalt ions were quantitatively recovered at the range of 25–400 ml. At the higher volumes than 500 ml, the recoveries for analytes were not quantitative. Thus, a sample volume in the range of 25–400 ml for simultaneous preconcentration of six analytes could be used in our procedure. The preconcentration factor for simultaneous preconcentration is calculated by the ratio of the highest sample volume for each analytes (400 ml) and the lowest eluent volume (5 ml). The preconcentration factor was 80.

3.7. Effect of divers ions

The influences of possible matrix ions in the environmental samples and some transition metals on the recoveries of ana-

Table 2
Influences of some foreign ions on the recoveries of analytes ($N=3$)

Ion	Added as	Concentration (mg l ⁻¹)	Recovery (%)					
			Cu	Cd	Pb	Zn	Ni	Co
Na ⁺	NaCl	20000	97 ± 3 ^a	96 ± 3	95 ± 3	96 ± 3	97 ± 3	96 ± 3
K ⁺	KCl	5000	98 ± 2	97 ± 3	97 ± 3	96 ± 2	95 ± 2	95 ± 2
Ca ²⁺	CaCl ₂	5000	97 ± 3	95 ± 3	96 ± 3	98 ± 3	96 ± 3	98 ± 3
Mg ²⁺	MgCl ₂	5000	95 ± 3	96 ± 3	97 ± 3	96 ± 3	97 ± 2	95 ± 3
Cl ⁻	NaCl	30000	96 ± 3	96 ± 2	95 ± 2	96 ± 2	95 ± 2	96 ± 3
F ⁻	NaF	1000	97 ± 3	98 ± 3	98 ± 3	96 ± 3	97 ± 2	98 ± 2
NO ₃ ⁻	KNO ₃	3000	95 ± 2	97 ± 3	97 ± 3	97 ± 3	97 ± 3	96 ± 3
SO ₄ ²⁻	Na ₂ SO ₄	3000	97 ± 3	97 ± 3	96 ± 2	95 ± 2	96 ± 2	95 ± 3
PO ₄ ³⁻	Na ₃ PO ₄	3000	96 ± 3	96 ± 3	97 ± 3	96 ± 2	97 ± 3	98 ± 3
CH ₃ COO ⁻	CH ₃ COONa	1000	96 ± 2	97 ± 3	96 ± 3	95 ± 3	97 ± 3	96 ± 3
HCO ₃ ⁻	NaHCO ₃	1000	97 ± 3	96 ± 3	96 ± 2	95 ± 2	96 ± 2	95 ± 2
Al ³⁺	Al ₂ (SO ₄) ₃	50	98 ± 3	95 ± 2	96 ± 3	97 ± 2	95 ± 3	96 ± 3
Fe ³⁺	FeCl ₃	50	97 ± 2	96 ± 3	97 ± 3	96 ± 3	95 ± 3	96 ± 3
Mn ²⁺	MnSO ₄	50	96 ± 3	97 ± 3	95 ± 3	96 ± 3	95 ± 3	97 ± 3
Ag ⁺	AgNO ₃	50	95 ± 3	96 ± 2	95 ± 3	96 ± 2	96 ± 3	95 ± 2

^a Mean ± standard deviations.

Table 3
The results for reference standard materials ($N=4$)

Element	LGC 6010 Hard drinking water ($\mu\text{g l}^{-1}$)		NIST SRM 1515 Apple leaves ($\mu\text{g g}^{-1}$)		NIST RM 8418 Wheat gluten ($\mu\text{g g}^{-1}$)	
	Certified value	Our value	Certified value	Our value	Certified value	Our value
Cu	–	BDL	5.64	5.80 ± 1.2^a	5.94	5.98 ± 0.45
Cd	–	BDL	(0.013) ^b	0.015 ± 0.001	0.064	0.062 ± 0.005
Pb	97	93.5 ± 4.2	0.47	0.45 ± 0.04	0.1	0.15 ± 0.01
Zn	590	570 ± 20	12.5	12.8 ± 0.9	53.8	57.5 ± 2.7
Ni	51	49.6 ± 2.5	0.91	0.89 ± 0.05	0.13	0.16 ± 0.01
Co	–	BDL	(0.09) ^b	0.10 ± 0.01	0.01	BDL

BDL: below the detection limit.

^a Mean expressed as 95% tolerance limit.

^b The values in the parentheses are not certified.

lytes on multiwalled carbon nanotubes were also examined. A 50 ml portion of sample solution containing analytes and a given amounts of foreign ions were concentrated. The experimental results are shown in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the preconcentration and determination of analytes. The ions normally present in natural waters do not interfere under the experimental conditions used. Some of the transition metals given in Table 2 at mg l^{-1} levels were not interfered on the recoveries of the analyte ions on MWNTs. This results show that the proposed preconcentration/separation method could be applied to the highly saline samples and the samples that contains some transition metals at mg l^{-1} levels.

3.8. Adsorption capacity

In order to study the adsorption capacity of multiwalled carbon nanotubes, 0.1 g MWNTs was added 50 ml of solution

containing 1.0 mg of metal ion at pH 2.0. 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 MWNTs for analytes was found as: Cu: 8.4 mg g^{-1} , Cd: 9.5 mg g^{-1} , Pb: 10.3 mg g^{-1} , Zn: 14.2 mg g^{-1} , Ni: 8.9 mg g^{-1} and Co: 7.3 mg g^{-1} . The stability of multiwalled carbon nanotubes was excellent. On storing for six mounts its properties and sorption capacity do not change significantly. The adsorption of metal-APDC chelates is related with the physical interaction of the surface of the nanotubes and the metal-APDC chelates.

3.9. Limit of detections

The detection limit (LOD) of the presented solid phase extraction study was calculated under optimal experimental conditions after application of the preconcentration procedure to

Table 4
The application of the presented procedure for natural water samples ($N=4$)

Element	Added ($\mu\text{g l}^{-1}$)	Tap water		Spring water		Sea water	
		Found ($\mu\text{g l}^{-1}$)	Recovery (%)	Found ($\mu\text{g l}^{-1}$)	Recovery (%)	Found ($\mu\text{g l}^{-1}$)	Recovery (%)
Cu	–	4.6 ± 0.3^a	–	1.6 ± 0.1	–	1.7 ± 0.1	–
	5	9.3 ± 0.5	97	6.3 ± 0.4	95	6.4 ± 0.5	96
	10	14.2 ± 0.9	97	11.1 ± 0.8	96	11.3 ± 0.4	97
Cd	–	1.5 ± 0.1	–	2.4 ± 0.2	–	1.2 ± 0.1	–
	5	6.2 ± 0.3	95	7.1 ± 0.4	96	5.9 ± 0.3	95
	10	11.2 ± 0.7	97	16.8 ± 0.6	98	10.8 ± 0.5	96
Pb	–	9.9 ± 0.5	–	13.3 ± 0.7	–	3.3 ± 0.2	–
	5	14.2 ± 0.9	95	17.9 ± 0.6	98	8.1 ± 0.5	98
	10	19.4 ± 0.8	97	22.7 ± 0.9	97	12.9 ± 0.7	97
Zn	–	8.4 ± 0.8	–	9.3 ± 0.6	–	4.9 ± 0.2	–
	5	13.1 ± 0.9	98	13.9 ± 0.5	97	9.5 ± 0.5	96
	10	17.9 ± 0.8	97	18.8 ± 0.8	97	14.4 ± 0.7	97
Ni	–	6.6 ± 0.3	–	5.9 ± 0.4	–	12.1 ± 1.2	–
	5	11.2 ± 0.5	97	10.4 ± 0.6	95	16.7 ± 1.1	98
	10	16.1 ± 0.4	97	15.3 ± 0.5	96	21.6 ± 1.4	98
Co	–	2.4 ± 0.2	–	5.1 ± 0.3	–	6.5 ± 0.4	–
	5	7.1 ± 0.3	96	9.9 ± 0.4	98	11.1 ± 0.6	97
	10	12.1 ± 0.5	98	14.7 ± 0.8	97	16.2 ± 0.8	98

^a Mean \pm standard deviations.

Table 5
The application of presented method in real samples for contents of analyte ions ($N=4$)

Element	Tomato sauce ($\mu\text{g g}^{-1}$)	Canned fish ($\mu\text{g g}^{-1}$)	Tobacco ($\mu\text{g g}^{-1}$)	Chickpea ($\mu\text{g g}^{-1}$)
Cu	3.4 ± 0.2^a	0.95 ± 0.06	6.1 ± 0.5	3.4 ± 0.2
Cd	0.35 ± 0.03	0.19 ± 0.02	0.49 ± 0.03	0.20 ± 0.02
Pb	0.36 ± 0.02	0.56 ± 0.04	1.9 ± 0.1	1.2 ± 0.1
Zn	35.8 ± 2.2	25.1 ± 1.5	18.9 ± 1.4	19.5 ± 1.3
Ni	1.9 ± 0.2	2.6 ± 0.2	3.9 ± 0.2	1.1 ± 0.1
Co	1.8 ± 0.1	0.87 ± 0.06	0.95 ± 0.08	0.36 ± 0.03

BDL: below the detection limit.

^a Mean expressed as 95% tolerance limit.

blank solutions. The detection limits, defined as the concentration equivalent to three times the standard deviation ($N=13$) of the reagent blank were found as: Cu: $0.30 \mu\text{g l}^{-1}$, Cd: $0.45 \mu\text{g l}^{-1}$, Pb: $0.60 \mu\text{g l}^{-1}$, Zn: $0.35 \mu\text{g l}^{-1}$, Ni: $0.57 \mu\text{g l}^{-1}$ and Co: $0.40 \mu\text{g l}^{-1}$.

3.10. Applications of the presented procedure

The method was applied to NIST RM 8418 Wheat gluten and NIST SRM 1515 Apple leaves standard reference materials after microwave digestion and also applied to LGC 6010 Hard drinking water. The results were given in Table 3. The results are in good agreement with the certified values for the analytes.

Table 7
Comparative data from some recent studies on preconcentration

Analytes	System	Eluent	Preconcentration factor	Detection limit ($\mu\text{g l}^{-1}$)	R.S.D. (%)	Reference
Pb	Octadecyl bonded silica membrane disk modified with Cyanex302	$1 \text{ mol l}^{-1} \text{ HNO}_3$	400	1.0	0.4	[1]
Co, Cu, Ni, Zn, Cd	Activated carbon/2-([1-(2-hydroxynaphthyl)methylidene] amino) benzoic acid (HNMABA)	$1 \text{ mol l}^{-1} \text{ HNO}_3$ in acetone	100–310	0.75–3.82	<5	[9]
Pb, Ni, Cu, Mn	Amberlite XAD 7/sodium bispiperidine-1,1'-carbottetrathioate (Na-BPCTT)	$1 \text{ mol l}^{-1} \text{ HNO}_3$	50	2.8×10^{-6} – $3.6 \times 10^{-6} \text{ g ml}^{-1}$	<3	[13]
Cu, Cd, Pb, Zn, Mn, Fe, Cr, Ni, Co	Chromosorb 108/bathocuproinedisulfonic acid	$2 \text{ mol l}^{-1} \text{ HNO}_3$	80	0.16–0.60	1–17	[28]
Cd, Cu	Amberlite XAD-2/2-aminothiophenol	$0.5 \text{ mol l}^{-1} \text{ HCl}$	14–28	0.14–0.54	<5	[44]
Mn	Naphthalene/1-(2-pyridylazo)-2-naphthol (PAN)	Dimethylformamide	20	5	3.8	[45]
Cd, Cu, Co, Fe, Pb, Ni, Zn	Diaion HP-2MG/dithizone	$2 \text{ mol l}^{-1} \text{ HNO}_3$ in acetone	375	0.08–0.25	<9	[46]
Cu, Cd, Pb, Zn, Ni, Co	Multiwalled carbon nanotubes/ APDC	$1 \text{ mol l}^{-1} \text{ HNO}_3$ in acetone	80	0.30–0.60	<5	Present work

Table 6
Optimum preconcentration conditions in experimental studies

Parameters	Optimum conditions
pH	2–6
Eluent type	$1 \text{ mol l}^{-1} \text{ HNO}_3$ in acetone
Eluent volume (ml)	8
Amount of ligand (mg)	1–5
Flow rate of sample (ml min^{-1})	1–6
Flow rate of eluent (ml min^{-1})	1–7
Nanotube amount (g)	0.2–0.4
Sample volume (ml)	25–500 For copper and nickel, 25–400 for cadmium, lead, zinc and cobalt
Enrichment factor	80

The procedure presented was also applied to the determination of analytes in natural water samples. Various amounts of analytes were also spiked to these water samples. The results were given 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 copper, cadmium, lead, zinc, nickel and cobalt ions in both spiked and water samples.

Also the application of the proposed solid phase extraction procedure for the determination of analyte ions was performed to the microwave digested environmental samples. The results were given in Table 5.

4. Conclusion

Multiwalled carbon nanotubes were used as solid phase extractor for heavy metal ions at trace levels in the presented paper. The conditions for quantitative and reproducible preconcentration, elution and FAAS determinations were studied. Under conditions given in Table 6, the determination of Cu(II), Cd(II), Pb(II), Zn(II), Ni(II) and Co(II) yields quantitative recoveries on MWNTs. The method is simple, accurate can be applied for the determination of analytes in environmental samples. The comparison of the results found in the presented study and some works in literature was given in Table 7. The system showed reproducibility and reliability in analytical data, with an R.S.D. value of lower than 5% on triplicate experiment. Three-hundred milligrams of multiwalled carbon nanotubes can be used as high as greater than 250 experiments without any loss in its sorption behavior.

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