Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry

Mehrorang Ghaedi *, Farshid Ahmadi, Ardeshir Shokrollahi

Chemistry Department, Yasouj University, Yasouj 75914-353, Iran

Abstract

A sensitive and simple method for the simultaneous preconcentration of nutritionally important minerals in real samples has been reported. The method is based on the formation of metal complexes by 4,6-dihydroxy-2-mercaptopyrimidine (DHMP) loaded on activated carbon. The metals content on the complexes are then eluted using 5 mL 2 M HNO_3 in acetone, which are detected by AAS at resonance line. In this procedure, minerals such as Cu, Ni, Pb and Co could be analyzed in one run by caring out the simultaneous separation and quantification of them. At optimum condition the response are linear over concentration range of 0.04–1.1 $\mu g\,mL^{-1}$ for Ni^{2+} and 0.04–1.0 $\mu g\,mL^{-1}$ for Cu^{2+}, Pb^{2+} and Co^{2+}. The detection limits of each element are expressed as the amount of analytes in $ng\,mL^{-1}$ giving a signal to noise ratio of 3 are equal to 3.5, 3.4, 2.9 and 8.4 for Ni^{2+}, Co^{2+}, Cu^{2+} and Pb^{2+}. The sorption capacity was determined by saturating 0.5 g solid phase. The loading capacity are 0.54, 0.53, 0.63 and 0.45 $mg\,g^{-1}$ for Ni^{2+}, Co^{2+}, Cu^{2+} and Pb^{2+}. The ability of method for repeatable recovery of trace ion are 99.0, 98.9, 99.2 and 98.8 with R.S.D. of 1.4, 1.3, 1.2 and 1.4 for Ni^{2+}, Co^{2+}, Cu^{2+} and Pb^{2+}. The low detection limits of these elements in this technique make it a superior alternative to UV–vis and in several applications, also an alternative to ICP-MS techniques. The method has been successfully applied for these metals content evaluation in some real samples including natural water, leaves of spinach and cow liver.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Heavy metal; 4,6-Dihydroxy-2-mercaptopyrimidine (DHMP); Atomic absorption spectrometry; Activated carbon

1. Introduction

In the analysis of trace metal ions present in various samples such as natural and waste water, biological and alloy samples, the direct determination with various instrumental methods is not possible owing to matrix effect and low concentration of metal ions in a sample. In trace analysis, therefore, a preconcentration and/or separation of trace elements from the matrix are frequently necessary to improve the detection limit and selectivity.

Various techniques have been applied for the determination of trace heavy metals in aqueous samples. Direct instrumental analysis of these samples is difficult because of complex formation and significant matrices, which invariably influence normal instrumental analysis. In addition, some metals have low concentrations, which are near or below the limit of detection of the

instrument. However, the low level of trace elements in drinking waters is not compatible with the detection limit of AAS. Preconcentration can solve the above two problems and leads to simplified heavy metal determination.

There are many methods of preconcentration, including co-precipitation, solvent extraction, electrochemical deposition, membrane extraction, and solid phase extraction.

Solid phase extraction has several advantages over other separation techniques in view of: (i) trace and major concentrations of trace ions present in hazardous samples can be removed with equal ease; (ii) higher enrichment factors; (iii) reusability of the adsorbent; (iv) absence of emulsion; (v) minimal costs due to low consumption of reagents; (vi) ease of automation; (vii) environmental friendly; (viii) safety with respect to hazardous samples. Accordingly, several solid phase extractants have been employed for enrichment of traces of elements from dilute solutions. A number of supports and chelating ligands have been widely used in the design of chelating resins for the preconcentration and separation of trace metal ions from various matrices. The most prominent among the sup-

* Corresponding author. Tel.: +98 741 2223048; fax: +98 741 2223048.
 E-mail address: m_ghaedi@mail.yu.ac.ir (M. Ghaedi).
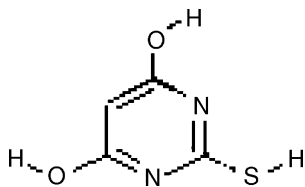
Scheme 1. Schematic diagram of 4,6-dihydroxy-2-mercaptopyrimidine structures.

ports used are Amberlite XAD resins [1], activated carbon, [2], SDS coated alumina [3], modified chromosorb [4] and sepiolite [5].

Among them activated carbon, which are characterized by high adsorption capacity, allowing application under broad pre-concentration conditions has widespread application for trace element preconcentration. Metal ions to be preconcentrated on activated carbon as a hydrophobic adsorbent need to be transformed corresponding metal chelates or precipitate [6–12] or metal hydroxides [13], which could be adsorbed on activated carbon. Metal chelates could provide higher selectivity and high enrichment factors for such a preconcentration and separation. The mechanism involved in the adsorption of ions as trace compounds by activated carbon is not completely known. The mechanism of sorption is still under investigation and the adsorption of heavy metals on AC could be explained using Langmuir and Freundlich equations. It was assumed that the sorption is quantitative when the chelate contains systems of π-electrons in the molecule and when the centers for binding on carbon and those for the metal ions are spatially separated so that their orbital do not have a substantial influence [14]. The major advantage of these models is their simplicity; however, the models fail to describe accurately the adsorption equilibrium under varying conditions, such as pH and ionic strength. The adsorption equilibrium studies have revealed that pH is the dominant parameter controlling the adsorption [15]. Therefore, activated carbon (AC) has been used as a collector, permitting the pre-concentration and separation of low levels of analytes in several matrices [16–24]. As shown in Scheme 1, due to the existence of a donating nitrogen atom as well as =S (SH) group and =O (OH) group and NH group in DHMP was expected to increase both the stability and selectivity of its complex toward ions including copper, nickel, cobalt and lead ion over other metal ions, especially alkali and alkaline earth cations. It is occurred to us that the presence of some constituents with non-cyclic sulfur-containing ligand in addition to nitrogen and oxygen in addition to the π-electrons results in selective interaction with these ions

while oxygen atoms of the ligands mostly interact with this ion as a soft acid through ion–dipole interactions and soft atoms such sulfur and nitrogen through soft–soft interaction, while all resulting in fast complexation and higher sensitivity.

Here authors report a method for preconcentration of trace elements, viz., Co, Ni, Cu, and Pb on a activated carbon modified with DHMP. The sorbed elements were eluted with 5 mL, 2 mol L^{-1} HNO$_3$. The effluents were further analyzed by AAS for evaluating their metals content.

2. Methods and materials

2.1. Reagents

Acids and bases were of the highest purity available from Merck and used as received. Doubly distilled deionized water was used throughout. Analytical grade nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, barium, sodium and potassium (all from Merck) were of the highest purity available and used without any further purification. The ligand 4,6-dihydroxy-2-mercaptopyrimidine (DHMP) was purchased from Merck Company. The pH 6.0 was adjusted by addition of appropriate amount of dilute nitric acid or potassium hydroxide to solutions. Activated carbon powder (Merck) was treated with 20% nitric acid, washed with de-ionized water and oven-dried at 110 °C.

2.2. Instruments

The evaluation of ions content were carried out on a Shimadzu 680 A or a Perkin-Elmer 603 atomic absorption spectrometer with a hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air–acetylene flame. The conditions for FAAS determination of these ions are presented in Table 1. A Metrohm 691 pH/Ion meter with a combined glass–calomel electrode was used for adjustment of test solution pH. A Shimadzu UV–vis 160 spectrophotometer has been used for measuring spectrophotometric data.

2.3. Preparation of DHMP coated activated carbon

SPE tubes and frits were soaked in 1% nitric acid overnight and then washed with water. A Pyrex glass column containing 0.5 g of activated carbon in water suspension was 40 cm long and 0.75 cm in internal diameter. The bed height in the column was approximately 1 cm. The AC (500 mg) was impregnated with DHMP by percolating 2 mL of 1% (w/v) DHMP

Table 1
Hollow cathode lamp conditions and flame conditions for FAAS

Element	Slit (nm)	Wavelength (nm)	Lamp current (mA)	Flow rate of flame gases (L min^{-1})	
				Air	Acetylene
Cu	0.5	324.8	3	8.0	1.8
Co	0.2	240.7	8	8	2.2
Ni	0.2	232.0	4	8	1.7
Pb	1.0	283.3	5	8.0	2.0

(20 mg) solution through the column packed with AC at a flow rate of 0.2 mL min^{-1}. The filtrate was collected and analyzed for un-adsorbed DHMP with the UV–vis spectrophotometer at 280 nm. The column was then washed twice with 5 mL water and the filtrates were analyzed for DHMP that was released. The retained amount of DHMP on the AC column was 110 mg g^{-1}.

2.4. Pretreatment of real samples

2.4.1. Digestion of leaves of spinach

Leaves of spinach were purchased from Gachsaran Iran. Afterwards, they dried and were taken in small mesh. A 40 g leaves of spinach was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3 mL 30% H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 2–4 mL 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 6.0 made up to 250 mL by addition of diluted KOH. The dissolved solution was suitably diluted and metals concentration was determined after suitable preconcentration using AAS.

2.4.2. Determination of metal ions in water samples

Water samples were collected from spring water Tangari spring, Yasouj, Iran and Beshar River, Yasouj, Iran; tap water and wastewater are collected from Gachsaran, Iran. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm. The organic content of the water samples were oxidized in the presence of 1% H_2O_2 and addition of concentrated nitric acid. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles. For the preconcentration procedure, pH of the 800 mL of water samples was adjusted to 6 and the sample passed through the column at flow rate of 6 mL min^{-1}. The metals, which retained on activated carbon by complexation with DHMP loaded on AC, were eluted with 5 mL of 2 mol L^{-1} HNO$_3$ in acetone. The effluent was sent to FAAS for evaluation of their metal content evaluation.

2.4.3. Digestion of the liver sample

A 50 g of liver were taken and dried for 48 h in an oven at 120 °C to remove the water content and to obtain a constant weight (about 68% water). Dried liver sample transferred into a glass flask. For the digestion of the sample, a concentrated acid mixture of 3 mL H_2SO_4, 15 mL $HClO_4$, 15 mL HNO_3 was added and left to stand over night. The solution was kept in an oil bath at 50 °C until the foaming stopped. Then the temperature was increased to 150 °C and heating was continued until the evolution of brown fumes of nitrogen oxides ceased. When a dark brown in mixture was appeared, the flask was cooled for about 2 min then a 5 mL of nitric acid had to be added. Heating was continued until nitrogen oxides fumes were longer given off.

Appearance of white fume of perchloric acid in 1 mL solution is an indication of complete digestion.

2.5. Preconcentration procedure

The pH of the solution (500–1000 mL) was adjusted to ~6.0 with hydrochloric acid and passed through the DHMP loaded-AC column at a flow rate of 6 mL min^{-1} with the aid of a suction pump. The analyte was then eluted with 5 mL of 2 M nitric acid in acetone. The metal ions content of the eluent was measured by flame-AAS. The same eluate was used to determine all analytes, while the eluate introduced into the chamber by discrete injection. The metals quantified one each time. The effects of sample volume, amount of DHMP, AC, pH and working solution ionic strength on the recoveries of metal ions were investigated.

3. Results and discussion

In order to show that complexation between ions and DHMP is responsible for selective, sensitive and reversible preconcentration of mention ions, the copper complexation with ligand, as model has been investigated. Since these mention ions have similar property, similar results for them can be achieved. In preliminary experiments typical complexation between copper ion and DHMP was examined using spectrophotometry, and the nature of respective complex was investigated using the mole ratio method under the established experimental conditions by Kin fit program [25]. In order to confirm this result and ascertain the nature and structure of the extracted species, to the fixed amount of DHMP different mole ratio of copper ion was added and corresponding data are presented in Figs. 1 and 2. At mole ratio of 2, indicating the association of two DHMP molecules with the one molecule of copper ion. The stability constant of copper ion and DHMP has been investigated using spectrophotometry as a general accurate and powerful method. According to the results of Table 2, it can bee seen that the DHMP is a suitable sorbent with reversible sorption/desorption (medium formation constant), which facilitate both process is superior to those modified activated carbon.
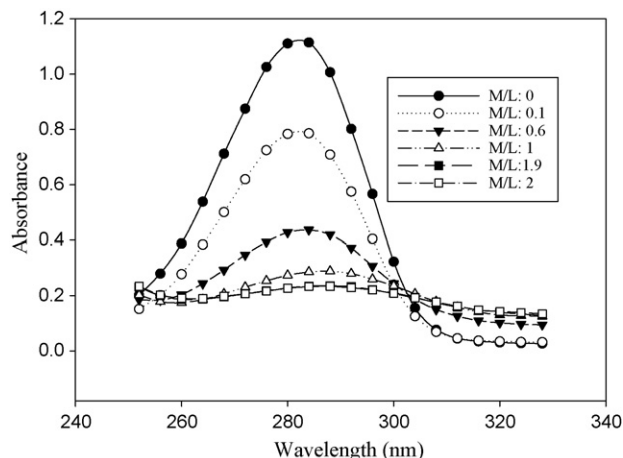

Fig. 1. Spectra of complex of DHMP (1×10^{-3} M) with copper ion (1×10^{-3} M) in acetonitril in different mole ratio.

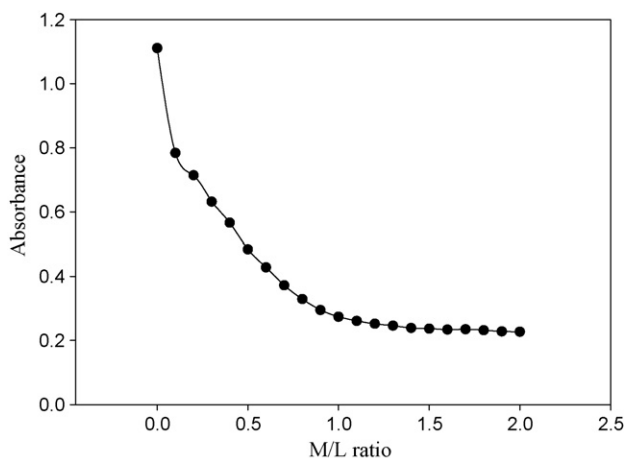Fig. 2. UV–vis spectra of 1×10^{-3} M of DHMP in acetonitrile and various concentration of Cu^{2+} 1×10^{-3} M, mole ratio plot.

Fig. 3. Effect of pH on recovery of metal ions at optimum conditions according to Table 5.

Table 2
Logarithm of stability constants assembling for the interaction of Cu^{2+} with DHMP in acetonitrile

Complex nature		$\log \beta$
Cu^{2+}	DHMP	
1	1	5.000 ± 0.004
1	2	8.001 ± 0.003

The efficiency of the DHMP-AC column for the sorption of metals was studied by using 500 mg of DHMP-AC in comparison with 500 mg of AC for preconcentration of metals in a model solution, starting with 50 μg of each metal ions in 250 mL of solution, the quantity of metals ion in the eluent was determined by FAAS. The percentage sorption of the metals retained on the sorbents was calculated from the difference between the starting amount of each metal (μg) (N_s) and the amount of metal (μg) left in the sample (N_f) according to Eq. (1).

$$\text{sorption} (\%) = \frac{N_s - N_f}{N_s} \times 100 \qquad (1)$$

The DHMP-AC can retain all the metal ions while the untreated AC cannot quantitatively retain Co, Ni, Cu and Pb. Evidently; the preconcentration of the metals with the untreated AC is not suitable for Co, Ni, Cu and Pb. Therefore, DHMP-AC seems to be a better sorbent in simultaneous sorption of the studied elements. The purpose of this work is to investigate the feasibility of absorption of these ions on activated carbon modified with DHMP. For obtaining maximum signal for evaluation of these ion contents, the effective parameters viz. pH of sample, amount of ligand and solid phase, type and concentration of eluting agent and flow rate must be optimized.

3.1. Optimization of variables

In optimization of variables 250 mL of 0.2 μg mL^{-1} of ions are used as sample solution. In the adsorption step, an appropriate amount of activated carbon should be used in order to obtain quantitative retention of metals. On the other hand, an excess
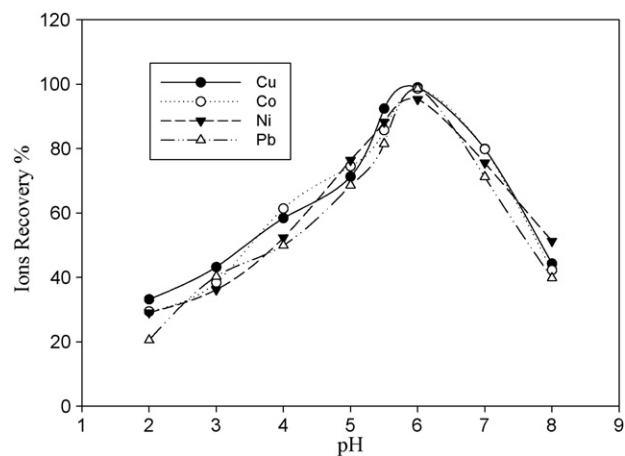
amount of the sorbent also prevents the quantitative elution of the retained metals by a small volume of eluent. For this reason, the effect of the amount of activated carbon and the eluent volume were examined. The effects of the amount of activated carbon at fix value of DHMP on the sorption of metal ions at pH 6 were examined in the range of 100–800 mg. The results demonstrated that, quantitative recoveries (>95%) of the working elements were observed in the range of 400–500 mg. Above 500 mg, the recoveries were below 95% with 10 mL of the eluent. In the proposed procedure, 500 mg of activated carbon is recommended.

As is well known, pH value of the solution has significant influence on the overall performance of the retention of the metal ions on activated carbon. The effect of pH on the preconcentration of metals on AC loaded with DHMP was studied by determination of individual elements. Fifty micrograms (250 mL 0.2 μg mL^{-1}) of each element were preconcentrated in the pH range of 2.0–8.0 (by addition of diluted KOH or HCl) by introducing 20 mg of DHMP on the activated carbon. The elution was performed with 5 mL of 2 mol L^{-1} HNO$_3$ in acetone. The data corresponding to each element was shown in Fig. 3. The results obtained indicated that the ions could be retained quantitatively by the modified activated carbon at the pH 6.0. So the pH 6.0 ± 0.1 has been selected for the determination of metals content. The decrease in signal at pH > 6.0 is probably due to the precipitation of ions as their related hydroxide and at pH < 6 may be due to competition of hydronium ion toward complexation with PUT, which lead to the decrease in the recovery. To achieve high efficiency and good selectivity, a pH of ~6.0 was selected for subsequent work.

The elution of a group of analytes could be sometimes troublesome owing to irreversible binding of some elements. In addition, desorption step leads to sample dilution and causes decrease of the analyte enrichment factor. An appropriate eluent for metal desorption was selected by taking into account the following considerations: (i) the eluent should desorb the metals or chelate complexes, (ii) should be suitable for the subsequent determination technique. Organic solvents and inorganic acids have been found to meet the requirements. In a set of simi-

Table 3
Effect of type and concentration of eluting agent on ions recovery

Eluent	Recovery (%)			
	Co^{2+}	Ni^{2+}	Pb^{2+}	Cu^{2+}
5 mL 4 M HCl	69.4	54.6	55.6	59.4
5 mL 4 M HNO$_3$	99.7	99.1	98.8	99.2
5 mL 4 M H$_2$SO$_4$	64.3	68.3	62.3	61.3
5 mL 4 M H$_3$PO$_4$	41.4	39.3	40.8	43.6
5 mL 1 M HNO$_3$[a]	72.3	79.2	78.9	80.6
5 mL 2 M HNO$_3$[a]	98.8	99.1	98.9	99.0
5 mL 3 M HNO$_3$[a]	98.9	99.2	99.4	99.3
3 mL 2 M HNO$_3$[a]	85.6	87.6	89.7	87.1
4 mL 2 M HNO$_3$[a]	94.6	95.4	96.2	97.3
6 mL 2 M HNO$_3$[a]	99.6	98.3	98.6	98.5

[a] Solution were prepared in acetone.

lar experiments, the standard solution for preconcentration was 0.2 mg L^{-1} of above mention ions (pH 6, 250 mL). The eluents chosen were 4 M sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid and 1–3 M nitric acid in acetone. The effectiveness of metal desorption from DHMP-AC was evaluated from the recovery (%) of ions. The recovery (%) in this section was calculated from the amount of metals (mg) in the starting solution (N_s) and the amount of metals (mg) eluted from the column (N_f) according to Eq. (1). The results are summarized in Table 3.

According to Table 3, solvents could elute ions with recoveries (%) ranging from 39.3–99.6%. It is clear that 2 M nitric acid in acetone was the best eluent allowing 98.8–99.0% recovery and 1.6–1.9% R.S.D. Thus, this solvent mixture was chosen for desorption of all heavy metals studied in further experiments. The recovery of Co, Cu, Ni and Pb was investigated. Two hundred and fifty millilitres of solution was percolated through the column with a flow rate of 4 mL min^{-1}. The elution step was performed using a flow rate of 0.6 mL min^{-1}. The recoveries of Co, Cu, Ni and Pb using 2 M nitric acid in acetone as eluent are shown in Table 3. The results show that the recoveries higher than 98.5% with R.S.D. values less than 2% with low blank value could be obtained for all metal ions, while using acids with further concentration lead to higher blank value and higher detection limit.

The volume of the eluent was varied from 2 to 6 mL. In the case of 500 mg of DHMP-AC, the volume of eluent >5 did not affect the recoveries of the metals. In this study, 500 mg of DHMP-AC and 5 mL of eluent are ideal for the preconcentration of metal at a concentration of 50 μg or less in the solution having volumes up to 1300 mL.

In order to determine the concentration of the DHMP required for quantitative recoveries, the proposed method was applied, changing the DHMP concentration from 5 to 25 mg per 500 mg AC. It was found that, the recovery of the metal ions increased with increasing concentrations of DHMP added and reached a constant value with at least 20 mg. On this basis, studies were carried out at a DHMP concentration of 20 mg. This concentration of ligand is enough for the preconcentration procedure because of the very low level of the investigated metal ion concentrations in natural waters.

The influence of flow rate on the adsorption of trace metals was studied. Flow rate in the range of 2–4 mL min^{-1} had no
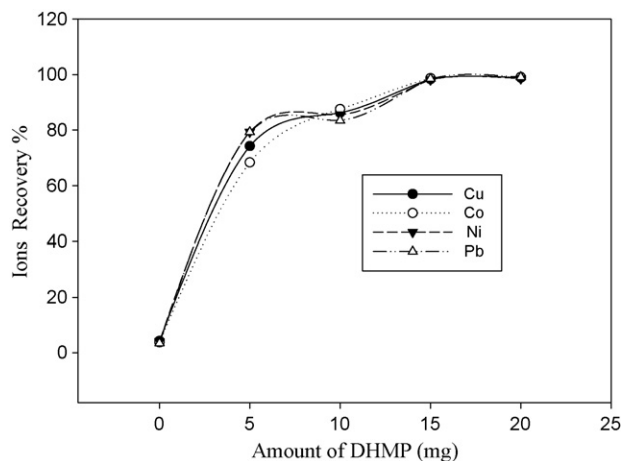

Fig. 4. Effect of amount of DHMP on recovery of metal ions at optimum conditions according to Table 5.

significant effect on the recoveries of the investigated elements. All subsequent experiments were performed at 4 mL min^{-1} flow rate.

In order to explore the possibility of enriching low concentrations of the analytes from the large sample volume, the effect of the sample solution volume on the metal sorption was studied by passing 250–1600 mL volumes through the activated carbon column at a 4 mL min^{-1} flow rate. In this work, the amounts of analyte added were constant. The results were given in Fig. 3. The adsorption of the metal ions with 500 mg activated carbon was not affected by sample volume below 1300 mL. Above this volume the percent sorption decreased for the analytes. In the present study 1300 mL of sample solution was adopted for the preconcentration of the investigated ions from drinking water samples, the adsorbed metals can be eluted with 5 mL of 2 M HNO$_3$ in acetone and a preconcentration factor of 260 is achieved by this technique (Fig. 4).

Common cations such as sodium, calcium, and magnesium are always found in water samples and have the capability to compete with many metal ions to complex with ligands, and common anions such as nitrate and chloride have the ability to bind with metal ions. Therefore, in their presence the efficiency of the impregnated ligand to bind metal ions may be reduced resulting in a reduction of the recovery.

The effects of matrix ions in water samples on the recovery of Cu, Co, Pb and Ni were also investigated (Table 4). There are

Table 4
Effects of the matrix ions on the recoveries of the examined metal ions ($n = 3$)

Ion	Added as	Tolerance limit ion (mg L^{-1})
Na$^+$	NaCl	1000
K$^+$	KCl	1000
Cl$^-$	NaCl	1000
Mg^{2+}	MgCl$_2$	600
HCO$_3$$^-$	NaHCO$_3$	1000
PO$_4$$^{3-}$	Na$_3$PO$_4$	500
Zn^{2+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, Ag$^+$, Al^{3+}, Cr^{3+}, Hg^{2+}	Nitrate salt	100

Table 5
Optimum value of method

Parameter	Optimum value
pH	6.0
Amount of DHMP (mg)	20
Amount of AC (g)	0.5
Eluting agent	5 mL of 2 mol L^{-1} HNO$_3$ in acetone
Flow rate (mL min^{-1})	4
Volume of sample (mL)	250

no interferences in the presence of large amounts of alkaline, alkaline earth metals and main anions in the water samples. The matrix metal ions are not retained on the column because of their very low stability constants of DHMP complexes. The optimum conditions of method are presented in Table 5.

At optimum condition the response are linear over concentration range of 0.04–1.1 μg mL^{-1} for Ni^{2+} and 0.04–1.0 for Cu^{2+}, Pb^{2+} and Co^{2+}. The sorption capacity was determined by saturating 1 g of solid phase in bath method. The loading capacities are 0.54, 0.53, 0.63 and 0.45 mg g^{-1} for Ni^{2+}, Co^{2+}, Cu^{2+} and Pb^{2+}. The ability of method for repeatable recovery of trace ion are 99.0, 98.9, 99.2 and 98.8 with R.S.D. of 1.4, 1.3, 1.2 and 1.4 for Ni^{2+}, Co^{2+}, Cu^{2+} and Pb^{2+}. The method detection limits were calculated by three times the standard deviation ($n = 15$) of the blank. The values were 3.4 μg L^{-1} for Co, 2.9 μg L^{-1} for Cu, 3.5 μg L^{-1} for Ni and 8.4 μg L^{-1} for Pb. These limits were based on 50 mL of blank undergoing the preconcentration. They can be improved by increasing the sample volume.

3.2. Recovery of spikes from real samples

The recoveries of the trace metal ions from a water samples were studied. As can be seen in Tables 6–8, satisfactory results were obtained for the elements examined. These results confirm the validity of the proposed method for the preconcentration of the investigated ions. The proposed method was applied for the determination of Co, Cu, Ni, and Pb in natural water samples, leaves of spinach and liver samples. The results are given in Tables 6–8. The recoveries of the metal ions were in the order of 98–104%. The R.S.D. values were less than 3%.

Table 6
Recovery studies of trace metal ions in leaves of spinach

Analyte	Added (μg g^{-1})	Found (μg g^{-1})	R.S.D. (%)	Recovery (%)
Co	0	56.3	2.2	–
	75	132.3	0.9	101.3
Ni	0	80.6	1.4	–
	75	154.6	0.8	98.7
Cu	0	70.3	1.6	–
	75	144.1	0.9	98.4
Pb	0	45.6	1.8	–
	75	121.9	1.0	101.75

Table 7
Recovery of trace elements from spiked liver sample after preconcentration on activated carbon modified with DHMP ($n = 3$)

Analyte	Added (μg g^{-1})	Found (μg g^{-1})	R.S.D. (%)	Recovery (%)
Co	0	1.45	1.5	–
	5	6.62	1.0	103.4
Ni	0	1.57	1.7	–
	5	6.68	1.1	102.2
Cu	0	6.9	0.9	–
	5	12.1	0.6	104.0
Pb	0	0.73	1.4	–
	5	5.78	1.0	101.0

Table 8
Recovery of trace elements from spiked spring water sample after preconcentration on activated carbon modified with DHMP

Analyte	Added (μg L^{-1})	Found (μg L^{-1})	R.S.D. (%)	Recovery (%)
	0	BL	–	–
Co	50	63.4	1.4	–
	75	90.0	0.9	111.9
	0	BL	–	–
Ni	50	83.4	1.5	–
	75	109.2	1.0	102.4
	0	43.2	–	–
Cu	50	94.5	1.3	102.6
	75	120.2	0.9	102.8
	0	BL	2.0	–
Pb	50	72.3	1.5	–
	75	98.3	0.9	104

BL: below linear range.

4. Conclusion

DHMP loaded on activated carbon is a sensitive and accurate method for the determination of Co (II), Cu (II), Ni (II), and Pb (II) in low concentrations. The results presented (Tables 1–8) have confirmed its applicability to the separation and preconcentration of these ion contents. This method is simple and there is no need for an elaborate cleanup procedure, since the adsorbed metals are simply eluted with 5 mL of 2 mol L^{-1} HNO$_3$ in acetone. The adsorbent for Co (II), Cu (II), Ni (II), and Pb (II) preconcentration can be used for at least five successive analyses without a considerable change. The method due to advantages such as high reliability, reproducibility, sensitivity, and high tolerance limit of common ions and low detection limit is a powerful tool for rapid and sensitive determination of these ions ion in various media. The accuracy and precision of the proposed SPE method was reported in term of recovery (%) ranging from 98 to 104%, and R.S.D. (%) ranging from 0.6 to 3.0%.

References

[1] S.L.C. Ferreira, C.F. Brito, A.F. Dantas, N.M.L. Araujo, A.C.S. Costa, Nickel determination in saline matrices by ICP-AES after sorption on Amberlite XAD-2 loaded with PAN, Talanta 48 (1999) 1173–1179.

[2] S. Cerutti, S. Moyano, J.A. Gásquez, J. Stripeikis, R.A. Olsina, L.D. Martinez, On-line preconcentration of cobalt in drinking water using a minicolumn packed with activated carbon coupled to electrothermal atomic absorption spectrometric determination, Spectrochim. Acta, Part B 58 (2003) 2015–2021.

[3] M. Ghaedi, E. Asadpour, A. Vafaie, Simultaneous preconcentration determination of copper, nickel, cobalt, lead and iron content using a surfactant coated alumina, Bull. Chem. Soc. Jpn. 79 (2006) 432–436.

[4] M. Ghaedi, M.R. Fathi, A. Shokrollahi, F. Shajarat, Highly selective sensitive preconcentration of mercury ion by cold vapor atomic absorption spectroscopy, Anal. Lett. 39 (2006) 1171–1185.

[5] M. Soylak, S. Saracoglu, L. Elci, M. Dogan, Solid phase preconcentration and separation of copper, nickel and lead in haemodialysis concentrates and urine on Amberlite XAD-1180 resin, Kuwait J. Sci. Eng. 30 (2003) 95–109.

[6] I. Narin, M. Soylak, L. Elci, M. Dogan, Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column, Talanta 52 (2000) 1041–1046.

[7] R.E. Santelli, M. Gallego, M. Valcarcel, Preconcentration and atomic absorption determination of copper traces in waters by on-line adsorption-elution on an activated carbon minicolumn, Talanta 41 (1994) 817–823.

[8] M. Ghaedi, H. Parham, K. Mortazavi, M. Janbezar, Preconcentration, Extraction of copper on activated carbon using alpha-benzoinoxime and pyrimidin 2-thiole, J. Saudi Chem. Soc. 10 (2006) 23–32.

[9] D. Pozebon, V.L. Dressler, A.J. Curtius, Determination of copper, cadmium, lead, bismuth and selenium (IV) in sea water by electrothermal vaporization and inductively coupled plasma mass spectrometry after on-line separation, J. Anal. Atom. Spectr. 13 (1998) 363–369.

[10] J. Shiowatana, K. Benyatianb, A. Siripinyanond, Determination of Cd, Co, Hg and Ni in seawater after enrichment on activated carbon by slurry sampling electrothermal AAS, Atom. Spectr. 21 (2000) 179–186.

[11] M. Soylak, M. Dogan, Column preconcentration of trace amounts of copper on activated carbon from natural water samples, Anal. Lett. 29 (1996) 635–643.

[12] M. Soylak, I. Narin, L. Elci, M. Dogan, Atomic absorption spectrometric determination of copper, cobalt, cadmium, lead, nickel and chromium in table salt samples after preconcentration on activated carbon, Kuwait J. Sci. Eng. 28 (2001) 361–370.

[13] H. Koshima, H. Onishi, Adsorption of metal ions on activated carbon from aqueous solutions at pH 1–13, Talanta 33 (1986) 391–395.

[14] E. Piperaki, H. Berndt, E. Jackwerth, Investigations on the sorption of metal chelates on activated carbon, Anal. Chim. Acta 100 (1978) 589–596.

[15] J.P. Chen, M. Lin, Surface charge and metal ion adsorption on an H-type activated carbon: experimental observation and modeling simulation by the surface complex formation approach, Carbon 39 (2001) 1491–1504.

[16] M. Ghaedi, F. Ahmadi, H. Karimi, S. Gharaghani, Preconcentration and extraction of copper on activated carbon using 4-amino-2, 3-dimethyl-1-phenyl-3-pyrazoline or 4-(4-methoxybenzylidenimin) thiophenole, Korean J. Chem. 50 (2006) 23–31.

[17] M. Ghaedi, F. Ahmadi, H. Karimi, S. Gharaghani, Preconcentration and extraction of copper on activated carbon using 4-amino-2, 3-dimethyl-1-phenyl-3-pyrazoline or benzil dioxime, Asian J. Chem., in press.

[18] S. Cerutti, M.F. Silva, J.A. Gasquez, R.A. Olsina, L.D. Martinez, On-line preconcentrationydetermination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma optical emission spectrometer, Spectrochim. Acta: Part B 58 (2003) 43–50.

[19] E.A. Takara, S.D. Pasini-Cabello, S. Cerutti, J.A. G'asquez, L.D. Martinez, On-line preconcentration/determination of copper in parenteral solutions using activated carbon by inductively coupled plasma optical emission spectrometry, J. Pharmaceut. Biomed. Anal. 39 (2005) 735–739.

[20] M. Soylak, Determination of trace amounts of copper in metallic aluminium samples after separation and preconcentration on an activated carbon column, Fresenius Environ. Bull. 7 (1998) 383–387.

[21] K. Jankowski, J. Yao, K. Kasiura, A. Jackowska, A. Sieradzka, Multi-element determination of heavy metals in water samples by continuous powder introduction microwave-induced plasma atomic emission spectrometry after preconcentration on activated carbon, Spectrochim. Acta: Part B 60 (2005) 369–375.

[22] P. Daorattanachai, F. Unob, A. Imyim, Multi-element preconcentration of heavy metal ions from aqueous solution by APDC impregnated activated carbon, Talanta 67 (2005) 59–64.

[23] I. Narin, M. Soylak, M. Dogan, Trace enrichment and atomic absorption spectrometric determination of lead, copper, cadmium and nickel in drinking water samples by use of an activated carbon column, Anal. Lett. 30 (1997) 2801–2810.

[24] G. Chakrapani, D.S.R. Murty, P.L. Mohanta, R. Rangaswamy, Sorption of PAR-metal complexes on activated carbon as a rapid preconcentration method for the determination of Cu, Co, Cd, Cr, Ni, Pb and V in ground water, J. Geochem. Explor. 63 (1998) 145.

[25] A. Safavi, S. Rastegarzadeh, Spectrophotometric study of stabilities of copper, zinc, nickel and cobalt with 1, 2-bis methyl(2-aminocyclopentene carbodithioate) ethane in binary *n, n*-dimethyl formamide dichloromethane mixtures, Anal. Sci. 15 (1999) 173–175.