



# Sorbent extraction of 4-(2-thiazolylazo) resorcinol (TAR)–metal chelates on Diaion SP-850 adsorption resin in order to preconcentration/separation

Mustafa Soylak\*, Erkan Yilmaz

Erciyes University, Faculty of Science, Department of Chemistry, 38039 Kayseri, Turkey

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## ABSTRACT

A sensitive and simple separation–enrichment technique for the determination of trace amounts of some metal ions was described. By the passage of aqueous samples including Fe(III), Cu(II), Ni(II) and Co(II) ions–4-(2-thiazolylazo) resorcinol (TAR) chelates through Diaion SP-850 column, metal chelates adsorb quantitatively and almost all matrix elements were passed through the column to drain. Quantitative recoveries for analyte ions were obtained at pH 6 at 3 ml/min flow rate of sample solution in 0.5 g Diaion SP-850 filled glass column. The investigations were also carried out on the interferences from other concomitant ions in the sorption process. After optimization, a preconcentration factor of 60 and a recovery values as % higher than 95 were achieved. The detection limit ( $N=10$ , 3 sigma) for Fe(III), Cu(II), Ni(II) and Co(II) were found as 3.6, 1.1, 2.8 and 2.3  $\mu\text{g l}^{-1}$ , respectively. The applications to the determination of iron, copper, nickel and cobalt in real samples and the validation of the analytical methodology employing NIST SRM 1549 milk powder, NIST RM 8433 Corn Bran and BCR 144R Sewage sludge of domestic origin as certified reference materials were performed.

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## 1. Introduction

The accumulation of heavy metals like Cd, Pb, Cu, Zn, Cr, Fe and Ni in environmental and food samples is an important problem for human beings [1–6]. Instrumental techniques such as atomic absorption spectrometry, atomic emission spectrometry, inductively coupled plasma–mass spectrometry, electroanalytical techniques [7–13] are used for the determination of heavy metals in real samples. However, there is two main problems in these determinations are lower elements concentrations than the qualification limits of the instrument and the negative or positive effects of concomitant ions [14–19]. Generally in order to solve these problems, separation–preconcentration methods including solvent extraction, cloud point extraction, membrane filtration, flotation, electro-deposition and other methods are used by the researchers [20–27].

Solid phase extraction is a popular technique for separation and preconcentration of heavy metal ions [28–31]. It very important and need much more attention for the preconcentration and selective separation of trace heavy metal ions from the environmental samples because of some its some advantages including its simplicity, to obtain high preconcentration factor, environmental friendly, etc. [32–35]. Some adsorbents including zeolites [36], acti-

vated carbon [37,38], amberlite resins [39–41], chromosorb [42], clinoptilolite [43], etc. have been used for the solid phase extraction of traces heavy metals in environmental samples prior to their instrumental analysis.

4-(2-Thiazolylazo) resorcinol (TAR) is a spectrophotometric reagent for the determination of metal ions [44,45]. Its metal chelates have been also used for the preconcentration of metal ions by solid phase extraction [46–48]. According to our literature survey, 4-(2-thiazolylazo) resorcinol (TAR)–metal chelates–Diaion SP-850 combination is not used for the preconcentration–separation of traces metal ions in the food and environmental samples.

The aim of presented work was to develop a solid phase extraction method for the separation and preconcentration of Fe(III), Cu(II), Ni(II) and Co(II) ions as 4-(2-thiazolylazo) resorcinol chelates prior to atomic absorption spectrometric determination. The chemical variables affecting the sensitivity of the presented preconcentration procedure were studied in detail.

## 2. Experimental

### 2.1. Apparatus

The instrumental detection system used in this work was a PerkinElmer Model 3110 flame atomic absorption spectrometer (Norwalk, CT, USA). All measurements were carried out in an air/acetylene flame. 10 cm long slot-burner heads, hollow cathode lamps were used. The operating parameters for working elements

\* Corresponding author. Tel.: +90 352 437 4933; fax: +90 352 437 4933.  
E-mail addresses: [soylak@erciyes.edu.tr](mailto:soylak@erciyes.edu.tr), [msoylak@gmail.com](mailto:msoylak@gmail.com) (M. Soylak).

were set as recommended by the manufacturer. All measurements were carried out without background correction. A pH meter, Nel pH-900 (Ankara, Turkey) Model glass-electrode was employed for measuring pH values in the aqueous phase. The pure water used all experiments was purified in a Human model RO 180 (HUMAN Corp., Seoul, Korea), resulting water with a conductivity of  $1 \mu\text{S cm}^{-1}$ .

## 2.2. Reagents

Otherwise stated analytical-grade acids and other chemicals were used in this study obtained from Merck, Darmstadt, Germany. The calibration curve was established using the standard solutions of investigated analyte elements prepared in  $1 \text{ mol l}^{-1}$   $\text{HNO}_3$  by dilution from  $1000 \text{ mg l}^{-1}$  stock solutions (Merck). The calibration standards for analytes were not submitted to the separation–preconcentration procedure.

The chelating agent was 4-(2-thiazolylazo) resorcinol (Merck, Darmstadt, Germany). 0.1% (m/v) of TAR solution was daily prepared in a water/ethanol (25/75, v/v) mixture. The certified reference materials from various origins (NIST SRM 1549 milk powder, NIST RM 8433 Corn Bran and BCR 144R Sewage sludge of domestic origin) were used in the experiments.

Diaion SP-850 is an aromatic type adsorbent. It is based on crosslinked polystyrenic matrix. Its surface area is  $1000 \text{ m}^2 \text{ g}^{-1}$ . Diaion SP-850 is widely used in different industrial fields; extraction of antibiotic intermediates from fermentation broth, separation–enrichment of peptides, or food additives, debittering of citrus juice [49,50]. Diaion SP-850 was purchased from Sigma Chem. Co. St. Louis, MO, USA. It (20–60 mesh) was washed successively with methanol, water,  $1 \text{ mol l}^{-1}$   $\text{HNO}_3$  in acetone, water,  $1 \text{ mol l}^{-1}$  NaOH, and water, sequentially.

A glass column containing 500 mg of Diaion SP-850 in water suspension was 10 cm long and 1.0 cm in diameter. The bed height in the column was approximately 2.0 cm. The resin on the column was preconditioned with pH 6.0 buffer solution prior to percolation of the sample.

Sodium phosphate buffer ( $0.1 \text{ mol l}^{-1}$ ) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers ( $0.1 \text{ mol l}^{-1}$ ) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6. Ammonium chloride buffer solutions ( $0.1 \text{ mol l}^{-1}$ ) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8.

## 2.3. Model works

Model solutions containing analyte ions were adjusted to desired pH. Then 4-(2-thiazolylazo) resorcinol was added to form the metal-4-(2-thiazolylazo) resorcinol chelates. After 5–10 min, the solution was loaded to the Diaion SP-850 column. The flow of sample solution through the column was gravitationally performed. After passage of the solution finished, the column was washed with a chelating agent solution adjusted to the working pH. Subsequently, metal-4-(2-thiazolylazo) resorcinol chelates retained on Diaion SP-850, were eluted at  $4 \text{ ml min}^{-1}$  of flow rate with 10 ml of  $1 \text{ M HNO}_3$  in acetone. The effluent was evaporated to near dryness and made up to 5.0 ml with  $1 \text{ M HNO}_3$ . The levels of the investigated analyte ions in the samples were determined by AAS.

## 2.4. Analysis of real samples

0.5 g of certified reference material (NIST SRM 1549 milk powder, NIST RM 8433 Corn Bran and BCR 144R Sewage sludge of

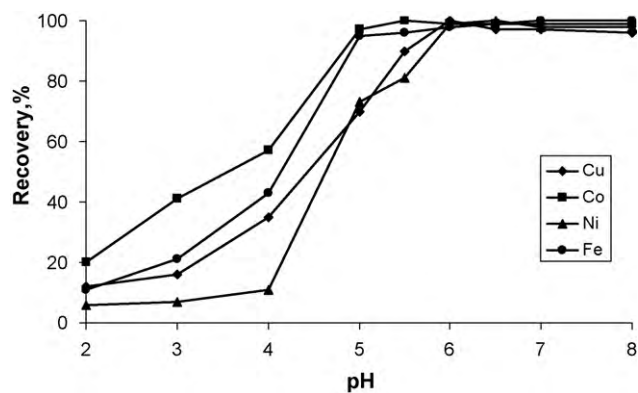


Fig. 1. The influence of the pH on the recovery of analyte ions (chelating agent: TAR, eluent:  $1 \text{ mol l}^{-1}$   $\text{HNO}_3$  in acetone,  $N=3$ ).

domestic origin), black tea and rice samples was digested with 10 ml concentrated  $\text{HNO}_3$  at  $95^\circ\text{C}$ . The mixture was evaporated almost to dryness and mixed with 3 ml of  $\text{H}_2\text{O}_2$ . Then it was again evaporated to dryness. After evaporation 8–9 ml of distilled water was added and the sample was mixed. The resulting mixture was filtered through a blue band filter paper. The filtrate was diluted to 25 ml with distilled water. Then the procedure given in Section 2.3 was applied. The analytes in final solution were determined with flame AAS.

The water sample analyzed was filtered through a cellulose membrane filter (Millipore) of  $0.45 \mu\text{m}$  pore size. The pH of the samples was adjusted to 6. Then TAR solution was added. The sample was passed through the column. The TAR chelates adsorbed on column were eluted with  $1 \text{ M HNO}_3$  in acetone. The effluent was evaporated to near dryness and made up to 5.0 ml with  $1 \text{ M HNO}_3$ . The levels of the investigated analyte ions in the samples were determined by AAS.

## 3. Results and discussion

### 3.1. Effect of pH

The pH of the aqueous phase is one of the most important factors in a solid phase extraction procedure for the quantitative recoveries [51–53]. The influences of the pH on Fe(III), Cu(II), Ni(II) and Co(II)–TAR chelates on the sorption onto Diaion SP-850 resin was investigated over the range from 2.0 to 8.0 keeping other parameters constant. The results are depicted in Fig. 1. The analyte ions were effectively adsorbed in pH range 6.0–8.0. It was possible to carry out the determination of both ions at pH 6.0. In order to control the pH during the analytical procedure, it was adjusted to 6.0 with a buffer solution of acetate/acetic acid.

### 3.2. Influences of the amounts of ligand

The effects of the amounts of TAR on the quantitative recoveries of the analyte ions on Diaion SP-850 were also examined in the range of 0.0–1.0 mg of TAR. The results are depicted in Fig. 2. The recoveries of nickel and cobalt were below 40% without TAR. Over 0.25 and 0.50 mg of TAR, cobalt and nickel were quantitatively adsorbed, respectively. Copper and iron ions were quantitatively recovered without ligand and with ligand. In order to recover all analyte ions quantitatively with together, all further studies were performed by using 0.50 mg of TAR.

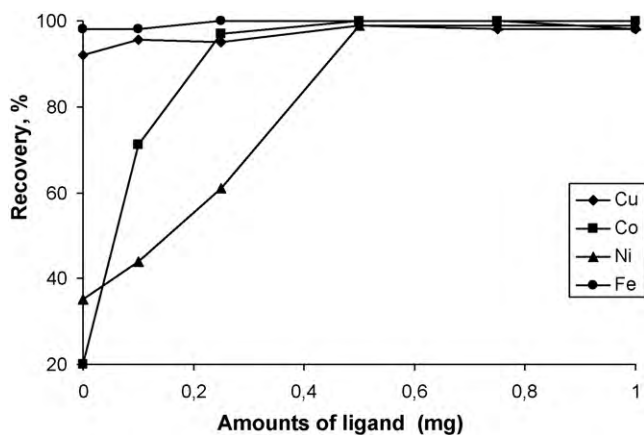


Fig. 2. Influences of amounts of TAR on the recoveries of analyte ions (eluent:  $1 \text{ mol l}^{-1} \text{ HNO}_3$  in acetone,  $N=3$ ).

### 3.3. Effect of eluent

Various eluents were examined to obtain quantitative recovery values for analyte ions from Diaion SP-850 glass column. The results are summarized in Table 1. The recoveries of analyte ions were quantitative only with  $1 \text{ M HNO}_3$  in acetone. The recoveries for the analyte ions were not quantitative with other eluents given in Table 1.  $1 \text{ M HNO}_3$  in acetone was used as eluent all further works for quantitative recovery of metal ions from Diaion SP-850 column.

Some experiments were carried out in order to choose a proper eluent volume for the retained analyte ions. The recovery values for analyte ions from the column were greater than 95%, in the eluent volume range of 10.0 ml. In the eluent volume lower than 10.0 ml, because of insufficient eluent volume, the recoveries of the analyte ions were not quantitative. The effluent (acetone in eluent) was evaporated to near dryness and made up to 5.0 ml with  $1 \text{ M HNO}_3$ . The final volume for AAS determinations was 5 ml.

### 3.4. Flow rates

Under optimal constant conditions, the model solutions of 50 ml were passed through the column with rates in the range  $0.75\text{--}4.0 \text{ ml min}^{-1}$  and the flow rate of the solutions was increased by the application of vacuum via a water jet. It was observed that the recovery was not changed significantly up to  $3.0 \text{ ml min}^{-1}$  and the flow rate  $3.0 \text{ ml min}^{-1}$  was selected for further experiments.

The flow rates of eluent solution were investigated in the range of  $1.0\text{--}4.0 \text{ ml min}^{-1}$  under optimal constant conditions. After  $4.0 \text{ ml min}^{-1}$  of eluent solution, the recovery values of the analytes were not quantitative. For the all experiments,  $4.0 \text{ ml min}^{-1}$  was selected as eluent flow rate.

Table 1

Effects of various eluents on the recoveries of the analytes ( $N=3$ , eluent volume: 10 ml).

	Recovery (%)			
	Fe	Co	Ni	Cu
1 M $\text{HNO}_3$	$64 \pm 1^a$	$19 \pm 1$	$93 \pm 1$	$92 \pm 1$
2 M $\text{HNO}_3$	$77 \pm 1$	$15 \pm 2$	$98 \pm 1$	$72 \pm 2$
1 M HCl	$93 \pm 3$	$19 \pm 1$	$73 \pm 1$	$85 \pm 1$
2 M HCl	$94 \pm 2$	$60 \pm 1$	$80 \pm 2$	$90 \pm 2$
1 M HCl in acetone	$82 \pm 1$	$94 \pm 2$	$99 \pm 1$	$90 \pm 1$
2 M HCl in acetone	$75 \pm 2$	$98 \pm 1$	$92 \pm 1$	$98 \pm 1$
1 M $\text{HNO}_3$ in acetone	$95 \pm 1$	$98 \pm 1$	$95 \pm 2$	$95 \pm 1$
2 M $\text{HNO}_3$ in acetone	$80 \pm 2$	$97 \pm 2$	$98 \pm 2$	$85 \pm 3$

<sup>a</sup> Mean  $\pm$  standard deviation.

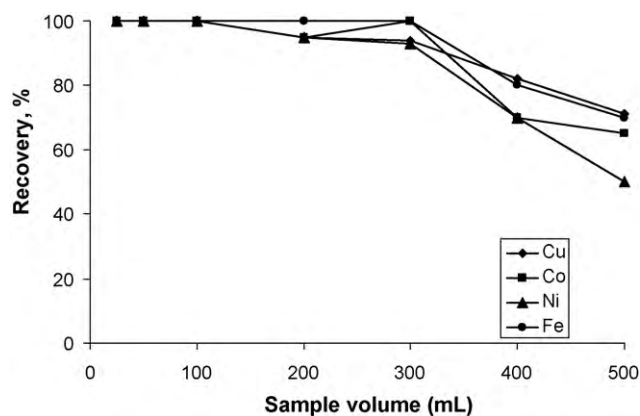


Fig. 3. The recovery values as a function of sample volume (chelating agent: TAR, eluent:  $1 \text{ mol l}^{-1} \text{ HNO}_3$  in acetone,  $N=3$ ).

### 3.5. Effects of sample volume

In order to obtain high preconcentration factor in the solid phase extraction studies, the solid phase extraction technique is a common procedure for extraction and separation of metal ions from large sample volumes [54–57]. The effect of the sample solution volume on the metal sorption was also studied at pH 6 by passing 25–500 ml volumes through the column. The recovery values as a function of sample volume were shown in Fig. 3. The adsorption of the metal ions with 500 mg of Diaion SP-850 was not affected by sample volume below 300 ml. Above 300 ml the percent sorption decreased for the analytes. Therefore a preconcentration factor of 60 can be achieved when using 300 ml of the sample and 5.0 ml of final volume.

### 3.6. Effect of matrix

The effect of common coexisting ions on the recoveries of the analyte ions on Diaion SP-850 was also investigated. The experimental results are summarized in Table 2. The results show that the presences of interfering anions and cations have no obvious influence on the coprecipitation of the studied metal ions under optimum conditions. Also some of the transition metal ions at  $\text{mg l}^{-1}$  levels were not interfered on the quantitative recoveries of the analyte ions. The investigation of many alkaline, earth alkaline and metallic ions as concomitants showed that the sorption of metal–TAR chelates by Diaion SP-850 was relatively found selective.

### 3.7. Detection limits

The limits of detection (LOD) of the proposed procedure for the determination of analyte elements were studied under the optimal experimental conditions. The detection limits, defined as the concentration equivalent to three times the standard deviation of blank ( $n=10$ ,  $X_L = (X_b + 3s)/PF$ ,  $X_L$ : limit of detection,  $X_b$ : blank value, PF: preconcentration factor) of the reagent blank [58–60], were  $1.1 \mu\text{g l}^{-1}$  for copper,  $2.3 \mu\text{g l}^{-1}$  for cobalt,  $2.8 \mu\text{g l}^{-1}$  for nickel and  $3.6 \mu\text{g l}^{-1}$  for iron.

### 3.8. Addition/recovery tests

The tests of addition/recovery in the experiments for analyte ions were performed for a river and tap water samples. Different amounts of the investigated metal ions were spiked to these samples in order to estimate the accuracy of the presented procedure. The results are given in Table 3. Good agreement was obtained between the added and found analyte content using the recom-

**Table 2**  
Matrix effects ( $N=3$ ).

Ion	Added As	Concentration ( $\mu\text{g/ml}$ )	Recovery (%)			
			Cu	Co	Ni	Fe
Mg <sup>2+</sup>	Mg(NO <sub>3</sub> ) <sub>2</sub>	3000	95 ± 1 <sup>a</sup>	95 ± 1	95 ± 2	100 ± 1
Ca <sup>2+</sup>	CaCl <sub>2</sub>	2500	95 ± 2	99 ± 0	100 ± 1	100 ± 0
K <sup>+</sup>	KCl	2500	95 ± 2	100 ± 1	95 ± 1	100 ± 1
Na <sup>+</sup>	NaCl	5000	100 ± 1	100 ± 0	98 ± 2	100 ± 1
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	20	97 ± 1	99 ± 1	96 ± 2	98 ± 1
Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	40	95 ± 1	100 ± 0	100 ± 1	100 ± 0
Cu <sup>2+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	10	–	95 ± 2	98 ± 2	99 ± 1
Co <sup>2+</sup>	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5	98 ± 0	–	96 ± 1	97 ± 2
Ni <sup>2+</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5	95 ± 2	97 ± 0	–	98 ± 1
Fe <sup>3+</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	15	96 ± 2	97 ± 1	99 ± 2	–
Cl <sup>–</sup>	NaCl	7500	95 ± 1	99 ± 1	95 ± 1	100 ± 1
HPO <sub>4</sub> <sup>2–</sup>	Na <sub>2</sub> HPO <sub>4</sub> ·7H <sub>2</sub> O	2500	95 ± 1	98 ± 1	95 ± 2	95 ± 1
I <sup>–</sup>	NaI	2500	100 ± 1	100 ± 1	95 ± 2	100 ± 0
NO <sub>3</sub> <sup>–</sup>	KNO <sub>3</sub>	3500	98 ± 1	100 ± 0	100 ± 1	100 ± 1
CO <sub>3</sub> <sup>2–</sup>	Na <sub>2</sub> CO <sub>3</sub>	1500	95 ± 2	95 ± 1	95 ± 1	100 ± 0
PO <sub>4</sub> <sup>3–</sup>	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	2500	98 ± 1	95 ± 1	96 ± 1	100 ± 1
SO <sub>4</sub> <sup>2–</sup>	Na <sub>2</sub> SO <sub>4</sub>	2500	97 ± 0	99 ± 0	95 ± 2	95 ± 2
F <sup>–</sup>	NaF	1000	96 ± 1	100 ± 0	95 ± 0	98 ± 1

<sup>a</sup> Mean ± standard deviation.

mended procedure. The standard deviation values for the spiked samples were in the range of 1–5%. These values were quantitative (>95%) and it shows that the presented method can be applied for the separation/preconcentration of analyte ions in the real environmental samples.

The validation of the presented procedure is performed by the analysis of three certified reference materials (NIST SRM 1549 milk powder, NIST RM 8433 Corn Bran and BCR 144R Sewage sludge of domestic origin) for analytes. The certified and observed values for certified reference materials are given in Table 4. The results found were in good agreement with the certified values of CRMs.

### 3.9. Application to real samples

The solid phase extraction procedure presented for Fe(III), Cu(II), Ni(II) and Co(II) was applied to some water and food samples. The results were given in Table 5 for water samples and in Table 6 for food samples.

**Table 3**  
Tests of addition and recovery for natural water samples.

Added ( $\mu\text{g}$ )	Water from Zamantı River		Tap water from Nigde	
	Found ( $\mu\text{g}$ )	Recovery (%)	Found ( $\mu\text{g}$ )	Recovery (%)
Fe 0	54.4 ± 1.0 <sup>a</sup>	–	3.2 ± 0.3	–
	5	98	8.3 ± 0.4	102
	10	101	13.1 ± 0.1	99
	20	104	22.1 ± 0.2	95
	40	100	44.5 ± 1.1	103
Cu 0	1.1 ± 0.1	–	1.0 ± 0.1	–
	5	98	5.8 ± 0.4	96
	10	99	10.5 ± 0.6	95
	20	100	21.3 ± 1.5	101
	40	103	41.0 ± 0.2	100
Co 0	GSA	–	GSA	–
	5	96	5.1 ± 0.3	102
	10	93	10.5 ± 1.2	105
	20	100	20.8 ± 2.0	104
	40	99	40.5 ± 0.5	101
Ni 0	2.5 ± 0.1	–	GSA	–
	5	96	5.0 ± 0.2	100
	10	96	9.9 ± 0.8	99
	20	99	20.0 ± 0.9	100
	40	98	40.5 ± 1.1	101

<sup>a</sup> Mean ± standard deviation.**Table 4**  
The results for reference standard materials ( $N=5$ ).

Element	Our value	Certified value
SRM 1549 milk powder (mg/kg)		
Cu	0.7 ± 0.1 <sup>a</sup>	0.7
Fe	1.8 ± 0.3	1.78
SRM 8433 Corn Bran powder (mg/kg)		
Cu	2.4 ± 0.1	2.47 ± 0.40
Fe	13.7 ± 0.3	14.8 ± 1.8
Ni	BDL	0.158 ± 0.054
BCR 144R Sewage sludge of domestic origin powder (mg/kg)		
Cu	308.0 ± 0.7	305.0 ± 0.2
Fe	7.0 ± 0.1 g/kg	7.21 ± 0.02 g/kg
Ni	47.7 ± 1.1	45.5 ± 0.3
Co	14.5 ± 0.3	15.0 ± 0.6

BDL: below the detection limit.

<sup>a</sup> Mean ± standard deviation.**Table 5**  
The application of the presented method in natural water samples for contents of analyte ions ( $N=4$ ).

Sample	Concentration ( $\mu\text{g/l}$ )			
	Cu	Fe	Ni	Co
Water from Zamantı River	5.5 ± 0.2 <sup>a</sup>	222 ± 4	12.5 ± 0.5	BDL
Tap water from Nigde	4.9 ± 0.3	15.9 ± 0.2	BDL	BDL

BDL: Below the detection limit.

<sup>a</sup> Mean ± standard deviation.**Table 6**  
The application of the presented method in natural water samples for contents of analyte ions ( $N=4$ ).

Örnek	Concentration ( $\mu\text{g/g}$ )			
	Cu	Fe	Ni	Co
Rice	1.0 ± 0.1 <sup>a</sup>	4.8 ± 0.1	BDL	BDL
Black tea	11.4 ± 0.8	34.3 ± 1.2	7.4 ± 1.0	BDL

BDL: below the detection limit.

<sup>a</sup> Mean ± standard deviation.



**Table 7**  
Comparative data from some recent studies on preconcentration of heavy metal ions by sorbent extraction.

Analytes	System	Eluent	PF	Detection limit ( $\mu\text{g l}^{-1}$ )	RSD (%)	Ref.
Cu	Polyurethane foam/2-(6'-methyl-2'-benzothiazolylazo) chromotropic acid	$5 \times 10^{-3} \text{ mol l}^{-1}$ HCl	14.1	1.2	<6.3	[61]
Co, Ni	5,7-Dichloroquinone-8-ol embedded styrene-ethylene glycol dimethacrylate polymer	$2.0 \text{ mol l}^{-1}$ HCl	200	2.0–2.0	<3	[62]
Cd, Pb	Dowex Optipore V-493/dibenzylthiocarbamate	$1.0 \text{ mol l}^{-1}$ $\text{HNO}_3$	50	0.43–0.65	3	[63]
Cu, Fe, Pb	2-((2-Aminoethylamino) methyl)phenol-functionalized activated carbon	$1.0 \text{ mol l}^{-1}$ $\text{HNO}_3$	50–100	0.16–0.41	1.9–2.7	[64]
Co, Ni, Cu, Zn, Pb	Phydroxybenzoic acid modified Amberlite XAD-4	$2.0 \text{ mol l}^{-1}$ HCl	260–460	0.47–1.35	<5	[65]
Cd, Cu	Amberlite XAD-2/2-aminothiophenol	$0.5 \text{ mol l}^{-1}$ HCl	14–28	0.14–0.54	<5	[66]
Cu, Cd, Pb, Zn, Mn, Fe, Cr, Ni, Co	Chromosorb 108/bathocuproinedisulfonic acid	$2.0 \text{ mol l}^{-1}$ $\text{HNO}_3$	80	0.16–0.60	1–17	[67]
Fe(III), Cu(II), Ni(II) and Co(II)	Diaion SP-850/4-(2-thiazolylazo) resorcinol	$0 \text{ mol l}^{-1}$ $\text{HNO}_3$ in acetone	60	1.1–3.6	<5	Present work

PF: preconcentration factor.

#### 4. Conclusion

The proposed column preconcentration method is simple, accurate, selective, and efficient as it reduces to a large extent the total dissolved salts in the sample solution arising from the matrix. The precision and recovery (>95%) were satisfactory. The working pH (6) for all the metal ions is slightly acidic and therefore there is no possibility of their hydrolysis. The proposed preconcentration/separation method could be applied to other highly saline samples and the samples contain some transition metal ions. The presented system was also successful in preconcentrating metal ions from large sample volume. The comparative information from some recent studies on preconcentration of heavy metals by various techniques for the figure of the merits is given in Table 7. The analytical performance of the presented method is comparable with other preconcentration methods. The detection limits of investigated elements are superior to those of some preconcentration/separation techniques for analyses. The method is relatively rapid as compared with previously reported procedures for the enrichment of traces metal ions.

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