A multi-element solid-phase extraction method for trace metals determination in environmental samples on Amberlite XAD-2000

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Abstract

A method for the preconcentration of some transition elements at trace level was proposed using a column filled with Amberlite XAD-2000 resin. Metal ions were adsorbed on XAD-2000 as their diethyldithiocarbamate chelates, then analytes retained on the resin were eluted by $1 \, mol \, L^{-1}$ nitric acid in acetone and determined by flame atomic absorption spectrometry (FAAS). The influences of some analytical parameters including pH of sample solution, ligand amount, the type, concentration and volume of elution solution, flow rates of the sample and eluent solutions, adsorption capacity of the resin and sample volume on the preconcentration efficiency have been investigated. The influences of some matrix elements were also examined. The detection limit ($N = 20$, 3 sigma) for Mn(II), Fe(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II) were found as 0.20, 0.35, 0.25, 0.20, 0.20, 0.15, 0.45 and $0.25 \, \mu g \, L^{-1}$, respectively. The validation of the procedure was carried out by analysis of certified reference materials. The proposed method was applied to natural waters and kale vegetable (*Brassica oleracea* var. *acephala*).
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1. Introduction

The determination of trace metals in the environmental samples including natural waters have been continuously performed in order to designate the level of pollution as the number of ecological and health problems associated with environmental contamination continues to rise [1–3]. The direct determination of the trace metals by atomic spectroscopic methods, such as flame atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) is often difficult due to their extremely low concentrations and matrix interferences, therefore a preconcentration method is required [1,4]. The preconcentration techniques such as solid-phase extraction (SPE) [5–7], liquid–liquid extraction [8],

coprecipitation [9], ion-exchange [10], electrochemical deposition [11], cloud point extraction [12] and flotation [13] etc. have been widely used for the preconcentration and separation of trace metal ions.

Solid-phase extraction is preferred on account of the fast, simple and direct application in micro liter volume without any sample loss, higher preconcentration factor, rapid phase separation, time and cost saving [14]. The basic principle of SPE of trace metal ions is the transfer of analytes from aqueous phase to the active sites of solid phase. For this purpose, various adsorbents including activated carbon [15,16], silica gel [17], microcrystalline naphthalene [18,19], C_{18} cartridges [20], Chelex-100 [21], Alumina [22], polyurethane foam [23,24] have been used.

Among solid-phase adsorbents, Amberlite XAD resins are very useful for preconcentration-separation of metal complexes [25–29] because of their good physical properties such as their porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structure, and good adsorbent

properties for great amounts of uncharged compounds. Amberlite XAD-2000 is a polystyrene–divinylbenzene copolymer. Some properties of Amberlite XAD-2000 are specific surface area: $620 \, m^2 \, g^{-1}$, dipole moment: 0.3, pore size: 4.5 nm and bead size: 20–50 mesh [29–33]. These properties are important advantage for Amberlite XAD resin than other Amberlite XAD resins like XAD-4 and XAD-16. Due to these properties, it has selected as a solid-phase extraction materials for metal chelates for the presented work.

In this study, a simple and sensitive separation and preconcentration procedure has been investigated by using a column loaded with Amberlite XAD-2000 resin for the determination of Mn(II), Fe(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II) ions in natural waters and kale vegetable (*Brassica oleracea* var. *acephala*) collected from various locations in Trabzon-Turkey.

2. Experimental

2.1. Instruments

A Unicam AA-929 atomic absorption spectrophotometer equipped with single element hollow cathode lamps and an air/acetylene burner was used for the determination of trace metals. The instrumental parameters were those recommended by the manufacturer. The wavelengths (nm) selected for the determination of the analytes were as follows: Cr 357.9, Mn 279.5, Fe 248.3, Co 240.7, Ni 232.0, Cu 324.8, Zn 213.9, Cd 228.8 and Pb 217.0. Hanna 211 pH meter with glass electrode was used for the pH adjustments. Milestone Ethos D microwave oven with closed vessel and 1450 psi maximum pressure was used for digestion of plant materials.

2.2. Reagents and solutions

All chemicals were analytical reagent-grade (Merck and Fluka) and all solutions were prepared in distilled/deionized water. Amberlite XAD-2000 and sodium diethyldithiocarbamate (Na-DDTC) were purchased from Sigma Chem. Co., St. Louis. Stock solutions of all metals with a concentration of $1000 \, mg \, L^{-1}$ in $0.5 \, mol \, L^{-1}$ HNO_3 were used except for Cr(VI) where $K_2Cr_2O_7$ salt was dissolved in water. The model and standard solutions of the metals were prepared by diluting from the stock solutions using suitable ratios. 0.1% (w/V) solution of Na-DDTC in ethanol was used as a chelating agent. Trace metal in drinking water standard reference material (CRM-TMDW-500) and CRM NIES No. 7 Tea Leaves were obtained from High-Purity Standards, Inc. and The National Institute for Environmental Studies, respectively.

The calibration curves for analyte ions were drawn after setting various parameters of FAAS including wavelength, slit width, lamp current at an optimum level. The optimum concentration ranges and regression equations for analytes were given in Table 1. The statistical calculations are based on the average of triplicate readings for a standard solution the analyte ions. The precision of the method was investigated by using the model solutions containing the spiked elements on the optimal conditions of the method (Table 1). The calibration standards were not submitted to the preconcentration procedure.

pH 2 buffer solution was prepared by mixing of appropriate volume of $1 \, mol \, L^{-1}$ sodium sulfate and $1 \, mol \, L^{-1}$ sodium hydrogen sulfate solutions (Merck and Fluka). Acetate buffers prepared by mixing different amounts of $1 \, mol \, L^{-1}$ sodium acetate and $1 \, mol \, L^{-1}$ acetic acid (Merck and Fluka) were used to maintain the pH between 4 and 6. Ammonium chloride buffer solutions ($0.1 \, mol \, L^{-1}$) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions (Merck and Fluka) to result in solutions of pH 8–10. pH 12 was obtained by mixing of appropriate amounts of $0.1 \, mol \, L^{-1}$ sodium dihydrogen phosphate and $0.1 \, mol \, L^{-1}$ sodium hydroxide solutions (Merck and Fluka).

2.3. Column preparation

A glass column (10 cm length and 1.0 cm diameter), with a porous disk and a stopcock, has been used for preconcentration of the metals. Before 250 mg of ground and sieved (150–200 μm) XAD-2000 resin was placed in the column, it was washed successively with $1 \, mol \, L^{-1}$ NaOH, water, $1 \, mol \, L^{-1}$ HNO_3, water, acetone and water. After each use, the resin in the column was washed thoroughly with water and related buffer solution, and then stored in water for further applications.

2.4. Sampling

Water samples were stored in polyethylene bottles that were thoroughly washed with detergent, tap water, HNO_3,

Table 1
Analytical characteristics of the calibration curves of the analytes

Analyte	Correlation coefficient	Linear range (mg/L)	Regression equation	Precision (R.S.D. %)
Copper	0.9999	0.06–6.0	$A = 0.0522C + 0.0008$	2.0
Cadmium	0.9998	0.05–1.1	$A = 0.1482C - 0.0002$	1.7
Lead	0.9995	0.15–12.0	$A = 0.0192C + 0.0017$	4.8
Zinc	0.9977	0.05–2.0	$A = 0.1574C + 0.0016$	5.6
Nickel	0.9989	0.1–5.0	$A = 0.0308C + 0.0009$	3.2
Cobalt	0.9994	0.1–6.0	$A = 0.0299C + 0.0013$	2.9
Iron	0.9983	0.1–7.0	$A = 0.0296C + 0.0021$	3.6
Manganese	0.9996	0.04–7.0	$A = 0.0639C + 0.0018$	2.3

A: absorbance, *C*: concentration of analyte.

distilled/deionised water, respectively prior to collection. They were collected from four main sources: (1) Tap water, which provides drinking water for Karadeniz Technical University in Turkey, (2) the branches of Kalyan River (Ciftdere, Temelli and Kustul stream), which will supply drinking water to Trabzon city in the future, (3) Degirmendere River, (4) Vegetable sample; kale (*Brassica oleracea* var. *acephala*) from Yomra (Trabzon) in Turkey.

The water samples were acidified with HNO_3 and filtered through a nitrocellulose membrane with 0.45 µm of pore size. Kale leaves were dried in an oven for 20 h at 105 °C and fine powdered in an agate mortar.

2.5. Preconcentration procedure

The proposed method was tested with model solutions prior to the determination of the trace metals in the real samples. 50 mL of model solutions containing 25 µg of Cr(VI), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II), 10 µg of Zn(II), 50 µg of Pb(II) and 5.0 µg of Cd were prepared. First, pH of the model solutions were adjusted to the desired values (in the range 2–12) by the addition of 2–5 mL of buffer solution. Then 5.0 mL of chelating agent, Na-DDTC was added. The resultant solution was passed completely through the column with a flow rate of 20 mL min^{-1} and after that, the column was rinsed with 10 mL of water. The retained species (metal-DDTC) on the resin was eluted with 7.5 mL of 1 mol L^{-1} HNO_3 in acetone. The eluat was evaporated to near dryness on a hot plate at ~40 °C and quantitatively completed to 5.0 mL with 1 mol L^{-1} HNO_3. Finally the solution was analyzed by FAAS.

2.6. Application to real samples

CRM No. 7 Tea Leaves certified reference material was digested in microwave oven after 1.500 g of fine powdered and dried tea leaves was weighed into teflon beakers and 8 mL of HNO_3, 1 mL of H_2O_2 and 0.5 mL HF were added into the beakers. The pH was adjusted to 8 after volume of the solution was completed to 50 mL and then the proposed method was applied.

1.00 g of fine powdered and dried kale sample was weighed into Teflon vessel and 8 mL of HNO_3, 1 mL of H_2O_2 and 0.5 mL of concentrated HF were added. Then, the content of the vessel was digested by microwave irradiation. The residue diluted to 50.0 mL with deionized water. A blank digest was carried out in the same way.

50 mL of CRM TMDW-500 Drinking Water certified reference material and 500 mL from other water samples were taken and the pHs of water samples and kale samples were adjusted to 8. Then, preconcentration procedure given above was applied.

3. Results and discussion

3.1. The effect of pH on recovery of the metals

The influences of pH on the recoveries of analyte ions on XAD-2000 were investigated in the pH range 2–12. The change
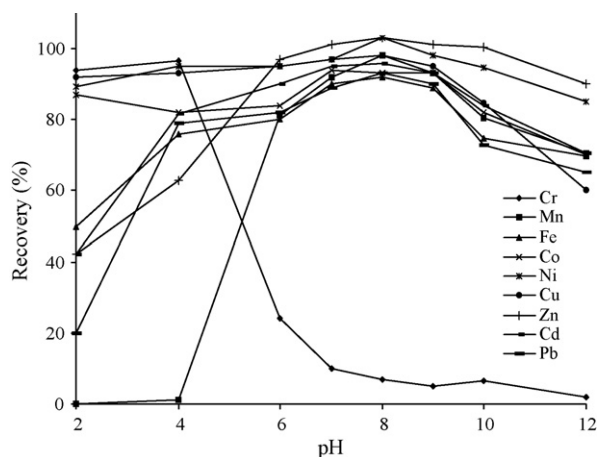

Fig. 1. The variation of pH with the recovery of the metal ions (eluent: 7.5 mL of 1 mol L^{-1} HNO_3 in acetone, complexing agent: 5 mL of 0.1% Na-DDTC, resin quantity: 250 mg, sample volume: 50 mL, sample flow rate: 20 mL min^{-1}, $N = 5$).

of recovery of metals with pH is shown in Fig. 1. The analyte ions were quantitatively recovered in the pH range of 7.0–9.0 except zinc, manganese and chromium. Quantitative recovery values for zinc and manganese were obtained in the pH range 7–10. At the pH range of 2–4, chromium(VI) was recovered quantitatively as DDTC chelates. According to the results the optimum pH was determined as 8 for all the analytes except for Cr(VI).

3.2. Effect of ligant amount

The effects of DDTC amounts on the adsorption of studied metals on the resin were investigated. The recoveries of metals were <15%, when DDTC was not added to the solution. The recovery values increased with the addition of DDTC. The optimum values were obtained after 4.0 mg (4 mL of 0.1% (w/v)) of DDTC for all metal. After this point the recoveries were quantitative in all working range of DDTC. In all further studies, 5.0 mg (5.0 mL of 0.1% (w/v)) of DDTC was used.

3.3. Eluent type and volume

Various acids and organic solvents were used to identify the best eluent for the adsorbed metal-DDTC chelates on Amberlite XAD-2000. The results were summarized in Table 2. Among the solvents studied, especially the acids with acetone provided higher recovery efficiency compared to the acids in aqueous and alcoholic solutions and therefore the highest recoveries were obtained for nitric acid and HCl in acetone. Finally, 1 mol L^{-1} HNO_3 in acetone was specified as the eluent for the desorption of metal chelates from XAD-2000 and was used for the optimization of the other parameters.

The effects of 1 mol L^{-1} M HNO_3 solutions in acetone with volumes 2.5, 5.0, 7.5, 10.0 and 15.0 mL were investigated and quantitative recoveries were obtained after 5.0 mL of the

Table 2
The influences of eluent type on the recoveries (pH 8, sample volume: 50 mL, $N = 3$)

Type of eluent	Recovery (%)							
	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
1 mol L^{-1} HCl	78 ± 4	63 ± 3	<5	<5	<5	53 ± 2	35 ± 2	55 ± 3
1 mol L^{-1} HCl in ethanol	94 ± 3	85 ± 2	10 ± 0	85 ± 2	42 ± 2	95 ± 2	93 ± 2	80 ± 3
1 mol L^{-1} HCl in acetone	96 ± 2	87 ± 4	91 ± 1	97 ± 3	98 ± 2	105 ± 2	96 ± 3	83 ± 3
1 mol L^{-1} acetic acid	72 ± 3	21 ± 1	<5	<5	<5	<5	12 ± 1	84 ± 1
1 mol L^{-1} acetic acid in ethanol	87 ± 3	36 ± 2	41 ± 2	65 ± 2	45 ± 2	75 ± 4	92 ± 3	18 ± 1
1 mol L^{-1} acetic acid in acetone	64 ± 2	71 ± 2	89 ± 3	100 ± 3	97 ± 1	88 ± 4	95 ± 3	81 ± 4
1 mol L^{-1} HNO$_3$	64 ± 2	71 ± 2	<5	<5	<5	82 ± 4	75 ± 2	52 ± 3
1 mol L^{-1} HNO$_3$ in ethanol	95 ± 1	84 ± 3	38 ± 2	93 ± 4	86 ± 2	90 ± 5	86 ± 2	79 ± 4
1 mol L^{-1} HNO$_3$ in acetone	98 ± 2	92 ± 1	93 ± 2	103 ± 3	98 ± 4	103 ± 4	96 ± 3	93 ± 4
Chloroform	47 ± 2	6 ± 0	68 ± 3	81 ± 3	81 ± 2	91 ± 3	90 ± 3	62 ± 3
Acetone	50 ± 3	10 ± 0	80 ± 3	98 ± 2	92 ± 3	89 ± 4	87 ± 3	76 ± 4

eluent. The optimum eluent volume is specified as 7.5 mL for the subsequent studies.

3.4. Effect of flow rate of sample and eluent solutions

The rate of the flow of model solutions through the column is one of the factors affecting the duration of the determination and directly related to the contact of the solution with the resin thereby providing information about the adsorption rate of the complexes on the resin. The model solutions of 50 mL were passed through the column with rates in the range 1–20 mL min^{-1} and the flow rate of the solutions was increased by the application of vacuum via a waterjet. It was observed that the recovery was not changed significantly up to 20 mL min^{-1} and the flow rate 20 mL min^{-1} was selected for further experiments.

The flow rates of eluent solution were investigated in the range of 1–15 mL min^{-1}. After 10 mL min^{-1} of eluent solution, the recovery values of the analytes were not quantitative. For the all experiments, 5 mL min^{-1} was selected as eluent flow rate.

3.5. Sample volume

Due to the low concentrations of trace metals in real samples, by using samples with large volumes, the trace metals in these volumes should be taken into smaller volumes for high preconcentration factor. Hence, the maximum sample volume was optimized by the investigation of the recovery of trace metals in various sample volumes in the range 50–1000 mL. The results were given in Fig. 2. The recoveries of the analytes were quantitative until 500 mL and decreased especially for Mn and Fe above 500 mL of sample volume. In this study, the final solution volume was 5 mL, therefore the preconcentration factors were 100 for the analytes.

3.6. Matrix effects

The investigation about the matrix components of the real samples are an important point in the preconcentration-

separation studies [34–38]. In order to identify the effects of some matrix ions on the recoveries of the analytes on Amberlite XAD-2000 resin, model solutions contain the chlorine salts of Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} ions, some anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$), and transition metal ions with various concentrations were prepared then the preconcentration procedure given Experimental was applied. The results were given in Table 3. The efficiency of the recovery was not affected whether these ions exist individually or as a whole. Hence, the presented method can be applied to real samples including sea water and samples containing transition metals at mg L^{-1} since it was not affected by high concentrations of alkaline and earth alkaline ions.

3.7. Adsorption capacity of the resin

The adsorption capacity is the maximum metal quantity taken up by 1 g of resin and given by mg metal g^{-1} resin or miliequivalent gram (meg). In order to determine this, 100–5000 μg of analytes were loaded to the column containing 250 mg of resin and recoveries were investigated. Then, Langmuir isotherms were plotted in order to determine the resin capacity. Langmuir adsorption isotherm is one of the most well-known and applied
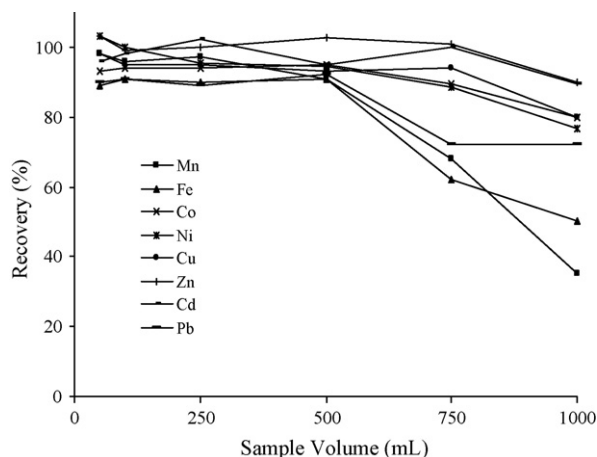

Fig. 2. Effects of sample volume on the recoveries of the analytes (pH 8, $N = 3$).

Table 3
The matrix ions and the recovery of the metal ions (pH 8, sample volume: 50 mL, $N = 3$)

Ion	Concentration (mg L^{-1})	Salt	Recovery (%)							
			Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Na$^+$	500	NaCl	90 ± 3	88 ± 4	99 ± 3	103 ± 2	95 ± 3	91 ± 5	92 ± 3	88 ± 3
	1000		92 ± 2	89 ± 4	94 ± 4	101 ± 3	97 ± 3	96 ± 4	94 ± 2	92 ± 3
	10000		94 ± 3	90 ± 4	95 ± 4	98 ± 2	95 ± 3	95 ± 4	95 ± 2	91 ± 4
K$^+$	250	KCl	92 ± 2	91 ± 3	90 ± 3	99 ± 2	97 ± 2	96 ± 4	94 ± 2	89 ± 4
	500		95 ± 3	92 ± 3	92 ± 4	102 ± 3	99 ± 4	99 ± 4	99 ± 2	89 ± 3
	1000		96 ± 2	89 ± 3	91 ± 4	99 ± 3	100 ± 4	103 ± 4	98 ± 1	90 ± 3
Ca^{2+}	250	CaCl$_2$	96 ± 2	90 ± 3	92 ± 3	103 ± 4	101 ± 4	94 ± 4	100 ± 3	91 ± 3
	500		98 ± 3	91 ± 2	96 ± 2	96 ± 3	102 ± 4	102 ± 4	96 ± 3	90 ± 3
	1000		97 ± 4	89 ± 2	93 ± 2	97 ± 4	98 ± 4	94 ± 5	95 ± 3	92 ± 4
Mg^{2+}	250	MgCl$_2$	96 ± 4	92 ± 2	90 ± 2	103 ± 3	101 ± 3	95 ± 4	99 ± 3	89 ± 4
	500		94 ± 4	91 ± 3	90 ± 1	99 ± 2	102 ± 3	97 ± 4	97 ± 4	90 ± 3
	1000		92 ± 4	92 ± 4	93 ± 4	100 ± 5	103 ± 4	99 ± 4	100 ± 4	91 ± 4
Cl$^-$	20000	NaCl	97 ± 2	91 ± 5	97 ± 2	101 ± 3	98 ± 3	97 ± 4	95 ± 4	89 ± 3
NO$_3^-$	5000	KNO$_3$	98 ± 3	89 ± 4	96 ± 3	100 ± 4	96 ± 3	100 ± 5	93 ± 2	91 ± 3
SO$_4^{2-}$	2500	Na$_2$SO$_4$	94 ± 4	93 ± 3	95 ± 4	99 ± 2	94 ± 2	102 ± 4	95 ± 3	96 ± 4
Al^{3+}	10	Al$_2$(SO$_4$)$_3$	96 ± 3	91 ± 3	95 ± 4	101 ± 4	100 ± 4	97 ± 4	96 ± 2	91 ± 3
Hg^{2+}	10	Hg(NO$_3$)$_2$	98 ± 4	90 ± 3	95 ± 2	97 ± 3	99 ± 2	99 ± 4	97 ± 3	91 ± 5
Cr^{3+}	10	Cr(NO$_3$)$_3$	100 ± 4	92 ± 4	93 ± 4	100 ± 4	96 ± 3	96 ± 3	100 ± 4	93 ± 4
Mn^{2+}	10	Mn(NO$_3$)$_2$	–	91 ± 3	96 ± 3	100 ± 3	97 ± 3	98 ± 4	97 ± 1	92 ± 5
Fe^{3+}	10	Fe(NO$_3$)$_3$	92 ± 2	–	92 ± 3	99 ± 3	93 ± 4	94 ± 5	96 ± 2	88 ± 5
Co^{2+}	10	Co(NO$_3$)$_2$	94 ± 3	93 ± 4	–	102 ± 4	100 ± 2	95 ± 5	97 ± 2	92 ± 4
Ni^{2+}	10	Ni(NO$_3$)$_2$	96 ± 3	90 ± 4	92 ± 4	–	97 ± 2	94 ± 4	93 ± 4	90 ± 3
Cu^{2+}	10	Cu(NO$_3$)$_2$	97 ± 2	94 ± 5	96 ± 3	100 ± 4	–	98 ± 4	94 ± 3	92 ± 3
Zn^{2+}	10	Zn(NO$_3$)$_2$	99 ± 4	89 ± 3	93 ± 2	98 ± 3	96 ± 1	–	99 ± 3	94 ± 4
Cd^{2+}	10	Cd(NO$_3$)$_2$	96 ± 4	91 ± 3	94 ± 3	99 ± 2	100 ± 3	102 ± 4	–	90 ± 4
Pb^{2+}	10	Pb(NO$_3$)$_2$	95 ± 1	90 ± 4	94 ± 4	98 ± 4	101 ± 4	101 ± 3	98 ± 2	–
Mixed[a]			95 ± 4	89 ± 4	96 ± 4	103 ± 4	101 ± 4	103 ± 5	97 ± 3	96 ± 5

[a] Mixed: The solution containing 10,000 mg L^{-1} Na$^+$, 1000 mg L^{-1} K$^+$, Ca^{2+} and Mg^{2+}, 20,000 mg L^{-1} Cl$^-$, 5000 mg L^{-1} NO$_3^-$, 2500 mg L^{-1} SO$_4^{2-}$, 2.5 mg L^{-1} of Al^{3+}, Bi^{3+}, Hg^{2+} ions.

adsorption isotherms and described by the equation below:

$$q_e = \frac{q_{max} a_L C_e}{1 + a_L C_e} \quad (1)$$

where q_e is the amount of metal adsorbed per unit weight of the resin (mg g^{-1}) at equilibrium, C_e the final concentration in the solution (mg L^{-1}), q_{max} the maximum adsorption at monolayer coverage (mg g^{-1}), and a_L the adsorption equilibrium constant which is related to energy of adsorption (L mg^{-1}). The equation given above can be rearranged as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{a_L q_{max}} \quad (2)$$

A plot of C_e/q_e versus C_e shows linearity, hence Langmuir constants q_{max} and a_L can be calculated from the gradient and intercept of the plot, respectively.

The amount of maximum metal (q_{max}) adsorbed on 1.0 g of Amberlite XAD-2000 was calculated as mg g^{-1} from the plots obtained for each metal. The results obtained from the adsorption capacity experiments for Cu, Fe, Zn, Mn, Cd, Pb, Ni and Co were 5.63, 5.40, 4.80, 4.76, 4.41, 6.42, 3.80, and 6.08 mg g^{-1}, respectively.

Amberlite XAD-2000 is a styrene–divinylbenzene copolymer. The adsorption on XAD-2000 is based on molecular adsorption. The metals are adsorbed as metal-DDTC chelates. The desorption of the metal chelates are performed by using 1 mol L^{-1} HNO$_3$ in acetone to breakdown the physical interactions between resin and metal chelates.

3.8. Accuracy of the presented procedure

The limits of detection (LOD) of the proposed preconcentration method for the determination of investigated elements were studied by passing 50 mL of blank solutions from the column under the optimal experimental conditions by using the regression equation of each analytes. The detection limit ($N = 20$, blank + 3s, where s is standard deviation of blank estimation) for Mn(II), Fe(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II) were found as 0.20, 0.35, 0.25, 0.20, 0.20, 0.15, 0.45 and 0.25 μg L^{-1}, respectively.

To estimate the accuracy of the procedure, different amounts of the investigated metal ions were spiked into 50 mL of various natural waters. The resulting solutions were submitted to the presented procedure given in Experimental. The results

Table 4
The accuracy test results for spiked recovery (pH 8, sample volume: 50 mL, $N = 3$)

Analyte	Added (µg)	Ciftdere stream		Degirmendere stream		Kustul stream		Temelli stream		Tap water	
		Found (µg)	Recovery (%)	Found (µg)	Recovery (%)	Found (µg)	Recovery (%)	Found (µg)	Recovery (%)	Found (µg)	Recovery (%)
Mn	0	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
	10	9.8 ± 0.3	98	9.5 ± 0.2	95	9.9 ± 0.4	99	9.7 ± 0.2	97	9.7 ± 0.3	97
	25	23.8 ± 1.2	95	24.3 ± 1.1	97	24.3 ± 0.8	97	24.0 ± 0.8	96	24.0 ± 1.1	96
Fe	0	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
	10	9.1 ± 0.2	91	9.2 ± 0.3	92	9.0 ± 0.5	90	9.2 ± 0.3	92	9.3 ± 0.4	93
	25	22.5 ± 0.8	90	22.7 ± 0.6	91	22.6 ± 0.8	90	22.3 ± 0.6	89	22.9 ± 0.5	92
Co	0	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
	10	9.6 ± 0.1	96	9.4 ± 0.3	94	9.7 ± 0.3	97	9.6 ± 0.4	96	9.9 ± 0.3	99
	25	24.5 ± 0.6	98	24.5 ± 1.0	98	23.8 ± 1.1	95	24.8 ± 0.9	99	24.5 ± 0.4	98
Ni	0	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
	10	10.0 ± 0.4	100	9.6 ± 0.1	96	10.1 ± 0.5	101	9.6 ± 0.3	96	9.7 ± 0.1	97
	25	24.5 ± 1.1	98	24.8 ± 0.9	99	23.8 ± 1.2	95	24.6 ± 0.7	98	24.8 ± 0.7	99
Cu	0	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
	10	9.7 ± 0.2	97	10.2 ± 0.3	102	9.8 ± 0.4	98	9.9 ± 0.5	99	10.1 ± 0.4	101
	25	25.3 ± 0.8	101	24.8 ± 0.8	99	25.3 ± 1.0	101	25.8 ± 0.9	103	25.0 ± 0.9	100
Zn	0	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
	10	9.4 ± 0.4	94	9.4 ± 0.2	94	9.6 ± 0.4	96	9.7 ± 0.2	97	9.7 ± 0.2	97
	25	25.5 ± 1.0	102	24.0 ± 1.2	96	23.5 ± 0.5	94	25.0 ± 1.1	100	23.3 ± 0.6	93
Cd	0	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
	10	9.7 ± 0.2	97	9.6 ± 0.3	96	9.3 ± 0.3	93	9.5 ± 0.4	95	9.6 ± 0.3	96
	25	23.8 ± 0.7	95	24.0 ± 1.1	96	23.0 ± 0.9	92	23.8 ± 1.0	95	23.5 ± 0.7	94
Pb	0	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
	10	9.1 ± 0.5	91	9.4 ± 0.4	94	9.1 ± 0.3	91	9.0 ± 0.3	90	9.3 ± 0.3	93
	25	22.6 ± 0.5	90	22.9 ± 0.7	92	22.5 ± 0.7	90	22.9 ± 0.7	92	23.0 ± 1.0	92

BDL: below the detection limit.

Table 5
Analysis of the Certified Reference Materials for the determination of analytes after application presented procedure

	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
CRM TMDW-500 Drinking Water								
Certified value ($\mu g\,L^{-1}$)	40.0 ± 0.2	100.0 ± 0.5	25.0 ± 0.1	60.0 ± 0.3	20.0 ± 0.1	70.0 ± 0.4	10.0 ± 0.05	40.0 ± 0.2
Amount found ($\mu g\,L^{-1}$)[a]	38.0 ± 1.1	92.0 ± 5.1	23.6 ± 0.6	60.2 ± 2.9	19.7 ± 0.5	70.7 ± 5.3	9.8 ± 0.4	37.3 ± 3.1
CRM NIES[b] No. 7 Tea Leaves								
Certified value ($\mu g\,g^{-1}$)	700 ± 25	–[c]	0.12[c]	6.5 ± 0.3	7.0 ± 0.3	33 ± 3	0.030 ± 0.003	0.80 ± 0.03
Amount found ($\mu g\,g^{-1}$)[a]	650 ± 26	ND	BDL	6.3 ± 0.4	6.7 ± 0.4	31 ± 3	BDL	0.73 ± 0.07

ND: not determined.
[a] The confidence interval was calculated at $P = 0.95$ ($N = 3$).
[b] NIES, The National Institute for Environmental Studies.
[c] Not certified.

Table 6
Trace metals contents of real water samples with the proposed method (pH 8, sample volume: 500 mL, $N = 3$)

Samples	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Ciftdere stream ($\mu g\,L^{-1}$)	0.73 ± 0.04	33.6 ± 1.1	0.56 ± 0.03	2.21 ± 0.09	9.0 ± 0.3	24.7 ± 0.5	14.0 ± 0.7	2.56 ± 0.10
Degirmendere stream ($\mu g\,L^{-1}$)	2.22 ± 0.09	275 ± 8	0.89 ± 0.05	2.00 ± 0.07	6.67 ± 0.22	5.0 ± 0.2	3.40 ± 0.11	1.95 ± 0.06
Kustul stream ($\mu g\,L^{-1}$)	0.51 ± 0.02	29.0 ± 1.0	0.37 ± 0.01	0.58 ± 0.03	2.31 ± 0.08	12.3 ± 0.5	2.10 ± 0.07	0.76 ± 0.04
Temelli stream ($\mu g\,L^{-1}$)	0.88 ± 0.05	46.6 ± 2.2	0.40 ± 0.02	1.77 ± 0.03	7.68 ± 0.15	18.4 ± 0.6	1.51 ± 0.04	1.95 ± 0.03
Tap water ($\mu g\,L^{-1}$)	1.00 ± 0.03	3.0 ± 0.2	0.66 ± 0.02	0.27 ± 0.01	0.96 ± 0.03	10.1 ± 0.5	BDL	BDL

were given in Table 4. The recovery percentages of analyte ions were evaluated and the results showed that the real sample matrixes did not affect the recovery of the trace metals (Table 4).

Table 7
Levels of analytes in kale vegetable (*Brassica oleracea* var. *acephala*) after application of preconcentration procedure

Analyte	Added ($\mu g/g$)	Found ($\mu g/g$)	Recovery (%)
Mn	0	41.0 ± 1.2	–
	10	50.8 ± 1.5	98
	25	64.5 ± 2.1	94
Fe	0	108.0 ± 6.5	–
	10	117.0 ± 6.8	90
	25	130.8 ± 6.1	91
Co	0	BDL	–
	10	9.1 ± 0.2	91
	25	23.3 ± 0.7	93
Ni	0	1.50 ± 0.06	–
	10	11.4 ± 0.3	99
	25	26.8 ± 1.1	101
Cu	0	2.75 ± 0.12	–
	10	12.8 ± 0.4	100
	25	27.9 ± 1.4	101
Zn	0	33.0 ± 1.1	–
	10	43.2 ± 0.9	102
	25	58.8 ± 1.4	103
Cd	0	BDL	–
	10	9.5 ± 0.4	95
	25	24.3 ± 0.9	97
Pb	0	BDL	–
	10	9.1 ± 0.3	91
	25	22.6 ± 0.8	90

3.9. Application of the method

The method presented was checked to two different reference materials (NIES No. 7 Tea Leaves and CRM TMDW-500 Drinking Water) for the determination of analyte ions. The certified values and obtained results are given in Table 5. The results reveal good agreement between the observed values and certified values.

The method was applied to natural water samples collected from the various locations in Trabzon-Turkey. The results are shown in Table 6. The metal concentration levels in drinking waters and river waters determined by this method were compatible with the standard levels published by World Health Organization [39]. The procedure presented for analytes was also applied to various microwave-assisted digested kale vegetable (*Brassica oleracea* var. *acephala*). The results are given in Table 7.

4. Conclusion

The presented method is simple, time saving, economical. XAD-2000 in the column used for preconcentration can be used approximately 200 times. After 200 times, the recoveries of the metal-chelates were not quantitative. The resin may be loss of its adsorption properties after usage 200 times for preconcentration. The separation-preconcentration step takes about 30 min for 500 mL of water sample solution. The possible interference of alkaline and earth alkaline ions to the analysis were investigated and since an important interference was not encountered.

Comparison of Amberlite XAD–2000/diethyldithiocarbamate (DDTC) and Amberlite XAD–2000/1-(2-pyridylazo)-2-naphthol (PAN) methods for solid-phase extraction of metal ions is given in Table 8. Eight elements were quantitatively

Table 8

Comparison of Amberlite XAD–2000/diethyldithiocarbamate (DDTC) and Amberlite XAD–2000/1-(2-pyridylazo)-2-naphthol (PAN) methods for solid-phase extraction of metal ions

System	Analytes	Eluent	PF	DL, $\mu g\,L^{-1}$	Ref.
XAD–2000/1-(2-pyridylazo)-2-naphthol (PAN)	Cr(III), Cu(II), Ni(II), Pb(II)	1 mol L^{-1} HNO$_3$ in acetone	250	–	[30]
XAD–2000/diethyldithiocarbamate (DDTC)	Mn(II), Fe(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II), Ni(II)	1 mol L^{-1} HNO$_3$ in acetone	100	0.15–0.45	This work

DL: detection limit.

recovered in the presented work while four elements were recovered in the XAD-2000/1-(2-pyridylazo)-2-naphthol (PAN) method [30]. 1 mol L^{-1} HNO$_3$ in acetone was effective eluent for both methods. The influences of the matrix components were higher tolerable levels than the XAD-2000/1-(2-pyridylazo)-2-naphthol (PAN) method.

Acknowledgements

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