

Scientific paper

Simultaneous Preconcentration of Trace Metals in Environmental Samples Using Amberlite XAD-2010/8-Hydroxyquinoline System

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Abstract

A simple and sensitive system for simultaneous preconcentration of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pb(II) and Cd(II) at trace level by flame atomic absorption spectrometry (FAAS) is proposed. Amberlite XAD-2010 packed in a column was used as sorbent. Analyte ions were sorbed in the column as their 8-hydroxyquinoline chelates; they could then be eluted by 1 mol L⁻¹ HNO₃ in acetone. The analytical conditions including pH, amounts of 8-hydroxyquinoline, sample volume etc. on the quantitative recoveries of the analytes were investigated. The effects of the concomitants ions on the recoveries of the analytes column were also studied. The detection limits, corresponding to three times the standard deviation of the blank, were found to be in the range of 0.10–0.40 µg L⁻¹. The accuracy of the procedure was measured by analyte determinations in certified reference materials (CRM NIES No. 7 Tea Leaves and TMDW-500 Drinking Water). The applications of the presented system were performed by the analysis of some environmental samples including water samples.

Keywords: Amberlite XAD-2010, solid phase extraction, preconcentration, FAAS

1. Introduction

The determination of trace heavy metal contents of environmental materials including natural water and food samples have been continuously performed to put forward the level of pollution levels of the environment by trace metals.^{1–4} For the direct determination of heavy metals in environmental samples, a number of sensitive instrumental methods including atomic spectroscopic methods are available, which, however, can suffer from interferences by the matrix of the samples. Also other important problem is lower concentration of the analytes than the limit of detection of the instruments. Due to these points, a separation-preconcentration step for heavy metals is often necessary before determination of the analytes.^{5–7} The most widely used techniques for the separation-preconcentration of trace elements include solvent extraction,^{8,9} coprecipitation,^{10,11} electrochemical deposition,^{12,13} cloud point extraction,^{14,15} ion-exchange^{16,17} and membrane filtration^{18,19}.

Solid phase extraction is an attractive method for the preconcentration and separation of trace heavy metal ions among these preconcentration techniques. The application of solid-phase extraction is due to its advantages, such as simplicity, high enrichment factor, easy application to the flow injection systems, easy regeneration for multiple sorption-desorption cycles, significantly reduces the consumption and exposure to solvent, disposal costs, and extraction time and good reproducibility in the sorption characteristics.^{20–22} Up to now, several kinds of sorbents, such as activated carbon,⁵ polymeric supports,^{6,7} Diaion HP-20,²³ naphthalene,²⁴ octadecyl bonded silica membrane disk²⁵ etc. have been used for the preconcentration and determination of traces metal ions.

Amberlite XAD resin family is an important place in the solid phase extraction studies for heavy metal ions in the environmental samples. The family belongs to two main groups: polystyrene-divinyl benzene based resins in-

cluding XAD-1, XAD-2, XAD-4, XAD-16, XAD-1180 and XAD-2000, and polyacrylic acid ester based resins including XAD-7, XAD-8 and XAD-11. The affinity of Amberlite XAD resins for absorbable compounds correlates with their specific surface area, polarity and specific pore volume.^{26,27}

Amberlite XAD-2010, and Amberlite XAD-2000 are polystyrene-divinyl benzene based resins. Some properties of these two resin are given in Table 1. The literature survey revealed that XAD-2000 and XAD-2010 are used for the preconcentration and isolation of organic materials at trace levels;^{28,29} however, only a few studies with these resins were performed by our working group have been used for the preconcentration of trace metals.^{30–32} Due to limited usage of these resins, for the present work, Amberlite XAD-2010 was selected as solid phase extractor for metal ions.

Table 1: Comparison of the resins in terms of some chemical properties

Resin	Surface area (m ² g ⁻¹)	Pore diameter (Å)	Bead mesh size	Pore volume (mL g ⁻¹)
XAD-2000	580	42	20–60	0.64
XAD-2010	660	280	20–60	1.80

In the presented study, a preconcentration-separation procedure based on solid phase extraction has been established for the flame atomic absorption spectrometric determination of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pb(II) and Cd(II) ions in environmental samples to show possible usage of Amberlite XAD-2010 as solid phase extractor. The analytical parameters, including pH of the solution, modification of the adsorbent, sample volume, eluent and effects of interfering ions were investigated.

2. Experimental

2.1. Instrumental

The measurements of metal ions were performed with a Unicam Model AA-929 flame atomic absorption spectrometer equipped with a single element hollow-cathode lamps and 5.0 cm of an air/acetylene burner head. The instrumental parameters were those recommended by the manufacturer. The selected wavelengths (nm) for analytes are 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

A digital pH meter (Hanna Instruments Model pH 211) with glass electrode was used for all pH measurements. Milestone Ethos D microwave oven with closed vessels and 1450 psi max pressure was used for digestion of moss and rock materials.

2.2. Reagents and Solutions

Distilled-deionized water from a water purification system was used to prepare all solutions. All reagents were of analytical reagent grade. The laboratory glassware were kept overnight in 1 mol L⁻¹ nitric acid solutions. Afterwards, they were rinsed thoroughly with distilled-deionized water and left to dry. Metal working solutions at mg L⁻¹ level were prepared daily by diluting 1000 mg L⁻¹ of stock solutions (Merck and Fluka). Amberlite XAD-2010 and 8-hydroxyquinoline (8-HQ) were purchased from Sigma Chem. Co., St. Louis. 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 pHs of the solutions were adjusted with the buffer solutions. The 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). pH of the buffer and the buffered solutions were controlled with the pH meter.

2.3. Sampling

The polyethylene bottles (5 L) used for sampling river from Degirmendere River in Trabzon-Turkey and drinking water from Karadeniz Technical University in Trabzon-Turkey. The bottles were successively precleaned with detergent, distilled-deionized water, 1 mol L⁻¹ HNO₃, and distilled-deionized water. The water samples were taken in June, 2006. High-purity HNO₃ was added to keep the final acidity of the water at about pH 2 after sampling. The samples were filtered through a Millipore cellulose membrane (pore size 0.45 μm) immediately after sampling and stored at 4 °C.

Moss samples collected from Hopa-Artvin, Turkey were dried in an oven for 20 h at 80 °C and ground into fine powder in an agat mortar. Rock samples were collected from Kumbet Plateau, Giresun-Turkey. Rock sample was crushed, ground and left to dry in an oven for 3 h at 105 °C.

2.4. Preparation of Column

A glass column (10 cm × 1.0 cm i.d.), with a porous disk and a stopcock, packed with 250 mg of the resin bead was employed. Before placed in the column, ground and

sieved (150–200 μm) XAD-2010 resin was washed successively with 1 mol L⁻¹ NaOH, water, 1 mol L⁻¹ HNO₃, water, acetone and water.^{33,34} 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. 5. Model Workings

A solution containing 25 μg of 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(II) in a volume of 50 mL was prepared. pH was adjusted to the desired value (in the range 2–10) and 5 mL of 0.1% (w/v) chelating agent (8-HQ) was added to the solution. After waiting for 10 minutes for the formation of metal-8-HQ chelates, the solution was passed through the column packed with Amberlite XAD-2010, at a flow rate of 20 mL min⁻¹. Then, the metal chelates were stripped from the resin column with 10 mL of 1 mol L⁻¹ HNO₃ in acetone. The acetone in the eluent solution was evaporated to near dryness on a hot plate at ~40 °C. The residue was quantitatively completed to 10 mL with 1 mol L⁻¹ HNO₃. Total time for the procedure is approximately 30 minutes. Finally the solution was analyzed by FAAS.

2. 6. The Application of the Method to Real Samples

CRM NIES No. 7 Tea Leaves standard reference material was digested in closed microwave digestion system prior to application of presented procedure. 1.00 g of fine powdered and dried sample was weighed into Teflon vessel and 8 mL of HNO₃, 1 mL of H₂O₂ 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 distilled-deionized water. A blank digest was carried out in the same way. Then the preconcentration procedure given above was applied to the final solution. The final volume was made to 5 mL and the solution was analyzed by FAAS.

The preconcentration procedure was also applied to CRM TMDW-500 Drinking Water standard reference material (100 mL), drinking and river waters (1000 mL) after adjusting pH to 8. Then the preconcentration procedure given above was applied to the final solutions. The final volume was made to 10 mL and the solution was analyzed by FAAS.

0.500 g of fine powdered moss and rock samples were digested with 6 mL of HNO₃ + 2 mL of H₂O₂ and 4.5 mL of HCl + 1.5 mL of HNO₃ + 2 mL of HF, respectively, in microwave oven at 45 bar pressure. After digestion, the suspension from rock sample was filtered through a blue band filter paper. The clear solutions obtained from moss and rock samples were completed to 50.0 mL with distilled-deionized water. After preconcentration step, final

volumes of solid samples and water samples were made up to 5 and 10 mL, respectively.

3. Results and Discussion

3. 1. Effect of pH on the Retention of Analytes

The pH study was carried out to investigate its effect on the retention of metal ions on Amberlite XAD-2010/8-HQ resin column by applying the proposed procedure at the range 2–12. The results are depicted in Figure 1. Copper was quantitatively recovered in the pH range of 2–12. Quantitative recoveries were obtained in the pH range of 6–12 for nickel, cadmium, lead and cobalt while zinc, manganese and cobalt were recovered in the pH range of 8–12. According to the results the optimum pH was selected as 8 for all the metals.

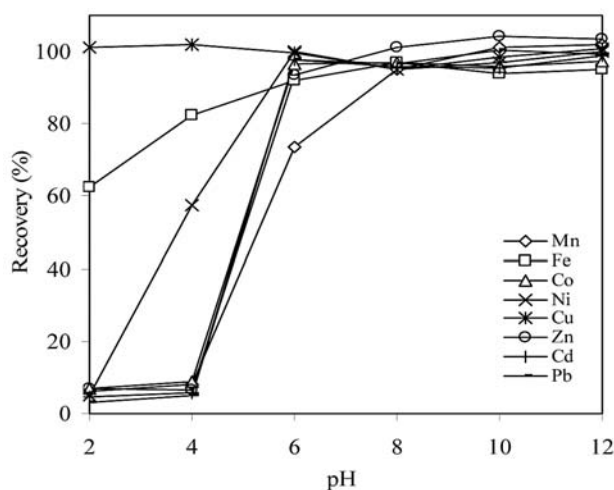


Figure 1. Effect of pH on the retention of metal ions (Eluent: 1 mol L⁻¹ HNO₃ in acetone, complexing agent: 5 mL of 0.1% 8-HQ, sample flow rate: 20 mL min⁻¹, N=4)

3. 2. Influences of the Amounts of Ligand

The influences of the amounts of 8-hydroxyquinoline also investigated. In order to determine this, amount of 8-HQ on the retention was examined from 1.25 to 25 mg. Various amounts of 8-HQ were added to the model solutions and preconcentration procedure was applied.

The recoveries of the metals were < 15%, when 8-HQ was not added to the solution. The recovery values increased with the addition of 8-HQ. The quantitative values were obtained after 5.0 mg (5 mL of 0.1% (w/v)) of 8-HQ (Figure 2). After this point the recoveries were quantitative in all working range of 8-HQ. For all further works, 5.0 mg of 8-hydroxyquinoline was added.

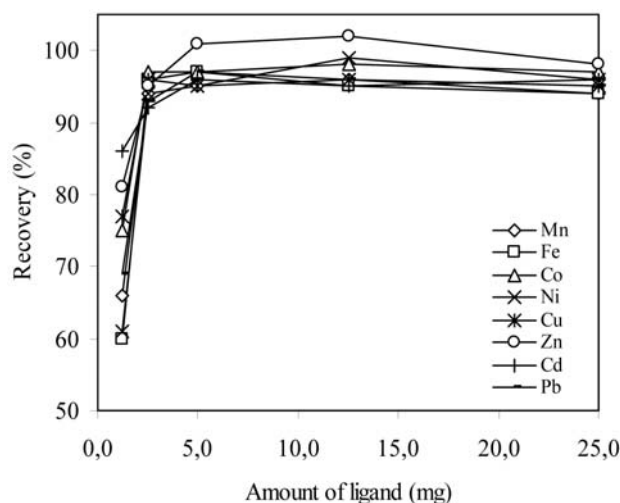


Figure 2. Effect of amount of ligand (Eluent: 1 mol L⁻¹ HNO₃ in acetone, pH: 8, N=3)

3. 3. Effect of Eluent Type and Volume

One of the most important parameters affecting the recoveries of trace metals is selection of a suitable eluent. Thus, various acids and organic solvents were used to identify the best eluent for desorption of the metal/8-HQ chelates adsorbed on the resin and the percentage of recovery for each metal was determined. 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 HNO₃ and HCl in acetone. 1 mol L⁻¹ HNO₃ in acetone was chosen as the eluent owing to its effective elution of the ad-

sorbed analyte complex. The influence of volume of 1 mol L⁻¹ HNO₃ in acetone was also examined (Table 3). The optimum eluent volume is specified as 10 mL for the subsequent studies.

3. 4. The Effect of the Sample Flow Rate

The flow rate 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^{35–38} thereby providing information about the adsorption rate of the complexes on the resin. 50 mL of the model solutions containing certain amounts of corresponding metal ions were passed through the column with rates in the range 1–30 mL min⁻¹ and the flow rate of the solutions was increased by the application of vacuum via a waterjet. The retention of Mn(II), Fe(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II) as 8-HQ complexes were almost independent from flow rates when flow rates were within 1.0 and 30.0 mL min⁻¹. A sample flow rate of 20.0 mL min⁻¹ was selected. This rate is high enough to load the sample in a moderate short time and allowing metal/8-HQ chelates to interact with XAD-2010.

3. 5. The Effect of the Sample Volume

Because of low concentrations in real samples, large sample volume is generally required for effective preconcentration and determination of trace metals. Therefore, the effect of sample volume on the recoveries of the analytes were investigated by using model solutions containing the same amount of trace metals in the volume range of 50–2500 mL which were passed through the column under optimum conditions. The results were given in

Table 2: The eluent type and the recovery of analytes (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 in acetone	99 ± 3	99 ± 4	94 ± 3	94 ± 2	94 ± 2	100 ± 6	97 ± 2	98 ± 4
1 mol L ⁻¹ HNO ₃ in acetone	95 ± 3	97 ± 4	97 ± 2	95 ± 2	95 ± 3	101 ± 6	96 ± 2	97 ± 4
1 mol L ⁻¹ HNO ₃ in water	90 ± 3	80 ± 4	38 ± 2	84 ± 3	80 ± 3	89 ± 7	70 ± 3	93 ± 5
1 mol L ⁻¹ HCl in water	80 ± 3	80 ± 5	44 ± 2	80 ± 4	78 ± 3	62 ± 5	64 ± 3	94 ± 5
Acetone	58 ± 3	77 ± 4	88 ± 2	74 ± 3	42 ± 2	92 ± 7	72 ± 3	79 ± 4
Ethanol	46 ± 2	65 ± 3	76 ± 3	70 ± 3	37 ± 2	86 ± 6	24 ± 1	36 ± 4

Table 3: The eluent volume and the recovery of the metal ions (pH: 8, N = 3)

Eluent vol. (mL)	Recovery (%)							
	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
2.5	84 ± 3	79 ± 3	76 ± 2	80 ± 3	78 ± 3	80 ± 4	75 ± 3	77 ± 4
5.0	90 ± 3	93 ± 3	89 ± 3	94 ± 1	86 ± 2	87 ± 4	83 ± 3	76 ± 4
7.5	94 ± 2	98 ± 4	95 ± 3	97 ± 2	93 ± 3	101 ± 6	97 ± 2	87 ± 5
10.0	95 ± 3	97 ± 4	97 ± 2	95 ± 2	95 ± 3	101 ± 6	96 ± 2	97 ± 4
12.5	95 ± 1	100 ± 4	98 ± 3	99 ± 3	96 ± 4	100 ± 6	96 ± 1	96 ± 4
15.0	97 ± 3	99 ± 5	96 ± 3	97 ± 3	96 ± 3	97 ± 5	101 ± 3	96 ± 5

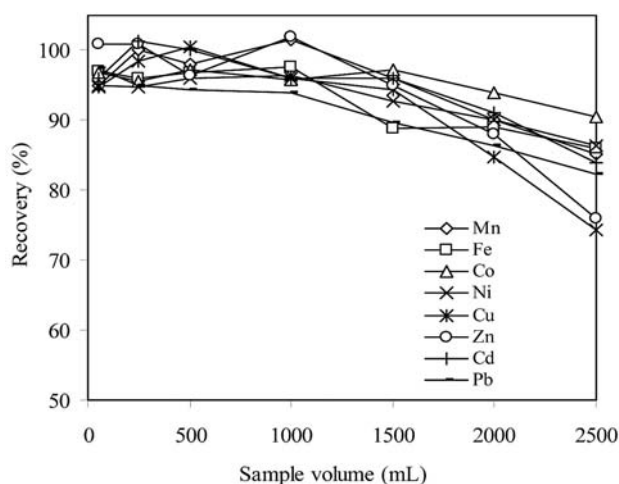


Figure 3. Effect of sample volume (pH: 8, N=3)

Figure 3. The recoveries were found to be stable until 1000–1500 mL. As a result, sample volume was selected 1000 mL especially for real water samples. In this study, the final solution volume to be measured by FAAS was 10 mL, therefore the preconcentration factors were 100 for eight metal ions.

3. 6. Effect of Foreign Ions

To assess the usefulness of the proposed method, the effects of representative potential interfering species especially alkaline and earth alkaline ions on the recoveries of analytes were also tested. The model solutions containing fixed amount of trace metal ions together with either individual matrix ions or mixed matrix ions in various concentrations were prepared and the preconcentration procedure was applied. The results were given in

Table 4. Commonly encountered matrix components such as alkali and alkaline earth elements generally do not form stable complexes and are not retained on the resin, however their high concentrations may affect recoveries of trace metals. The results showed that trace metals were not affected by the medium containing either individual or mixed ions.

3. 7. Adsorption Capacity of the Resin

The adsorption capacity is the maximum metal quantity taken up by 1 gram of resin and given by mg metal g^{-1} resin or meg. To determine this, 100–6000 μg of analyte metals 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 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 ($L mg^{-1}$ or $L mol^{-1}$).

The equation given above can be rearranged as follows:

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

Table 4: 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	96 ± 3	94 ± 5	98 ± 4	101 ± 5	100 ± 3	102 ± 5	97 ± 3	96 ± 4
	1000		94 ± 4	95 ± 5	97 ± 3	96 ± 4	95 ± 3	97 ± 5	96 ± 2	94 ± 5
	10000		94 ± 3	92 ± 5	99 ± 3	97 ± 4	93 ± 2	99 ± 4	95 ± 2	92 ± 6
K ⁺	250	KCl	97 ± 4	95 ± 5	100 ± 3	98 ± 3	99 ± 3	101 ± 5	97 ± 3	95 ± 4
	500		96 ± 4	96 ± 5	98 ± 2	100 ± 3	95 ± 4	102 ± 6	98 ± 2	94 ± 4
	1000		95 ± 5	96 ± 4	98 ± 2	98 ± 2	99 ± 4	101 ± 7	99 ± 2	95 ± 5
Ca ²⁺	250	CaCl ₂	94 ± 4	93 ± 4	100 ± 3	99 ± 2	101 ± 5	103 ± 5	97 ± 1	96 ± 4
	500		95 ± 5	97 ± 4	98 ± 3	96 ± 4	97 ± 4	97 ± 5	100 ± 2	94 ± 3
	1000		96 ± 4	101 ± 6	100 ± 4	99 ± 3	98 ± 4	103 ± 4	99 ± 3	96 ± 4
Mg ²⁺	250	MgCl ₂	95 ± 3	97 ± 5	99 ± 3	101 ± 4	100 ± 3	101 ± 5	100 ± 3	95 ± 5
	500		94 ± 4	95 ± 3	98 ± 3	100 ± 4	99 ± 4	102 ± 5	97 ± 2	97 ± 4
	1000		95 ± 5	94 ± 4	96 ± 2	100 ± 5	97 ± 3	96 ± 5	95 ± 2	93 ± 5
Mixed*			101 ± 5	102 ± 5	96 ± 4	99 ± 4	96 ± 3	102 ± 6	97 ± 4	96 ± 5
Mixed**			98 ± 4	101 ± 5	98 ± 4	95 ± 5	97 ± 4	102 ± 6	96 ± 3	96 ± 6

* Sample containing 1000 $mg L^{-1}$ of Ca²⁺, Mg²⁺, Na⁺ and K⁺

** Sample containing 10000 $mg L^{-1}$ of Na⁺, 500 $mg L^{-1}$ of SO₄²⁻, 12500 $mg L^{-1}$ of Cl⁻, 10000 $mg L^{-1}$ of NO₃⁻

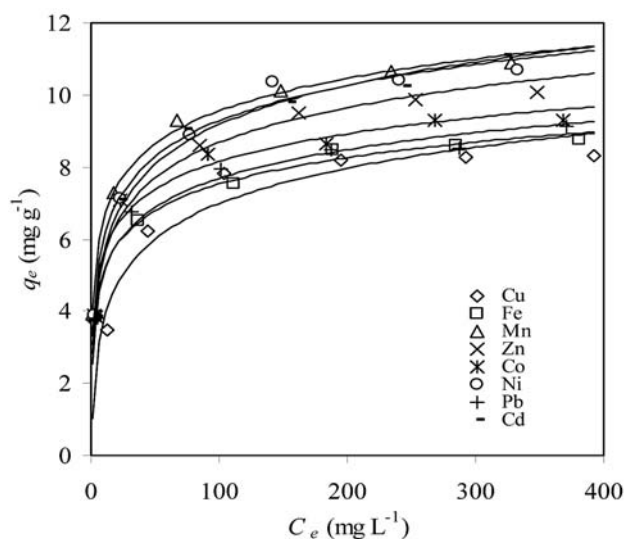


Figure 4. Langmuir isotherm; C_e vs q_e

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 resin was calculated as mg g^{-1} from Langmuir isotherms (Figure 4 and 5). The results are given in Table 5.

3. 8. Figure of Merits

Analytical recoveries for the investigated ions was assessed for two concentration levels, after spiking two water samples (50 mL of tap and river water) with analyte quantities of 10 and 25 μg for each metal. As can be seen Table 6, good recoveries were reached for all elements.

The detection limit (DL) was calculated as three times the standard deviation of twenty replicate measure-

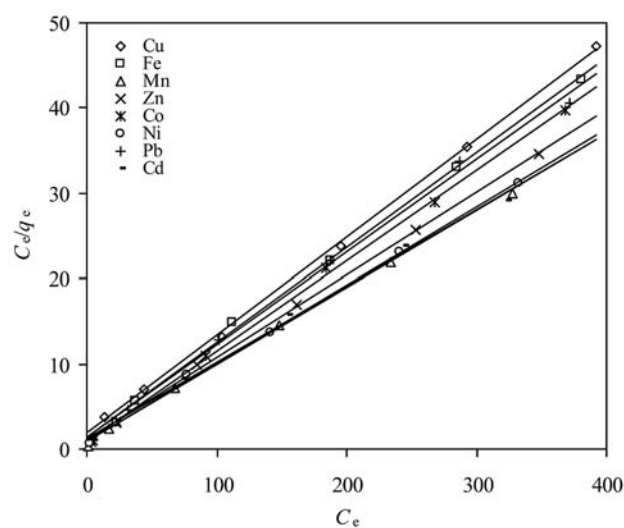


Figure 5. Langmuir isotherm; C_e/q_e vs C_e

ments of blank sample with the preconcentration step. The detection limits were calculated by dividing the instrumental detection limit by preconcentration factor. The results were given in Table 7. To find the precision of the method for analytes, the procedure was repeated ten times under optimum conditions and it was presented as RSD%. The calculated values for statistical evaluation of the method are given in Table 7. The working range for flame atomic absorption spectrometric determinations were also given in Table 7.

3. 9. The Application of the Method to Real Samples

The accuracy of the method was verified by analyzing CRM NIES No. 7 Tea Leaves and TMDW-500 Drinking Water Certified Reference Materials. Results (Table

Table 5: Adsorption capacity of the resin and Langmuir constants from Figure 5

	Cu	Fe	Mn	Zn	Co	Ni	Pb	Cd
Equation; $y = mx + n$	$y = 0.11x + 1.80$	$y = 0.11x + 1.37$	$y = 0.09x + 0.81$	$y = 0.10x + 1.11$	$y = 0.11x + 0.93$	$y = 0.09x + 0.97$	$y = 0.11x + 1.33$	$y = 0.09x + 1.31$
R^2	0.9994	0.9985	0.9988	0.9993	0.9988	0.9987	0.9974	0.9962
$q_{\max}; 1/m$ (mg g^{-1})	8.7	9.0	11.1	10.3	9.5	11.0	9.2	11.2
$\alpha_L; 1/(q_{\max} \cdot n)$ (L mol^{-1})	$\sim 4.0 \times 10^3$	$\sim 4.5 \times 10^3$	$\sim 6.0 \times 10^3$	$\sim 5.7 \times 10^3$	$\sim 6.7 \times 10^3$	$\sim 5.5 \times 10^3$	$\sim 1.7 \times 10^4$	$\sim 7.6 \times 10^3$

Table 7: Figure of merits of the method

Statistical parameters	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Detection limit ($\mu\text{g L}^{-1}$)	0.14	0.30	0.25	0.23	0.17	0.10	0.12	0.40
Relative standard deviation, RSD (%)	2.1	3.8	3.2	2.8	2.1	6.4	1.9	5.1
Working range (mg L^{-1})	0.05–5.0	0.10–7.0	0.08–6.0	0.07–5.0	0.06–5.0	0.04–2.0	0.04–1.1	0.13–8.0

Table 6: The accuracy test results for spiked recovery (pH: 8, sample volume: 50 mL, $N = 3$)

	Added (μg)	Degirmendere River		Tap water	
		Found (μg)	R (%)	Found (μg)	R (%)
Mn	0	8.0 ± 0.3	–	BDL	–
	10	17.0 ± 0.5	94	9.7 ± 0.2	97
	25	32.0 ± 1.3	97	24.0 ± 0.7	96
Fe	0	21.0 ± 1.1	–	BDL	–
	10	29.5 ± 1.3	95	9.6 ± 0.4	96
	25	42.5 ± 2.3	93	25.5 ± 1.2	102
Co	0	0.30 ± 0.01	–	BDL	–
	10	9.7 ± 0.3	94	9.9 ± 0.3	99
	25	24.5 ± 1.0	97	24.5 ± 0.7	98
Ni	0	0.40 ± 0.02	–	BDL	–
	10	10.0 ± 0.3	96	9.7 ± 0.2	97
	25	24.8 ± 1.0	98	24.6 ± 0.7	98
Cu	0	1.10 ± 0.05	–	BDL	–
	10	11.2 ± 0.3	101	9.6 ± 0.2	96
	25	25.8 ± 0.7	99	25.0 ± 0.8	100
Zn	0	1.40 ± 0.08	–	0.70 ± 0.05	–
	10	11.9 ± 0.7	104	10.9 ± 0.6	102
	25	27.0 ± 1.3	102	24.3 ± 1.0	95
Cd	0	0.70 ± 0.02	–	BDL	–
	10	10.6 ± 0.3	99	9.6 ± 0.1	96
	25	25.0 ± 0.7	97	23.5 ± 0.7	94
Pb	0	0.50 ± 0.04	–	BDL	–
	10	9.5 ± 0.4	90	9.5 ± 0.4	95
	25	24.6 ± 1.3	96	24.2 ± 1.0	97

BDL: Below the detection limit

8) reveal good agreement between the observed values and certified values.

The proposed preconcentration method was applied to rock, moss, and water samples under the optimum conditions. The results are given in Table 9.

4. Conclusions

A simple, accurate and fast preconcentration-separation procedure based on adsorption Mn(II), Fe(II), Co(II),

Cu(II), Cd(II), Zn(II), Pb(II) and Ni(II) as their 8-HQ chelates on Amberlite XAD-2010 resin prior to their atomic absorption spectrometric determinations is described. The procedure offers a useful multielement enrichment technique in various samples with acceptable accuracy and precision. Amberlite XAD-2010 on the column could be used all thought of the studies without any lost of its adsorption properties. The possibilities of using the extraction system in solid phase XAD-2010/8-HQ for the preconcentration and separation of the metallic cations in solutions with relatively high contents of salts are extended.

Table 8: 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 ($\mu\text{g L}^{-1}$)	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
^a Amount found ($\mu\text{g L}^{-1}$)	38.0 ± 1.3	93.8 ± 5.6	23.8 ± 0.8	55.0 ± 2.6	20.2 ± 0.7	65.6 ± 4.3	9.7 ± 0.3	38.0 ± 2.6
Recovery %	95	94	95	92	101	94	97	95
CRM NIES ^b No.7 Tea Leaves								
Certified value ($\mu\text{g g}^{-1}$)	700 ± 25	– ^c	0.12^c	6.5 ± 0.3	7.0 ± 0.3	33 ± 3	0.030 ± 0.003	0.80 ± 0.03
^a Amount found ($\mu\text{g g}^{-1}$)	660 ± 32	ND	BDL	6.2 ± 0.4	6.8 ± 0.5	34.0 ± 4.0	BDL	0.74 ± 0.07
Recovery %	94	–	–	95	97	103	–	93

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

Table 9: Trace metals contents of real samples with the proposed method (volumes of water samples: 1000 mL, N: 3)

Samples	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
River water ($\mu\text{g L}^{-1}$)	149 \pm 4	402 \pm 18	6.9 \pm 0.3	7.5 \pm 0.3	20.3 \pm 0.4	32 \pm 3	12.1 \pm 0.3	8.6 \pm 0.4
Tap water ($\mu\text{g L}^{-1}$)	1.3 \pm 0.04	10.1 \pm 0.4	BDL	BDL	1.5 \pm 0.05	16 \pm 1	BDL	BDL
Moss ($\mu\text{g g}^{-1}$)	447 \pm 22	2550 \pm 115	7.2 \pm 0.3	85.5 \pm 4.4	91.6 \pm 3.7	194 \pm 17.4	4.7 \pm 0.2	46.3 \pm 4.1
*Rock ($\mu\text{g g}^{-1}$)	282 \pm 13	7960 \pm 456	BDL	BDL	980 \pm 38	15.9 \pm 1.2	BDL	BDL

* Trace metal contents of rock sample was determined by ACME Analytical Lab. (ISO 9002 Accredited Co.) in CANADA as follows: Mn 309, Fe 8700, Co 1.9, Ni 4.1, Cu 1096, Zn 13.6, Cd 0.02, Pb: 1.11 mg kg⁻¹

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Povzetek

V članku smo opisali enostavno in občutljivo metodo za simultano predkoncentracijo Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pb(II) in Cd(II) ionov v sledeh za določanje s plamensko atomsko spektroskopijo. Kot sorbent v koloni smo uporabili Amberlite XAD-2010. Ioni se v koloni sorbirajo kot hidrati 8-hidroksikinolina, ki jih izperemo z 1M raztopino HNO₃ v acetonu. Raziskovali smo pogoje (pH, potrebna količina 8-hidroksikinolina, volumen vzorca itd.) pri katerih so pogoji tako določanja ionov kot tudi regeneracije kolone optimalni. Ugotovili smo, da je metoda uporabna v območju koncentracije ionov 0.10–0.40 µg L⁻¹. Natančnost metode smo preverili z vzorci s certifikatom (CRM NIES No. 7 Tea Leaves and TMDW-500 Drinking Water) in jo nato uporabili za določanje ionov v sledeh v nekaterih vzorcih iz okolja, vključno z vodo.