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Preconcentration of Trace Elements on Amberlite XAD-4 Resin Functionalised with 1,2-bis (o-aminophenylthio) Ethane and Their Determination by FAAS in Environmental Samples

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The use of chemically modified XAD-4-1,2-bis (o-aminophenylthio) ethane chelating resin for preconcentrating Cr^{6+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, and Ni^{2+} was studied using flame atomic absorption spectrometry (FAAS) for metal monitoring in environmental samples. Cd^{2+}, Zn^{2+}, Pb^{2+}, and Ni^{2+} ions were quantitatively recovered at the rate of 96.0%, 101.0%, 101.0%, and 95.0%, respectively (RSD < 5%), from the studied solutions. The procedure is based on the retention of analytes on a short column of 1,2-bis (o-aminophenylthio) ethane-XAD-4 chelating resin from a buffered sample solution and subsequent elution with 1 M HNO_3.Various parameters, such as pH, eluent type, and concentration, flow rate of sample solution and matrix interference effect on the retention of the metal ions have been studied. The optimum pH for the sorption of the above-mentioned metal ions was about 6. The adsorption and batch capacity of adsorbent and loading half time ($t_{1/2}$) for Ni^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} were established. The limit of detection was 3.0 $\mu g\ L^{-1}$ for Pb^{2+} and Ni^{2+}, 0.6 $\mu g\ L^{-1}$ for Cd^{2+}, and 0.3 $\mu g\ L^{-1}$ for Zn^{2+}. The validation of the procedure was carried out by analysis of certified reference materials and standard addition. The proposed enrichment method was applied to environmental samples from Trabzon.

Key Words: Water, trace element, preconcentration, Amberlite XAD-4, FAAS, 1,2-bis (o-aminophenylthio) ethane, chelating resin

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Introduction

The industrial use of metals leads to increased metal concentrations in air, water, and soil. Unlike organic pollutants, metals are non-biodegradable and therefore accumulate in living organisms. Trace elements are widespread in the environment and can enter the food chain. Some trace elements are essential and play important roles in human metabolism. On the other hand, at higher concentrations all of the metals are recognised as potentially toxic. Therefore, accurate determination of trace elements in the environment is very important.[1] For this purpose, instruments such as ICP-MS, ICP-OES, and ETAAS, which are highly sensitive, were developed. Nevertheless, although these instruments have high sensitivity, in cases of low metal concentration they are greatly affected by the matrix effect. Thus, the preconcentration process is needed in order to separate the analytes from the mixed matrix and to decrease the quantification limits. After the preconcentration process, without the need for costly instruments such as ICP-MS, analyses can be performed by using economical instruments such as FAAS.[2]

A wide variety of procedures have been proposed for diverse matrices, depending on the nature of the sample, the type and concentration of the analyte, and the methods used for determination. Preconcentration techniques, such as solid-phase extraction (SPE),[3−5] liquid-liquid extraction,[6,7] co-precipitation,[8,9] ion exchange,[10] electrochemical deposition,[11,12] cloud point extraction,[13] and flotation,[14] have been widely used for the preconcentration and separation of trace element ions.

Recently, the SPE technique has received increased attention in comparison to the traditional liquid-liquid extraction technique. SPE is preferred on account of its fast, simple, and direct application in microlitre volume without any sample loss, higher preconcentration factor, rapid phase separation, and time and cost efficiency.[15] The basic principle of SPE of trace element ions is the transfer of analytes from the aqueous phase to the active sites of the solid phase. For this purpose, various adsorbents, including activated carbon,[16] silica gel,[17,18] microcrystalline naphthalene,[19] C_{18} cartridges,[20] Chelex-100,[21] Alumina,[22] polyurethane foam,[23] and Amberlite XAD resins have been used. Among these adsorbents, Amberlite XAD resins (XAD-2, XAD-4, XAD-7, XAD-16, XAD-1180 and XAD-2000) are very useful for the preconcentration of metal complexes.[24−32] A large number of studies on the preconcentration of metals using XAD resins have been conducted during the last 20 years. These studies have included the complexation of ligands, bacteria, and algae with metals and the adsorption of the resultant chelates on the resin, as well as the saturation of the resin with ligands, bacteria, and algae, followed by the transfer of the metal solutions with known pH through the resin.[2,28,33,34] During the last few years, studies have been carried out on chelating the resin over the covalent bonds by ligands that have metal adsorption capacity and the adsorption of the metals on the resultant sorbent. This method often involves the transformation of the resin into diazonium form and the bonding of the resin to the ligand by the resultant -N=N- bonds.[35−39] Based on these studies it can be concluded that preconcentration using the chelating resin process has some advantages, such as good selectivity, preconcentration factor, binding energy and mechanical stability, easy regeneration for multiple sorption-desorption cycles and good reproducibility in sorption characteristics compared to other methods.[40] XAD resins, as the copolymer backbone for the immobilisation of chelating ligands, have some physical superiority, such as porosity, uniform pore size distribution, high surface area and durability, and chemical stability towards acids, bases, and oxidising agents, as compared to other resins.[39] The literature describes many chelating ion-exchangers that were synthesised from XAD-2,[24,41,42] XAD-4,[39,43−45] XAD-7,[40] XAD-16,[46−49] and XAD-1180[50] copolymers that are suitable for metal ion separation and preconcentration from aqueous solution.

In the present study, a simple and sensitive separation and preconcentration procedure was investigated by using a column loaded with 1,2-bis (o-aminophenylthio) ethane-functionalised Amberlite XAD-4 resin, in which the chelating ligand is bound to the copolymer via the -N=N- covalent linkage, for the determination of some trace element ions (Pb^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+}) in water samples taken from various locations in Trabzon, Turkey. The strong metal binding property of 1,2-bis (o-aminophenylthio) ethane combined with the insolubility of the metal complexes result in the high sorption capacity of the new matrix for the preconcentration and determination of metals in saline water, natural water, and plant samples. The proposed method was applied to the determination of trace element ions in artificial seawater, drinking water, and plant samples. Additionally, various parameters, such as pH, eluent type, volume and concentration, flow rate of the sample solution, volume of the sample solution, matrix interference effect, adsorption and batch capacity of the resin, as well as the accuracy of the method were studied.

Experimental

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 elements. The instrumental parameters were those recommended by the manufacturer. The wavelengths (nm) selected for the determination of the analytes were as follows: Ni: 232.0; Zn: 213.9; Cd: 228.8; Pb: 217. A Hanna 211 pH meter with a glass electrode was used for the pH adjustments. Infrared (IR) spectra were recorded on a Spectrum One Fourier transform infrared (FTIR) spectrometer and elemental analyses were performed on a Hewlett-Packard 185 CHN analyser. An NÜVE SL 350 mechanical shaker with speed control was used for batch experiments. A Milestone Ethos D microwave oven was used for digestion of tea leaves and kale samples. A glass mini-column (10 cm × 1.0 cm) with a porous disk and a stopcock was used for preconcentration of the metals.

Reagents and Solutions

In this study, all chemicals and solutions were analytical reagent grade and were purchased from Merck and Fluka. All solutions were prepared in distilled/de-ionised water. Stock solutions of the studied metals (Pb^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+}) at the concentration of 1000 mg L^{-1} in 0.5 M HNO_3 were used. The model and standard solutions of the metals were prepared by appropriately diluting the stock solutions. Buffer solutions were used for pH adjustment. For this, solutions containing suitable amounts of Na_2SO_4-$NaHSO_4$ for pH 2, HAc-NH_4Ac for pH 4-6, NH_3-NH_4Cl for pH 8-10, and NaOH-Na_2HPO_4 for pH 12 were prepared in water. Amberlite XAD-4 resin (Sigma Chemical Co.) was purchased as 20-60 mesh particle size with 725 m^2 g^{-1} of surface area.

Synthesis and Characterisation of the XAD-ABA Sorbent

The XAD-4-1,2-bis (o-aminophenylthio) ethane sorbent (resin) was prepared by nitrating 5 g of Amberlite XAD-4 copolymer with a mixture of 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 with constant stirring in a 60 °C oil bath for 30 min. The reaction mixture was poured into ice-water, the nitrated resin was filtered off and then washed with water until the effluents were neutral. The resin was refluxed at

90 °C for 10 h with a mixture of 40 g of $SnCl_2$, 45 mL of concentrated HCl and 50 mL of ethanol. The product was filtered off, washed with water, and then washed with 2 M NaOH to release the amino polymer:

$$(RNH_3)_2SnCl_6 + 8OH^- \rightarrow 2RNH_2 + SnO_3^{2-} + 6Cl^- + 5H_2O$$

The amino polymer was treated with 2 M HCl, the excess HCl was removed by washing with water, and then it was suspended in 350 mL of ice-water. The reaction mixture was treated with 1 mL portions of 1 M HCl -1 M $NaNO_2$ until a durable blue colour formed on the starch iodide paper. The polymer was thus converted to diazonium salt, washed with cold water, and treated with a solution containing 1 g of 1,2-bis (o-aminophenylthio) ethane in 200 mL water and 100 mL of glacial acetic acid at 0-3 °C. The final mixture was kept at this temperature for 24 h until the reaction was complete. The dark brown grains were filtered off and washed, as suggested by Tewari and Singh.[39,41] The reaction sequences for various stages of the preparation of the Amberlite XAD-4 resin functionalised with 1,2-bis (o-aminophenylthio) ethane are shown in Figure 1.

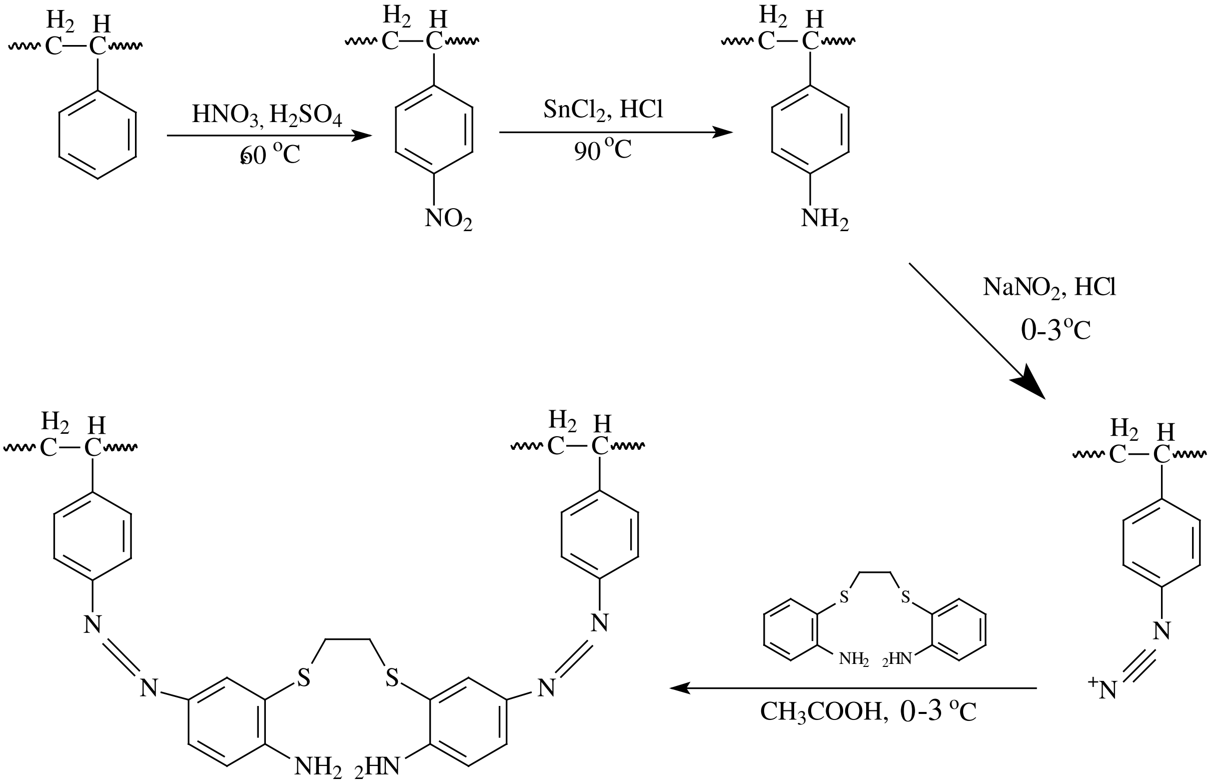

Figure 1. The synthesis and chemical structure of XAD-4-1,2-bis (o-aminophenylthio) ethane chelate resin.

The Characterisation of the 1,2-bis (o-aminophenylthio) Ethane-Functionalised Amberlite XAD-4 Copolymer with FTIR

IR spectra of free Amberlite XAD-4, 1,2-bis (o-aminophenylthio) ethane and functionalised Amberlite XAD-4 copolymer were studied using the potassium bromide technique. Additional peaks in the IR spectrum of the functionalised Amberlite XAD-4 resin that do not appear in the spectrum of the free Amberlite XAD-4 are at 3456, 3358, 1606, 1526, 1440, and 1250 cm^{-1}, which appear to originate due to modification of the resin by the ligand and are characteristic of -NH$_{2(st)}$,

-NH$_{2(d-inplane)}$ stretching (st), deformation (d) and -N=N-, CH$_2$-S-C, C-N vibrations, respectively (Figure 2). Data obtained from CHN elemental analysis (C: 67.27%; H: 3.98%; N: 15.83%) were comparable with the theoretically calculated values (C: 66.14%; H: 4.72%; N: 16.54%). CHN analysis confirmed that one 1,2-bis(o-aminophenylthio) ethane molecule is present in the resin per repeat unit of the polymeric matrix. A structure according to these data is shown in Figure 1.

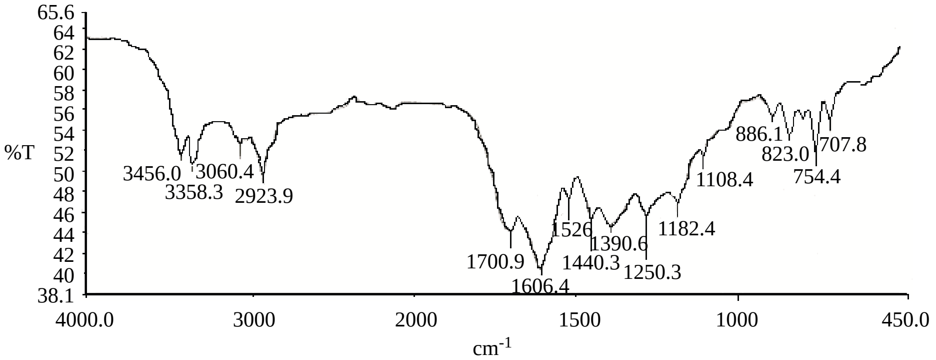

Figure 2. IR spectra of Amberlite XAD-4 resin functionalised with 1,2-bis (o-aminophenylthio) ethane.

Column Preparation

A glass mini-column (10 cm × 1.0 cm) with a porous disc and a stopcock was used for preconcentration of the metals. Before chelating the XAD-4 resin it was washed successively with 1 M NaOH, water, 1 M HNO$_3$, water, and acetone and water. Before placing 250 mg of Amberlite XAD-4-1,2-bis (o-aminophenylthio) ethane sorbent into the column, a small amount of glass wool was placed in the lower part of the column and then the sorbent in another layer of glass wool was placed in the upper part of the column to prevent loss of the XAD-4-1,2-bis (o-aminophenylthio) ethane resin. Then, the sorbent was washed with ethanol and 1 M HNO$_3$. The resin was thoroughly washed with H$_2$O until the effluents were neutral. After each use, the resin in the column was washed thoroughly with water, 1 M HNO$_3$ and related buffer solution, and then stored in water for further applications.

Preconcentration Procedure

The proposed method was tested with model solutions prior to the determination of the trace elements in the real samples. We prepared 50 mL of model solutions containing 25 μg of Ni^{2+}, 10 μg of Zn^{2+}, 50 μg of Pb^{2+}, and 5.0 μg of Cd^{2+}. The pH of the model solutions was adjusted to the desired values (range: 2-12) by the addition of 2-5 mL of buffer solution. The resultant solution was passed completely through the column at a flow rate of 10 mL min^{-1} and then the column was rinsed with 10 mL of water. The retained species on the resin was eluted with 7.5 mL of 1 M HNO$_3$ solution. The eluate was quantitatively completed to 10 mL with 1 M HNO$_3$. Finally, the solution was analysed by FAAS.

Application to the Certified Reference Material

Analysis of NIES No. 7, Tea Leaves

We decomposed 1 g of reference material (NIES No. 7, tea leaves) and kale sample with a mixture of 6 mL of concentrated HNO_3, 2 mL of H_2O_2, and 0.5 mL HF in an Ethos microwave system. Digestion conditions for the microwave system were (45 bar) 1 min at 250 W, 1 min at 0 W, 6 min at 600 W, 5 min at 250 W and 5-min vent, respectively. All sample solutions were clear. The volume of the samples was completed to approximately 50 mL with distilled water. This solution was analysed by using the preconcentration procedure described above. The retained species on the resin was eluted with 7.5 mL of 1 M HNO_3 solution. The eluate was evaporated on a hot plate until nearly dry. The residue was diluted to 5.0 mL with 1.0 M HNO_3.

Analysis of CRM-TMDW-500, Drinking Water Standard

A 50-mL aliquot of reference material sample was analysed using the preconcentration procedure described above. The retained species on the resin was stripped with 7.5 mL of 1 M HNO_3 solution. After the eluate was evaporated on a hot plate until nearly dry, the residue was diluted to 5.0 mL with 1.0 M HNO_3.

Batch Capacity of the Resin

We brought 50 mL of 10 mg mL^{-1} working solution of the metals to pH 6 and transferred it to polyethylene bottles. To each was added 0.1 g of XAD-4-1,2-bis (o-aminophenylthio) ethane, and each was stoppered and agitated for 1, 3, 5, 10, 30, 60, and 120 min at room temperature. At the end of each batch contact, the metal-loaded sorbent was filtered off and the metal remaining in the filtrate was stripped with 1 M HNO_3, diluted to 10 mL with 1 M HNO_3, and then measured by FAAS.

Adsorption Capacity of the Resin

The adsorption capacity is the maximum metal quantity taken up by 1 g of resin and is given as mg of metal g^{-1} resin or meg (milli-equivalent gram). In order to determine this, test solutions of Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} weighing in the range 100-500,000 μg were loaded to the column containing 250 mg of chelated resin and recoveries were investigated. Langmuir isotherms were plotted in order to determine the resin capacity.

The Langmuir adsorption isotherm is one of the most well-known and applied adsorption isotherms, and is described by the equation below:

$$q_e = \frac{q\text{max}\, a_L C_e}{1 + a_L C_e} \tag{1}$$

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

The equation given above can be rearranged as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q\text{max}} + \frac{1}{a_L q\text{max}} \tag{2}$$

A plot of C_e/q_eversusC_e shows linearity; hence, the Langmuir constants, q_{max} and a_L, can be calculated from the slope and intercept of the plot. From the plots obtained for each metal, the amount of maximum total metal (q_{max}) adsorbed on 1.0 g of resin is calculated.

Sampling Procedure

Samples were taken from a tap at Karadeniz Technical University (drinking water) and from streams of the Kalyan River Basin, which will supply drinking water to Trabzon city in the future. Polyethylene bottles were used for sample storage and were thoroughly washed with detergent, tap water, HNO_3, and then distilled/de-ionised water prior to collection of the water samples. Finally, the water samples were acidified with HNO_3 and filtered through a nitrocellulose membrane with a pore size of 0.45 μm.

A vegetable sample, kale (*Brassica oleracea* var. *acephala*) was collected from Sürmene (Trabzon). Kale leaves were dried in an oven for 20 h at 105 °C and finely powdered in an agate mortar.

Results and Discussion

The Effect of pH on Recovery of the Metals

The efficiency of recovery of each metal was investigated in the pH range of 2-12. According to the recovery results (Ni^{2+}: 95.0%; Zn^{2+}: 101.0%; Cd^{2+}: 96.0%; Pb^{2+}: 101.0%) the optimum pH was 6 for all the metals. In addition, it was revealed that the HAc-NH_4Ac buffer used for pH 6 did not have a negative effect; hence, the following optimisation work was carried out at this pH. The change in the recovery of metals according to pH is shown in Figure 3.

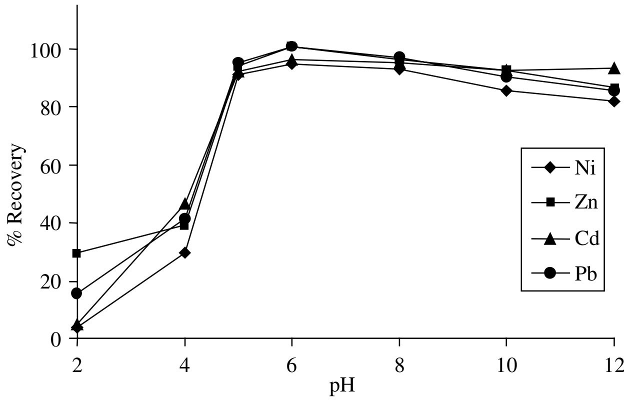

Figure 3. The effect of pH on the recovery of the metal ions (N = 3, V = 50 mL, RSD < 5%).

The Effect of Eluent Type and Concentration

Various acids were used to identify the best eluent for the metal accumulated on Amberlite XAD-4-1,2-bis (o-aminophenylthio) ethane resin and the percentage of recovery for each of them was determined. Among the eluents studied, the 1 M HNO_3 and 1 M HCl:1 M HNO_3 mixture provided the highest recovery efficiency. Finally, 1 M HNO_3 was specified as the eluent and this solution was used for the optimisation of the other parameters (Table 1).

Table 1. The effect of eluent solution type on the recovery of the metal ions (N = 3, V = 50 mL, RSD < 5%).

Type of eluent	Conc. (M)	Recovery, %			
		Ni	Zn	Cd	Pb
HCl in water	1	95	88	88	94
HAc* in water	1	71	60	83	36
HNO_3 in water	0.5	90	93	96	97
	1	95	101	96	101
	2	90	88	91	92
HCl : HNO_3 in water	1:1	94	102	95	100

*Acetic acid

The optimisation of the concentration of nitric acid was carried out with 0.50, 1.00, and 2.00 M HNO_3 solutions, and a high recovery rate was achieved for all the concentrations studied, except for the 2.00 M HNO_3 solution, for which the recovery rate decreased. For the subsequent studies, the optimum eluent concentration was selected as 1 M HNO_3 (Table 1).

The Effect of the Volume of the Eluent

The effects of 1 M HNO_3 with 2.5, 5.0, 7.5, 10.0, and 15.0 mL volumes were investigated, and a high recovery rate was obtained for all the volumes, except 2.5 mL (Table 2). The optimum eluent volume was specified as 7.5 mL for the subsequent studies.

Table 2. The effect of eluent volume on the recovery of the metal ions (N = 3, V = 50 mL, RSD < 5%).

Eluent volume (mL)	Recovery, %			
	Ni	Zn	Cd	Pb
2.5	86	64	81	92
5.0	90	94	93	98
7.5	95	101	96	101
10.0	92	100	98	98
15.0	95	97	93	96

The Effect of the Flow rate of the Solution

The flow rate of the model solutions through the column is one of the factors affecting the duration of the determination. The flow rate through the column is directly related to the contact of the solution with the resin; hence, model solutions of 50 mL were passed through the column with rates in the range of 1-20 mL min^{-1}. In order to increase the flow rate of the solutions, a vacuum was applied to the column with a water jet. With the flow rates chosen, it was observed that the recovery did not change significantly, except for the flow rate of 15-20 mL min^{-1}. Thus, the flow rate of 10.0 mL min^{-1} was chosen for all the subsequent experiments. The results obtained are shown in Figure 4.

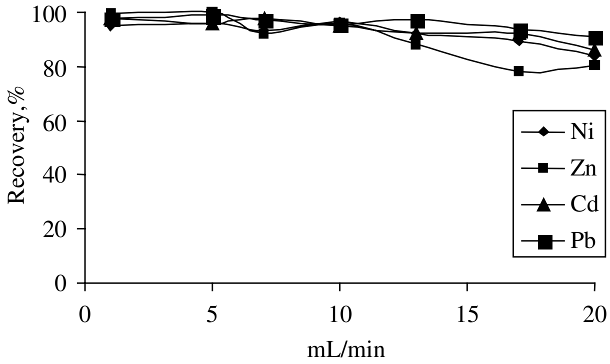

Figure 4. The effect of the flow rate of the solution (N = 3, V = 50 mL, RSD < 5%).

The effect of the matrix ions (Salt effect)

The Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-} ions at various concentrations were added to the preconcentration medium in order to identify the effects of these ions on trace element recovery. The efficiency of recovery was not affected, regardless of whether these ions existed individually or altogether, defined as a mixed salty solution, containing 20,000 mg L^{-1} of Na^+, 1000 mg L^{-1} of K^+, 1000 mg L^{-1} of Ca^{2+}, 1000 mg L^{-1} of Mg^{2+}, 1250 mg L^{-1} of Cl^-, 1500 mg L^{-1} of NO_3^-, and 2000 mg L^{-1} of SO_4^{2-} ions (Table 3). Hence, this method can be applied to sea water since it was not affected by high concentrations of Na^+ or Mg^{2+}.

Table 3. The effect of matrix ions on metal ion recovery (N = 3, V = 50 mL, RSD < 5%).

Ions	Conc. (mg L^{-1})	Recovery, %			
		Ni	Zn	Cd	Pb
Na^+	20000	96.2	101.2	96.4	98.2
K^+	1000	95.3	99.5	94.7	97.4
Ca^{2+}	1000	97.1	98.2	98.2	95.6
Mg^{2+}	1000	95.3	100.2	96.3	98.3
Cl^-	1250	97.2	97.6	97.3	96.8
SO_4^{2-}	1500	96.5	98.5	96.1	95.3
NO_3^-	2000	95.2	98.7	95.6	94.8
Mixed salty solution		95.4	99.0	96.0	96.7

Adsorption and batch capacity of the resin and loading half-time

The adsorption capacity of the Amberlite XAD-4-1,2-bis (o-aminophenylthio) ethane resin was obtained between 48.5 and 416.0 mg g^{-1} for the studied metals (Table 4).

The sorption percentages of the tested metal(II) cations are shown as a function of time in Figure 5. Batch capacity of the Amberlite XAD-4-1,2-bis (o-aminophenylthio) ethane resin was obtained between 60.0 and 625.0 mg g^{-1} for the studied metals. Sorption was complete within 10 min for all the metal ions. The sorption half-time was 2.5 min for all the metal ions, except Pb^{2+} (5 min). Both of these half-times and batch capacities are tabulated in Table 4. The proposed method developed using Amberlite XAD-4 resin chelated with 1,2- bis (o-aminophenylthio) ethane has a high sorption capacity and is very fast, with a loading half time, $t_{1/2,}$ of less then 5 min.

Table 4. Adsorption and batch capacities, and loading half-time (N = 3, RSD < 5%).

Element	Adsorption Capacity (mg g^{-1})	Batch Capacity (mg g^{-1})	Loading Half-Time (min)
Ni	48.5	60.0	2.5
Zn	28.0	47.0	2.5
Cd	46.0	85.0	2.5
Pb	416.0	625.0	5.0

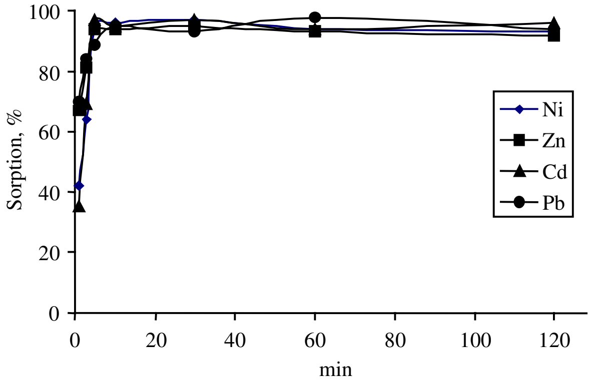

Figure 5. The rate of Pb^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} sorption on XAD-4-1,2-bis (o-aminophenylthio) ethane (N = 3, V = 50 mL, RSD < 5%).

The effect of the volume of the sample

As the concentrations of trace elements in real samples are too low, by using samples with large volumes the trace elements in these volumes should be taken into smaller volumes for determination of these metals with high accuracy. Hence, the maximum sample volume was optimised by the investigation of the recovery of trace elements (25 μg for Ni^{2+}, 10 μg for Zn^{2+}, 50 μg for Pb^{2+} and 5.0 μg for Cd^{2+}) in various sample volumes ranging from 50 to 2000 mL. Consequently, the recovery rates were stable until 1000 mL for Ni^{2+}, Cd^{2+}, and Zn^{2+}, and until 1500 mL for Pb^{2+}. All the studied metals were observed to decrease above 1500 mL of sample volume (Figure 6). The highest preconcentration factor was 150 for analyte ions when the final volume was 10 mL.

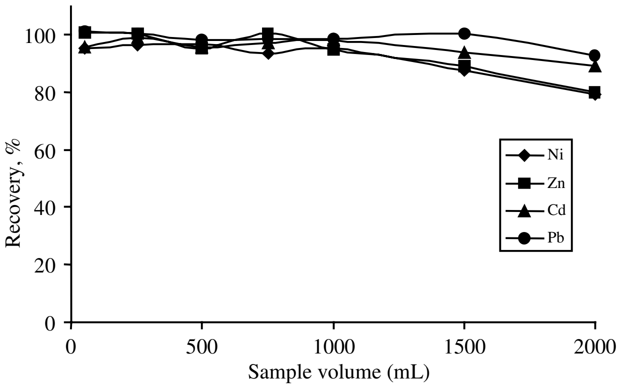

Figure 6. The effect of sample volume on the recovery of the metal ions (N = 3, RSD < 5%).

The validation of the method

In order to demonstrate the validity and accuracy of the proposed enrichment and determination method, the analytes were determined in standard reference materials of tea leaves (NIES No. 7) and drinking water (CRM-TMDW-500). All the results were in the range of 95% confidence level. The results are summarised in Table 5. As can be seen from the table, the accuracy of the method was very satisfactory; the relative error was lower than 5%.

Table 5. Analysis of the certified reference materials.

NIES[a] No. 7 CRM Tea Leaves	Ni	Cd	Zn	Pb
Certified value (μg g^{-1})	6.5 ± 0.3	0.030 ± 0.003	33 ± 3	0.80 ± 0.03
Amount found (μg g^{-1})[b]	6.6 ± 0.5	ND[d]	33.8 ± 2	0.77 ± 0.08
Recovery %	102	-	102	96
CRM-TMDW-500[c]				
Certified value (μg L^{-1})	60 ± 0.3	10 ± 0.05	70 ± 0.35	40 ± 0.2
Amount found (μg L^{-1}) 50 mL[b]	61 ± 0.2	9.7 ± 0.03	70.2 ± 0.42	38.9 ± 0.1
Recovery %	102	97	100	97

[a] The National Institute for Environmental Studies.

[b] The confidence interval was calculated at P = 0.95 (N = 4).

[c] Certified reference material trace elements in drinking water.

[d] Not detected

The application of the method to water and plant samples

The method, after being optimised in terms of the parameters described above, was applied to real samples collected from 3 branches of the Kalyan River (Çiftdere, Temelli, and Kuştül Stream), the Değirmendere River, tap water, artificial sea water and from kale, which was selected as the vegetable sample. The kale sample was digested according to procedure mentioned above. The estimation of all the 4 metal ions was made with and without (referred as direct determination) standard addition (S.A.) by passing 1000 mL of water sample and 50 mL of kale sample solution (spiked with 5-15 μg of each of the 4 metal ions in the case of the standard addition method) through the column filled with 0.25 g of XAD-4-1,2-bis (o- aminophenylthio) ethane resin after adjusting the pH to an optimum value and determining the metal ion as described in the recommended column procedure. The elution was made with 7.5 mL of 1 M HNO_3 and completed to 10 mL of 1 M HNO_3. The results obtained by FAAS are given in Table 6 in which the relative standard deviation was evaluated as $< 5\%$ and reflects the suitability of the present resin for water analysis. The concentrations reported in Table 6, as estimated by the S.A. method, are the values obtained by subtracting the amount of metal added for spiking from the total of metal recovered. The similarity of the results of direct and S.A. methods indicates the reliability of the present results of metal analyses in the water samples and the plant sample.

Limit of detection and quantification

The detection limits (blank + 3σ, where σ is standard deviation of blank estimation) for Cd^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} are 0.6, 3.0, 0.3, and 3.0 μg L^{-1}, respectively, and the corresponding quantification limits (blank + 10 σ) for the studied metals are 0.8, 3.4, 0.4, and 3.3 μg L^{-1}, respectively.

Comparison with Other Methods

A comparison of the optimum conditions of the proposed method with other preconcentration methods in which Amberlite XAD-4 resin was coated or chelated with various ligands is given in Table 7. As can be seen from the data in Table 7, the proposed method developed using Amberlite XAD-4 resin chelated with 1,2-bis (o-aminophenylthio) ethane has a high sorption capacity, flow rate, loading half time and enrichment factor for lead, cadmium, zinc, and nickel, as compared to the other methods reported in Table 7. The sorption capacity for cadmium and zinc is lower when compared with a previously reported method based on the modification of Amberlite XAD-4 with 1-hydrazinophthalazine.[52] The method provides quantitative recovery for Cd^{2+}, Zn^{2+}, Pb^{2+}, and Ni^{2+} of 96%, 101%, 101%, and 95%, respectively.

Conclusion

In this paper a novel trace element analysis method was proposed. The applicability of the method to environmental samples (plant sample (kale), and drinking and surface waters (streams, rivers, and lakes)) with a preconcentration factor of 100 for Cd^{2+}, Ni^{2+}, and Zn^{2+}, and 150 for Pb^{2+} was tested and reliable results were achieved. Additionally, it was determined that Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-} ions did not interfere with our analysis since no important interference affecting the analysis was encountered; therefore, it was concluded that this analysis could also be applied to salty waters such as sea water.

The validation of the method was tested using standard reference materials (tea leaves (NIES No. 7) and drinking water (CRM-TMDW-500)), and the results were very satisfactory; the relative error was lower than 5%.

In this study, the results show that the sorbent used in all the optimisation parameters studied was more active towards Pb^{2+} compared to the other metals in question. The results obtained from both adsorption capacity and batch capacity studies clearly confirmed this finding. The adsorption capacity and batch capacity of Pb^{2+}, with values of 416 and 625 mg g^{-1}, respectively, was approximately 10 times greater than that of the other metals studied. Moreover, the adsorption rate was very fast, with a loading half time, $t_{1/2}$, of less than 5 min.

Table 6. Trace element content of real water samples determined with the proposed method (V = 1000 mL, N = 3, RSD < 5%).

Sampling locations		Ni		Zn		Cd		Pb	
		Concentration (μg L^{-1})	RSD (%)	Concentration (μg L^{-1})	RSD (%)	Concentration (μg L^{-1})	RSD (%)	Concentration (μg L^{-1})	RSD (%)
Çiftdere	Direct[1]	1.64	2.7	20.94	3.2	0.35	4.1	2.38	2.2
	S.A.[2]	1.57	2.4	21.23	3.4	0.32	3.7	2.45	2.5
Kutül	Direct	2.10	4.4	13.60	2.1	0.19	4.1	1.52	2.8
	S.A.	2.30	4.2	13.12	2.7	0.21	4.6	1.47	3.1
Temelli	Direct	0.93	2.5	12.85	2.7	0.22	3.6	1.57	2.4
	S.A.	1.10	2.3	13.10	3.2	0.20	4.0	1.49	2.8
D.River	Direct	1.60	2.7	3.40	3.7	0.24	4.1	2.31	2.5
	S.A.	1.52	2.3	3.50	4.1	0.21	3.8	2.21	2.1
Tap Water	Direct	1.30	2.7	8.20	2.7	0.20	3.4	1.61	2.7
	S.A.	1.22	2.3	8.50	3.1	0.23	3.9	1.69	3.2
Kale (μg g^{-1})[4]	Direct	2.32	2.1	22.0	3.2	ND	-	ND	-
	S.A.	2.15	1.98	19.0	3.4	ND	-	ND	-
Artificial Sea Water[5]	Direct	1.51	2.3	20.10	3.1	0.54	3.4	1.95	2.6
	S.A.	1.42	2.4	19.87	2.9	0.56	3.5	2.01	2.9

[1] Recommended procedure applied without standard addition.

[2] Recommended procedure applied with standard addition.

[3] Relative standard deviation is for three determinations.

[4] Sample volume: 50 mL

[5] 1.5 μg **L**$^{-1}$ Ni^{2+}, 20 μg **L**$^{-1}$ Zn^{2+}, 0.5 μg **L**$^{-1}$ Cd^{2+}, 2 μg **L**$^{-1}$$Pb^{2+}$ in mixed salty solution.

Table 7. Comparison of optimum conditions of different ligands chelated^a or coated^b with XAD-4.

Experimental parameter	Immobilised ligand																			
	1,2-bis(o-aminophenyl thio)ethane^a				o-aminobenzoic acid^a				1-hydrazinophthalazine^a				Ammonium pyrrolidine dithiocarbamate^b				Morpholine dithiocarbamate^b			
	Pb	Cd	Ni	Zn	Pb	Cd	Ni	Zn	Pb	Cd	Ni	Zn	Pb	Cd	Ni	Zn	Pb	Cd	Ni	Zn
pH	6	6	6	6	6	6	6	6	6.5	7.5	8.5	7.0	5	5	5	5	8	8	8	8
Flow rate (mL min^{-1})	10	10	10	10	5	5	5	5	2	2	2	2	0.6	0.6	0.6	0.6	1.2	1.2	1.2	1.2
HNO_3^{1} or HCl^2 concentration for desorption (mol L^{-1})	1^1	1^1	1^1	1^1	1^1	1^1	1^1	1^1	1^2	1^2	1^2	1^2	4^1	4^1	4^1	4^1	2^1	2^1	2^1	2^1
Adsorption capasity of resin (mg g^{-1})	416	46	48.5	28	12.4	9.4	6.8	7.9	178	107	48.1	48.5	10.3	9.47	7.21	10.6	10.4	10.0	10.3	10.3
Loading half time, $t_{1/2}$ (min)	5	2.5	2.5	2.5	15	15	15	30	5	5	5	5	3.0	3.2	5.2	2.5	2.5	2.9	3.0	2.6
Average recovery (%)	101	96	95	101	98	97.2	96	97	98	98	99	99	99	98	98	99	99	97	98	99
Relative standard deviation (%)	< 5%	< 5%	< 5%	< 5%	< 5%	< 5%	< 5%	< 5%	< 5%	< 5%	< 5%	< 5%	< 4%	< 4%	< 4%	< 4%	< 4%	< 4%	< 4%	< 4%
Enrichment factor	150	100	100	100	400	400	200	400	50	50	50	50	160	180	130	215	160	120	90	150
Limit of detection (µg L^{-1})	3	0.6	3	0.3	2.5	2.5	5.0	2.5	-	-	-	-	0.6	0.1	0.4	0.5	0.9	2	1.5	1.5
Reference	This work				39				52				2				51			

The novel method is simple, time efficient, economical, and has wide ranging applicability. For example, the XAD-4-1,2-bis (o-aminophenylthio) ethane chelating resin (0.25 g) in the column used for preconcentration can be used 50 times and the preconcentration step takes about 1.5 h for a 1000 mL sample solution.

Since trace elements exist both in low concentrations and in complicated matrix media, the applied preconcentration method not only increased their concentration 100-150 fold, but also provided a cleaner matrix; therefore, the metal concentrations were determined easily and with high accuracy in the level of μg L^{-1}. The metal concentration levels in drinking water determined by this method were compatible with the standard levels published by the World Health Organisation (WHO), Environmental Protection Agency (EPA), and TS (Turkish Standards)-266.[53−55]

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