Preconcentration–separation of Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} in real samples by solid phase extraction of a calix[4] resorcinarene modified Amberlite XAD-16 resin

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ABSTRACT

A new method is described for the simultaneous preconcentration of trace metal ions. The method is based on the adsorption of Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} ions on 2,4,6,8-tetra(2-hydroxyphenyl)-1,3,5,7(1,3)tetrabenzenzcyclooctaphane-14,16,34,36,54, 56,74,76-octol (salicylaldehyde calix[4] resorcinarenes) (new resorcinarenes derivative) modified on Amberlite XAD-16. The adsorbed analyte ions were eluted with 6 mL 3 M HCl in acetone solution, which then were determined by atomic absorption spectroscopy. The influences of the analytical parameters including pH, ligand amount and solid phase ingredient, eluting solution conditions and sample volume were investigated. Common coexisting ions did not interfere with the separation and determination. The preconcentration factor is 208. The sorbent exhibited excellent stability and its sorption capacity under optimum conditions has been found to be more than 60 µg of ions per gram of sorbent. The relative standard deviation under optimum conditions is lower than 4.10%. The accuracy of the method was estimated by using different real samples.

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1. Introduction

Lower levels of the heavy metals than the quantitation limits of the instrumental techniques and higher levels of the concomitant ions in the real samples are two important problems for metal determinations in environmental samples by using measurement techniques [1–5]. Because of these limitations, monitoring of environmental pollutants at ultra-trace levels by instrumental techniques like atomic absorption spectroscopy, atomic emission spectroscopy, etc. needs an effective sample preconcentration step [6–9]. Because of these limitations, monitoring environmental pollutants at ultra-trace level by instrumental techniques like atomic absorption spectroscopy atomic emission spectroscopy, etc. needs an effective sample preconcentration step [6–9].

Solid phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental waters because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [10–16]. In SPE procedure,

the choice of appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor [17–21]. For this reason, modification and impregnation techniques of solid phase have long been used to increase the surface adsorption capacity, to enhance the removal efficiency and also to add selectivity to the solid phase [22–29].

The synthesis of resins by the reaction of commercial resin with a suitable chelating agent and sorption characterization of chelating resin, available for interesting metal ions have been extensively carried out. The studies on the synthesis resins by the reaction with a commercial resin and a suitable chelating agent and sorption characterization of chelating resin available for interesting metal ions have been extensively carried out in a number of analytical laboratories. According to our literature knowledge, up to now, no systematic investigation on the preparation of chelating resin by combination of Amberlite XAD-16 with the proposed reagent on the adsorption characteristics and its application in trace metal analysis have been performed.

The purpose of this work was to investigate the feasibility of adsorption of metal ions including, Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} ions on SDS coated Amberlite XAD-16 modified with new resorcinarenes derivative. The effective parameters viz. pH of sample, amount of new resorcinarenes derivative and solid phase, type and concentration of eluting agent and flow rate were optimized.

2. Experimental

2.1. Instruments

The measurements of metal ions were performed with a Perkin-Elmer AA Analyst 300 (Shelton Ct, USA) atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths using an air–acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691 pH/ion meter with a combined glass–calomel electrode was used for adjustment of test solution pH.

2.2. Reagents and solutions

Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, chromium, magnesium, calcium, strontium, barium, silver, sodium and potassium and all surfactant including sodium dodecyl sulfate (SDS), Triton X-100, Triton X-114, cetyltrimethylammonium bromide (CTAB), N,N-dodecyltrimethylammonium bromide (DTAB) were of the highest purity available from Merck (Dramsdt, Germany) and used without any further purification. The pH adjustment was done by addition of dilute hydrochloric acid or potassium hydroxide to prepare the desired pH solution.

2.3. Synthesis of new resorcinarenes derivative

Salicylaldehyde 0.03 g (0.25 mmol), resorcinol 0.55 g (5 mmol) and tungstate sulfuric acid 0.1315 g (0.25 mmol) were transferred to a round-bottom flask and stirred vigorously in an oil bath at 80 °C for 45 min. After completion of the reaction (TLC: carbon tetrachloride:ethylacetate 15:10) 100 mL methanol was added. Methanol was removed under water bath and simple distillation. The content of the flask was filtered, and filtrate was recrystallized by methanol–ethyl acetate to give 1.0165 g (95%) yellow solid which are presented in Scheme 1, m.p. 272–273 °C. IR (KBr), ν cm^{-1}: 3700–3000 (s, br), 1630 (s), 1500 (s), 1495 (s), 1490 (s), 1250 (m), 1100 (s), 950 (m), 850 (m), 750 (s). ^{1}H NMR (Varian, 400 MHz, DMSO-d_6) δ_H (ppm): 5.80 (s, 4H, CH), 5.95 (s, 4H, ArH *ortho* of OH), 6.30–6.70 (m, 20H, *meta* of OH and ArH of salicyl ring), 8.10 (s, 8H, OH of resorcinol), 8.30 (s, 4H, OH of salicyl ring).

2.4. Preparation of new resorcinarenes derivative coated Amberlite XAD-16

A Pyrex glass column containing 0.5 g of modified Amberlite XAD-16 in water suspension has 40 cm long and 0.75 cm in inter-
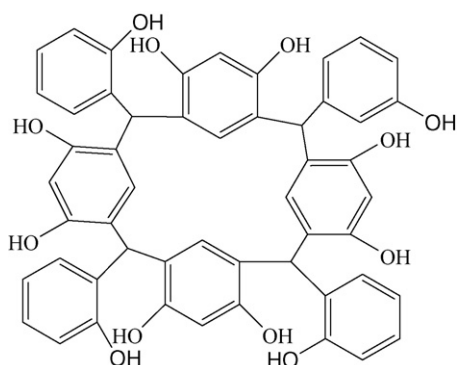
Scheme 1. Structure of ligand.

nal diameter. The bed height in the column was approximately 1 cm. The Amberlite XAD-16 (500 mg) was impregnated with new resorcinarenes derivative by percolating 3 mL of 1% (w/v) of this reagent (30 mg) and 60 mg SDS solution through the column packed with Amberlite XAD-16 at a flow rate of 0.2 mL min^{-1}. The filtrate was collected and analyzed for un-adsorbed new resorcinarenes derivative with the UV–VIS spectrophotometer at maximum wavelength of ligand. The column was then washed twice with 5 mL water and the filtrates were analyzed for ligand that was released. The new resorcinarenes derivative was retained on the Amberlite XAD-16 column completely. The pH of the solution (250–2000 mL) was adjusted to 6.0 by addition of dilute HNO3 or KOH and passed through the new resorcinarenes derivative loaded Amberlite XAD-16 column at a flow rate of 4 mLmin −1.

2.5. Preconcentration procedure

The pH of the solution (250–2000 mL) was adjusted to 6.0 by addition of dilute HNO$_3$ or KOH and passed through the new resorcinarenes derivative loaded Amberlite XAD- 16 column at a flow rate of 4 mL min^{-1}. The adsorbed analytes was then eluted with 6 mL of 3 mol L^{-1}M HCl in acetone. The metal ions content of the eluent was measured by flame-AAS.

2.6. Pretreatment of real samples

Vegetable samples (a mixture off our time with equal value) purchased from Omidyeh, Iran. Afterwards, they dried and were taken in small mesh. A 40 g leaves of spinach was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3 mL 30% (w/w) H$_2$O$_2$ again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 2–4 mL 70% (w/v) perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water and filtered. After adjustment of the pH at 6.0 by addition of KOH then made up to 250 mL with distilled water. Then the preconcentration procedure given above was applied.

Juices of alhaghi (hedysarum), fennel, and of tarune (commercially available from Farahbakhsh company in Mimand, Iran), which are used as protective drug for improving body function and river water samples collected from Omidiyeh, Iran were analyzed by the presented method. Before analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45 μm. The organic content of the water and juice samples were oxidized in the presence of 2 mL of 30% H$_2$O$_2$ and 5 mL concentrated nitric acid. After acidification with 1% (w/v) nitric acid, they were stored in polyethylene bottles. For the preconcentration procedure, pH of the 100 mL of water samples was adjusted to 6 and the sample passed through the column at flow rate of 4 mL min^{-1}. The metals, which retained on Amberlite XAD-16 by complexation with THPT-BCSCR, were eluted with 6 mL of 3 mol L^{-1} HCl in acetone. Then the preconcentration procedure given above was applied.

2.0 g of tobacco sample was digested with 4 mL of concentrated HNO$_3$ and 2 mL of 30% H$_2$O$_2$ in microwave system. Blank digestions were also performed at the same conditions. After digestion, the volume was made up to 100 mL with distilled water. The enrichment procedure given above was applied to the samples. The final volume was 5 mL. The metal concentrations in the final solutions were determined by flame AAS.

For the digestion of black tea samples, 2.0 g of tea was mixed with 6 mL of HNO$_3$:H$_2$SO$_4$:H$_2$O$_2$ (1:1:1) in microwave system. After digestion, the volume was made up to 100 mL with distilled water. Blanks were prepared in the same way as the sample, but omit-

ting the sample. The preconcentration procedure given above was applied.

One gram of sample (mushroom and wheat samples) was digested with 6 mL of HNO₃ (65%) and 2 mL of H₂O₂ (30%) in microwave digestion system and diluted to 10 mL with deionized water. A blank digest was carried out in the same way. Digestion conditions for microwave system for all samples were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 in for 400 W, 8 min for 550 W, ventilation 8 min, respectively. The preconcentration procedure given above was applied to the samples.

3. Results and discussion

The resulting complexes have attracted increasing attention, mainly due to their peculiar properties and their reactivity, mainly in the area of binding small molecules. This nature seems to be not only originated from their backbone structure of ligands but mainly from the use of ligand–O-donors on the complexation. The unique nature of ligand is enhanced by the existence of widely spread π-conjugation system. The extraction mechanism corresponds to a cation exchange, in which a complex is formed in the organic phase, and also liberating at the same time H⁺ ions in aqueous phase.

3.1. Influences of pH

The pH of the working media is a main analytical factor for the quantitative recoveries of metal ions by solid phase extraction [30–35]. The effect of pH on the preconcentration of metals on Amberlite XAD-16 loaded with new resorcinarenes derivative was studied by determination of individual elements. 50 μg of each element were preconcentrated in the pH range of 3.0–10.0 by introducing 30 mg of new resorcinarenes derivative on the 0.5 g Amberlite XAD-16 and respective results were shown in Fig. 1. The results obtained indicated that the ions could be retained quantitatively by the modified Amberlite XAD at the pH of 6. The decrease in signal at pH > 6 is probably due to the precipitation of ions as their related hydroxide precipitate or complex and at pH < 6 may be due to competition of hydronium ion toward complexation with new resorcinarenes derivative (hydroxyl group could be protonated) which lead to the decrease in the recovery. In order to control the pH during the analytical procedure, it was adjusted to 6 by addition of KOH and/or HNO₃. We only follow and control the initial pH of solution.

3.2. Effect of amount and type of surfactant

In order to prepare a stable repeatable and efficient solid phase, 250 mL of sample solution containing 50 μg of each metal ion were
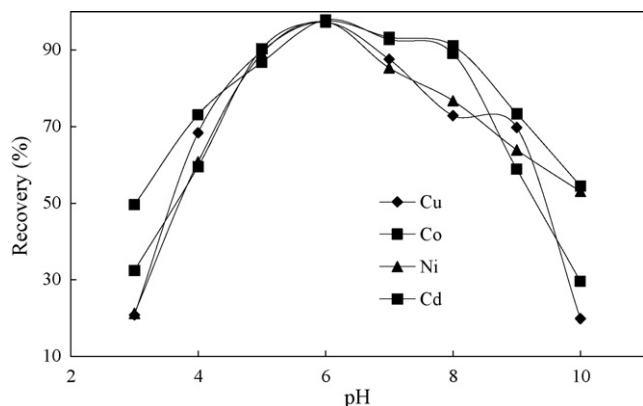
Table 1
Effect of type of surfactant on metal ions recovery.

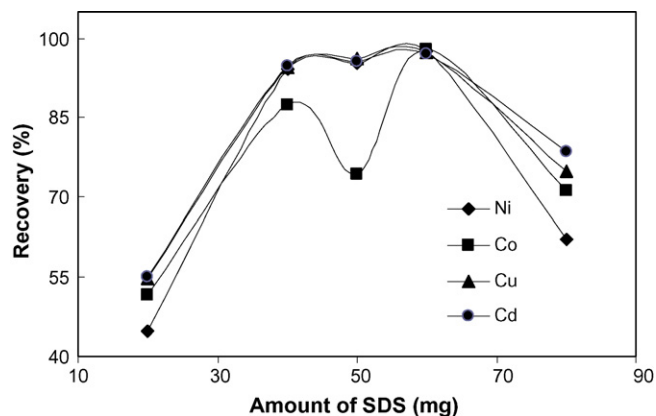| Surfactant	Recovery (%)			
	Co	Cu	Ni	Cd
DTAB	10.4	38.2	16.2	11.8
CTAB	9.6	25.2	15.4	7.6
Triton X-100	12.6	29	15.6	11.8
SDS	96.4	96.7	97.4	96.3

Fig. 2. Effect of SDS on the recovery values of the analytes (*N* = 3).

passed through solid phase (compromise of 60 mg of various type of surfactant including SDS, Triton X-100, CTAB and DTAB at fixed value of ligand (30 mg) and Amberlite XAD-16 (0.5 g) (Table 1). By modification of Amberlite (0.5 g) with sorbent at pH 6 according to experimental section in the presence of SDS maximum metal ions recovery could be obtained. The formation of minute amounts of ad-micelles was essential to achieve complete ad-solubilization of these ions as respective complex. At surfactant concentrations higher than about 60 mg a decrease in the percentage of ions retained was observed as a result of the formation of micelles. The adsorption amount began to decrease when the SDS added exceeded 60 mg for solid phase. It can be explained by the fact that with more SDS added the SDS molecules began to form micelles in the bulk aqueous solution; moreover, the micelles make the new resorcinarenes derivative distribute into the bulk solution again. At this value of SDS and ligand, there is a strong interactions between these reagents to strongly be coated on Amberlite XAD-16. As a result, it was more difficult for SDS-coated Amberlite XAD-16 to desorb ligand into aqueous solution (Fig. 2).

3.3. Effect of amount of ligand on metal ion recovery

The solid phase itself retained only <30% of these metal ions, while new resorcinarenes derivative-loaded Amberlite retained >70% of the mention metals contents from sample solutions. The SDS coated Amberlite modified by new resorcinarenes derivative is capable for quantitative retention of some heavy and transition metal ion. The synergic effects of new resorcinarenes derivative in the presence of SDS lead to increase in recovery, reproducibility and extraction efficiency of metal ions. The SDS has profound effects on increasing solid phase life-time, reducing the consumption of material and improve enrichment factor. On the other hand, the system in the absence of surfactant has low repeatability and efficiency Therefore, both new resorcinarenes derivative and SDS are beneficial for the efficient and sensitive recovery of metal ions.

In order to determine the concentration of new resorcinarenes derivative required for quantitative recoveries of metal ions, the proposed method was applied. Firstly, some works were carried
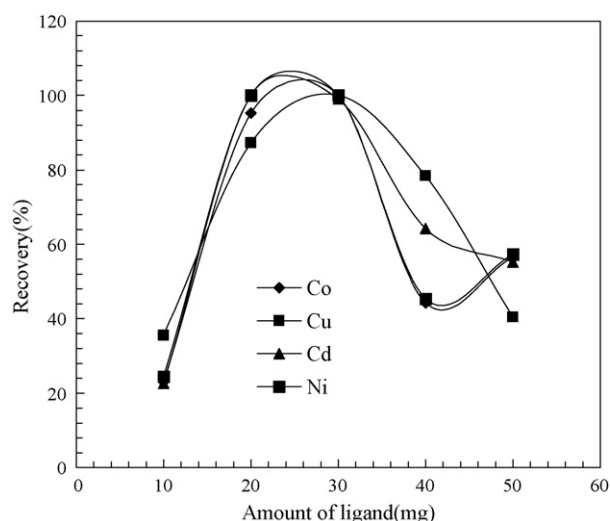

Fig. 1. Effect of pH on recoveries of analyte ions (*N* = 3).

Fig. 3. Effect of amount of ligand on recoveries ($N = 3$).

Table 2
Effect of amount of solid phase on metal ion recovery.

Amount of solid phase (g)	Co	Cu	Ni	Cd
0.2	73.2	68.3	68.1	54.8
0.3	60.3	73.2	84.3	66
0.4	89.3	81.7	88.9	74.3
0.5	95.6	97.4	97.6	96.4
0.6	96.4	96.7	97.4	96.3

out without ligand at pH 6. The analyte ions were not quantitatively recovered without ligand. Then the studies were performed with the various amount of new resorcinarenes derivative at pH 6. It was found that, the recovery of the metal ions increased with increasing concentrations of sorbent added and reached a constant value (95%) with at least 30 mg of this new resorcinarenes derivative. On this basis, studies were carried out at a new resorcinarenes derivative concentration of 30 mg. This concentration of new resorcinarenes derivative is enough for the separation–preconcentration procedure because of the very low level of the investigated metal ion concentrations in real samples (Fig. 3).

The influences of the amounts of modified solid phase filled to the column were also investigated (Table 2). It was observed that by increasing the amount of modified solid phase up to 0.5 g, the metal ions recovery were increased. Further increasing the amount of solid phase at fixed value of eluting solution (6 mL of 3 mol L^{-1} HCl in acetone), may be due to insufficiency of eluting solution recoveries is lower than 95%. In the proposed procedure, 0.5 g of modified solid phase is recommended.

3.4. Effect of eluting solution condition

In this experiment, a series of experiments were designed and performed to obtain a reasonable eluent to elute completely Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} ions after their enrichment by chelation with new resorcinarenes derivative from 250 mL sample solution. Various acids with various volumes were investigated to obtain the optimal eluent for further experiments. The results showed that HCl in acetone could accomplish the quantitative elution of target analytes, Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} ions chelated with from the resin (Table 3). For the sake of achieving better enrichment, the volume and concentration of eluent was optimized in the range of 2–6 mL and 1–6 mol L^{-1} of HCl in acetone for obtaining the optimal volume, and the data is given in Table 3. It is obvious that 6 mL 3 mol L^{-1} HCl in acetone is

Table 3
Effect of type and concentration of eluting agent on recovery of analytes ($N = 3$).

Eluent conditions	Recovery (%)			
	Co	Cu	Ni	Cd
HNO$_3$ (2 mol L^{-1})[a]	51.4	78	100	29.4
HCl (2 mol L^{-1})[a]	95.6	94.3	98.9	93.1
HClO$_4$ (2 mol L^{-1})[a]	57.8	22.6	100	61
HCl (3 mol L^{-1})[a]	100	100	100	99
H$_2$SO$_4$ (2 mol L^{-1})	69.4	23.4	100	27.4
5 mL (3 mol L^{-1} HCl)	85.8	51.8	100	55.0
6 mL (2 mol L^{-1} HCl)	91.5	97.9	91.6	95.5
8 mL (3 mol L^{-1} HCl)	60.2	80.7	78	31.5
10 mL (3 mol L^{-1} HCl)	56.2	48.5	58.8	58.6
6 mL (3 mol L^{-1} HCl)	97.8	96.9	97.4	98.1
6 mL (1 mol L^{-1} HCl)	68.3	73.4	79.8	80.4
6 mL (4 mol L^{-1} HCl)	97.5	97.3	97.6	98.0

[a] Volume of eluent were 6 mL, all solution in acetone.

sufficient for quantitative elution of the retained target compound from the solid phase.

3.5. Effect of sample volume

Since metal ions are generally at very low concentrations in a variety of samples of interest by the detection limit of FAAS, it is important to obtain high enrichment factors [36–45]. In order to explore the possibility of enriching low concentrations of ions from the large sample volume, the influences of the sample volume on the recovery of metal ions were also investigated. The amounts of metal ions in the model solution were 50 μg, to kept the metal ions concentrations constant while increasing the sample volume.

The effect of sample volume on the sorption of metal ions was also investigated by passing 250–2000 mL volumes through the modified solid phase column. The results are depicted at Fig. 4. The adsorption of all metal ions with 0.5 g resin was not affected by sample volume till 1250 mL.

3.6. Effect of flow rate

Sample and eluent flow rates are important parameters to obtain quantitative retention and elution of analyte ions, respectively. The influences of the flow rates were investigated in the range of 1–5 mL min^{-1}. The retentions for the analyte ions on Amberlite XAD-16 were virtually quantitative for sample flow rates (rate at which sample solution was introduced to the column) up to 4 mL min^{-1}. Variation of the elution flow rate (rate at which the sample solution came out of column) up to 1.0 mL min^{-1} has no
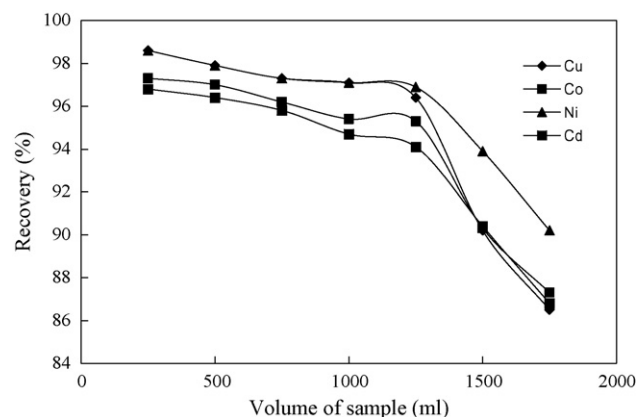

Fig. 4. Effect of sample volume ($N = 3$).

Table 4
Effects of the interferences ions on the recoveries of the examined metal ions.

Ion	Interfering ion to analyte mass ratio			
	Co	Cu	Ni	Cd
K	1000	1000	750	1000
Na	800	1000	750	900
Ba	750	1000	1000	750
Cr	750	1000	750	750
Hg	750	750	1000	750
Ag	1000	1000	750	750
Pb	1000	750	750	750
Mg	1000	750	1000	750
Mn	750	1000	1000	750

effect on the elution efficiency. In consequence, $4\,mL\,min^{-1}$ was selected as flow rate for sample loading and sample elution from the Amberlite XAD-16 resin.

3.7. Interference investigation

To assess the possible analytical applications of the recommended procedure, the effect of some foreign ions which interfere with the determination of metal ions by the THPTBCSCR method or/and often accompany analyte ions in various real samples was examined with the optimized conditions at above. For these studies, a fixed amount of metal ions was taken with different amounts of foreign ions and recommended procedure was followed. The recoveries of metal ions in these studies were higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding more than 5% in the determination of investigated analyte ions by the combination of the column solid phase extraction and the flame atomic absorption spectrometric determination methods. The results are summarized in Table 4. Common coexisting ions did not interfere with the separation and determination of understudy metal ions. Also, some of the transition metal ions at $mg\,L^{-1}$ levels were not interfered on the recoveries of the analyte ions. This results show that the proposed preconcentration/separation method could be applied to the highly saline samples and the samples that contains some transition metals at the tolerable levels.

3.8. Analytical features

By employing the optimum experimental conditions, the calibration graphs obtained for copper, cobalt, nickel, and cadmium, respectively, were given in Table 5. The enrichment factors calculated as the ratio of the slope of the calibration graph with and without preconcentration was 35, 30, 31 and 38 for Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions, while the preconcentration factor as the volume of initial solution (1250 mL) to the volume of eluting solution (6 mL) for all ions is 208.

The limit of detection (LOD) of a method is the lowest analyte concentration that produces a response detectable above the noise

Table 6
Recovery of trace elements from spiked environmental samples after application of presented procedure.

Sample	Ion	Added ($\mu g\,mL^{-1}$)	Found ($\mu g\,mL^{-1}$)	RSD (%)	Recovery (%)
Juice of tarune	Co	0	0.341	3.6	–
		0.2	0.536	3.0	97.5
	Cu	0	0.642	3.4	–
		0.2	0.849	2.8	103.5
	Ni	0	0.792	3.6	–
		0.2	0.985	2.7	96.5
	Cd	0	0.212	3.8	–
		0.2	0.408	3.0	98.5
Juice of fennel	Co	0	0.354	3.4	–
		0.2	0.559	2.8	102.5
	Cu	0	0.453	3.2	–
		0.2	0.658	2.6	102.5
	Ni	0	0.364	3.7	–
		0.2	0.560	3.0	98.0
	Cd	0	0.204	3.5	–
		0.2	0.409	2.9	102.5
Juice of alhaghi (hedysarum)	Co	0	0.206	3.6	–
		0.2	0.400	3.1	97.0
	Cu	0	0.361	3.4	–
		0.2	0.568	2.8	103.5
	Ni	0	0.418	3.3	–
		0.2	0.621	2.7	101.5
	Cd	0	0.188	3.5	–
		0.2	0.382	3.0	97.0
River water	Co	0	0.542	3.1	–
		0.2	0.749	2.5	103.5
	Cu	0	0.552	3.4	–
		0.2	0.745	2.9	96.5
	Ni	0	0.688	2.8	–
		0.2	0.898	2.3	105.0
	Cd	0	0.168	3.8	–
		0.2	0.374	3.1	103.0

level of the system, typically, three times the standard deviation (s) of the blank ($n = 5$), were found to be 1.8, 2.3, 2.2, 1.6 $\mu g\,L^{-1}$ for Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions. The empirical limit of quantification (LOQ) is the lowest level of analyte that can be accurately and precisely measured, were found to be 8 $\mu g\,L^{-1}$ for Co^{2+} and Ni^{2+} and 6 $\mu g\,L^{-1}$ for Cu^{2+} and Cd^{2+} ions this ion. Consumptive index (CI) is another efficient way to evaluate the performance of preconcentration system. CI is expressed by volume of analyte solution (V, mL) and the experimental preconcentration factor (EPF) ratio (CI = V/EPF), thus indicate the necessary volume to obtain one unit of enrichment factor. In addition, enrichment factor can be improved by using larger sample volumes. It is important to emphasize that CI values obtained in the present study are lower than that of the most procedure (Table 5).

The capacity of solid phase was investigated by batch method. In this regard, 0.5 g of modified solid phase at optimum value of experimental variable was contacted with 100 mL of 10 $\mu g\,mL^{-1}$

Table 5
Specification of presented method at optimum conditions for each element.

Parameters	Cu	Co	Ni	Cd
Linear range ($\mu g\,mL^{-1}$)	0.01–0.45	0.02–0.38	0.02–0.43	0.01–0.34
Regression equation	$y = 0.74x - 0.02$	$y = 0.37x - 0.01$	$y = 0.34x + 0.02$	$y = 2.31x - 0.03$
R^2	0.996	0.997	0.997	0.995
Limits of detection ($ng\,mL^{-1}$)	1.8	2.3	2.2	1.6
Loading capacity ($mg\,g^{-1}$)	68.5	61.9	61.9	62.5
Enrichment factor	35	30	31	38
Preconcentration factor		208		
RSD (%)	0.86	1.1	0.95	0.96
Recovery (%)	99.4	97.0	99.8	96.8
CI	0.024	0.021	0.021	0.027

Table 7
Recovery of trace elements from spiked environmental samples after application of presented procedure.

Sample	Ion	Added ($\mu g\,g^{-1}$)	Found ($\mu g\,g^{-1}$)	RSD (%)	Recovery (%)
Wheat	Co	0	0.406	3.2	–
		0.2	0.609	2.7	101.5
	Cu	0	0.376	3.4	–
		0.2	0.583	3.0	103.5
	Ni	0	0.381	3.3	–
		0.2	0.588	2.6	
	Cd	0	0.462	3.5	–
		0.2	0.669	3.0	103.5
Mushroom	Co	0	0.652	3.4	–
		0.2	0.845	2.6	96.5
	Cu	0	0.402	3.4	–
		0.2	0.608	2.8	103.0
	Ni	0	0.924	3.7	–
		0.2	1.129	3.0	102.5
	Cd	0	0.228	3.3	–
		0.2	0.434	2.7	103.0
Black tea	Co	0	0.676	3.5	–
		0.2	0.881	2.9	102.5
	Cu	0	0.132	3.6	–
		0.2	0.340	3.0	104.0
	Ni	0	0.598	3.3	–
		0.2	0.803	2.6	102.5
	Cd	0	0.144	3.4	–
		0.2	0.350	2.6	103.0
Tobacco	Co	0	0.646	3.2	–
		0.2	0.851	2.4	102.5
	Cu	0	0.412	3.2	–
		0.2	0.604	2.4	96.0
	Ni	0	0.714	3.1	–
		0.2	0.906	2.7	96.0
	Cd	0	0.171	3.1	–
		0.2	0.369	2.4	99.0
Vegetable	Co	0	0.348	3.8	–
		0.2	0.552	3.0	102.0
	Cu	0	0.308	4.0	–
		0.2	0.504	3.3	98.0
	Ni	0	0.342	3.7	–
		0.2	0.549	3.1	103.5
	Cd	0	0.206	3.8	–
		0.2	0.414	3.0	104.0

of metal ions for 1 h while stirring. After this, one portion of supernatant solution was analyzed by FAAS to evaluated un-retained metal ions. From the difference of initial and final analyte concentration and amount of solid phase loading capacity were examined and presented in Table 5, which indicate the ability of solid phase to recovered high amount of metal ions.

3.9. Accuracy and applications

In order to assess the applicability of the method to real samples, with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions from different matrices such as wheat, tobacco, vegetable, tea sample and some drug compound juice. Spiking experiments using standard addition method checked reliabilities. The percent of recoveries and relative standard deviation for each element in spiked vegetable, water samples are given in Tables 6 and 7. As seen, the results of three analyses of each sample show that, in all cases, the metal ions recovery is almost quantitative with a low RSD.

4. Conclusions

In the presented study, a new solid phase extraction technique was developed based on the preconcentration of Cu^{2+}, Co^{2+}, Ni^{2+}

and Cd^{2+} ions in environmental samples on SDS coated Amberlite XAD prior to the determination by FAAS. Under conditions given in Table 5, the determination of Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} ions yields quantitative recoveries. Conditions for quantitative and reproducible preconcentration, elution and FAAS determinations were studied. The method is simple, accurate, and economical and can be applied for the determination of these ions in environmental samples. The figure of merit of the purposed method is comparable to the other reported methods [39–45] and additionally, the method has the advantage of environment-friendly. The system showed reproducibility and reliability in analytical data, with an RSD value of lower than 5% on triplicate experiment. 0.5 g of modified solid phase can be used as high as greater than five experiments without any loss in its sorption behavior. The system was successful in preconcentration of analytes from large sample volume (1250 mL).

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