Solid-phase extraction method for preconcentration of trace amounts of some metal ions in environmental samples using silica gel modified by 2,4,6-trimorpholino-1,3,5-triazin

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ABSTRACT

A method was proposed for the preconcentration of some transition elements at trace levels using a column packed with silica gel modified by a synthetic ligand. Metal ions were adsorbed on 2,4,6-trimorpholino-1,3,5-triazin modified silica gel, then analytes retained on the adsorbent were eluted by $1 \, mol \, L^{-1}$ hydrochloric acid and determined by flame atomic absorption spectrometry (FAAS). The influences of some experimental parameters including pH of the sample solution, weight of adsorbent, type, concentration and volume of eluent, flow rates of the sample solution and eluent, and sample volume on the preconcentration efficiency have been investigated. The influences of some matrix elements were also examined. The method also was used for simultaneous preconcentration of these elements and the method was successfully applied to the preconcentration and determination of them. The detection limits of the method for Ni^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+} were 0.29, 0.20, 0.23 and, 0.30 $ng \, mL^{-1}$, respectively. The application of this modified silica gel to preconcentration of investigated cation from tap water, lake water, urine and apple leaves gave high accuracy and precision (relative standard deviation (R.S.D.) <3%).

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1. Introduction

Direct determination of metals in seawater samples or biological samples by atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry or inductively coupled plasma mass spectrometry is not always possible due to matrix interferences and the very low concentrations of metal ions. Therefore, a preconcentration/separation step is required [1–3]. To accomplish this task a solvent extraction, co-precipitation or solid-phase preconcentration technique can be applied.

Although liquid–liquid extraction has proven to be a reliable and efficient technique [4], it is a time, reagent and labor consuming procedure, which cannot be easily automated. Of additional concern is disposal of the solvent used, which creates a severe environmental problem. As a result, alternative methods, such as solid-phase extraction and co-precipitation, have been developed. Solid-phase has the advantages of simplicity, high preconcentration factor, and environmental friendly reagents used. The method employs similar principles of metal partitioning between solid and liquid phases. The sample is passed through a column containing a solid sorbent and retained metals are eluted from the solid-phase by an appropriate solvent. Since trace elements are attached to the solid-phase through van der Waals forces or hydrophobic interactions, which are not very strong, the addition of chelating agents to a sample prior to extraction is desired. Alternatively, functional chelating groups may be introduced into the sorbent. This may be done by synthesis of new sorbents containing such groups or chemical/physical bonding of chelating groups on existing materials (functionalization or coating). A variety of commercially available sorbents and chelating agents creates possibilities for modifications of existing methods and achieving high metal recoveries at reasonably high flow rates.

A survey of the literature revealed that various adsorbents such as thiol cotton [5,6], silinized glass beads resin [7], silica gel [8], activated carbon [9], C60–C70 fullerene [10] and microcrystalline naphthalene have been investigated for preconcentration of metal ions. It has been shown that the type of support material used is critical factor in the performance of the resulting supported reagent or catalyst. Two main factors should be considered when employing a material as a support. First, the material needs to be stable both thermally and chemically during the reaction process. Second, the structure of the support needs to be such that the active sites are well dispersed on its surface and that these sites are easily accessible.

One of the most effective sorbents is silica gel as this offers high thermal and chemical stability (except for a few small nucleophiles, notably OH⁻ and F⁻). In addition, silica can possess high surface areas [11], and with low cost. Thus, the chemical modification of

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silica gel for producing a valuable solid support could be recommended. Modified silica gels have also been used in the separation of trace metals from aqueous systems [12–14].

In this study we report the application of a 2,4,6-trimorpholino-1,3,5-triazin bonded silica gel as an efficient sorbent for preconcentration and determination of some transition metal ions by atomic absorption spectrometry (AAS).

2. Experimental

2.1. Apparatus

A Shimadzu model 670 atomic absorption spectrometer was used for determination of concentration of metal ions after elution. The conditions were used as given in Table 1. The flow rates of air and acetylene were set as recommended by the manufacturer.

2.2. Reagents

Triply distilled water was used and analytical reagent grade chemicals were purchased from Merck (Darmstadt, Germany) and Sigma–Aldrich (St. Loius, MO, USA) chemical companies. 2,4,6-Trimorpholino-1,3,5-triazin (Scheme 1) was prepared and purified according to ref. [15]. The sorbent 2,4,6-trimorpholino-1,3,5-triazin modified silica gel was prepared as described previously [12].

2.3. Analytical procedure

An accurately weighed sorbent was transferred into a glass column of 15 cm length and 1.0 cm diameter. The column was washed with triply distilled water. The pH of optimized volume of metal ion solution was adjusted by the drop-wise addition of dilute HNO_3. The solution was then passed through the column at a flow rate of 5 mL min^{-1}. Metal ion adsorbed on the column was then eluted with 2.0 mL of 1.0 mol L^{-1} HCl solution at an elution rate

Table 1
Operating parameters for determination of cations by flame atomic absorption spectroscopy

Element	Current (mA)	Wavelength (nm)	Slit (nm)
Ni	4	232.0	0.15
Co	6	240.7	0.20
Zn	4	213.9	0.50
Cd	4	228.8	0.30
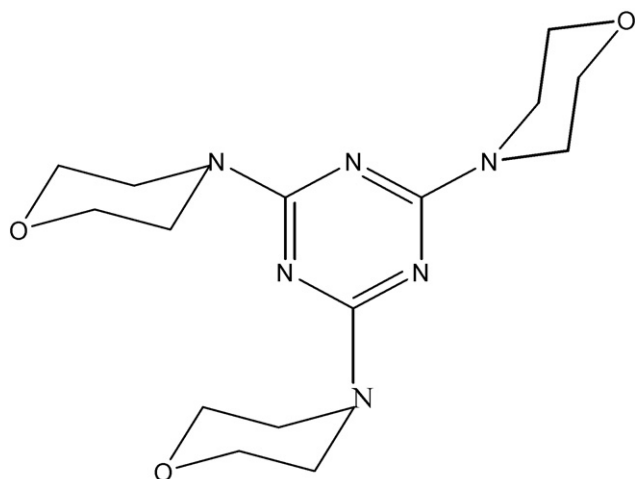
Scheme 1. 2,4,6-Trimorpholino-1,3,5-triazin.

of 1 mL min^{-1}. The metal concentration in the eluted solution was determined by FAAS.

2.4. Determination of nickel in apple leaves

Sample pretreatment was performed as described previously [16]. A 1.0 g sample was taken in a beaker and dissolved in 20 mL concentrational nitric acid with heating. The solution was cooled, diluted and filtered. The pH of the final solution was adjusted to 5 by suitable addition of NH_3 solution and the solution was finally diluted to 250 mL by distilled water in a calibrated flask. The nickel content of the solution was then determined after preconcentration as described above (in Section 2.3).

2.5. Determination of Co in urine samples

Sample pretreatment was performed as described previously [17]. A 10 mL portion of urine sample (or spiked urine sample) was treated with 10 mL of 2:1 HNO_3 and $HClO_4$ in a 50 mL beaker covered with a watch glass. The contents in the beaker were heated on a hot plate (20 min). The watch glass was removed and the acid evaporated to dryness at 150 °C. To the obtained white residue, 8 mL of $HClO_4$ was added, and the mixture was heated to dryness. All of the heating processes were carried out under a hood with necessary precautions. Five milliliters of 1 mol L^{-1} HCl were added, and the contents were heated at 150 °C for 1 min. The pH of the obtained clear solution was adjusted to 5 by NH_3 solution and the solution was finally diluted to 50 mL by distilled water in a calibrated flask. The preconcentration procedure given above was applied to the final solutions.

3. Results and discussion

Adsorption of each ion was investigated separately. Ions from solutions with different concentrations of cations were allowed to become adsorbed on the sorbent. Different parameters were optimized. The effect of pH of sample solution, the type and concentration of eluent, sample and eluent flow rates on the extraction efficiency, interfering effects of foreign species and capacity factor of the sorbent have been studied. The optimization procedure was carried out by varying a parameter while the others were kept constant.

3.1. Optimization of pH

The effect of pH of the test solution on the retention of Co^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions was studied. Aliquots of 5.0 mL of 5.0 μg mL^{-1} of each metal ion solution in the pH range of 3.0–9.0 were passed through a series of column containing 0.10 g sorbent and their concentrations were measured after elution. The results are shown in Fig. 1. The results of this study showed that metal ions were completely adsorbed on the sorbent over the pH range of 4.0–6.0. Therefore, pH 5.0 was chosen as the optimum pH for further studies. Diluted HNO_3 and NH_3 were used for adjusting the pH of solutions.

3.2. Effect of sample flow rate

The percent sorption of 5.0 mL of 5.0 μg mL^{-1} each metal ion on the sorbent surface as a function of sample solution flow rate was examined in the range of 0.5–12.0 mL min^{-1}. The retention of Co^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions on adsorbent was not affected by sample flow rates lower than 6 mL min^{-1}. However, at flow rates greater than 6 mL min^{-1}, there was a decrease in the percentage of sorption. This may be due to the insufficient contact time of the sample
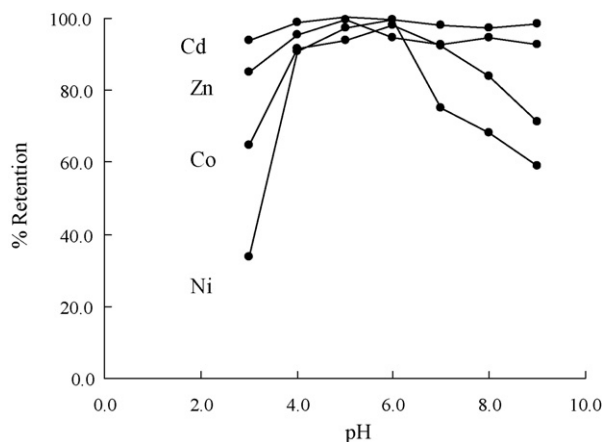
Fig. 1. Effect of pH of the metal ions solution on the percent of retention on sorbent. Experimental conditions: 5 mL 10.0 ng mL^{-1} metal ion solution at different pH, 0.10 g sorbent, flow rates of sample and eluent were 5 mL min^{-1} and 1 mL min^{-1}, respectively.

solution with the sorbent. Thus the experiments were performed at a sample flow rate of 5 mL min^{-1} which was the maximum flow rate attainable by the pump we used.

3.3. Choice of eluent

Studies were carried out to investigate the influence of different acids as eluents for desorbing metal ion from the sorbent surface. HNO$_3$ caused decomposition of the modified silica gel. HCl was chosen as an eluent owing to its effective elution of the adsorbed cations. Aliquots of 5.0 mL of 5.0 μg mL^{-1} metal ion solutions were passed through a series of columns containing 0.10 g of adsorbent. The amount of metal ion back-extracted into the liquid phase by each eluent was measured using FAAS. Recovery percentages of metal ions were calculated for each sample. The effect of eluent concentration in the range 0.025–1.500 mol L^{-1} of HCl on the absorbance of eluted solution was examined was also studied. The absorbance of all four ions was increased, as the HCl concentration increased up to 1.0 mol L^{-1} and remained constant above this concentration. Therefore, a concentration of 1.0 mol L^{-1} of HCl was selected for further studies.

The effect of the volume of eluent solution was also studied. The recovery percentage of metal ions increased by increasing the volume of HCl up to 2.0 mL and remained constant afterward. Therefore, optimum volume of the eluent was chosen as 2.0 mL. The flow rate of eluent was 1 mL min^{-1}.

3.4. Capacity of the sorbent

The capacity of the sorbent is an important factor that determines how much sorbent is required to quantitatively remove a specific amount of metal ion from the solution [18]. For investigation of adsorption isotherm of metal ions in solution, the same volume of metal ion solution with different concentrations of ion was passed from column that packed with 0.10 g of sorbent. The number of microgram adsorbed per gram of adsorbent (N_f) versus the equilibrium concentration of cation shows the process that conforms to the Langmuir model. Such isotherms are generally associated with monolayer adsorption. The Langmuir equation was used to calculate the maximum retention capacity (N_s) [19,20]. The general form of Langmuir isotherm is:

$$Y = \frac{KC_s}{1 + KC_s} \tag{1}$$

where Y is the fraction of adsorbent surface covered by adsorbed species, K a constant and C_s the equilibrium concentration of the cation solution. In our case, $Y = N_f/N_s$, where N_f represents the number of μg cation adsorbed per gram of adsorbent (μg g^{-1}) at equilibrium concentration, C_s and N_s is the maximum amount of solute adsorbed per gram of surface (μg g^{-1}) which depends on the number of adsorption sites. After linearization of the Langmuir isotherm, Eq. (1), we obtain:

$$\frac{C_s}{N_f} = \left(\frac{C_s}{N_s}\right) + \left(\frac{1}{KN_s}\right) \tag{2}$$

All these adsorption studies were based on the linearization form of the Lanmguir isotherm derived from C_s/N_f as a function of C_s. This plot gives a straight line with slope equal to $1/N_s$, and intercept equal to $1/KN_s$. Therefore, the Langmuir isotherm is an adequate description of the adsorption of metal ion on sorbent. The maximum retention capacity (N_s) for cation–surface interaction was determined from the slope. The results showed that the capacity factor were 590, 833, 670, and 526 μg g^{-1} for Cd^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}, respectively.

Adsorption of the investigated metal cations on a blank column that was packed with silica gel instead of modified silica gel was also studied. It was found that adsorption of metal ions on blank column is not significant.

3.5. Effect of sample volume

The effect of the sample volume on the adsorption of metal ions on 0.10 g of sorbent was studied by passing sample volumes of 10.0–250.0 mL containing the same amount of metal ion (25 μg) through the column. The amount of metal was measured after elution of adsorbed metal by 2.0 mL of HCl solution. The signal of each eluted solution was compared with calibration curve data which was achieved from determination method and the recoveries of cations were calculated. The results are given in Table 2. As the reported recoveries show, sample volume did not affect on the adsorption of cobalt and nickel up to 200 mL and on the adsorption of cadmium and zink up to 100 mL. In order to determine low concentrations of metal ions, all the experiments for cobalt and nickel were carried out with 200 mL sample solution and for cadmium and zink with 100 mL sample solution. As the amount of metal ions in sample solution was measured after elution of adsorbed metal ions by 2 mL of HCl, and as the recoveries are almost 100%, the preconcentration factor is 100, 100, 50, 50 for Ni, Co, Cd and Zn, respectively.

Table 2
The effect of sample volume on the recovery of cations

Sample volume	Recovery (%)			
	Co	Ni	Cd	Zn
10	100.1	99.4	100.1	97.5
50	97.8	99.9	99.3	98.5
100	99.8	98.9	99.7	98.9
175	99.3	99.1	95.4	84.6
200	98.8	98.6	91.3	79.8
250	96.7	93.4	85.6	72.4

Table 3
Analytical features of proposed method

Cation	Equation	Linear range (ng mL^{-1})	Detection limit (ng mL^{-1})	R^2 ($n = 8$)
Cd^{2+}	$A = 0.0186C + 0.0097$	1.00–50.00	0.23	0.9980
Co^{2+}	$A = 0.0054C + 0.0026$	5.00–100.00	0.20	0.9983
Ni^{2+}	$A = 0.0027C + 0.0017$	5.00–125.00	0.29	0.9987
Zn^{2+}	$A = 0.0187C + 0.0044$	0.50–20.00	0.34	0.9957

Table 4
Accuracy and precision of the proposed method

Cation	Concentration (ng mL^{-1})	Relative error (%)	R.S.D. (%), $n = 5$
Ni^{2+}	10.00	−2.64	2.37
	50.00	−1.37	1.65
Co^{2+}	10.00	1.96	1.75
	50.00	0.95	1.41
Cd^{2+}	5.00	−3.02	2.71
	50.00	−2.05	1.86
Zn^{2+}	5.00	−3.41	2.95
	50.00	−2.54	2.23

Table 5
Determination of cations in natural water samples by the proposed method ($n = 5$)

Sample	Amount of cation (µg L^{-1})				Recovery	
	Added		Found			
	Ni^{2+}	Co^{2+}	Ni^{2+}	Co^{2+}	Ni^{2+}	Co^{2+}
Tap water	0.00	0.00	n.d.[a]	n.d.	–	–
	10.00	10.00	9.70 ± 0.71	9.80 ± 0.62	97.0	98.0
	50.00	50.00	49.14 ± 0.82	49.44 ± 0.71	98.2	98.8
Spring water	0.00	0.00	n.d.	n.d.	–	–
	10.00	10.00	10.50 ± 0.62	10.10 ± 0.52	105.0	101.0
	50.00	50.00	49.81 ± 1.83	49.60 ± 1.12	99.6	99.20

[a] Not detected.

Table 6
The application of proposed method in real samples ($n = 5$)

Cation	Added (µg L^{-1})	Found (µg L^{-1})	Recovery
Cd^{2+} in Caspian Sea water	–	1.36 ± 0.05	–
	5.00	6.17 ± 0.15	96.2
Zn^{2+} in Caspian Sea water	–	4.63 ± 0.09	–
	5.00	9.21 ± 0.33	91.6
Ni^{2+} in apple leaves	–	3.52 ± 0.22	–
	5.00	8.43 ± 0.41	98.2
Co^{2+} in urine	–	15.51 ± 0.71	–
	5.00	20.30 ± 0.90	95.8

3.6. Effect of foreign ions

The effect of different cations and anions was investigated on percentage recovery of 10.0 ng mL^{-1} of metal ion in 5 mL of solution by the proposed method and various amounts of foreign ions were prepared and the procedure described in the experimental section was applied. Any deviation of ±5% or more from the absorbance value of the standard solution was taken as interference. The follow-

ing ions did not interfere at 100 mg L^{-1} on the preconcentration and determination of 10.0 ng mL^{-1} metal ions: Ca^{2+}, Mg^{2+}, Pb^{2+}, Mn^{2+} and Cu^{2+}. Fe^{3+} interfered at 5 mg L^{-1}, SO$_4^{2-}$ interfered at 10 mg L^{-1}, PO$_4^{3-}$ interfered at 100 mg L^{-1} on determination of Ni^{2+} and Co^{2+} interfered at 10 mg L^{-1} on determination of Zn^{2+} and Cd^{2+}. The results indicated that high concentrations of all the ions tested did not interfere with separation and determination of these cations.

3.7. 3.7 Simultaneous preconcentration

Solution (500 mL) containing 30.0, 35.0, 25.0 and 10.0 ng mL^{-1} of Cd, Co, Ni and Zn ions, respectively, was prepared and passed through the column containing 0.1 g sorbent. The metal ions were eluted with 4 mL of HCl solution (1.0 mol L^{-1}) and Cd, Co, Ni and Zn concentrations were determined by FAAS. The recoveries are 93.4%, 99.2%, 92.6%, 94.8% for Cd, Co, Ni and Zn ions, respectively. This indicates the proposed method is suitable for simultaneous preconcentration and separation of Cd, Co, Ni and Zn and allows the determination of trace amounts of theses elements by FAAS which is an available instrument in almost every laboratory.

3.8. Analytical characteristics

From measurements made under the optimum conditions described above, the calibration graphs were developed. The calibration equations are given in Table 3. The limit of detection, defined as $C_L = |3S_B|m$, where C_L, S_B and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively. To evaluate the accuracy and precision of the method, two different concentrations of standard samples with several repeating were used. The results are given in Table 4. As Table 4 shows, the relative standard deviation (R.S.D.) for the determination of different concentrations of cations was in the range 1.65–2.95%. The prepared sorbent was subjected to several loadings with the sample solution and subsequent elution with eluent. The capacity of the adsorbent did not change after six cycles of sorption and desorption.

3.9. Analytical applications

The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples of the spring water and tap water with different concentrations of cations. The results are given in Table 5. The accuracy and applicability of the proposed method has been applied to the determination of Zn and Cd in Caspian sea water sample, Ni in apple leaves, and Co in urine sample. The results are given in Table 6 and indicate the success-

Table 7
Comparison data from some recent solid-phase extraction studies by flame atomic absorption spectrometry

Analytes	Sorbent	Detection limit (µg L^{-1})	Liner range (µg L^{-1})	References
Cu, Cd, Pb, Zn, Ni, Co	Chromosorb 108/bathocuproinedisulphonic acid	0.16–0.6	20–10,000	[21]
Co, Ni	5,7-Dichloroquinolinone-8-ol embedded styrene-ethylene glycol dimethacrylate polymer	2.0	0–500	[22]
Cu, Cd, Pb, Ni, Co	Modified silica gel with aminothioamido-anthraquinone	0.95–22.5	–	[23]
Cd, Fe, Co, Ni, Zn, Cu	Pyrocatechol modified amberlite XAD-2 resin	5–25	500–10,000	[24]
Cd, Fe, Co, Ni, Zn, Cu, Pb	Cellulose functionalized with 8-hydroxyquinoline	0.79–2.59	–	[25]
Cr, Fe, Cu, Ni, Co, Zn	Salicyl aldehyde, 1,3-propan diimine (BSPDI) loaded on activated carbon	0.27–0.33	0.02–0.8	[26]
Cu, Pb, Fe, Co, Cr	Chelex-100	2.9–15.0	0–6000	[27]
Cu, Co, Ni, Cd	2,4,6-Trimorpholino-1,3,5-triazin bonded silica gel	0.20–0.30	0.5–125.0	Proposed method

ful applicability of the proposed method for the determination of these cations in real samples.

4. Conclusion

Solid-phase extraction with 2,4,6-trimorpholino-1,3,5-triazin bonded silica gel is an effective separation and preconcentration technique for trace elements. The method has the advantages of being simple and inexpensive. This proposed preconcentration method has a high enrichment factor which develops possibility of determining concentration levels as low as sub micro amounts of cations. A comparison between the proposed method with some existing methods reported for preconcentration of metal ions by solid-phase extraction method [21–27] is given in Table 7. As Table 7 shows, The proposed method shows comparable capacity level, lower detection limit, and wider linear range and is a convenient, safe, simple, rapid and inexpensive method for the determination of trace quantities of these cations in real samples with satisfactory results.

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