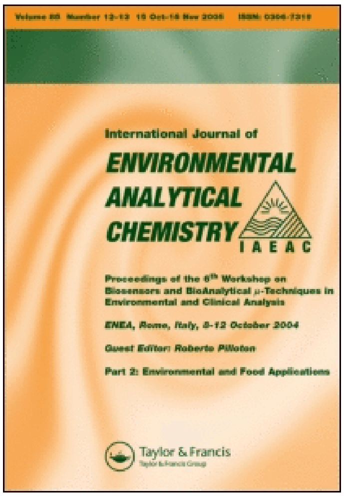

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Column-mode separation and pre-concentration of some heavy metal ions by solvent-impregnated resins containing quinizarin before the determination by flame atomic absorption spectrometry

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Column-mode separation and pre-concentration of some heavy metal ions by solvent-impregnated resins containing quinizarin before the determination by flame atomic absorption spectrometry

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A simultaneous separation and pre-concentration of Cd(II), Cu(II), Ni(II) and Zn(II) ions from natural water samples for subsequent flame atomic absorption spectrometric determination was proposed. The procedure is based on sorption of the metal ions at the buffering pH of 9.5, on a short column filled with Amberlite XAD-16 impregnated with the complexing agent of 1,4-dihydroxyanthraquinone (quinizarin). The determinations, without the interference of the co-existing substances, were carried out after metals elution with 5 mL of 0.5 mol L^{-1} HCl. A pre-concentration factor of nearly 100 was obtained using aliquots of 500 mL of the sample solution. For the optimisation of the procedure, effects of sample and eluent flow rate, eluent concentration and its volume were investigated. Beer's law was obeyed in the range of 5.0×10^{-9} to 1.0×10^{-7} mol L^{-1} for Cd(II) and Zn(II), 5.0×10^{-8} to 1.0×10^{-6} mol L^{-1} for Cu(II) and Ni(II) ions. The relative standard deviations of the determinations were <1.87%. The limit of detections for Cd(II), Cu(II), Ni(II) and Zn(II) were found to be 1.3×10^{-9}, 7.1×10^{-9}, 1.3×10^{-8} and 1.8×10^{-9} mol L^{-1}, respectively. The practical applicability of the method was confirmed using a synthetic certificated reference material and spiked natural water samples.

Keywords: solvent-impregnated resins; quinizarin; Amberlite XAD-16; column-mode separation; flame atomic absorption spectrometry

1. Introduction

The determination of low concentration of metal ions by flame atomic absorption spectrometry (FAAS) usually requires separation and pre-concentration steps due to insufficient sensitivity or matrix interference. In the last decade, solid phase extraction has become an eminent technique for this purpose [1,2]. New types of materials, such as highly cross-linked polymers and chemically modified polymers, have been developed for more effective extraction [3–5]. Some of these sorbents exhibit co-extraction behaviour so that the extraction process involves many matrix species. As a result, the necessity to develop selective chelating sorbents has become an attractive area of research. Based on this, polymeric chelating ion-exchange resins that exhibit high selectivity have been developed [6–14]. However, industrial application of these resins in large scale is uneconomic, which is related to complex and time-consuming industrial manufacturing. Moreover, these

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resins are usually suffering from low metal ion loading capacities, expensive chemical regeneration and tedious recycling procedures.

Solvent-impregnated resins (SIR), which were firstly studied for metal extraction processes by Warshawsky [15] and Grinstead [16], are alternative route to synthetic polymeric chelating resins. SIRs are simply prepared by immobilisation of a complexing solvent extraction reagent within the matrix structure of polymer adsorbents by physical contact. It is possible to obtain a whole range of SIRs using various combinations of polymeric supports and liquid extractants [17–27]. They combine the advantageous features of both liquid–liquid extraction and ion-exchange techniques. These include (i) application of the readily available extractants that benefit from the unique specificity and selectivity properties, (ii) the feasibility to describe the mechanism of interaction of metal ions with the extractants, (iii) lack of third phase formation, (iv) the possibility of treating with complicated solutions and (v) simply adopting to a continuous separation process. The only limitation of SIRs is the loss of extractant from the polymer matrix during the application since there is no covalent bond between the extractant and the polymer matrix. Hence, it seems, application of SIRs is unacceptable in view of economic and environmental pollution. Recently, some efforts have been made to increase the chemical stability of SIRs [28,29]. Consequently, any attempt to improve the stability of SIRs and prepare high stable SIRs can be an attractive area of research.

1,4-dihydroxyanthraquinone (quinizarin, QNZ) have been reported as an effective chelating reagent for some metal ions [30–32]. Recently, we have developed a batch-mode solid-phase FAAS procedure for the determination of Cd(II), Cu(II), Ni(II) and Zn(II) ions in natural water samples [33]. The procedure was based on employing the SIR that was readily prepared through impregnation of QNZ in/on Amberlite XAD-16. This SIR exhibits a good stability against sorption/desorption processes without any significant mass loss for a long time. The results showed that the analytes can be reacted with the QNZ impregnated and retain on the SIR. After separating the resin beads, the analytes were eluted with hydrochloric acid and determined by FAAS. Though batch-mode solid-phase extraction offers some benefits in comparison with solvent extraction, it suffers from disadvantages such as, damage of the resin bead during the stirring process, tedious steps of separation of the resin beads from the sample solution and eluent, losing the resin beads during the process and gradual release of the impregnated reagent during the regeneration step. On the other hand, this method is not adapted to use in industrial processes. All of these restrictions are eliminated by using the column-mode extraction. Hence, the possibility of developing sensitive and selective column-mode procedure for simultaneous separation and pre-concentration of the above metal ions was explored using the QNZ impregnated resins. The determination process was subsequently performed by FAAS. The procedure was validated by analysis of a standard reference material (SRM 1643d) and spiked natural water samples.

2. Experimental

2.1 *Instrumentation*

A Shimadzu AA 6300 flame atomic absorption spectrometer equipped with a deuterium arc was used for determination of metal ions of interest. The instrumental operating parameters for the determinations were those recommended by the manufacturer. A Corning model 130 pH-meter was used for pH measurements. The flow of liquids through the short column was controlled with an Eyela SMP-23 peristaltic pump and a 6-port valve (V-451, Upchurch). A Sartorius membrane filter of pore size 0.45 μm was used for filtration of the natural water samples.

2.2 *Materials and solutions*

All the reagents used were of analytical grade (99.99%, E. Merck, Darmstadt, Germany). All solutions were prepared with ultra pure water (Millipore) and all the experiments were performed with deionised distilled water. The glassware used was cleaned by overnight soaking in solution of $3\,\mathrm{mol\,L^{-1}}$ HNO_3 and then rinsing with deionised distilled water. Stock solutions of Cd(II), Cu(II), Ni(II) and Zn(II) at concentrations of $1 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ were prepared separately by dissolving appropriate amounts of nitrate salts in 1.0% HNO_3. The working solutions with the desired concentrations were made daily using the stock solutions. Solutions of ammonia and ammonium nitrate were prepared with equal concentrations of $1\,\mathrm{mol\,L^{-1}}$ for buffering the experimental solutions at the pH of interest.

2.3 *Preparation of the SIR*

Preparation and characterisation of the SIR has been described in the previous paper [33]. In order to remove any type of adsorbed ion that maybe present on surface of the resin beads of SIR, they were kept in solution of $4\,\mathrm{mol\,L^{-1}}$ HCl for 24 h prior to use.

2.4 *Procedure*

A portion of 1.00 g of the SIR was packed in an acrylate column (4 mm i.d. and 70 mm long), which was used in place of an injection loop. Both the ends of the column were fritted with Teflon wool to prevent loss of the resin beads during the sorption/desorption process. The bed length of resin in the column was about 55 mm. Working solutions containing the analytes with the concentrations exceeding the detection limits of the metal ions were prepared in which the pH and ionic strength were adjusted to 9.50 and $0.01\,\mathrm{mol\,L^{-1}}$, respectively, using the ammonia and ammonium solutions. Periodically, aliquots of 500 mL of the prepared solutions were passed through the column at a flow rate of $10.0\,\mathrm{mL\,min^{-1}}$. The column was washed with 10 mL of distilled water to remove free matrix substances and then the metal ions sorbed on the SIR were stripped off from the column with 5 mL of $0.5\,\mathrm{mol\,L^{-1}}$ HCl at a flow rate of $3\,\mathrm{mL\ min^{-1}}$. The subsequent determinations were carried out by FAAS. The column was regenerated by passing 10 mL of distilled water at the same flow rate.

3. Results and discussion

3.1 *Effect of pH and ionic strength on metal sorption*

As pointed out in our previous work [33], sorption of the metal ions from the sample solution could be carried out at the optimum pH and ionic strength of 9.5 and $0.01\,\mathrm{mol\,L^{-1}}$, respectively. In treatment with the column-mode separation, to find the optimum pH and ionic strength, the investigation was repeated again. The results obtained confirmed that the maximum sorption can be carried out at the same conditions. Therefore, pH and ionic strength of all standard and sample solutions were adjusted to

9.5 and 0.01 mol L^{-1}, respectively. It should be considered that the interested metal ions are capable to form moderately stable complexes with OH^- as $M(OH)^+$ at weak basic media [34] and finally precipitate as $M(OH)_2$ by increasing the pH of the solutions. Evidently, in such conditions, the procedure cannot perform properly. To prevent from undesirable precipitation of the metal ions, the sorption process was carried out at the presence of ammonia i.e. the solutions were buffered with ammonium/ammonia system. Obviously, at this condition, the metal ions are present as soluble species, $M(NH_3)_4^{2+}$, at the working pH of the solution. The sorption process, which involves replacement of the metal ions with the counter ions present in the resin phase, can be accomplished with the following reactions:

$$M(NH_3)_4^{2+} \leftrightarrows M^{2+} + 4NH_3$$

$$\overline{(QH_2)_n} + M^{2+} \leftrightarrows \overline{(QH_2)_{n-2}M(QH)_2} + 2H^+$$

$$H^+ + NH_3 \leftrightarrows NH_4^+$$

where the bar denote the species in the organic phase of the impregnated resin and QH_2 represents the impregnated QNZ. As it is observed, the sorption process involves complex formation between the metal ions and QNZ, which can be occurred only at the basic media.

3.2 *Desorption studies*

As pointed out in the previous work [33], among the various types of acidic reagents that were examined for desorption of the metal ions, hydrochloric acid was preferred owing to protect SIR from damage. In addition, desorption process is accelerated because of formation of moderately stable complexes between the released metal ions and chloride ions. Hence, a number of experiments with a flow rate of 1 $cm^3 min^{-1}$ were carried out in which the recoveries of the metal ions were investigated subjected to change in concentration, and volume of hydrochloric acid solution as the eluent. The results obtained are summarised in Table 1. As it is shown, quantitative recoveries (>95%) were obtained for all the metal ions with 0.5 mol L^{-1} HCl as the eluent.

3.3 *Sample and eluent flow rates*

The sample and eluent flow rates are important parameters to obtain quantitative retention and elution, respectively. The effect of sample volume flow rate on sorption of metal ions of interest was studied in the range of 2–14 mL min^{-1} using the feed solution containing the metal ions with the concentrations of 4×10^{-7} mol L^{-1} for Zn(II) and Cd(II), and 8×10^{-7} mol L^{-1} for Ni(II) and Cu(II). The flow rate slower than 2.0 mL min^{-1} was not studied to avoid a long time of the analysis. As shown in Figure 1, all metal ions of interest can be sorbed quantitatively by the SIRs at a flow rate of 2.0–10.0 mL min^{-1}. Above 10.0 mL min^{-1}, the recovery for Ni(II) ions was less than 95%, as this metal ion probably could not equilibrate properly with the resin bed. In practice, to obtain the maximum recovery for all the metal ions, the experiments were carried out at the sorption flow rate of 10 $cm^3 min^{-1}$.

For elution, as it is shown in Figure 2, these metal ions can be eluted quantitatively by the resin at a flow rate of 1.0–3.5 mL min^{-1}. Above 3.5 mL min^{-1}, the recovery for

Table 1. Effect of concentration and volume of hydrochloric acid as the eluent on the recoveries of metal ions of interest at the conditions where, volume of the solution: 500 mL, C_{Cd} and $C_{Zn} = 2 \times 10^{-7}$, C_{Cu} and $C_{Ni} = 4 \times 10^{-7}$, pH = 9.5, ionic strength: 0.01 mol L^{-1}, elution flow rate: 3.5 mL min^{-1}. The results are mean of three measurements ± SD.

		Recovery ± SD (%)			
C_{HCl} (mol L^{-1})	V_{HCl} (mL)	Cd(II)	Cu(II)	Ni(II)	Zn(II)
0.05	5	54.11 ± 0.25	68.01 ± 0.25	67.40 ± 0.35	60.75 ± 0.32
0.05	10	67.02 ± 0.21	76.31 ± 0.21	78.55 ± 0.28	69.58 ± 0.28
0.08	5	85.20 ± 0.18	83.00 ± 0.17	84.01 ± 0.25	70.00 ± 0.24
0.08	10	94.13 ± 0.14	89.19 ± 0.23	89.07 ± 0.25	76.92 ± 0.21
0.10	5	90.05 ± 0.12	85.04 ± 0.21	88.70 ± 0.21	77.09 ± 0.18
0.10	10	96.26 ± 0.15	93.12 ± 0.18	92.32 ± 0.15	91.24 ± 0.18
0.25	5	95.15 ± 0.13	95.03 ± 0.15	96.07 ± 0.15	97.09 ± 0.15
0.25	10	97.86 ± 0.12	97.34 ± 0.13	97.12 ± 0.11	97.41 ± 0.12
0.50	5	99.98 ± 0.10	98.15 ± 0.12	97.06 ± 0.12	98.96 ± 0.12
0.50	10	99.99 ± 0.08	99.10 ± 0.10	98.02 ± 0.14	99.52 ± 0.10
0.80	3	71.97 ± 0.23	76.01 ± 0.27	66.28 ± 0.35	68.95 ± 0.28
0.80	5	99.97 ± 0.05	99.56 ± 0.11	97.18 ± 0.12	98.98 ± 0.10
1.50	3	82.15 ± 0.21	82.24 ± 0.31	72.38 ± 0.20	75.64 ± 0.18
1.50	5	99.98 ± 0.10	99.85 ± 0.10	97.07 ± 0.12	98.96 ± 0.10
2.00	3	86.35 ± 0.21	89.56 ± 0.16	83.57 ± 0.24	85.06 ± 0.20
2.00	5	99.98 ± 0.12	99.78 ± 0.14	98.13 ± 0.15	99.12 ± 0.15

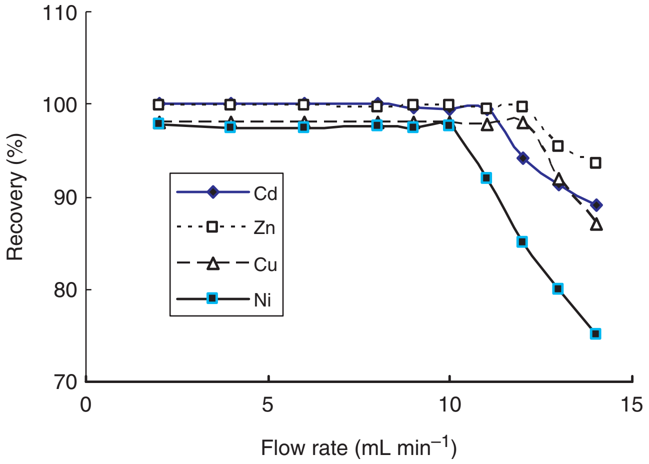

Figure 1. Effect of sample flow rate on the recoveries of the metal ions on QNZ impregnated resin (volume of the solution: 500 mL, C_{Cd} and $C_{Zn} = 2 \times 10^{-7}$ and C_{Cu} and $C_{Ni} = 4 \times 10^{-7}$, pH = 9.5, eluent: 5 mL 0.5 mol L^{-1} HCl, elution flow rate: 3.5 mL min^{-1}, $N = 3$).

Ni(II) was <95%. In practice, to obtain a better reproducibility, all further studies were performed at eluent flow rates of 3 mL min^{-1}. When the effects of flow rates of sample were examined, the eluent flow rate was kept constant as 2 mL min^{-1}. Conversely, the flow rate of sample was kept as 10 mL min^{-1}, to find the optimum conditions of the eluent flow rate.

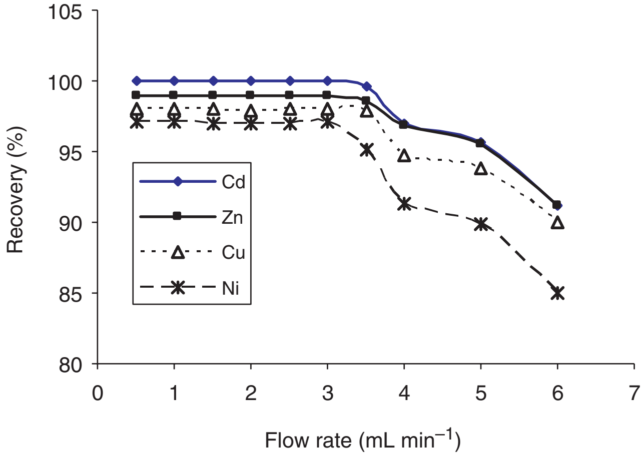

Figure 2. Effect of the eluent flow rate on the recoveries of the metal ions on QNZ impregnated resin (sample flow rate: 10 mL min^{-1}, other conditions as in Figure 1).

Table 2. Selectivity factors for different metal ion couples determined at the conditions that 500 mL of solution containing binary mixture of the metal ions was passed through the column. The other conditions are mentioned in this article. The results are mean of three measurements ± SD.

$\alpha^{Cu^{2+}}_{Zn^{2+}}$	$\alpha^{Cu^{2+}}_{Cd^{2+}}$	$\alpha^{Cu^{2+}}_{Ni^{2+}}$	$\alpha^{Cd^{2+}}_{Zn^{2+}}$	$\alpha^{Ni^{2+}}_{Zn^{2+}}$	$\alpha^{Ni^{2+}}_{Cd^{2+}}$
2.15 ± 0.03	1.82 ± 0.02	1.67 ± 0.02	1.21 ± 0.03	1.55 ± 0.02	1.34 ± 0.03

3.4 *Selectivity factor for metal separation*

In order to determine the selectivity factors of each of the metal ions respect to the others, a series of solutions containing binary mixture of the metal ions with equal concentrations of 1×10^{-4} mol L^{-1} were prepared and portions of 500 mL of these solutions were passed through the column. After eluting the fractions of sorbed metal ions with 5 mL of 0.5 mol L^{-1} HCl, both sorbed/residual fractions were analysed by FAAS. The selectivity factor for each of the binary systems was then calculated according to the following expression:

$$\alpha^{M_2}_{M_1} = \frac{Y_{M_2}}{Y_{M_1}} \frac{X_{M_1}}{X_{M_2}}$$

where Y and X are the equivalent fractions of the ions under separation in the resin and solution phases, respectively. Indices 1 and 2 are chosen to represent the binary metal ions so that $\alpha > 1$. As it is pointed out from Table 2, the selectivity factor values for Cu/Zn, Cu/Cd ion pairs are higher than the others.

3.5 *Dynamic sorption capacity and pre-concentration factor*

The sorption capacities of the SIR for all metal ions of interest were evaluated in our previous work at the batch experimental conditions [33]. In the present work, the dynamic sorption capacities of the SIR for each one of these metal ions were calculated using the breakthrough curves, which they were recorded as C/C_0 (ratio of eluent concentration to that of the influent) *versus* effluent volume. The experiments were carried out by recommended procedure using the metal ion solution at $1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ concentration and a column containing 0.1 g of the SIR. The upper parts of these breakthrough curves up to the horizontal line where $C/C_0 = 1$ were integrated, and the areas (in mL) found were multiplied by C_0 and 10 to yield the dynamic capacities, i.e. the amount of metal sorbed by 1.0 g of the SIR. The dynamic capacities obtained were 209.5, 245.8, 192.4 and 281.6 $\mu\mathrm{mol\,g^{-1}}$ for Cd(II), Cu(II), Ni(II) and Zn(II) ions, respectively. The difference between the above quantities may be attributed to the distribution coefficients of these metal ions, which in turn are related to stability constants of the metal-QNZ chelates.

The pre-concentration factor was studied by recommended procedure using increasing volume of metal ion solution up to 4500 mL and keeping the amount of each of the metal ions constant to 5×10^{-7} mol. It was found that the recoveries were >95% in the sample volume range of 100–3000 mL for Ni(II) and 100–3500 mL for the others. The pre-concentration factor is calculated by the ratio of the highest sample volume and the eluent volume (5 mL). The results of the pre-concentration factors and recoveries for each of the metal ion are summarised in Table 3. As it is seen, the pre-concentration factors are very high for all metal ions of interest so that ultra-trace amounts of these metal ions can be determined using high volume samples. However, it should be considered that the sorption process is taken a long time when an excessive volume is passing through the column. On the other hand, as it is observed in Table 3, the reproducibility is moderately diminished by increasing the sample volume. Hence, it was preferred to use aliquots of 500 mL for the sorption process. In such conditions, the experimental pre-concentration factor is nearly equal to 100 for all metal ions of interest.

3.6 *Analytical performance*

Under the optimum conditions, the calibration curves for the determination of these metal ions were linear over the ranges of 5.0×10^{-9} to $1.0 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$ for Cd(II) and Zn(II), and 5.0×10^{-8} to $1.0 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$ for Cu(II) and Ni(II) contents. The linear equations along with regressions (R^2) are as follows:

$$\begin{aligned}
\mathrm{Cd(II)}:&\quad A = 2.5466 \times 10^6 C + 0.0016; \quad R^2 = 0.9996\\
\mathrm{Zn(II)}:&\quad A = 1.9839 \times 10^6 C + 0.0011; \quad R^2 = 0.9997\\
\mathrm{Cu(II)}:&\quad A = 4.6940 \times 10^5 C + 0.0013; \quad R^2 = 0.9998\\
\mathrm{Ni(II)}:&\quad A = 2.8615 \times 10^5 C + 0.0014; \quad R^2 = 0.9987
\end{aligned}$$

where A is the peak area of absorbance and C is the concentration in $\mathrm{mol\,L^{-1}}$. All the statistical calculations were obtained based on the average of triplicate reading for each standard solution in the given ranges.

The quantities of limit of detection (blank + 3σ), where σ is SD of the blank estimations, were evaluated as given in the parentheses: Cd ($1.3 \times 10^{-9}\,\mathrm{mol\,L^{-1}}$), Zn ($1.8 \times 10^{-9}\,\mathrm{mol\,L^{-1}}$), Cu ($7.1 \times 10^{-9}\,\mathrm{mol\,L^{-1}}$), and Ni ($1.3 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$).

The relative standard deviation values were measured by seven successive sorption/desorption cycles using the solutions with the concentration of $5 \times 10^{-8}\,\mathrm{mol\,L^{-1}}$

Table 3. Effect of sample volume on the recoveries of the metal ions on QNZ-impregnated resin at the condition where, eluent: 5 mL 0.5 mol L^{-1} HCl. Other conditions are as discussed in Table 1. The results are mean of three measurements ± SD.

Sample volume (mL)	Concentration (mol L^{-1})	Final volume (mL)	Pre-concentration factor	Recovery ± SD (%)			
				Cd(II)	Cu(II)	Ni(II)	Zn(II)
100	5.00×10^{-6}	5	20	99.99 ± 0.05	98.03 ± 0.10	97.02 ± 0.10	98.97 ± 0.08
500	1.00×10^{-6}	5	100	99.98 ± 0.10	98.05 ± 0.10	97.03 ± 0.10	98.95 ± 0.10
1000	5.00×10^{-7}	5	200	99.97 ± 0.16	98.00 ± 0.15	97.01 ± 0.18	98.96 ± 0.14
2000	2.50×10^{-7}	5	400	99.98 ± 0.22	97.98 ± 0.20	97.02 ± 0.24	98.96 ± 0.21
3000	3.33×10^{-7}	5	600	99.98 ± 0.25	97.96 ± 0.24	96.58 ± 0.27	98.95 ± 0.25
3500	1.43×10^{-7}	5	700	99.89 ± 0.25	97.95 ± 0.31	91.08 ± 0.42	98.88 ± 0.28
4000	1.25×10^{-7}	5	800	94.20 ± 0.31	92.06 ± 0.32	87.07 ± 0.45	93.21 ± 0.32
4500	1.11×10^{-7}	5	900	91.03 ± 0.35	90.09 ± 0.32	83.11 ± 0.45	90.01 ± 0.30

(Cd(II) and Zn(II)), and 5×10^{-7} mol L^{-1} (Cu(II) and Ni(II)). The obtained results were as 1.51%, 1.32%, 1.63% and 1.87% for Cd(II), Zn(II), Cu(II) and Ni(II) ions, respectively.

3.7 *Effects of matrix ions interferences*

To evaluate the analytical applications of the recommended procedure, the effect of some foreign ions which interfere with the determination of these metal ions was examined. For this purpose, fixed amounts of metal ions of interest with equal concentrations of 1.0×10^{-7} mol L^{-1} were taken with different amounts of foreign ions and the recommended procedure was followed. The tolerance limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of metal ion of interest by the combination of the column solid phase extraction and FAAS determinations. The results are summarised in Table 4. As it is observed, some ions including Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-} and CO_3^{2-} as essential constituents of natural water are tolerated in the concentration range of 5.0×10^{-4} to 1.5×10^{-2}. The results also show that commonly occurring ions in water samples like SO_4^{2-}, I^{-}, PO_4^{3-}, Al^{3+}, Co^{2+} and Hg^{2+} have no pronounced interference effect even at much higher concentrations. On the other

Table 4. Tolerance level of the interfering ions on determination of the analytes at the conditions that 500 mL of solution containing metal ions of interest with equal concentrations of 1.0×10^{-7} mol L^{-1} and each of the examined ions was passed through the column. The other conditions are mentioned in this article. The results are mean of three measurements ± SD.

			Recovery ± SD (%)			
Ion	Added as	Concentration (mol L^{-1})	Cd^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}
Na^{+}	NaCl	1.5×10^{-2}	98.61 ± 0.12	98.17 ± 0.11	97.02 ± 0.11	98.70 ± 0.10
K^{+}	KCl	1.5×10^{-2}	98.36 ± 0.13	99.21 ± 0.11	96.59 ± 0.14	99.24 ± 0.11
NH_4^{+}	NH_4Cl	1.5×10^{-2}	99.29 ± 0.12	98.63 ± 0.10	96.90 ± 0.12	99.15 ± 0.10
Ca^{2+}	$CaCl_2$	5.0×10^{-4}	95.58 ± 0.11	98.05 ± 0.12	96.12 ± 0.11	98.63 ± 0.12
Mg^{2+}	$MgCl_2$	5.0×10^{-4}	96.22 ± 0.11	98.42 ± 0.11	96.35 ± 0.10	96.57 ± 0.11
Cl^{-}	NH_4Cl	1.5×10^{-2}	99.29 ± 0.12	99.21 ± 0.11	96.90 ± 0.12	98.65 ± 0.11
NO_3^{-}	KNO_3	1.5×10^{-2}	98.31 ± 0.11	98.25 ± 0.12	97.87 ± 0.11	98.78 ± 0.10
CO_3^{2-}	Na_2CO_3	1.0×10^{-3}	96.09 ± 0.13	96.18 ± 0.14	95.21 ± 0.13	96.17 ± 0.12
SO_4^{2-}	Na_2SO_4	1.0×10^{-3}	96.38 ± 0.12	97.29 ± 0.11	95.08 ± 0.12	96.29 ± 0.11
I^{-}	KI	1.0×10^{-3}	102.27 ± 0.11	100.54 ± 0.11	98.37 ± 0.11	100.68 ± 0.10
PO_4^{3-}	Na_3PO_4	5.0×10^{-4}	103.13 ± 0.14	101.23 ± 0.10	98.12 ± 0.11	101.45 ± 0.10
Al^{3+}	$AlCl_3$	5.0×10^{-4}	95.24 ± 0.11	95.11 ± 0.11	95.11 ± 0.10	96.07 ± 0.10
$Fe^{3+ a}$	$FeCl_3$	5.0×10^{-4}	96.17 ± 0.11	96.48 ± 0.12	96.23 ± 0.14	96.35 ± 0.11
Co^{2+}	$Co(NO_3)_2$	5.0×10^{-4}	96.35 ± 0.10	95.17 ± 0.10	95.04 ± 0.13	96.23 ± 0.12
$Mn^{2+ a}$	$Mn(NO_3)_2$	5.0×10^{-4}	98.18 ± 0.13	95.08 ± 0.11	96.55 ± 0.11	98.61 ± 0.12
Cd^{2+}	$Cd(NO_3)_2$	1.0×10^{-4}	–	41.13 ± 0.15	49.84 ± 0.11	65.58 ± 0.15
Cu^{2+}	$Cu(NO_3)_2$	1.0×10^{-4}	63.82 ± 0.11	–	56.27 ± 0.10	73.42 ± 0.13
Ni^{2+}	$Ni(NO_3)_2$	1.0×10^{-4}	74.51 ± 0.14	55.26 ± 0.12	–	76.33 ± 0.11
Zn^{2+}	$Zn(NO_3)_2$	1.0×10^{-4}	47.23 ± 0.12	43.65 ± 0.13	41.12 ± 0.14	–
$Pb^{2+ a}$	$Pb(NO_3)_2$	1.0×10^{-4}	95.34 ± 0.11	95.32 ± 0.12	95.91 ± 0.13	95.37 ± 0.14
Hg^{2+}	$\mu g(NO_3)_2$	1.0×10^{-5}	96.12 ± 0.14	95.28 ± 0.14	95.36 ± 0.11	96.89 ± 0.12

Note: [a]The majority of these ions were precipitated as hydroxide; hence, they were removed by filtering before the sorption process.

hand, a number of cations, such as Fe^{3+}, Mn^{2+} and Pb^{2+} could be eliminated through the precipitation as hydroxo species at the working pH and separated by filtration. So, they have no adverse effect on the determination, even when present initially at high considerable concentrations.

3.8 *Analysis of real samples*

In order to investigate the validity of the proposed method, a synthetic water sample was prepared conforming to the composition of SRM 1643d, by following just the literature considerations [35]. The results of the expected and found values of the interested metal ions' concentrations are shown in Table 5. Satisfactory recoveries, being in the range of 94.4%–99.1%, were obtained. The agreement between found and expected values of the metal ions' concentrations demonstrated that the described method was accurate for trace

Table 5. Application of the proposed method to the determination of the analytes in 500 mL aliquots of the synthetic certified sample of SRM 1643d.

	Concentration (μg L^{-1})		
Metal ion	Expected	Found ($n=3$)	Recovery (%)
Cd^{2+}	6.47	6.41 ± 0.11	99.1
Cu^{2+}	20.5	19.68 ± 0.37	96.0
Ni^{2+}	58.1	54.83 ± 1.21	94.4
Zn^{2+}	72.48	71.12 ± 1.47	98.1

Table 6. The chemical composition of the natural water samples, which were collected from the water sources of Kashmar city and used for investigation of applicability of the proposed method. All values are in milligrams per litre unless specified otherwise.

Measurand	Spring water	Tap water	Well water
Alkalinity, total (as $CaCO_3$)	14.3 ± 2.4	156 ± 2.4	177.2 ± 2.4
Ammonia (as N; μg L^{-1})	2.1 ± 0.4	27.2 ± 0.4	58.5 ± 0.4
Boron (μg L^{-1})	10.0 ± 2.2	85.3 ± 3.4	54.4 ± 3.1
Calcium	32.4 ± 1.7	76.9 ± 2.8	64.8 ± 2.1
Chloride	18.6 ± 1.4	83.6 ± 1.8	56.7 ± 1.1
Dissolved inorganic carbon	20.7 ± 1.6	34.3 ± 1.7	43.1 ± 2.0
Dissolved organic carbon	1.1 ± 0.4	3.6 ± 0.4	1.6 ± 0.4
Fluoride (μg L^{-1})	21 ± 2	50 ± 2	42 ± 2
Hardness, total (as $CaCO_3$)	126.3 ± 2.7	218.1 ± 3.4	338.5 ± 3.5
Magnesium	12.7 ± 1.8	22.7 ± 1.5	30.2 ± 1.4
Nitrate + Nitrite	0.5 ± 0.2	5.6 ± 0.2	5.6 ± 0.2
pH	7.38 ± 0.01	7.83 ± 0.01	8.37 ± 0.01
Potassium	1.0 ± 0.1	3.1 ± 0.1	3.3 ± 0.1
Silica (as Si)	0.4 ± 0.1	2.2 ± 0.1	1.1 ± 0.1
Sodium	14.4 ± 0.1	38.1 ± 0.1	29.2 ± 0.1
Sulphate (as SO_4)	12.8 ± 0.5	57.5 ± 0.5	62.3 ± 0.6
Total Kjeldahl nitrogen (μg L^{-1})	72 ± 5	110 ± 7	117 ± 6

Table 7. Determination of the investigated metal ions in natural water samples at the conditions that 500 mL of the sample was examined according to the proposed method. The results are mean of three measurements ± SD.

	Spiked (μg)				Found[a] ± s (μg)				Recovery (%)			
Sample	Cd^{2+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Ni^{2+}
Sping water	–	–	–	–	1.19 ± 0.04	13.14 ± 0.05	–	–	–	–	–	–
	5.62	3.27	6.35	5.87	6.74 ± 0.04	16.46 ± 0.05	6.28 ± 0.04	5.79 ± 0.04	98. 8	101.7	98.9	98.7
Tap water	–	–	–	–	–	0.39 ± 0.03	–	–	–	–	–	–
	5.62	3.27	6.35	5.87	5.70 ± 0.06	3.63 ± 0.04	6.23 ± 0.05	5.74 ± 0.5	101.4	99.2	98.1	97.8
Well water	–	–	–	–	1.57 ± 0.05	1.34 ± 0.05	–	–	–	–	–	–
	5.62	3.27	6.35	5.87	7.28 ± 0.05	3.26 ± 0.04	6.32 ± 0. 5	5.76 ± 0.5	101.6	99.3	99.5	98.1

Note: [a]Average and SD of three determinations.

Table 8. Comparison of dynamic sorption capacities of the prepared SIR with other impregnated or immobilised chelating resins.

Supporter	Ligand	Metal ion (μmol g^{-1}) Cd(II)	Cu(II)	Ni(II)	Zn(II)	References
	Impregnated					
Amberlite XAD-16	Quinizarin	209.5	245.8	192.4	281.6	This work
Polyethylene	1-(2-Pyridylazo)-2-naphthol	0.75	0.75	–	0.75	[36]
	Immobilised					
Chromosorb 108	Bathocuproinedisulfonic acid	31.1	118.0	83.5	81.1	[37]
Amberlite XAD-2	2-(Methylthio)aniline	210.6	139.2	239.9	129.5	[38]
Amberlite XAD-2	2-Aminoacetylthiophenol	190.4	379.2	299.9	299.7	[39]
Chloromethylated	Imidazolylazobenzene	131.0	290.1	9.0	38.0	[40]
Polysryrene	1,4-Bis(imidazolylazo)benzene	361.0	148.0	7.0	61.0	[40]

Table 9. Comparison of pre-concentration factors of the prepared SIR with other impregnated or immobilised chelating resins.

Supporter	Impregnated ligand	Metal ion (μg g^{-1}) Cd(II)	Cu(II)	Ni(II)	Zn(II)	References
	Impregnated					
Amberlite XAD-16	Quinizarin	700	700	600	700	This work
Polyethylene	1-(2-Pyridylazo)-2-naphthol	10	10	–	10	[36]
Ambersorb 563	1-(2-Pyridylazo)-2-naphthol	125	125	125	125	[41]
Activated carbon	APDC	125	125	125	–	[42]
	Immobilised					
Chromosorb 108	Bathocuproinedisulfonic acid	80	80	80	80	[37]
Amberlite XAD-2	2-(Methylthio)aniline	300	100	400	150	[38]
Amberlite XAD-2	2-Aminoacetylthiophenol	400	100	400	150	[39]

analysis of such metal ions in the complex matrices. The proposed method was also applied to determine metal ions of interest in several natural water samples collected from water sources of Kashmar, a city in province of Khorassan Razavi. The chemical compositions of these water samples are detailed in Table 6. Before the treatment, they were filtered through a membrane filter with a pore size of 0.45 µm and then 500-mL aliquots of the samples were applied to analysis. The accuracy of the determinations was investigated using the spiked water samples with these metal ions at various concentrations. The obtained results are summarised in Table 7. As observed from the results, the recoveries for the added amounts to the spiked sample solutions were in the range 97.8%–101.7%, which confirmed satisfactorily applicability of the proposed method for complicated environmental samples.

3.9 *Comparison with other methods*

The dynamic sorption capacity and pre-concentration factors of the prepared SIR are compared with those of other important impregnated or immobilised resins in

Tables 8 and 9, respectively. The prepared resin exhibits better than or comparable pre-concentration and capacity values to a large number of the metal–matrix combinations. The shorter loading time for the examined metal ions is another advantage of this SIR system.

4. Conclusion

A procedure for the determination of trace amounts of Cd(II), Cu(II), Ni(II) and Zn(II) ions is described, which combines FAAS with simultaneous pre-concentration of the analytes by a high stable SIR. The proposed method has the following advantages: simple, rapid and low analysis cost. Instead of the use of fresh solvent as an extracting phase for each sample, the reusability of the SIR was as high as greater than 800 cycles without any loss in its sorption behaviour. The system was also successful in pre-concentrating metal ions from large sample volume. The analytical performance of the presented method is better than or comparable with other pre-concentration methods. The detection limits of investigated elements are superior to those of some pre-concentration/separation techniques for analyses [43–48]. The matrix effects with the method were reasonably tolerable. The elution was easily performed with 0.5 M HCl. The good features of the proposed method showed that it is a convenient and low cost one. Also the method is relatively rapid as compared with previously reported procedures for the enrichment of traces metal ions.

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