

## Preconcentration and Determination of Lead, Cadmium and Nickel from Water Samples Using a Polyethylene Glycol Dye Immobilized on Poly(hydroxyethylmethacrylate) Microspheres

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A simple and sensitive preconcentration analysis-atomic absorption spectrometric procedure is described for the determination of lead, cadmium and nickel. The method is based upon on-line preconcentration of metal ions on a minicolumn of Cibacron Blue F3-GA immobilized on poly(hydroxyethylmethacrylate), poly(HEMA). The enrichment factors obtained were 42 for lead, 52 for cadmium and 63 for nickel (sample volume 10 mL and sample flow rate 5 mL/min). The relative standard deviations ( $n = 10$ ), in 10 mL sample solutions containing 100  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 10  $\mu\text{g/L}$   $\text{Cd}^{2+}$  and 100  $\mu\text{g/L}$   $\text{Ni}^{2+}$  were 8.9, 3.7 and 3.5%, respectively. The limits of detection (blank + 3s) ( $n = 10$ ), were found to be 12.01  $\mu\text{g/L}$  for  $\text{Pb}^{2+}$ , 1.34  $\mu\text{g/L}$  for  $\text{Cd}^{2+}$  and 28.73  $\mu\text{g/L}$  for  $\text{Ni}^{2+}$ . The accuracy of the system was checked with certified and tap water samples spiked with known amounts of metal ions. No significant difference was found between the achieved results and the certified values.

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Heavy metals in the environment are generally a source of pollution. The determination of ultra trace of metals in environmental samples plays an important role in the environmental pollution monitoring, due to their toxicity. Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the preconcentration of trace elements before their analysis due to their low concentrations in numerous samples (especially water samples). For this, several methods have been proposed and used for preconcentration and separation of trace elements according to the nature of the samples, the concentrations of the analytes and the measurement techniques.<sup>1</sup> Among the various preconcentration methods, solid phase extraction (SPE) is another approach that offers a number of important benefits. It reduces solvent usage and exposure, disposal costs and extraction time for sample preparation. Consequently, in recent years SPE has been successfully used for the separation and sensitive determination of metal ions, mainly in water samples. Until now, XAD resins,<sup>2,3</sup> activated carbon,<sup>4,5</sup> ion-exchange resins, chelating resins<sup>6,7</sup> and various polymers have been used as solid-phase material.<sup>8-10</sup>

A large number of chelating polymers incorporating a variety of ligands (*e.g.* polyethyleneimine, iminodiacetate, amidoxime, phosphoric acid, dithiocarbamate, sulfonic/carboxylic groups) have been prepared and their analytical properties have been investigated.<sup>12-15</sup> Recently, incorporating textile dyes into polymer matrix has been reported in a series of publications.<sup>16,17</sup> The idea of using different reactive dyes stems from the fact that textile dyes are very reactive with different chemical substances including metal ions. In addition, reactive textile dyes may be easily modified by existing chemical methods to facilitate desorption under mild conditions.

In this study, the polyethylene glycol dye, Cibacron Blue F3-GA, were immobilized on poly(hydroxyethylmethacrylate) microspheres as a sorbent for preconcentration of lead, cadmium and nickel ions from aqueous media. The poly(HEMA) microspheres were selected as the basic polymer matrix which carries functional hydroxyl groups for further modification. It is a non-toxic and hydrophilic material which is often employed as a sorbent. Cibacron Blue F3-GA was used as the dye-ligand for binding of lead, cadmium and nickel ions. The purpose of our study is to demonstrate the feasibility of using Cibacron Blue F3-GA immobilized poly(HEMA) resin as a solid-phase extractant for preconcentration of lead, cadmium and nickel found at trace level in water samples. In the procedure, the analytes were retained on a short column of Cibacron Blue F3-GA immobilized poly(HEMA) resin from a sample solution and then eluted from the resin column with nitric acid. In the development of the procedure, several parameters relevant to the retention and elution of the analytes were examined. The presented procedure was applied to tap water samples and to two different reference standard materials (LGC6010, Hard Drinking Water and SPS-SW2 Batch 108, Surface Water) to test the performance of the system.

### Experimental

#### Apparatus

Details of the preparation and characterization of the poly(HEMA) microbeads and Cibacron Blue F3-GA attachment to the poly(HEMA) microbeads were reported elsewhere.<sup>18</sup> A Perkin Elmer AA 800 atomic absorption spectrophotometer that includes a deuterium lamp correction was used for the determination of Pb, Cd and Ni. The working current/wavelength values for lead, cadmium and nickel were 10 mA/283.3 nm, 4 mA/228.8 nm and 25 mA/341.5 nm, respectively. A Fisher

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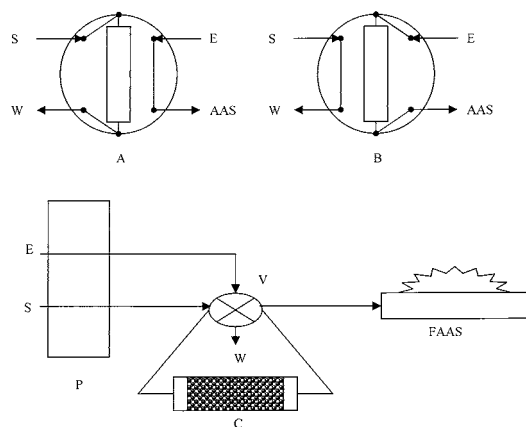


Fig. 1 Schematic diagram of the flow system used for preconcentration and determination of metal ions: S, sample (5.0 mL/min); E, eluent (0.2 mol/L HNO<sub>3</sub>, 5.0 mL/min); P, peristaltic pump; C, Cibacron Blue F3-GA immobilized poly(HEMA) minicolumn; V, four-way valve; FAAS, flame atomic absorption spectrometer; and W, waste. (A) Four-way valve in the preconcentration step. (B) Four-way valve in the elution position.

Scientific Accumet Model 15 pH meter was used to measure pH values. An Alitea S2-Mini peristaltic pump provided with Tygon tubes was used to transport all solutions.

#### Reagents

Standard solutions of 1000 mg/L Pb<sup>2+</sup>, Cd<sup>2+</sup> or Ni<sup>2+</sup> were separately prepared from Pb(NO<sub>3</sub>)<sub>2</sub> (Merck), Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Merck) or Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck) in deionized water. From these solutions, other dilute standard solutions were prepared daily. Deionized water of 18.1 MΩ/cm resistivity was obtained from a Banstead, Nanopure Diamond purification system. Nitric acid (Carlo Erba) and pure sodium hydroxide pellets (Merck) was used to adjust the sample pH.

#### Continuous flow system

A diagram of the flow system is shown in Fig. 1. The flow system was made up of a peristaltic pump fitted with Tygon tubes, one four-way valve and a minicolumn packed with Cibacron Blue F3-GA immobilized poly(HEMA) (2 mm i.d., 20 mm bed height), coupled to an atomic absorption spectrometer.<sup>19</sup> The flow system was operated in a time-based mode, in which a sample solution (S) pumped at 1.0–8.0 mL/min was percolated through a minicolumn containing a solid sorbent. Then metal ions are held by the Cibacron Blue F3-GA immobilized poly(HEMA), and the remaining solution was discharged. By switching the valve, one could pump a stream of a 0.2 mol/L HNO<sub>3</sub> (E) through the column for displacement of metal ions. The eluate was taken direct to the nebulizer-burner system of an atomic absorption spectrometer.

## Results and Discussion

#### Structure of the Cibacron Blue F3-GA attached poly(HEMA) microspheres

Cibacron Blue F3-GA molecules were covalently attached to the polymeric microspheres. The chemical structure of Cibacron Blue F3-GA is given in Fig. 2. It is accepted that ether linkages were formed between the reactive triazine ring of the dye and hydroxyl groups of the sorbent. Elemental analyses of the unmodified poly(HEMA) microspheres and those with

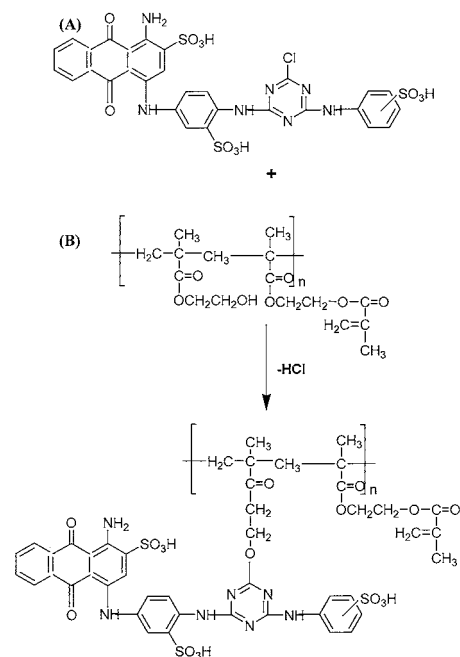


Fig. 2 The chemical reaction between Cibacron Blue F3-GA (A) and poly(HEMA) microspheres (B).

Cibacron Blue F3-GA attached performed. The attachment of the dye was found to be 22.3 μmol/g from the nitrogen stoichiometry. Cibacron Blue F3-GA leakage was also investigated; no leakage was observed from any of the dye-attached microspheres, even over a long period of time (more than 2 months). Cibacron Blue F3-GA was covalently coupled to the microspheres *via* the nucleophilic substitution reaction between the chloride of its triazine ring and the hydroxyl groups of the HEMA, under basic conditions. The chemical reaction between Cibacron Blue F3-GA and poly(HEMA) microspheres is shown in Fig. 2.

The continuous flow system was optimized by using the univariate method in order to determine the best chemical and flow conditions for the determination of metal ions with a maximum sensitivity.

#### Capacity of Cibacron Blue F3-GA immobilized poly(HEMA) microbeads resin

To investigate the adsorption capacity of the Cibacron Blue F3-GA immobilized poly(HEMA) microbeads, we allowed to 20 mL of each metal ion solution (pH adjusted to 5.5) at different initial concentrations to interact with 0.05 g of dye-attached poly(HEMA) microbeads for 30 min.

The amount of metal ions adsorbed per unit mass of the polymer increased with the initial concentration of metal ions, as expected. In order to reach the saturation of the active sites on the sorbent, in other terms to obtain the adsorption capacities of the dye attached microbeads for the interested metal ions, the initial concentrations of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions were increased up to 400 mg/L and the initial concentration of Ni<sup>2+</sup> ions was increased up to 600 mg/L. The adsorption capacities of Cibacron Blue F3-GA immobilized poly(HEMA) microbeads were 16.96 ± 2.05, 8.50 ± 1.38 and 26.12 ± 2.52 mg/g resin for Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup>, respectively.

#### Effect of the amount of resin

To test the effect of resin amount on quantitative retention of

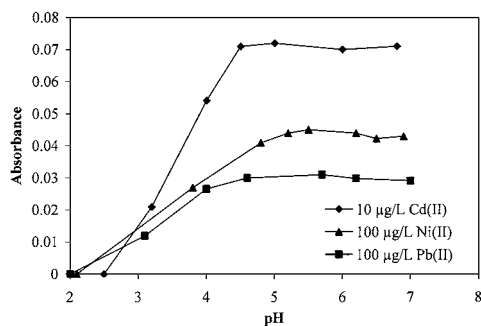


Fig. 3 The effect of the pH on the retention of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  by Cibacron Blue F3-GA immobilized poly(HEMA) microbeads (sample volume, 10 mL; eluent, 0.2 M  $\text{HNO}_3$ ;  $n = 3$ ).

analytes, we added different amounts of Cibacron Blue F3-GA immobilized poly(HEMA) microbead (ranging from 25 to 100 mg) to the mini-column. The results for 10 mL of 100  $\mu\text{g/L}$   $\text{Ni}^{2+}$  eluted with 0.2 mol/L  $\text{HNO}_3$ , indicated very similar peak shapes and heights for the resin amounts of 25–75 mg. Accordingly, the mini-column (2 mm i.d.) was filled with 50 mg (20 mm bed height) of Cibacron Blue F3-GA immobilized poly(HEMA) microbead resin in further experiments. When the amount of resin is more than 75 mg, the absorbance signal decreased by 20% and was broadened. This caused a problem in terms of sample flow resistance.

#### Effect of pH on the preconcentration

The effect of pH on the retention of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions was examined over a pH range of 2–7. Ten milliliters of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  standard solutions containing 100  $\mu\text{g/L}$ , 10  $\mu\text{g/L}$  and 100  $\mu\text{g/L}$  of the ions respectively, were loaded onto the column after pH adjustment with  $\text{HNO}_3$  and  $\text{NaOH}$ . The flow rate of the sample solutions was 5 mL/min. The results are depicted in Fig. 3. As can be seen from this figure, the maximum amount of lead, cadmium and nickel retention on Cibacron Blue F3-GA immobilized poly(HEMA) microbead resin is observed at  $\text{pH} > 4.5$ . Therefore, a pH above 4.5 was chosen throughout the subsequent experiments, considering that, at lower values, complexation and retention were probably incomplete.

#### Effect of sample solution flow rate

The degree of metal ion sorption on a mini-column packed with Cibacron Blue F3-GA immobilized poly(HEMA) microbead resin packed mini-column was studied at varying flow rates of the metal ion solutions. The optimum flow rate for loading the three metal ions was between 1.0 and 11.0 mL/min. The flow rates  $< 1 \text{ mL min}^{-1}$  were not employed to avoid the long extraction time. Results showed that the analytical signals did not vary significantly with the sample flow rate. That meant that the lead, cadmium and nickel sorption kinetics were very fast. A flow rate of 5.0 mL/min was chosen.

#### Effect of sample volume on the preconcentration

For the analysis of a real sample using preconcentration, the sample volume is one of the most important parameters for obtaining high enrichment factors. In this study, the effect of sample volume on the sorption behavior of the analytes was investigated by passing a sample solution in the range of 5–1000 mL containing  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions (1, 0.1 and 1  $\mu\text{g}$ , respectively) into the mini-column and comparing the absorbance values of metal ions. The results showed that the enrichment

Table 1 Effects of ions in determination of lead, cadmium and nickel by Cibacron Blue F3-GA immobilized poly(HEMA) microbeads in the continuous system

| Ion                | Added as                     | Tolerance limit/ $\mu\text{g L}^{-1}$ |       |       |
|--------------------|------------------------------|---------------------------------------|-------|-------|
|                    |                              | Pb                                    | Cd    | Ni    |
| $\text{Na}^+$      | NaCl                         | 500000                                | 70000 | 70000 |
| $\text{K}^+$       | KCl                          | 70000                                 | 10000 | 8000  |
| $\text{Al}^{3+}$   | $\text{AlCl}_3$              | 2000                                  | 400   | 900   |
| $\text{Cl}^-$      | $\text{NH}_4\text{Cl}$       | 300000                                | 50000 | 60000 |
| $\text{SO}_4^{2-}$ | $(\text{NH}_4)_2\text{SO}_4$ | 60000                                 | 8000  | 6000  |
| $\text{Cu}^{2+}$   | $\text{Cu}(\text{NO}_3)_2$   | 6000                                  | 600   | 2000  |
| $\text{Cd}^{2+}$   | $\text{Cd}(\text{NO}_3)_2$   | 40000                                 | —     | 2000  |
| $\text{Ni}^{2+}$   | $\text{Ni}(\text{NO}_3)_2$   | 600                                   | 400   | —     |
| $\text{Pb}^{2+}$   | $\text{Pb}(\text{NO}_3)_2$   | —                                     | 500   | 5000  |
| $\text{Cr}^{3+}$   | $\text{Cr}(\text{NO}_3)_3$   | 1000                                  | 100   | 600   |
| $\text{Fe}^{3+}$   | $\text{Fe}(\text{NO}_3)_3$   | 1000                                  | 1300  | 2000  |
| $\text{Zn}^{2+}$   | $\text{Zn}(\text{NO}_3)_2$   | 5000                                  | 2000  | 3000  |

Sample volume, 10 mL; eluent, 0.2 M  $\text{HNO}_3$ ;  $n = 3$ .

factors can be decreased by one order of magnitude by increasing the sample volume. The adsorption of metal ions was not affected by sample volume up to 500 mL. The enrichment factors of 2265, 2350 and 3550 for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$ , respectively, were reached with the present method when the sample volume was 500 mL and the elution rate was 5.0 mL/min.

#### Effect of the concentration of the eluent

The effect of eluent concentration is an important factor in solid phase extraction studies. The effects of various concentrations of nitric acid (between 0.025 and 0.5 mol/L) on the desorption of 100  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 10  $\mu\text{g/L}$   $\text{Cd}^{2+}$  and 100  $\mu\text{g/L}$   $\text{Ni}^{2+}$ , were studied. It was observed that there is an increase in the absorbance values up to the eluent concentration of about 0.1 mol/L. Accordingly, 0.2 mol/L  $\text{HNO}_3$  solution was selected as eluent for elution of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions in further studies.

#### Effect of the eluent flow rate

The influences of the flow rate of eluent solution on the desorption of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions from the minicolumn were investigated in the range of 1 mL/min to 10.5 mL/min after loading the column with 100  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 10  $\mu\text{g/L}$   $\text{Cd}^{2+}$  and 100  $\mu\text{g/L}$   $\text{Ni}^{2+}$  at 5.0 mL/min. The analytical signals obtained remain constant with increasing flow rates, probably due to the high desorption kinetics. A flow rate of 5.0 mL/min was selected in the subsequent studies because it did not cause air bubbles during aspiration.

#### Effects of other ions

One of the main problems in the atomic spectroscopic techniques is interference effects of the matrix of the analyzed samples. The influences of possible matrix ions in the natural water samples were also examined. For this purpose, interferent ions were added individually to a solution containing 100  $\mu\text{g/L}$   $\text{Pb}^{2+}$ , 10  $\mu\text{g/L}$   $\text{Cd}^{2+}$  and 100  $\mu\text{g/L}$   $\text{Ni}^{2+}$ . A set of 10 mL of solutions containing varying amounts of interferent ions and the metal ion of interest were taken and the same adsorption/elution procedure was applied. The results are given in Table 1. The tolerance limit is defined as the ion concentration causing a relative error smaller than  $\pm 5\%$  related to the preconcentration and determination of analytes. In all cases, the presence of the interferent decreased the interested metal ion signal by

Table 2 Recovery efficiencies of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> from tap water samples

| Element | Added/ $\mu\text{g L}^{-1}$ | Found/ $\mu\text{g L}^{-1}$ ( $\bar{x} \pm \text{S.D.}$ ) <sup>a</sup> | Rec., % |
|---------|-----------------------------|--|---------|
| Pb      | 0                           | BDL <sup>b</sup>   | —       |
|         | 20                          | 19.58 $\pm$ 0.02   | 97.9    |
|         | 30                          | 30.93 $\pm$ 0.04   | 103.1   |
|         | 40                          | 38.42 $\pm$ 0.05   | 96.05   |
| Cd      | 0                           | BDL <sup>b</sup>   | —       |
|         | 2.5                         | 2.48 $\pm$ 0.02  | 99.3    |
|         | 5                           | 5.06 $\pm$ 0.03  | 101.2   |
|         | 10                          | 9.86 $\pm$ 0.05  | 98.6    |
| Ni      | 0                           | BDL <sup>b</sup>   | —       |
|         | 30                          | 29.04 $\pm$ 0.01   | 96.8    |
|         | 40                          | 40.36 $\pm$ 0.02   | 100.9   |
|         | 50                          | 49.95 $\pm$ 0.04   | 99.9    |

a. S.D., standard deviation.

b. BDL, below detection limit.

Sample volume, 10 mL; eluent, 0.2 M HNO<sub>3</sub>;  $n = 3$ .

competition for the active sites present on the resin.

The ions normally present in water do not interfere under the experimental conditions used. Also, some transition metals at mg/L levels did not interfere with the preconcentration of the analyte ions. These results show that the proposed preconcentration method could be applied to the saline samples and to the samples that contain some transition metals including Zn<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup> and Cr<sup>3+</sup> at mg/L levels.

#### Reusability of the Cibacron Blue F3-GA immobilized poly(HEMA) resin

The reusability of the resin was tested by loading metal ions several times on minicolumn from a solution having different concentration of analyte ions at different flow rates and then adsorbed ions were eluted by the recommended procedure. It was found that the adsorption capacity after 30 cycles of adsorption and desorption does not vary more than 2%. Therefore multiple use of this resin is feasible. Similar results were obtained by the batch method.

#### Analytical features

**Enrichment factor, precision, LOD, LOQ.** Using the optimized conditions of preconcentration and elution, calibration graphs were prepared for lead (12.5 - 200  $\mu\text{g/L}$ ), cadmium (1.25 - 20  $\mu\text{g/L}$ ) and nickel (30 - 200  $\mu\text{g/L}$ ), and were found to be linear. The linear equations for lead, cadmium and nickel were  $A = 0.2878C + 0.0026$  ( $R^2 = 0.9966$ ,  $n = 5$ ),  $A = 6.914C + 0.0014$  ( $R^2 = 0.9998$ ,  $n = 5$ ) and  $A = 0.4230C + 0.0043$  ( $R^2 = 0.9989$ ,  $n = 5$ ), respectively. Here  $A$ , peak height absorbance and  $C$ , concentration in  $\mu\text{g/L}$ . All the statistical calculations are based on the average of triplicate readings for each standard solution.

The experimental enrichment factor was calculated as the ratio of the slopes of the calibration graphs obtained with and without preconcentration. The equations obtained by direct aspiration in FAAS for lead (1000 - 10000  $\mu\text{g/L}$ ), cadmium (100 - 1000  $\mu\text{g/L}$ ), and nickel (1000 - 10000  $\mu\text{g/L}$ ) were  $A = 0.006575C + 0.0011$  ( $R^2 = 0.9999$ ,  $n = 5$ ),  $A = 0.1339C + 0.0020$  ( $R^2 = 0.9999$ ,  $n = 5$ ) and  $A = 0.006610C + 0.0021$  ( $R^2 = 0.9999$ ,  $n = 5$ ), respectively. The enrichment factors obtained by calculating the ratio of the slopes of the two equations above, *i.e.*, with and without preconcentration, were 42 for lead, 52 for cadmium and 63 for nickel (sample volume 10 mL and sample flow rate 5 mL/min).

The precision of the proposed method, calculated as the

Table 3 Results of the analysis of standard reference materials (SPS-SW2 Batch 108, Surface Water and LGC6010, Hard Drinking Water) after application to preconcentration procedure

|    | SPS-SW2/ $\mu\text{g L}^{-1}$ |                  | LGC6010/ $\mu\text{g L}^{-1}$ |                |                  |
|----|-------------------------------|------------------|-------------------------------|----------------|------------------|
|    | Certified value               | Observed value   | Certified value               | Observed value |                  |
| Ni | 50.0 $\pm$ 0.3                | 48.18 $\pm$ 0.38 | Ni                            | 48 $\pm$ 4     | 46.42 $\pm$ 0.73 |
| Pb | 25.0 $\pm$ 0.1                | 24.08 $\pm$ 0.73 | Pb                            | 95 $\pm$ 3     | 93.33 $\pm$ 0.66 |
| Cd | 2.50 $\pm$ 0.02               | 2.47 $\pm$ 0.02  |                               |                |                  |

Sample volume, 10 mL;  $n = 5$ .

relative standard deviations in 10 mL sample solutions containing 100  $\mu\text{g/L}$  Pb<sup>2+</sup>, 10  $\mu\text{g/L}$  Cd<sup>2+</sup> and 100  $\mu\text{g/L}$  Ni<sup>2+</sup> were 8.9%, ( $n = 10$ ), 3.7%, ( $n = 10$ ) and 3.5% ( $n = 10$ ), respectively.

The limit of detection (blank + 3 $s$ , where  $s$  is standard deviation of blank estimation) ( $n = 10$ ), of a method is the lowest analyte concentration that produces a response detectable above the noise level of the system. This limit is reached where the precision of the method is unacceptable.<sup>3,20</sup> The limits of detection were found to be 12.01  $\mu\text{g/L}$  for Pb<sup>2+</sup>, 1.34  $\mu\text{g/L}$  for Cd<sup>2+</sup> and 28.73  $\mu\text{g/L}$  for Ni<sup>2+</sup>.

The limit of quantification (blank + 10 $s$ ) ( $n = 10$ ), is the lowest level of analyte that can be accurately and precisely measured. The limit of quantification was calculated as 12.69  $\mu\text{g/L}$  for Pb<sup>2+</sup>, 1.60  $\mu\text{g/L}$  for Cd<sup>2+</sup> and 28.97  $\mu\text{g/L}$  for Ni<sup>2+</sup>.

**Accuracy of the method.** Different amounts of interested metal ions were added to 10 mL of tap water in order to estimate the accuracy of the procedure. The resulting solutions were submitted to the preconcentration procedure given in experimental section. Results are shown in Table 2. A good agreement was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were always higher than 95%, thus assuring the accuracy of the procedure. These results confirm the validity of the proposed method.

**Application to real samples.** The column solid phase extraction method was applied to two different reference materials: LGC6010, Hard Drinking Water and SPS-SW2 Batch 108, Surface Water, for the determination of contents of Pb<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> ions. The certified and observed values for the LGC6010, Hard Drinking Water and SPS-SW2 Batch 108, Surface Water, are given in Table 3. The results in Table 3 are based on the average of five replicates. For 4 degrees of freedom, the table value of  $t$  at the 95% confidence level is 2.776. Good agreement was obtained between the estimated content by the proposed method and the certified values for the investigated analyte ions. If the concentration levels of the most common matrix constituents of the reference certified materials analyzed and the accuracy of the presented method are considered together, one can conclude that the proposed method is free from interferences of the various constituents.

**Comparative data from recent papers on solid-phase extraction.** In Table 4 are presented some preconcentration procedures for metal ion determinations, employing different sorbents with on-line column preconcentration systems. As can be seen from these data, our method is an effective approach in preconcentration and determination from sample matrices including tap, hard drinking, and surface water samples. The detection limits and enrichment factors of the investigated elements are superior to those of some preconcentration/separation techniques for analysis. The matrix effects with the method were reasonably tolerable. The elution was easily



Table 4 Comparison among several preconcentration methods for studied metal ions

| Trace element                   | Sorbent  | Rec., %    | Adsorptive capacity                                       | Enrichment factor          | LOD/ $\mu\text{g L}^{-1}$    | Ref.         |
|---------------------------------|--|------------|---|----------------------------|------------------------------|--------------|
| Bi/Cd/Co/Cu/Fe/<br>Ni/Pb + APDC | Chromosorb-102                                   | 95 - 110   | —   | 300                        | 0.10 - 11                    | 9            |
| Cu/Co/Ni                        | MPSP-loaded-SiO <sub>2</sub>                     | 94.6 - 101 | 43/45/49 $\mu\text{mol g}^{-1}$                           | 40                         | 60/40/70                     | 20           |
| Cu/Cd/Co/Pb/Zn/<br>Mn           | Quinalizarin-<br>functionalized-XAD-2            | 91 - 98    | 3.15/1.70/1.62/5.28/<br>1.42/0.94/2.19 $\text{mg g}^{-1}$ | 100/50/40/50/<br>100/65/65 | 2.0/1.3/5.0/<br>15.0/1.0/1.6 | 21           |
| Zn/Cd/Pb/Ni                     | PV-functionalized-<br>XAD-2                      | 98         | 1410/1270/620/1360 $\mu\text{g g}^{-1}$                   | 60/50/23/18                | —                            | 22           |
| Zn/Cd/Pb/Ni                     | Alizarin Red-S-<br>functionalized-XAD-2          | 95 - 100   | 511/124/306/124 $\mu\text{g g}^{-1}$                      | 40                         | 10                           | 23           |
| Cu/Cd/Co/Ni/Pb/<br>Zn/Mn/Fe     | Tiron-functionalized-<br>XAD-2                   | 91 - 99    | —   | 25 - 200                   | 0.5 - 24                     | 24           |
| Cd/Pb/Zn                        | Amberlite IRC-718                                | 63 - 104   | 1.06/0.096/1.77 $\text{mmol g}^{-1}$                      | 10                         | —                            | 25           |
| Cd/Co/Cu/Fe/Ni/Zn               | XO-loaded-XAD-7                                  | 96 - 100   | 1.6 - 2.6 $\text{mg g}^{-1}$                              | 10 - 200                   | 9/24/6/6/3/21                | 26           |
| Cd/Zn/Cu/Mn/Fe/<br>Ni/Co        | 8-HQ   | 67 - 108   | —   | 50 - 100                   | —                            | 27           |
| Pb/Cd/Ni                        | Cibacron Blue F3-GA<br>immobilized<br>poly(HEMA) | 97 - 101   | 16.96/8.50/26.12 $\text{mg g}^{-1}$                       | 42 - 63                    | 1.34 - 28.73                 | This<br>work |

performed with 0.2 M HNO<sub>3</sub>. The good feature of the proposed method is that it is relatively more rapid than previously reported procedures for the enrichment of trace metal ions. The resin on the column can be used at least 30 times.

## References

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