RESIDUES AND TRACE ELEMENTS

Simultaneous Preconcentration and Determination of Ni and Pb in Water Samples by Solid-Phase Extraction and Flame Atomic Absorption Spectrometry

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An analytical method for the preconcentration of nickel (Ni) and lead (Pb) in water samples on polystyrene-*graft*-ethylmethacrylate copolymer resin has been developed. The determinations of metal ions were performed by flame atomic absorption spectrometry. The experimental parameters, such as solution pH, sample flow rate, type and concentration of eluent, and amount of resin, were optimized for the preconcentration and recovery of Ni and Pb ions. Adsorbed ions on the resin were eluted by 6 mL of 2 M HNO_3. Under optimized conditions, the LOD was found to be 0.92 and 1.44 μg/L for Ni and Pb ions, respectively. The accuracy of the proposed procedure was tested by recovery studies and analysis of a standard reference material (GBW 08301, river sediment). The method was successfully applied to water samples.

Nickel (Ni) and lead (Pb) have no known essential role in living organisms and are toxic at even low concentrations. The World Health Organization has suggested that the maximum amount of Ni and Pb in drinking water should be 0.1 and 0.01 mg/L, respectively (1).

High Ni accumulation and absorption in organisms can cause various cancers, such as lung, nose, larynx, and prostate (2–6). Pb can accumulate in the human body over time and can cause serious damage to brain, kidney, nerves, and red blood cells. For infants, large amounts of Pb can cause delays in physical and mental development (7).

Direct analysis of some metals without using a separation-preconcentration technique is impossible due to interferences of the matrix and low LODs of most instruments (8). Therefore, a separation-preconcentration step is usually required for determination of metal ions with concentrations lower than the LOD of the technique. SPE has been widely used for the removal, separation, and preconcentration of metal ions. Various adsorbents, such as Amberlite and Duolite XAD resins, activated carbon, cellulose, modified silica gel, polymeric resin, and biomass, have been used (9–19). The synthesis of new adsorbents that are economical, selective, and have high capacity for the removal and separation of toxic heavy metal ions from water samples is a continuing research objective for control of environmental pollution (20).

Polystyrene-*graft*-ethylmethacrylate copolymer (GPSPEMA) is a new synthesized graft copolymer that is defined as a composition of PS-15Cl100 (15 and 100 includes *p*-chloromethyl styrene and monomer ratios, respectively) of poly (*S*-*g*-EMA) copolymer (21). It is synthesized from polystyrene-*co*-*p*-chloromethyl styrene, CuCl/1,2-dipiperidinoethane, and EMA monomers. It has physical, chemical, and thermal stability and a high surface area.

In the present work, a new separation method was developed for the preconcentration of trace Ni and Pb in water samples. GPSPEMA was first used as an adsorbent for the separation and preconcentration of heavy metals in water samples without using a chelating reagent. Required analytical parameters were investigated and optimized for GPSPEMA resin in a column. The developed method has been applied to analysis of water samples.

Experimental

Apparatus

A PerkinElmer (Shelton, CT) Analyst Model 700 flame atomic absorption spectrometry (FAAS) instrument with a hollow cathode lamp for the analyte elements, a deuterium background corrector, and an air-acetylene flame was used. The instrumental parameters used were resonance line wavelengths 232.0 and 283.3 nm, and slit widths 0.2 and 0.7 nm for Ni and Pb, respectively.

Reagents and Solutions

All reagents used were of analytical grade, and all solutions were prepared by using deionized water. GPSPEMA resin was obtained from Firat University (Elazig, Turkey), Physical Chemistry Division. Standard metal solutions were prepared from atomic absorption spectrometer stock solutions (1000 mg/L); Merck, Darmstadt, Germany). Other chemical reagents were obtained from Merck.

Preparation of GPSPEMA Resin

GPSPEMA was treated with nitric acid (2 M) and water, then washed with deionized water until the pH of the supernatant was

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neutral. Afterward, it was dried in an oven at 80°C. A polyvinyl chloride column (Sesim, Turkey) with a stopcock at the bottom and a reservoir of 250 mL (8 mm id and 120 mm in length) was used. A small amount of glass wool was placed at the bottom of the column to hold the resin, 0.5 g dried resin was placed inside, and another small glass wool plug was inserted onto the top of the resin. After each use, the resin was rinsed with 10 mL of 2 M HCl, 10 mL of 2 M HNO_3, and 50 mL water for 4 to 5 min for the removal of impurities (22–25).

Preconcentration Procedure

The column method was tested with model solutions, which were prepared as follows: 5 mL 1.0 mg/L Ni (II) and Pb (II) standard solutions were added to 2 mL acetate buffer (0.1 M, pH 5.0) solution in a 50 mL volumetric flask. The solution was diluted to the line with deionized water. Before use, the column was preconditioned with blank solution containing a buffer solution of the working pH. A test solution was permitted to flow through the column under gravity at a flow rate of 3 mL/min. The adsorbed ions on the column were eluted with 6 mL of 2 M HNO_3 solution at a flow rate of 4 mL/min. Ni and Pb were directly determined by FAAS using a calibration curve. A blank solution was analyzed under the same conditions.

Analysis of Water Samples

Commercial natural drinking water was obtained from a local market in Turkey. For the analysis, 600 mL aliquots of the water samples were used. Water samples were filtered by using Whatman (Florham Park, NJ) filter paper (No. 40), acetate buffer (pH 5.0) was added, and the sample was passed through the column. After the elution process, the metal concentrations were determined by FAAS.

Analysis of Standard Reference Material

Standard reference material (0.1 g; GBW 08301, river sediment; National Research Center for Certified Reference Materials, Beijing, China) was digested with 4 mL HNO_3 and 1 mL $HClO_4$ in a microwave digestion system (Vestel, Turkey) according to published procedures (26). A solution of the digested sample was transferred into a beaker and evaporated to dryness on a hot plate. Afterward, 25 mL distilled water was added and the solution was filtered through filter paper. The pH of this solution was adjusted to 5.0 by adding acetate buffer. The total volume was diluted to 50 mL with deionized water, and solutions were passed through the enrichment column. Then the given preconcentration procedure was applied. The blank digests were treated in the same way.

Results and Discussion

Effect of pH on Recovery of Metal Ions

The acidity of a solution has two effects on metal adsorption. First, protons in an acidic solution can protonate the binding sites of the resin. Second, the hydroxide ions in a basic solution may complex and precipitate many metals. Therefore, the effect of pH on the recovery of Ni and Pb ions on the resin was investigated in the pH range of 2–10. The prepared solutions at the working pH were passed through the column at a flow rate of 3 mL/min. The effect of the pH on the recovery values is summarized in Figure 1. As shown in the figure, the optimum recoveries were between pH 4.0 and 6.5 for Ni and 4.0 and 7.0 for Pb. Therefore, pH 5.0 was chosen as an optimum pH of the sodium acetate-acetic acid buffer for simultaneous preconcentration of Ni and Pb.

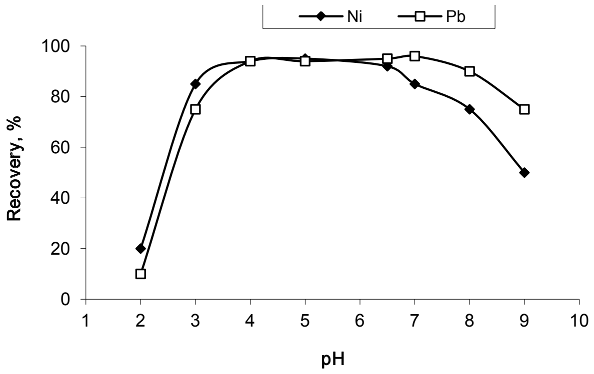

Figure 1. Effect of pH on the recovery of Ni and Pb.

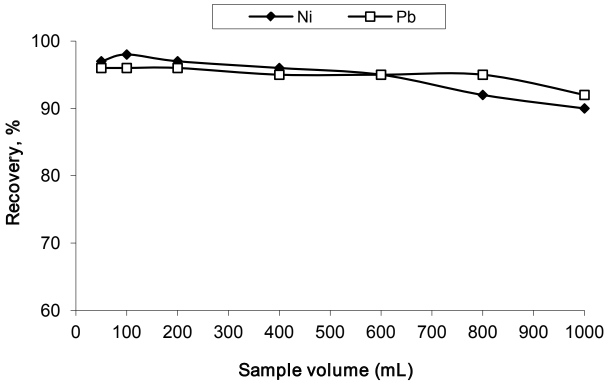

Figure 2. Effect of sample volume on the recovery of Ni and Pb.

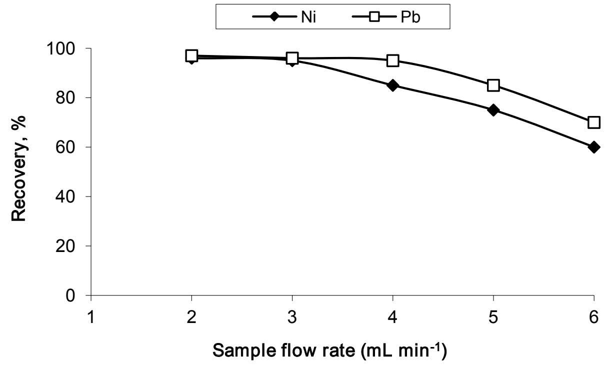

Figure 3. Effect of solution flow rate on the recovery of Ni and Pb.

Effect of Sample Volume

The selection of the sample volume is one of the important parameters in preconcentration studies, so the influence of the sample volume on Ni and Pb recovery was examined at a 3.0 mL/min flow rate. For this purpose, 50, 200, 400, 600, 800,

Table 1. Effect of type and concentration of eluting agent on Ni and Pb ion recovery

Eluent	Recovery, %[a] Ni	Pb
2 M HCl, 5 mL	90 ± 3	88 ± 2
2 M HCl, 6 mL	94 ± 2	92 ± 1
2 M HNO_3, 5 mL	95 ± 2	94 ± 2
2 M HNO_3, 6 mL	98 ± 2	100 ± 2
3 M HNO_3, 5 mL	96 ± 1	97 ± 1

[a] Results are mean ± SD of three replicate analyses.

Table 2. Effects of the matrix ions on the recoveries of Ni and Pb ions

Interfering ions	Concentration, mg/L	Recovery %[a] Ni	Pb
K^+	1000	99 ± 3	96 ± 2
Na^+	1000	100 ± 2	97 ± 2
Ca^{2+}	1000	97 ± 2	95 ± 2
Mg^{2+}	500	101 ± 2	94 ± 2
Mg^{2+}	1000	98 ± 2	85 ± 1
Cu^{2+}	10	103 ± 3	98 ± 2
Co^{2+}	10	96 ± 2	92 ± 2
Zn^{2+}	10	98 ± 2	96 ± 1
Cr^{3+}	10	97 ± 1	100 ± 2
Al^{3+}	10	96 ± 2	98 ± 2
Fe^{3+}	10	97 ± 3	96 ± 1
Cl^-	1000	98 ± 2	95 ± 3
NO_3^-	1000	99 ± 1	102 ± 2
SO_4^{2-}	100	97 ± 2	96 ± 2

[a] Results are mean ± SD of three replicate analyses.

and 1000 mL of the test solutions containing 2.5 µg of Ni and Pb were passed through the column at the optimum conditions. The results are shown in Figure 2. The recoveries were below 95% at sample volumes above 600 mL for Ni and above 800 mL for Pb. For the samples with volumes higher than 600 mL for Ni and 800 mL for Pb, the sorption of those ions was less than 95%. By analyzing 6 mL of the final solution after applying the preconcentration procedure (600 mL for Ni and 800 mL for Pb), enrichment factors were found to be 100 and 133 for Ni and Pb, respectively.

Effect of Sample Flow Rate

The interaction time between the metal ions and the resin is one of the critical parameters for the adsorption and recovery yield of metal ions. For this study, the effects of flow rate on the adsorption of Ni and Pb were investigated. To obtain maximum recoveries, different flow rates were tested for the retention of the Ni and Pb ions under optimum conditions. The metal ions were desorbed from the resin using 6 mL of 2 M HNO_3 solution. As shown in Figure 3, suitable flow rate of the solution was in the range of 1–3 mL/min for Ni and 1–4 mL/min for Pb. Therefore, an optimum flow rate of 3 mL/min was selected as the working solution flow rate to decrease enrichment time.

Effect of Eluent Type and Volume

Different volumes and concentrations of HCl and HNO_3 solutions were studied for maximum recoveries of Ni and Pb. The results showed that the maximum recovery of Ni and Pb was obtained using 6 mL of 2 M HNO_3 solution. The effects of various eluents on the recoveries of Ni and Pb ions are summarized in Table 1.

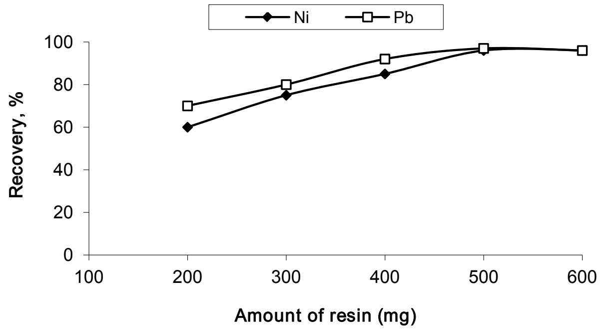

Figure 4. Effect of GPSPEMA resin amount on the recovery of Ni and Pb.

Effect of the Eluent Flow Rate

The speed of the recovery process is another important analytical parameter for preconcentration of trace metals. Therefore, the influence of eluent flow rate on the recoveries of Ni and Pb ions were examined in the range of 2–10 mL/min. The recoveries were below 95% at an eluent flow rate under 4 mL/min for both ions. To decrease the analysis time, an eluent flow rate of 4 mL/min was selected.

Effect of Resin Amount

The influence of the amount of the resin on recoveries of the metal ions was studied by adding the resin in the range between 200 and 600 mg into the adsorption column. Test solution (50 mL) containing 2.5 µg of Ni and Pb was passed through the column at the optimum conditions. The results showed that the optimum amount of sorbent was in the range of 500–600 mg for maximum extraction of Ni and Pb (Figure 4). From these results, the optimum amount of resin was selected as 500 mg, which was used in all further experiments.

Table 3. Results for certified reference material (GBW 08301, river sediment)

Element	Found, µg/g[a]	Certified, µg/g[a]	Recovery, %
Pb	78 ± 2.6	79 ± 12	98.7
Ni	33 ± 1.4	32[b]	103.1

[a] Mean ± SD from four determinations.

[b] Reference value.

Table 4. Applications of proposed method to water samples for determination of Ni and Pb ions

	Ni			Pb		
Sample	Added, µg/L	Found, µg/L [a]	Recovery, %	Added, µg/L	Found, µg/L [a]	Recovery, %
Commercial drinking water A	0	3.4 ± 0.5		0	2.2 ± 0.4	
	5.0	8.6 ± 0.7	97.6	5.0	7.4 ± 0.6	102.7
Commercial drinking water B	0	ND[b]		0	ND[b]	
	5.0	5.1 ± 0.6	98	5.0	5.0 ± 0.4	100
Tap water	0	4.1 ± 0.4		0	3.4 ± 0.5	
	5.0	9.3 ± 0.6	102.2	5.0	8.2 ± 0.6	97.6

[a] Mean ± ts/$\sqrt{N}$ at 95% confidence level.

[b] ND = Not determined.

Adsorption Capacity of the Resin

The metal ion uptake capacity of resin for Ni^{2+} and Pb^{2+} was determined by a batch method at the optimized pH (27). The adsorption capacity found for Ni and Pb was 12.5 and 16.4 mg/g, respectively.

Influence of Interfering Species

The effect of some ions present in water, i.e., K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Cu^{2+}, Cl^-, NO_3^-, and SO_4^{2-}, on the recoveries of Ni and Pb ions was investigated using the proposed method. In these experiments, 50 mL of solutions containing 2.5 µg of Ni and Pb and various amounts of possible interfering ions were treated according to the preconcentration procedure. The results are given in Table 2. As can be seen, added ions had no significant effect on the recovery of analyte ions.

Analytical Features

The analytical features of the proposed method, such as precision, mean recovery, and LOD, were examined. LOD for Ni and Pb was determined as 0.92 and 1.44 µg/L, respectively. Calculation of LOD was based on three times the SD of the 50 mL blank signals of 10 measurements. Precision of the method was obtained by analysis of 100 mL of test solutions containing 0.1 mg/L analyte ions under the optimized conditions. This procedure was performed seven times. The RSD values for Ni and Pb were 2.2 and 2.8%, respectively. The mean recovery values of the method for Ni and Pb were 96.8 and 98.4%, respectively.

The developed method was applied to standard reference material GBW 08301, river sediment, for the determination of Ni and Pb. The results, based on the average of four replicates, are given in Table 3 and show good agreement with the certified values.

Because the proposed method offers high sensitivity, low limit of determination, easy operation, and simple instrumentation, it can be recommended for Ni and Pb determination in various samples.

Applications of the Method for Determination of Ni and Pb

The developed method was applied to 600 mL of water samples. The validity of the proposed method was further proven by analyzing spiked Ni and Pb samples. For this purpose, known amounts of Ni and Pb solutions were added to samples. After homogenizing the samples and applying the procedure, Ni and Pb were determined by using the proposed method. Table 4 shows the experimental results of spiked Ni and Pb samples. The sufficiently good recoveries and low RSDs reflect the high accuracy and precision of the proposed preconcentration method.

Conclusions

In the present work, a new SPE method was developed for the separation and preconcentration of Ni and Pb in water samples. GPSPEMA resin was used as an adsorbent for enrichment of the metal ions. The proposed SPE method has a high enrichment factor, sufficiently good recoveries, a high tolerance limit for interfering ions, and a low LOD for simultaneous determination of Ni and Pb ions in various samples.

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