

Determination of lead and nickel in environmental samples by flame atomic absorption spectrometry after column solid-phase extraction on Ambersorb-572 with EDTA[☆]

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Abstract

Lead and nickel were preconcentrated as their ethylenediaminetetraacetic acid (EDTA) complexes from aqueous sample solutions using a column containing Ambersorb-572 and determined by flame atomic absorption spectrometry (FAAS). pH values, amount of solid phase, elution solution and flow rate of sample solution have been optimized in order to obtain quantitative recovery of the analytes. The effect of interfering ions on the recovery of the analytes has also been investigated. The recoveries of Pb and Ni under the optimum conditions were 99 ± 2 and $97 \pm 3\%$, respectively, at 95% confidence level. Seventy-five-fold (using 750 mL of sample solution and 10 mL of eluent) and 50-fold (using 500 mL of sample solution and 10 mL of eluent) preconcentration was obtained for Pb and Ni, respectively. Time of analysis is about 4.5 h (for obtaining enrichment factor of 75). By applying these enrichment factors, the analytical detection limits of Pb and Ni were found as 3.65 and 1.42 ng mL⁻¹, respectively. The capacity of the sorbent was found as 0.17 and 0.21 mmol g⁻¹ for Pb and Ni, respectively. The interferences of some cations, such as Mn²⁺, Co²⁺, Fe³⁺, Al³⁺, Zn²⁺, Cd²⁺, Ca²⁺, Mg²⁺, K⁺ and Na⁺ usually present in water samples were also studied. This procedure was applied to the determination of lead and nickel in parsley, green onion, sea water and waste water samples. The accuracy of the procedure was checked by determining Pb and Ni in standard reference tea leaves sample (GBW-07605). The results demonstrated good agreement with the certified values. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Since 1980s, mainly because of the decreasing use of leaded gasoline, exposure to lead has decreased dramatically [1]. However, in several countries lead exposure remains a considerable public health problem. Exposure to lead mainly occurs orally through food and water. Additional exposure may occur via contamination from soldered tin cans, lead-glazed glass or lead-painted glassware. In some countries, there may be considerable exposure through drinking water by contaminations from lead pipes [1]. Lead enters surface water from atmospheric fallout, run-off or wastewater. Most of the lead contamination

presents cumulative effect and if people maintain contact with lead for a long time, it could cause hazard for health even if it is in small concentrations. Lead contamination of foodstuffs and waters caused harmful effects on human health. The plants can absorb lead from the soil, fertilizers and air accumulating it in the tissue, thus it can reach the food chain of human. It decreased enzymatic activities and kidney functions and also causes neuromuscular difficulties [2]. There are legal restrictions concerning lead releasing to on the environmental samples in many countries. When vegetables and fruits were produced around industrial zone or when intensive use of fertilizers was employed to improve productivity, the monitoring of lead contaminations become important.

Nickel is widely used in electroplating, in the manufacture of Ni–Cd batteries, in rods for arc welding, in pigments for paints, in ceramics, in surgical and dental prostheses, in magnetic tapes and computer components and in nickel catalysts. Nickel enters waters from dissolution of rocks and soils, from biological

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cycles, from atmospheric fallout, especially from industrial processes and waste disposal [1]. Nickel was thought to be essential to plants and some domestic animals [3], but not considered to be a metal of biological importance until 1975, when Zerner discovered that urease was a nickel enzyme [4,5]. Nickel is essential constituent in plant urease [1]. Urease-rich legumes such as jack beans and soybeans generally contain high nickel concentrations [1]. Compared with other transition metals, nickel is a moderately toxic element. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including cancer of the respiratory system [6]. Moreover, nickel can cause a skin disorder known as nickel-eczema [7]. Therefore, it is necessary and important to develop sensitive methods for determining nickel in environmental, biological and food samples.

To assure that foods quality concerning trace metal contamination, food samples should be periodically analyzed. When vegetables and fruits were produced around industrial zone or when intensive use of fertilizers was employed to improve productivity the monitoring of trace metal contamination become important. Therefore, it is of importance to develop sensitive methods for determining trace metals in environmental and biological samples [8].

Lead and nickel could be determined directly in various samples by inductively coupled plasma atomic emission spectrometry (ICP-AES) or electrothermal atomic absorption spectrometry (ETAAS), which usually have a sufficiently low detection limit. Flame atomic absorption spectrometry (FAAS) available in most laboratories relatively simple, cheap and normally less subject to interferences than ICP-AES or ETAAS, can also be used for the determination of Pb and Ni. But, it requires the use of an enrichment and/or separation step in order to improve detection limit and selectivity. For this purpose, many enrichment methods have been proposed and used to separate and preconcentrate trace elements, according to nature of the samples, the concentration of the analytes and the measurement techniques [9]. Coprecipitation [10], liquid–liquid extraction [11], cloud-point extraction [12], ion-change [13], flotation [14] and solid-phase extraction (SPE) [15] are well-known procedures for the preconcentration and separation. SPE is the most effective multi-element preconcentration method because of its simplicity, rapidity and ability to attain a high enrichment factors. Therefore, the use of solid-phase extraction for the preconcentration and separation of trace metals from various matrices have recently increased. For this purpose, silica gel [16], activated carbon [17], Amberlite XAD resins [18–20], Chromosorb resins [21] and Ambersorb-572 [22,23] have been used as a solid-phase materials. However, in general, these materials have poor selectivity and sensitivity without using complexing agent or without modifying their surfaces with an appropriate ligand. If a complexing agent was used before extraction, high sensitivity and selectivity maybe obtained. Kendüzler and Türker used EDTA for Fe, 1,10-phenanthroline for Zn and Mn and 1-nitroso-2-naphthol-3,6-disulphonic acid for Cu and Cd as a complexing agent [22–24].

In the present study, EDTA was used as a complexing agent and the feasibility of using Ambersorb-572 resin as a

solid-phase extractor for the separation and preconcentration of Pb and Ni was investigated. The results showed that the analytes were easily retained in the form of metal–EDTA complexes on Ambersorb-572 resin from acidic aqueous solution. The proposed method was successfully applied to the analysis of various water and biological samples.

2. Experimental

2.1. Apparatus

A Varian GTA—97 Spectra AA 250 Plus atomic absorption spectrometer equipped with deuterium lamp background corrector was used for the analysis under the conditions suggested by the manufacturer. The instrumental parameters were as follows: wavelength, 217.0 and 232.0 nm; bandpass, 1.0 and 0.2 nm; lamp current, 5 and 4 mA; fuel flow rate, 2 and 2 L min⁻¹, for lead and nickel, respectively. All pH measurements were performed with a CRISON 20 model digital pH meter.

2.2. Reagents

Doubly distilled deionized water and analytical reagent grade chemicals were used unless otherwise specified. The laboratory glassware was kept overnight in a 5% nitric acid. After that it was rinsed thoroughly with water and dried. Lead and nickel stock solutions (1000 mg L⁻¹) were prepared by dissolving the appropriate amounts of Pb(NO₃)₂ (Merck) and Ni(NO₃)₂·6H₂O (Merck), respectively. Working solutions of the metal ions were prepared by suitable dilution of the stock solutions. 0.01 mol L⁻¹ ethylenediaminetetraacetic acid disodium salt dihydrid (EDTA) (C₁₀H₁₄N₂Na₂O₈·2H₂O) solution was prepared by dissolving 0.9306 g of EDTA in 250 mL of water. One mole per liter HNO₃, 2 mol L⁻¹ HNO₃, 1 mol L⁻¹ HCl and 2 mol L⁻¹ HCl solutions were prepared by dilution from concentrate solutions. Ambersorb-572 (Aldrich Chem., 1100 m² g⁻¹) was used after washing in methanol, 1 mol L⁻¹ HCl, 1 mol L⁻¹ HNO₃ and water, respectively. After that, it was dried about 4 h at 60 °C in an oven.

2.3. Column preparation

A glass column (150 mm length and 8 mm i.d.) with a glass-wool over its stopcock was used as a mini column. A total of 300 mg of Ambersorb-572 resin was slurried in water and then placed into the column. A small amount of glass-wool was placed on top to avoid disturbance the adsorbent during sample passage. The column was preconditioned by passing a blank solution having same pH with the sample solution prior to use. After each use, the resin in the column was washed with dilute HCl and with water, respectively, and stored in water for the next experiment.

2.4. General procedure for the sorption of lead and nickel on the column

The performance of the column preconcentration method was investigated with the synthetic sample solution before its

application to the real samples. A total of 100 mL synthetic sample solution containing 30 μg of Pb and 30 μg of Ni was taken and 1 mL of 0.01 mol L⁻¹ EDTA was added. The pH of the solution was adjusted to the optimum value determined experimentally (pH 2) with hydrochloric acid. The resulting solution was passed through the preconditioned column by a flow rate adjusted to the optimum value determined experimentally (ca. 3 mL min⁻¹). The retained metal ions were then eluted from the solid phase with 10 mL of 1 mol L⁻¹ HNO₃ solution. This solution was aspirated into an air–acetylene flame for the determination of Pb and Ni by FAAS. The Ambersorb-572 was used repeatedly (up to 50) after washing with 1 mol L⁻¹ solution and distilled water, respectively.

2.5. Preparation of samples

In order to check the accuracy of the proposed method certified reference material, tea leaves (GBW-07605), was used. As real samples, water (sea water and waste water) and vegetable (parsley and green onion) samples have been collected. Certified reference material and samples have been prepared as follows.

2.5.1. Dissolution of tea leaves

A portion (0.4 g) of standard reference tea leaves (GBW-07605) was taken in a 250 mL PTFE beaker. The sample was dissolved according to the method described in the previous study [25]. For dissolution, a minimal volume of 0.05 mol L⁻¹ nitric acid was added to moisten the sample thoroughly, followed by 10 mL of concentrated nitric acid. The beaker was heated on a hot plate at about 130 \pm 10 °C for 3 h. After cooling to room temperature, 3 mL hydrogen peroxide was added drop wise. The beaker was heated until complete decomposition of the sample. The resulting solution was transferred into 100 mL volumetric flask by washing the interior of the beaker with small portions of 0.05 mol L⁻¹ nitric acid, and the solution was diluted to the mark with 0.05 mol L⁻¹ nitric acid.

2.5.2. Dissolution of vegetable (parsley and green onion) samples

Parsley and green onion samples were collected in garden from Şanlıurfa. Firstly, the samples were cleaned with tap water and double distilled water, respectively. Then, the samples were dried at 110 °C. Vegetable samples (0.4 g) were dissolved according to the procedure given above for tea leaves.

2.5.3. Preparation of water (sea water and sewage water) samples

The surface sea water samples were taken from Mediterranean Sea, İskenderun, Turkey. Waste water samples were collected from the sewage in Şanlıurfa, Turkey. The water samples were filter first through the ordinary filter paper in order to separate coarse particles and suspended matter. Then, they were immediately filtered through a Millipore cellulose nitrate membrane (pore size 0.45 μm), acidified to pH 2 with HNO₃ and stored in polyethylene bottles previously cleaned with detergent, tap water, double distilled water, and dilute nitric acid, respectively, for further use.

3. Results and discussion

3.1. Optimization of the column conditions

The optimum sorption and desorption properties of Ambersorb-572 resin for Pb and Ni were found by using the column technique. Because quantitative recovery was not obtained for the analytes without using a chelating agent in our preliminary experiments (<50%), EDTA was used as chelating agent by taking into the results obtained by Ref. [22] for subsequent experiments. First, the effect of sample pH, amount of adsorbent, type and volume of elution solution, flow rate of sample solution, and volume of sample solution on the recovery of the analytes have been investigated.

3.1.1. Effect of pH

The effect of sample pH on the recovery of the analytes has been investigated. For that purpose, the pH values of synthetic sample solutions (Section 2.4) were adjusted to a range of 2–10 with HCl or NH₃. As can be seen from Fig. 1, quantitative recovery (>95%) was found in the pH range of 2–6 for both analytes. Since a wide range of pH is suitable for the preconcentration of the analytes, the use of buffer solutions were avoided. This minimizes a possible reduction in analytical sensitivity and interferences due to the buffer species.

3.1.2. Effect of the amount of adsorbent

The effect of amount of adsorbent on the recovery of the analytes was investigated in the range of 50–500 mg by using synthetic sample solution (Section 2.4). It was found that above 50 mg of adsorbent the recovery of analytes was gradually increased, but about 300 mg of adsorbent reached a plateau. Therefore, 300 mg of adsorbent was found to be optimum of all preconcentration purposes.

3.1.3. Effect of the type and volume of elution solutions

The effect of the kind and concentration of the eluent for elution of the analytes from Ambersorb-572 column was studied.

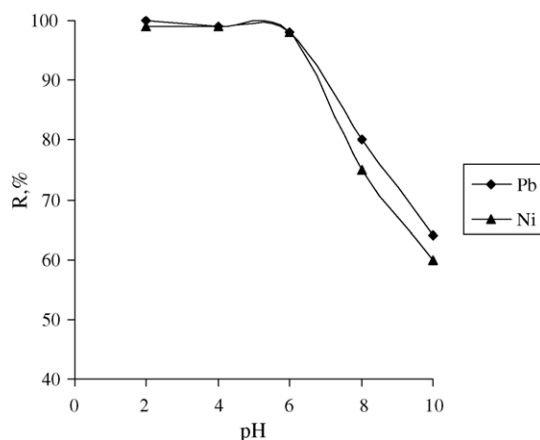


Fig. 1. The effect of pH on the recovery of Pb and Ni (amount of adsorbent: 300 mg, volume of sample solution: 100 mL, amount of Ni and Pb: 30 μg , chelating agent: 1 mL of 0.01 mol L⁻¹ EDTA, eluent: 10 mL of 1 mol L⁻¹ HNO₃, flow rate: 3 mL min⁻¹).

Table 1
The effect of the type and volume of elution solutions on the recovery of analytes

Element	Type of elution solution	Volume (mL)	Concentration (mol L ⁻¹)	Recovery ^a (%)
Pb	HCl	5	1	76
		10	1	88
	HNO ₃	5	1	82
		10	1	99
Ni	HCl	5	1	73
		10	1	87
	HNO ₃	5	1	78
		10	1	97

^a Mean of three determinations.

Lead and nickel retained on the adsorbent were eluted using various acid solutions. For this purpose, 5 and 10 mL of HCl and HNO₃ were examined as eluents. As can be seen from Table 1, 10 mL of 1 mol L⁻¹ HNO₃ was found to be satisfactory for Pb and Ni (recovery > 95%).

3.1.4. Effect of flow rate of sample solutions

The retention of analytes on an adsorbent depends upon the flow rate of sample solution was examined under optimum conditions (pH, eluent type, etc.) by using synthetic sample solution (Section 2.4). The solution was passed through the column with the flow rates adjusted in a range of 1–6 mL min⁻¹. The optimum flow rate was found as 3 mL min⁻¹ for Pb and 4 mL min⁻¹ for Ni. The flow rate of elution solution used was 3 mL min⁻¹.

3.1.5. Effect of the volume of sample solutions

In order to obtain higher preconcentration factor, the ratio of sample to eluent volumes should be increased by lowering the eluent volume and/or increasing the sample volume. Therefore, the maximum applicable sample solution was investigated by using increasing volume of metal ion solution and keeping the total amount of metal ions constant at 30 µg. Fifty, 100, 250, 500, 750 and 1000 mL of sample solutions containing 0.1, 0.30, 0.12, 0.06, 0.04 and 0.03 µg mL⁻¹ of both ions, respectively, were passed through the column. It was found that the dilution effect was not significant for the sample volumes up to 750 mL for Pb and 500 mL for Ni (Fig. 2). At higher sample volumes, the recoveries decreased gradually with increasing volume of sample solution. Because of the elution volume was 10 mL, a preconcentration factor was obtained 75 for Pb and 50 for Ni by assuming 100% recovery.

3.1.6. Effect of interfering ions

In order to investigate the effect of the interfering ions, alkaline and alkaline earth elements were added to the synthetic sample containing analytes. The interfering elements were added to the solution as their nitrate or chloride salts. The concentration of Pb and Ni is fixed at 0.3 µg mL⁻¹ and the concentration of interfering metal ions were adjusted in a range of 0.5–15,000 µg mL⁻¹. The results were given in Table 2. As can be seen in the table, no effect on the recovery of the investigated metal ions was found from Na⁺ (10,000 µg mL⁻¹), K⁺ and Mg²⁺ (500 µg mL⁻¹), Ca²⁺ (100 µg mL⁻¹) and Al³⁺, Zn²⁺, Co²⁺, Mn²⁺ and Cd²⁺ (50 µg mL⁻¹).

Table 2

The effect of some ions on the recovery of Pb and Ni (pH 2; eluent, 10 mL of 1 mol L⁻¹ HNO₃; flow rate of sample, 3 mL min⁻¹; sample volume, 100 mL; amount of Pb and Ni, 30 µg)

Interfering ions	Concentration (mg L ⁻¹)	R (%) ^a		Interfering ions	Concentration (mg L ⁻¹)	R (%) ^a	
		Pb	Ni			Pb	Ni
Na ⁺	–	99	97	K ⁺	–	99	97
	10	99	97		5	99	97
	100	99	97		10	99	97
	1000	98	96		50	98	96
	10000	97	96		500	98	96
Mg ²⁺	–	99	97	Ca ²⁺	–	99	97
	10	99	97		10	99	97
	100	98	97		50	98	96
	500	97	96		100	97	96
Al ³⁺	–	99	97	Fe ³⁺	–	99	98
	5	99	97		5	99	99
	10	99	96		10	97	98
	50	98	96		50	96	97
Zn ²⁺	–	99	97	Co ²⁺	–	99	97
	5	98	97		5	99	97
	10	97	96		10	98	96
	50	97	96		50	98	95
Mn ²⁺	–	99	97	Cd ²⁺	–	99	97
	5	98	97		5	99	97
	10	98	97		10	98	96
	50	97	96		50	97	96

^a Mean of three determinations.

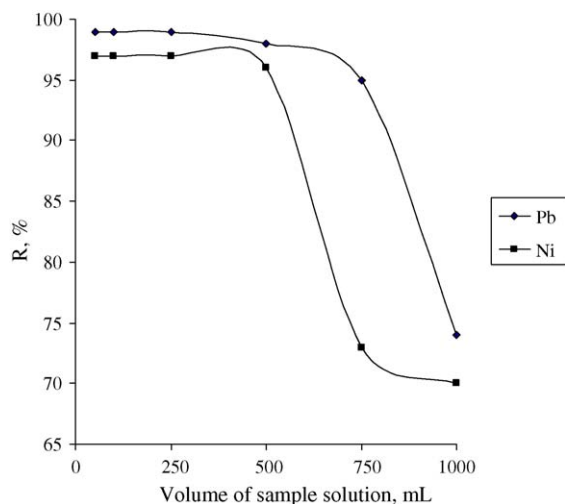


Fig. 2. Effect of sample volume on the recovery.

3.2. Sorption capacity of the resin

The maximum amount of the elements retained on the column was determined by passing growing concentration of the analytes through the column. The capacity study used was adapted from that recommended by Maqueira et al. [26]. Twenty-five milliliters of solution containing lead and nickel at concentrations in the range of 5–80 mg L⁻¹ was treated by using general column preconcentration procedure under optimum conditions determined before. But, 25 mL of elution solution was used in these capacity studies. The amount of lead and nickel adsorbed at each concentration level was determined from the following equation:

$$C = \frac{cV}{m}$$

where C is the amount of adsorbed lead and nickel, in micrograms per gram of sorbent, c the concentration of analyte eluted, in micrograms per milliliter of eluent, V the volume of solution, in milliliters, and m is the mass of sorbent, in grams. The breakthrough curve was obtained by plotting the lead and nickel concentration ($\mu\text{g mL}^{-1}$) in solution versus the amount of lead and nickel adsorbed per gram of sorbent ($\mu\text{g g}^{-1}$). The breakthrough capacity of lead and nickel evaluated from the breakthrough plot was 0.17 and 0.21 mmol g⁻¹, respectively.

3.3. Analytical parameters

The analytical performances of the proposed method were evaluated under the optimum conditions mentioned above (pH 2, chelating agent: 1 mL of 0.01 mol L⁻¹ EDTA, elution solution: 10 mL of 1 mol L⁻¹ HNO₃, flow rate of sample: 3 mL min⁻¹, volume of sample: 100 mL). For determining the precision of the method, the general procedure was performed successively by using synthetic sample solution (Section 2.4) and lead and nickel were determined in the elution solution by FAAS. The mean recovery for five determinations at the 95% confidence level was 99 ± 2 and 97 ± 3%, respectively. As can be seen from Table 3, the recoveries of the analytes are about 97–99% and the

Table 3

Precision of the method^a (pH 2; eluent, 10 mL of 1 mol L⁻¹ HNO₃; flow rate of sample, 3 mL min⁻¹; sample volume, 100 mL; amount of Pb and Ni, 30 μg)

Element	$R \pm ts/\sqrt{N}$ (%)	R.S.D. (%)
Pb	99 ± 2	2
Ni	97 ± 3	2

^a Mean of five determinations at 95% confidence level.

precision of the method is satisfactory. The relative standard deviation of recovery was about 2% ($N=5$).

The limit of detection (LOD) was also studied. Fifty milliliters of blank solution (absorbance below 0.001) was passed through the column under the optimum conditions determined and retained lead and nickel was eluted by again 50 mL of 1 mol L⁻¹ HNO₃. This solution was used for the determination of LOD. The instrumental detection limit based on three times the standard deviation of the blank signal ($\text{LOD}_i = 3\sigma/m$, $N=20$, where m is the slope of calibration curve and N is the number of replicates) was 274 $\mu\text{g L}^{-1}$ for lead and 71 $\mu\text{g L}^{-1}$ for nickel. The analytical detection limits were calculated by dividing the instrumental detection limits by the enrichment factor (in this study 75 for Pb and 50 for Ni) [27]. It may be concluded that by applying an enrichment factor of 75 and 50, the analytical detection limits were 3.65 and 1.42 $\mu\text{g L}^{-1}$ for lead and for nickel can be obtained.

3.4. Validation of the method

Certified reference material (tea leaves GBW-07605) were used for the validation of the proposed method. The results were compared with the certified values using t -test at 95% confidence level (Table 4). Good agreement was obtained between the estimated content found by the proposed method and the certified values for Pb and Ni. The difference between the certified values and found values are less than the uncertainty resulted in random errors at 95% confidence level. The results also indicate that the developed preconcentration method for Pb and Ni is not affected by potential interferences from the major matrix elements of the analyzed plant and alloy samples.

3.5. Application

The proposed method was applied to the analysis of water samples collected from Mediterranean Sea, İskenderun, Turkey, waste water samples collected from the sewage in Şanlıurfa, Turkey, and vegetable samples collected from Şanlıurfa, Turkey. The concentration of the analytes in the samples was below the

Table 4

Determination of lead and nickel in tea leaves (GBW 07605)

Sample	Element	Concentration ($\mu\text{g g}^{-1}$)		Relative error (%)
		Certified	Found ^a , $\bar{x} \pm ts/\sqrt{N}$	
GBW 07605	Pb	4.4 ± 0.2	4.2 ± 0.2	-6
	Ni	4.6 ± 0.3	4.4 ± 0.4	-2

^a Mean of five determinations at 95% confidence level.

Table 5
Determination of Pb and Ni in parsley and green onion

Sample	Element	Added ($\mu\text{g g}^{-1}$)	Found ^a ($\mu\text{g g}^{-1}$), $\bar{x} \pm ts/\sqrt{N}$	Relative error (%)
Parsley	Pb	–	41 \pm 1	–
		50	89 \pm 2	–3
	Ni	–	11.0 \pm 0.5	–
		10	20 \pm 1	–5
Green onion	Pb	–	13.1 \pm 0.7	–
		10	22 \pm 2	–5
	Ni	–	5.2 \pm 0.3	–
		10	14.6 \pm 0.9	–4

^a Mean of five determinations at 95% confidence level.

Table 6
Determination of Pb and Ni in waste water and sea water

Sample	Element	Added ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$), $\bar{x} \pm ts/\sqrt{N}$	Relative error (%)
Waste water	Pb	–	26 \pm 1	–
		20	44 \pm 2	–4
	Ni	–	14 \pm 1	–
		20	33 \pm 2	–3
Sea water	Pb	–	8.6 \pm 0.2	–
		20	27.2 \pm 0.5	–5
	Ni	–	4.4 \pm 0.3	–
		20	23.8 \pm 0.7	–3

^a Mean of five determinations at 95% confidence level.

detection limit of the method, as there was no spiking in the samples, the metallic ions could not be detected. In order to evaluate the accuracy of the procedure, recovery experiments were also carried out with spiked water samples because of certified reference materials for the analytes in such samples are not available. A 250 mL of sample was adjusted to the optimum pH and subjected to the recommended column procedure for the preconcentration and determination of analytes. The results are shown in Tables 5 and 6. The analytes could be determined with high accuracy (relative error < 5%) and precision. Thus, the present method is suitable for the preconcentration and determination of Pb and Ni in water samples and vegetable samples.

4. Conclusion

A simple, rapid, precise and accurate method was developed for the preconcentration and determination of Pb and Ni in various samples. Pb and Ni were quantitatively recovered from the column packed with Amborsorb-572 with their EDTA complexes with a high precision (R.S.D. < 2%). This method is very economical, only 300 mg of adsorbent is needed and repeated use is possible. Lead and nickel can be recovered successfully by using the proposed procedure in the presence of high concentrations of foreign cations such as Na^+ , K^+ , Mg^{2+} and Ca^{2+} from a strongly acidic medium. Moreover, as lead and nickel can be preconcentrated quantitatively over a wide

pH range (2–6), no buffer is required to control the pH values precisely, which minimizes contamination. The preconcentration technique used in this work is not only convenient, but also simple and the duration of preconcentration step is about 40 min including regeneration of sorbent for 100 mL of sample solution.

This method could be combined with other methods of analysis, such as ICP-AES, ICP-MS and electroanalytical methods, and used as an on-line preconcentration system.

References

- [1] E. Merian, M. Anke, M. Ihnat, M. Stoeppler, Elements and Their Compounds in the Environment, vol. 2, second ed., Wiley/VCH, Weinheim, 2004.
- [2] H.G. Seiler, H. Sigel, A. Sigel, Handbook on Toxicity of Inorganic Compounds, Marcel Dekker, New York, 1988.
- [3] K. Wang, Nickel Trace Elements in Life Science, Chinese Measurement Press, Peking, China, 1991.
- [4] B. Zerner, Recent advances in the chemistry of an old enzyme, urease, Bioorg. Chem. 19 (1991) 116–131.
- [5] R.K. Thauer, Nickel to the fore, Science 293 (2001) 1264–1265.
- [6] D. Templeton, Biological Monitoring of Chemical Exposure in the Workplace, World Health Organization, Geneva, 1990.
- [7] J. Kristiansen, J.M. Christensen, T. Henriksen, N.H. Nielsen, T. Menne, Determination of nickel in fingernails and forearm skin (stratum corneum), Anal. Chim. Acta 403 (2000) 265–272.
- [8] M.G. Pereira, M.A.Z. Arruda, Preconcentration of Cd(II) and Pb(II) using humic substances and flow systems coupled to flame atomic absorption spectrometry, Microchim. Acta 146 (2004) 215–222.
- [9] A. Mizuike, Enrichment Techniques for Inorganic Trace Analysis, Springer-Verlag, Berlin, 1983.
- [10] M. Soyak, S. Saracoglu, U. Divrikli, L. Elci, Coprecipitation of heavy metals with erbium hydroxide for their flame atomic absorption spectrometric determinations in environmental samples, Talanta 66 (2005) 1098–1102.
- [11] Y. Okamoto, Y. Nomura, H. Nakamura, K. Iwamaru, T. Fujiwara, T. Kamamaru, High preconcentration of ultra-trace metal ions by liquid–liquid extraction using water/oil/water emulsions as liquid surfactant membranes, Microchem. J. 65 (2000) 341–346.
- [12] V.O. Doroshuk, S.O. Lelyushok, V.B. Ishchenko, S.A. Kulichenko, Flame atomic absorption determination of manganese(II) in natural water after cloud point extraction, Talanta 64 (2004) 853–856.
- [13] F. Gode, E. Pehlivan, Removal of Cr(VI) from aqueous solution by two Lewatit-anion exchange resins, J. Hazard. Mater. 119 (2005) 175–182.
- [14] D. Zendelovska, G. Pavlovska, K. Cundeva, T. Stafilov, Electrothermal atomic absorption spectrometric determination of cobalt, copper, lead and nickel traces in aragonite following flotation and extraction separation, Talanta 54 (2001) 139–146.
- [15] Y. Guo, B. Din, Y.W. Liu, X.J. Chang, S.M. Meng, M.Z. Tian, Preconcentration of trace metals with 2-(methylthio)aniline-functionalized XAD-2 and their determination by flame atomic absorption spectrometry, Anal. Chim. Acta 504 (2004) 319–324.
- [16] Ş. Tokalhoğlu, T. Oymak, Ş. Kartal, Determination of palladium in various samples by atomic absorption spectrometry after preconcentration with dimethylglyoxime on silica gel, Anal. Chim. Acta 511 (2004) 255–260.
- [17] A.M. Starvin, T.P. Rao, Removal and recovery of mercury(II) from hazardous wastes using 1-(2-thiazolylazo)-2-naphthol functionalized activated carbon as solid phase extractant, J. Hazard. Mater. 113 (2004) 77–81.
- [18] A.R. Türker, S. Baytak, The use of *Escherichia coli* immobilised on Amberlite XAD-4 as solid phase extractor for metal preconcentration and determination by atomic absorption spectrometry, Anal. Sci. 20 (2004) 329–334.

- [19] S. Baytak, A.R. Türker, The use of *Agrobacterium tumefaciens* immobilized on Amberlite XAD-4 as a new biosorbent for the column preconcentration of iron(III), cobalt(II) manganese(II) and chromium(III), *Talanta* 65 (2005) 938–945.
- [20] Y.W. Liu, X.J. Chang, S. Wang, et al., Solid-phase spectrophotometric determination of nickel in water and vegetable samples at sub- μ g l⁽⁻¹⁾ level with o-carboxylphenyldiazoaminoazobenzene loaded XAD-4, *Talanta* 64 (2004) 160–166.
- [21] M. Tüzen, K. Parlar, M. Soylok, Enrichment/separation of cadmium(II) and lead(II) in environmental samples by solid-phase extraction, *J. Hazard. Mater.* 121 (2005) 79–87.
- [22] E. Kendüzler, A.R. Türker, Determination of iron, manganese and zinc in water samples by flame atomic absorption spectrophotometry after preconcentration with solid-phase extraction onto Ambersorb 572, *Anal. Sci.* 18 (2002) 917–921.
- [23] E. Kendüzler, A.R. Türker, Atomic absorption spectrophotometric determination of copper in waters, aluminium foil and tea samples after preconcentration with 1-nitroso-2-naphthol-3,6-disulfonic acid on Ambersorb 572, *Anal. Chim. Acta* 480 (2003) 259–266.
- [24] E. Kendüzler, A.R. Türker, Determination of trace cadmium in waters by flame atomic absorption spectrophotometry after preconcentration with 1-nitroso-2-naphthol-3,6-disulfonic acid on Ambersorb 572, *Ann. Chim.* 95 (2005) 77–81.
- [25] O. Acar, Determination of cadmium and lead in biological samples by Zeeman ETAAS using various chemical modifiers, *Talanta* 55 (2001) 613–622.
- [26] A. Maquieira, H.A.M. Elmahadi, R. Purchades, Immobilized cyanobacteria for online trace-metal enrichment by flow-injection atomic-absorption spectrometry, *Anal. Chem.* 66 (1994) 3632–3638.
- [27] M.A.A. Akl, I.M.M. Kenawy, R.R. Lasheen, Organically modified silica gel and flame atomic absorption spectrometry: employment for separation and preconcentration of nine trace heavy metals for their determination in natural aqueous systems, *Microchem. J.* 78 (2004) 143–156.