Enrichment and determination of Ni^{2+} ions in water samples with a diamino-4-(4-nitro-phenylazo)-1H-pyrazole (PDANP) by using FAAS

H. Ciftci [a,*], H. Yalcin [b], E. Eren [c], A. Olcucu [b], M. Sekerci [b]

[a] Ahi Evran University, Faculty of Science and Art, Department of Chemistry, Kirsehir, Turkey
[b] Firat University, Faculty of Science and Art, Department of Chemistry, Elazig, Turkey
[c] Bilecik University, Faculty of Science and Art, Department of Chemistry, Bilecik, Turkey

ARTICLE INFO

ABSTRACT

Nickel, as a heavy metal, is toxic for many living species. Thus, the determination of trace amounts of nickel in environmental samples is of great importance. In the present study, new, sensitive, simple and validated solid phase extraction method is developed for the determination of nickel. In recent study nickel was preconcentrated as diamino-4-(4-nitro-phenylazo)- 1H-pyrazole (PDANP) chelates (Ni-PDANP) from sample solutions using a column containing Amberlite XAD-7 and determined by flame atomic absorption spectrometry (FAAS). The optimum experimental parameters such as pH of the medium, sample flow rate, eluent and effect of matrix ions on the method efficiency were investigated. The optimum pH value for quantitative sorption of Ni–PDANP was found between 6.0 and 8.0. Elution process was performed by using 6 mL of 2 mol L^{-1} HCl. The sorption capacity of resin was determined to be 7.2 mg g^{-1} for Ni. The preconcentration factor was 125. In optimized conditions. A relative standard deviation and detection limit were found to be 2.8% and 0.44 µg L^{-1} respectively. The method was successfully applied to determine the trace amounts of nickel in tap water and mineral waters, and suitable recoveries were obtained (100.0–103.5%).

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Nickel is a toxic trace element of widespread distribution in the environment. It, usually, enters waters from waste disposals of different industrial processes such as electroplating, batteries, pigments for paints and ceramics, surgical and dental prostheses, magnetic tapes and computer components, catalysts and also it is emitted to the atmosphere from volcanoes and windblown dusts [1,2]. Long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. High levels of Ni in the diet may be associated with an increased risk of thyroid problems, cancer, and heart disease [3]. Epidemiological studies showed that the majority of the factors leading to the development of tumor in humans have arisen from environmental factors and 65–70% of all cancers in humans are associated with the environment, including the work environment, 30–40% with nutritional habits and only 2% with consequences of genetic predispositions [4,5]. Therefore, the development of novel and sensitive methods to determine the nickel content of environmental, biological and food samples is necessary and important [6].

The determination of nickel in environment and biological samples has been carried out by various instrumental techniques such as neutron activation analysis (NAA) [7], inductively coupled plasma optic emission spectrometry (ICP-OES) [8,9] inductively coupled plasma mass spectrometry (ICP-MS) [10], X-ray fluorescence spectroscopy [11] and chromatography [12,13]. Despite the sensitivity and selectivity of analytical techniques such as flame atomic absorption spectrometry (FAAS), there is a great necessity for preconcentration of metal prior to its determination, basically due to its low concentration or the effects of matrix in aqueous samples [14]. There are many methods to preconcentrate such as, coprecipitation, solvent extraction, electrochemical deposition, membrane extraction, and solid phase extraction [15]. Solid phase extraction (SPE) has become a preferred method at enrichment of many metal ions prior to their analysis by FAAS and other techniques. SPE is an attractive method that reduces consumption and exposure to solvent, disposal costs and extraction time [16,17].

In the present work, a novel method was developed for the determination of trace amount of nickel by using FAAS in different water samples. Ni–PDANP chelates can be adsorbed on resin in column and optimum experimental conditions on nickel recovery were investigated. Analytical parameters such as precision and accuracy of the method have also been determined. The developed method has been successfully used to determine the nickel in various samples.

* Corresponding author. Tel.: +90 386 211 4552; fax: +90 386 211 4525.
E-mail address: harunciftci@yahoo.com (H. Ciftci).

2. Experimental

2.1. Apparatus

A Perkin Elmer Analyst model 700 (Shelton, CT, USA) Flame Atomic Absorption Spectrometer (FAAS) with a hallow cathode lamp and a deuterium background corrector, at respective resonance line using an air–acetylene flame was used. The instrumental parameters for nickel determination were found as follows: wavelength 232.0 nm, lamp current 7.5 mA, bandpass 0.2 nm. Schott Lab-Star pH meter was used to measure the pH of solutions.

2.2. Reagents and solutions

All reagents used were of analytical grade and all solutions were prepared by using triple distilled and deionized water. Amberlite XAD-7 (surface area 450 $m^2 g^{-1}$ and bead size 20–40 mesh) was obtained from Aldrich (Milwaukee, USA). Standard PDANP solution of 0.04% (w/v) was prepared by dissolving 0.02 g of PDANP (99.9% purity) in 50 mL mixture of methanol–water (40:60% v/v). Metal solutions were prepared as atomic absorption standard solutions (1000 ± 2 mg L^{-1}). Nitric acid (65%w), hydrochloric acid (37%w), methanol, ethanol, acetonitrile (ACN) and other chemical reagents were purchased from Merck (Darmstadt, Germany). All chemicals were used without further purification. The glassware used was washed with potassium dichromate — sulfuric acid, NaOH, ethanol and finally soaked in dilute nitric acid overnight and thoroughly washed with distilled water. Amberlite XAD-7 was removed prior to its use by washing it thoroughly with 1 mol L^{-1} NaOH and 4 mol L^{-1} HCl respectively. Afterwards, it was washed with doubly distilled water and finally with a small amount of methanol.

Adsorption column were prepared according to literature [18]. The glass column was 12 cm length and 0.8 cm internal diameter. A small amount of glass wool was placed at the bottom of the column in order to hold the resin. 0.6 g dried resin was placed and another small glass wool plug was inserted onto the tap of the resin. The bed height of the resin in the column was approximately 2.0 cm. It was washed successively with water, methanol, 2 mol L^{-1} HCl and HNO₃ solutions, respectively.

2.3. Synthesis of diamino-4-(4-nitro-phenylazo)-1H-pyrazole

1,4-Diamino-benzene (0.56 g, 5.22 mmol) was dissolved in 100 mL methanol in a 250 mL round bottom flask. A solution of 1.12 g (10.44 mmol) of pyridine-2-carbaldehyde (1 mL) in 10 mL methanol was added drop-wise over a 20 min period with continuous stirring for 3 h at room temperature. Half of the methanol was removed by evaporation and the mixture was cooled in a salt ice-bath, the precipitate was filtered, washed with methanol and dried at room temperature. This reaction yield was obtained as 52% [19]. The reaction scheme of the synthesis is shown in Scheme 1.
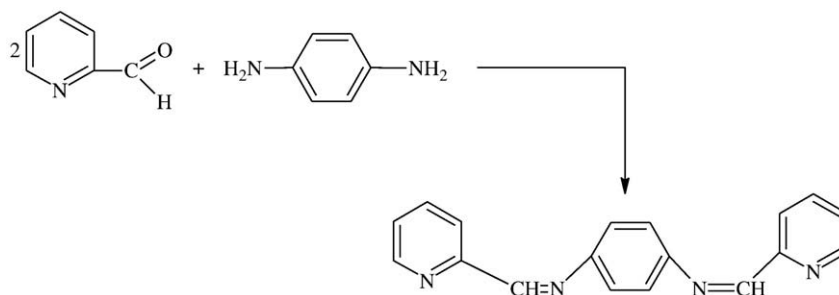
2.4. Preconcentration procedure

The method was tested by using standard test solutions before its application to the natural water samples. The standard test solutions were prepared as follows: 5 mL of 1.0 mg L^{-1} of Ni (II) standard solution added to 2.5 mL of standard PDANP solution and mixed with 2 mL buffer solutions in a volumetric flask. The pH was adjusted by adding 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH to the medium [20]. Acetate buffer (0.1 mol L^{-1}) was used in the pH range 3.0–6.0, phosphate buffer (0.1 mol L^{-1}) for the pH 6.8–9.0 and ammonium buffer (0.1 mol L^{-1}) was used in the pH range 9.0–10.0. Afterwards, final volume of sample was diluted to 50 mL with distilled water. Before use, the column was preconditioned with the buffer solution for each working pH. To formation of complexes, the standard test solutions in all of experiments were kept at 30 min. Then, this solution was permitted to flow through the column under gravity at flow rate of 2.5 mL min⁻¹. The adsorbed nickel ions on the column were eluted with 6 mL of 2 mol L^{-1} HCl solution that has a flow rate of 4 mL min⁻¹. Nickel was analyzed with method of direct calibration curve by FAAS. Device setting is controlled every five readings. A blank solution was also run under the same conditions without adding any nickel. In this study each measurement was repeated three times by FAAS.

2.5. Analysis of water samples

A tap water sample was collected from Elazig city line, a commercial natural drinking water and mineral water collected from local market in Elazig, Turkey. These samples were analyzed to its Ni content. The water samples were filtered through Whatman filter paper (No. 40). Then 2.5 mL of standard PDANP solution and 2 mL of phosphate buffer solutions were added. The pH of the solution was adjusted to 7.0 by using 0.1 mol L^{-1} HCl or NaOH solution and passed through the Amberlite XAD-7 column. After elution process, analyses of samples were performed according to recommended preconcentration procedure.

3. Results and discussion

In order to obtain quantitative recoveries of nickel on the XAD-7 polimer resin, in the separation/preconcentration procedure various analytical parameters, such as pH of sample solution, amount of resin, volume and type of elution solution, amount of ligand, flow rate of sample solution and volume of sample solution, were optimized. The possible interfering effects of other ions were also investigated. The recovery of analyte ion separated and preconcentrated on the column was calculated from the amounts of metal ion in the starting sample and the amount of metal ion in the eluent.

3.1. Effect of pH of the aqueous solution on the retention of Ni(II)

To determine the optimum pH range for sorption of nickel ions, seven standard sample solutions having pH in the range of 3.0–10.0 were passed through columns. The nickel ions was stripped by 6 mL of

Scheme 1. Synthesis of diamino-4-(4-nitro-phenylazo)-1H-pyrazole.

2 mol L^{-1} HCl solutions from column and determined by FAAS as described in the recommended procedure. The effects of the pH value on the recovery values were summarized in Fig. 1. As shown in the figure, at pH values lower than 6 and higher that 8, recovery values were found to be insufficient for analytical applications. This behavior of pH to recovery of nickel ions may be explained as follows: in alkaline medium, especially at pH values higher than 8 it is possible to be precipitated for nickel ions as related hydroxides. In solutions having a pH value lower than 6 a relatively high concentration of H$^+$ affects the active adsorption surface and hinders the adsorption of metal ions to surface and then lowers the recovery values of the proposed method [21]. Therefore, pH 7.0 was chosen as an optimum pH in phosphate buffer for analytical determination of nickel in further studies.

3.2. Influence of amount of diamino-4-(4-nitro-phenylazo)-1H-pyrazole

A series of studies were performed to test whether PDANP as a ligand has an effect on recovery values or not. Because, according to results of the studies carried out in PDANP-free medium, the recovery value was found to be about 22%. To this aim, different amounts of PDANP were added to the test solutions of which each contains 5.0 µg of Ni(II) and these test solutions were passed through the Amberlite XAD-7 column. The results were given in Fig. 2.

As seen from Fig. 2 recovery value of the proposed method increases with the amount of PDANP. Especially when the amount of PDANP is 0.5 mg or more, recovery values exceed 95%. Therefore, in further studies, 2.5 mL of standard PDANP solution of 0.04%, (w/v) was used.

This effect of PDANP on recovery may be explained as: PDANP could stimulate the adsorption of Ni(II) from the aqueous solution. It may be due to their unique characteristics, such as surface charge and sorption energy of the solution or exchange heavy metal on the solid surface [22].

3.3. Effect of sample volume

One of the important parameters in this kind of studies is the selection of the sample volume. The influence of the sample volume on recovery values was examined on XAD-7 column at a 2.5 mL min^{-1} flow rate. For this purpose; 50, 100, 250, 500, 750 and 1000 mL of the sample solutions (corresponding nickel ion concentrations are: 0.05, 0.025, 0.01, 0.005, 0.0033 and 0.0025 µg/mL) of which each contains 2.5 µg of nickel that was passed through the column at the optimum conditions. The results were given in Fig. 3. As can be seen from Fig. 3 at sample volume lower than 750 mL, Ni (II) ions present in the adsorption medium could interact with the binding sites, and the higher the recovery of the proposed method. The samples have volumes higher than 750 mL, probably because of the saturation of the adsorption sites and exceed the column capacity
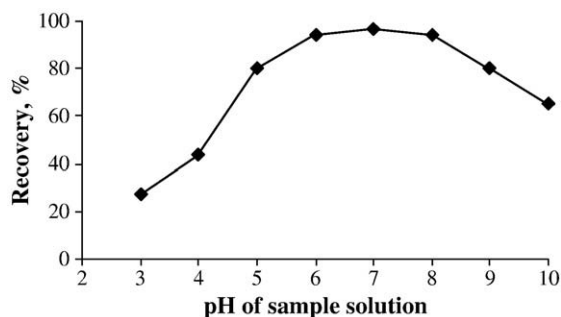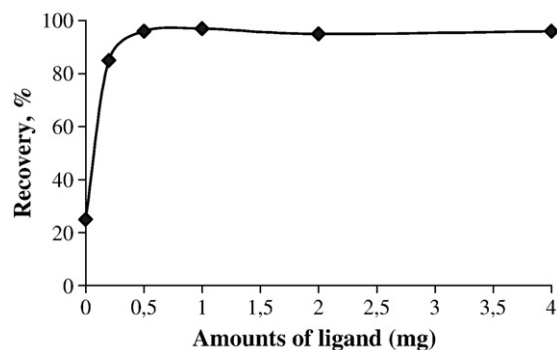

Fig. 2. The effect of PDANP amount on the recovery of nickel (sample volume: 50 mL, amount of nickel: 5 µg, eluent: 6 mL of 2 mol L^{-1} HCl solution, flow rate of sample: 2.5 mL min^{-1}, pH: 7.0, and sorbent: 600 mg, $N=3$).

recovery value that shows a trend of decreasing. Therefore, the optimum sample volume was obtained in the range of 50 mL and 750 mL for the quantitative determination of Ni (II) ion. Enrichment factor was found at 125 by analyzing 6 mL of the final solution after the preconcentration of 750 mL of the sample solution.

3.4. Effect of flow rate

After optimization of the sample volume, the influences of flow rate on the adsorption of nickel were investigated. The nickel was desorbed from the resin by using 6 mL of 2 mol L^{-1} HCl solutions. As shown in Fig. 4, when the flow rate was higher than 2.5 mL min^{-1}, the interaction time of Ni (II) ions to adsorbent was decreased and insufficient time of interaction decreases the amount of nickel ions in the eluent. Thus, it was found that the suitable flow rate of the solution was found to be in the range of 1–2.5 mL min^{-1} and the optimum flow rate of 2.5 mL min^{-1} was selected as the working solution flow rate to decrease analysis time.

3.5. Choice of eluent agents

In order to obtain maximum quantitative recoveries of nickel, various eluent and volume of reagent were studied. For this purpose ethanol, acetonitrile, HCl and HNO$_3$ solutions were used. The experimental results show that the maximum recovery for nickel was observed by using 6 mL of 2 mol L^{-1} HCl solutions. The effects of various eluents on the recoveries of nickel are summarized in Table 1.

3.6. Effect of resin amount

The influence of the amount of XAD-7 resin on recoveries for nickel was studied at different amounts of sorbent. To this aim, the XAD-7
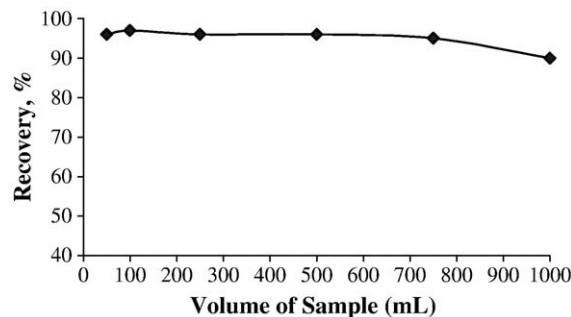

Fig. 1. The effect of pH on the recovery of nickel (sample volume: 50 mL, amount of nickel: 5 µg, eluent: 6 mL of 2 mol L^{-1} HCl solution, flow rate of sample: 2.5 mL min^{-1}, and sorbent: 600 mg, $N=3$).
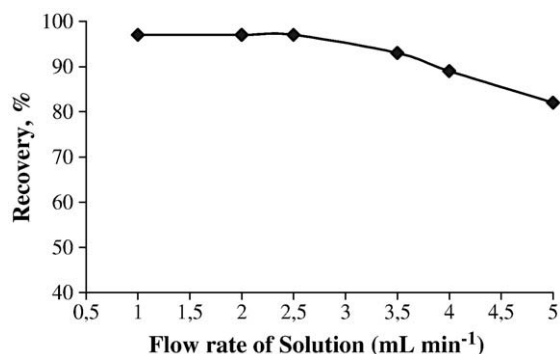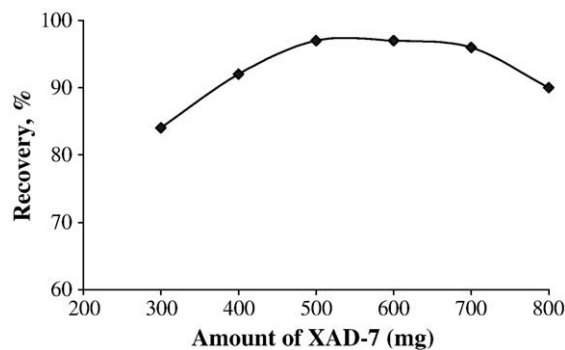

Fig. 3. The effect of sample volume on the recovery of nickel (amount of nickel: 2.5 µg, eluent: 6 mL of 2 mol L^{-1} HCl solution, flow rate of sample: 2.5 mL min^{-1}, pH: 7.0, and sorbent: 600 mg, $N=3$).

Fig. 4. The effect of solution flow rate on the recovery of nickel (sample volume: 50 mL, amount of nickel: 5 μg, eluent: 6 mL of 2 mol L^{-1} HCl solution, pH: 7.0, and sorbent: 600 mg, $N = 3$).

Fig. 5. The effect of XAD-7 amount on the recovery of nickel (sample volume: 50 mL, amount of nickel: 5 μg, eluent: 6 mL of 2 mol L^{-1} HCl solution, flow rate of sample: 2.5 mL min^{-1}, and pH: 7.0, $N = 3$).

resin was added in the range between 200 and 800 mg into the adsorption column. The test solution, that has volume of 50 mL and contains 5.0 μg of nickel, was passed through the column at optimum conditions. The results showed that the optimum amount of sorbent was found in the range from 500 to 800 mg for maximum extraction of Ni (II) (Fig. 5). To attain the expected increase in the recovery values with the amount of resin, the volume of the eluent should be increased in the same ratio at the same time.

In the current study the amount of resin upon the 800 mg, because of the eluent volume is held constant as 6 mL, and decrease in recovery values was obtained. From these results, optimum amount of resin was selected as 600 mg.

3.7. Influence of interfering species

The interference studies were performed using various possible interfering ions on the retentions of the investigated analyte. For this purpose, the influences of some cationic and anionic species were investigated. In these experiments, 50 mL of solutions of which each contains 5.0 μg of nickel and various amounts of possible interfering ions were treated according to the preconcentration procedure. The degree of interference effects were shown as the ratio of the recovery in the presence of interfering ions to that in their absence. The results were given in Table 2, and the recovery values showed that, in excess of 1000 mg L^{-1} of K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, Br$^-$, SO$_4^{2-}$ and 20 mg L^{-1} of Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+} ions have no significant interferences in the extraction and determination of nickel in sample solutions. The tolerance limit is defined as the ion concentration causing a relative error smaller than $\pm 5\%$ related to the preconcentration and determination of nickel.

3.8. Capacity of the resin

The capacity of Amberlite XAD-7 was determined for nickel ions by batch method. 1 g of the resin was equilibrated with nickel ion and 50 mL of PDANP solution containing 200 mg L^{-1} Ni ions and 10^{-3} mol L^{-1} PDANP for 3 h at optimum pH value. The nickel ions were stripped from the resin with 2 mol L^{-1} HCl solutions and determined to FAAS. It was investigated that the adsorption did not change significantly with contact time after 90 min. By using these parameters, the capacity of the XAD-7 resin has been calculated as 7.2 mg g^{-1} [23,24]. Different resins with sorption capacities and enrichment factors were given in Table 3.

3.9. Analytical performance

For the present study, the optimized experimental parameters and analytical performance of methods were given in Table 4. Under these experimental conditions the analytical features of the proposed method such as, linear range of calibration curve and limit of detection (LOD) were also examined. By using direct aspiration without the preconcentration step in FAAS applying the preconcentration system the linear range for nickel determination was between 0.2 and 3 mg L^{-1}. The calibration equation for nickel was found as $A = 0.0282\ C + 0.0064$ ($R^2 = 0.9976$). In this equation, A is absorbance corresponding to concentration C (mg L^{-1}) of Ni (II). The detection limit of this work was calculated after application of the preconcentration procedure to the 100 mL of blank solutions. The limit of detection (LOD) for nickel based on three times the standard deviations of the blank ($N = 10$) was calculated as 0.44 μg L^{-1}. The precision from seven repeated measurements of 50 mL of 5 μg L^{-1} of nickel solutions is excellent with RSD values of 2.8%. These values show that, the developed method is suitable for determination of nickel in different samples. The resin on the column can be used at least 250 times. The sufficiently good recoveries and low relative standard deviations reflect the high accuracy and precision of the proposed solid phase extraction.

Table 1
The effect of eluent types on the recovery of nickel (sample volume: 50 mL, amount of nickel: 5 μg, flow rate of sample: 2 mL min^{-1}, pH:7.0, and sorbent: 600 mg, $N = 3$).

Eluent	Recovery (%)[a]
2 mol L^{-1} HCl, 4 mL	92 ± 1
2 mol L^{-1} HCl, 6 mL	97 ± 2
2 mol L^{-1} HCl, 10 mL	96 ± 3
3 mol L^{-1} HCl, 6 mL	96 ± 2
2 mol L^{-1} HNO$_3$, 4 mL	88 ± 1
2 mol L^{-1} HNO$_3$, 6 mL	94 ± 2
2 mol L^{-1} HNO$_3$, 6 mL (in ethanol)	95 ± 2
2 mol L^{-1} HNO$_3$, 10 mL	95 ± 2
3 mol L^{-1} HNO$_3$, 6 mL	96 ± 2
6 mL ethanol	24 ± 2
6 mL acetonitrile	22 ± 1

[a] Mean ± standard deviation for three repeated measures.

Table 2
The effect of some ions on the recovery of nickel.

Ion	Concentration (mg L^{-1})	Recovery (%)[a]	Ion	Concentration (mg L^{-1})	Recovery (%)[a]
K$^+$	1000	98 ± 3	Co^{2+}	20	96 ± 2
Na$^+$	1000	100 ± 2	Zn^{2+}	20	100 ± 3
Ca^{2+}	1000	96 ± 2	Pb^{2+}	20	95 ± 2
Mg^{2+}	1000	94 ± 3	Al^{3+}	20	97 ± 2
Cl$^-$	1000	97 ± 2	Fe^{3+}	20	96 ± 2
SO$_4^{2-}$	1000	98 ± 2	Cr^{3+}	20	95 ± 2
Cu^{2+}	20	101 ± 2	Cd^{2+}	20	94 ± 2

[a] Mean ± standard deviation for three repeated measures.

Table 3
Comparison of adsorption capacities and enrichment factors for nickel.

Solid phase	Chelating agent	LOD ($\mu g\ L^{-1}$)	Adsorption capacity ($mg\ g^{-1}$)	Enrichment factor	References
Ambersorb 563	1-(2-pyridylazo) 2-naphtol	0.23	–	125	[25]
Cibacron Blue F3-GA	–	28.73	26.12	63	[26]
Immobilized poly(HEMA)					
(DVB)-ethylene glycol dimethacrylate	Quinoline-8-ol	2	–	200	[27]
Amberlite XAD-2	o-Amino phenol	7.5	3.24	65	[28]
Activated carbon	4,6-dihydroxy-2-mercaptopyrimidine	3.5	0.54	260	[29]
Amberlyst 36	–	0.86	143	100	[30]
XAD-7	PDANP	0.44	7.2	125	Present work

3.10. Determination of nickel in real samples

The validity of the proposed method was further proven by analyzing spiked nickel samples. For this aim, nickel solutions with the concentration between $2.0\ \mu g\ L^{-1}$ and $4.0\ \mu g\ L^{-1}$ were spiked to sample prepared by using 750 mL of water sample. After homogenizing the samples and applying the procedure, nickel was determined by direct calibration method. In calculations, analytical parameters derived from standard studies given in the proposed method were used. Table 5 shows the experimental results of spiked nickel samples. The relative standard deviations were less than 10%. Calculated recoveries for waters were found between 100.0 and 103.5%.

4. Conclusion

A novel solid phase extraction method involving PDANP was proposed for the determination of nickel content in different samples. The reagent PDANP is a good reagent for nickel ion enrichment and it is easy to be synthesized. The method has high tolerance limits for the matrix ions. The proposed method has distinct advantages such as simplicity, low cost, high precision and accuracy. The method developed has been successfully employed for the determination of the analytes in water samples.

Table 4
Analytical performance and optimum condition of the proposed method for determination of nickel.

pH	7
Amount of ligand (mg)	1
Amount of resin (mg)	600
Eluent volume (2 mol L^{-1} HCl) (mL)	6
Temperature	Ambient
Elue flow rate (mL min^{-1})	4
Sample flow rate (mL min^{-1})	2.5
Maximum sample volume (mL)	750
Enrichment factor	125
Linear range (mg L^{-1})	0.2–4.0
Regression equation (mg L^{-1})	$A = 0.0282\ C + 0.0064$
Correlation coefficient (R^2)	0.9976
Detection limit ($\mu g\ L^{-1}$)	0.44
Precision (R.S.D, $N = 7$) (%)	2.8

Table 5
The determination of nickel in different samples (initial volume for water samples: 750 mL).

Sample	Added	Found[a]	Recovery, %
Mineral water	–	$2.9 \pm 0.4\ \mu g\ L^{-1}$	–
	$2.0\ \mu g\ L^{-1}$	$4.9 \pm 0.5\ \mu g\ L^{-1}$	100
City line	–	$7.8 \pm 0.6\ \mu g\ L^{-1}$	–
	$4.0\ \mu g\ L^{-1}$	$12.2 \pm 0.8\ \mu g\ L^{-1}$	103.3
Commercial drink water	–	ND[b]	
	$4.0\ \mu g\ L^{-1}$	$4.1 \pm 0.4\ \mu g\ L^{-1}$	102.5

[a] Mean $\pm t \cdot$ SD/$\sqrt{N}$ with 95% confidence level ($N = 3$).
[b] ND: non determined.

References

[1] M. Stoeppler, Analysis of nickel in biological materials and natural waters, in: J.O. Nriagu (Ed.), John Wiley, New York, 1980, 29.
[2] E. Nieboer, D.M. Templeton, Nickel biogeochemistry, Sci. Total Environ. 148 (1994) 109–138.
[3] H. Ciftci, U. Bakal, The effect of lipoic acid on macro and trace metal levels in living tissues exposed to oxidative stress, Anticancer Agents Med. Chem. 9 (5) (2009) 560–569.
[4] I.B. Weinstein, The origins of human cancer, Cancer Res. 48 (1988) 4135–4143.
[5] M.R. Clemens, Klin Wochenschr, Free radicals in chemical carcinogenesis, Klin Wochenschr. 69 (1991) 1123–1134.
[6] S. Baytak, A.R. Turker, Determination of lead and nickel in environmental samples by flame atomic absorption spectrometry after column solid-phase extraction on Ambersorb-572 with EDTA, J. Hazard. Mater. B129 (2006) 130–136.
[7] F.Y. Iskander, T.L. Bauer, D.E. Klein, Determination of 28 elements in American cigarette tobacco by neutron-activation analysis, Analyst [London] 111 (1986) 107–109.
[8] A. Bakoglu, E. Bagci, H. Ciftci, Fatty acids, protein contents and metal composition of some feed crops from Turkey, J Food Agric. Environ. 7 (2) (2009) 343–346.
[9] H. Ciftci, E. Bagci, Protein contents and metal composition of some feed crops from Turkey, Int.J. ChemTech Res 1 (3) (2009) 577–580.
[10] K.A. Wagner, R.C. McDaniel, D. Self, Collection and preparation of sidestream cigarette smoke for trace elemental determinations by graphite furnace atomic absorption spectrometry and inductively coupled plasma mass spectrometry, J AOAC Int. 84 (2001) 1934–1940.
[11] K.H. Angeyo, J.P. Patel, J.M. Mangala, Measurement of trace element levels in Kenyan cigarettes with the energy dispersive X-ray fluorescence spectroscopy technique, J. Trace Microprobe Tech. 16 (1998) 233–246.
[12] H. Ciftci, A. Olcucu, A. Ozkaya, T. Ciftci, The optimization of analytical parameters for determination of iron, nickel and cobalt in plants with RP-HPLC, Asian J. Chem. 21 (2009) 2643–2652.
[13] M.A. Mirza, M.Y. Khuhawar, R. Arain, Determination of uranium, iron, copper, and nickel in rock and water samples by MEKC, J. Sep. Sci. 31 (16) (2008) 3037–3044.
[14] M. Faraji, Y. Yamini, S. Shariati, Application of cotton as a solid phase extraction sorbent for on-line preconcentration of copper in water samples prior to inductively coupled plasma optical emission spectrometry determination, J. Hazard. Mater. 166 (2–3) (2009) 1383–1388.
[15] M. Moors, D.L. Massart, R.D. McDowall, Analyte isolation by solid-phase extraction (SPE) on silica-bonded phases—classification and recommended practices, Pure Appl. Chem. 66 (1994) 277–304.
[16] V. Camel, Solid phase extraction of trace elements, Spectrochim. Acta Part B 58 (2003) 1177–1233.
[17] M.E. Mahmoud, I.M.M. Kenawy, MM.A.H. Hafez, R.R. Lashein, Removal, preconcentration and determination of trace heavy metal ions in water samples by AAS via chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidenepropylamine ion exchanger, Desalination 250 (2010) 62–70.
[18] E. Kenduzler, A.R. Turker, O. Yalcınkaya, Separation and preconcentration of trace manganese from various samples with Amberlyst 36 column and determination by flame atomic absorption spectrometry, Talanta 69 (2006) 835–840.
[19] N. Çolak, Metotreksat benzeri bileşiklerin sentezi, yapılarının aydınlatılması ve biyolojik aktivitelerinin incelenmesi, Gazi Üniversitesi, Fen Bilimleri Enstitüsü, Doktora tezi, 2005.
[20] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 4th ed., Longman, London, 1978, p. 318.
[21] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Bioresource Techno. 76 (2001) 63–65.
[22] V. Tharanitharan, K. Srinivasan, Removal of Ni(II) from water and wastewater using modified Duolite XAD-761 resin, Indian J. Chem. Techn. 16 (2009) 245–253.
[23] E. Eren, O. Cubuk, H. Ciftci, B. Eren, B. Caglar, Adsorption of basic dye from aqueous solutions by modified sepiolite: equilibrium, kinetics and thermodynamics study, Desalination 252 (2010) 88–96.
[24] H. Ciftci, Solid phase extraction method for the determination of cobalt in water samples on duolite XAD-761 resin using 4-(2-Pyridylazo) resorcinol by FAAS, Curr. Anal. Chem.2010, 6 (2), in press.
[25] I. Narin, M. Soylak, The uses of 1-(2-pyridylazo) 2-naphtol (PAN) impregnated Ambersorb 563 resin on the solid phase extraction of traces heavy metal ions and their determinations by atomic absorption spectrometry, Talanta 60 (2003) 215–222.

[26] C. Arpa, S. Bektas, Preconcentration and determination of lead, cadmium and nickel from water samples using a polyethylene glycol dye immobilized on poly (hydroxyethylmethacrylate) microspheres, Anal. Sci. 22 (2006) 1025–1029.

[27] R.S. Praveen, S. Daniel, T.P. Rao, Solid phase extraction preconcentration of cobalt and nickel with 5, 7-dichloroquinone-8-ol embedded styrene–ethylene glycol dimethacrylate polymer particles and determination by flame atomic absorption spectrometry (FAAS), Talanta 66 (2005) 513–520.

[28] M. Kumar, D.P.S. Rathore, A.K. Singh, Amberlite XAD-2 functionalized with o-aminophenol: synthesis and applications as extractant for copper(II), cobalt(II), cadmium(II), nickel(II), zinc(II) and lead(II), Talanta 51 (2000) 1187–1196.

[29] M. Ghaedi, F. Ahmadi, A. Shokrollahi, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, J. Hazard. Mater. 142 (2007) 272–278.

[30] E. Kenduzler, S. Baytak, O. Yalcınkaya, A.R. Turker, Application of factorial design in optimization of nickel preconcentration by solid phase extraction and its determination in water and food samples by flame atomic absorption spectrometry, Can. J. Anal. Sci. Spect. 52 (2007) 91–94.