A novel ionic liquid/micro-volume back extraction procedure combined with flame atomic absorption spectrometry for determination of trace nickel in samples of nutritional interest

Shayesteh Dadfarnia *, Ali Mohammad Haji Shabani, Mahboubeh Shirani Bidabadi, Abbas Ali Jafari

Department of Chemistry, Faculty of Science, Yazd University, 89195/74, Yazd, Iran

ABSTRACT

A simple, highly sensitive and environment-friendly method for the determination of trace amount of nickel ion in different matrices is proposed. In the preconcentration step, the nickel from 10 mL of an aqueous solution was extracted into 500 μL of ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [C$_4$MIM][PF$_6$], containing PAN as complexing agent. Subsequently, the PAN complex was back-extracted into 250 μL of nitric acid solution, and 100 μL of it was analyzed by flow injection flame atomic absorption spectrometry (FI-FAAS). The main parameter influencing the extraction and determination of nickel, such as pH, concentration of PAN, extraction time and temperature, ionic strength, and concentration of stripping acid solution, were optimized. An enhancement factor of 40.2 was achieved with 25 mL sample. The limit of detection (LOD) and quantification obtained under the optimum conditions were 12.5 and 41.0 μg L^{-1}, respectively. To validate the proposed methods two certified reference materials 681-I and BCR No. 288 were analyzed and the results were in good agreement with the certified values. The proposed method was successfully applied to determination of nickel in water samples, rice flour and black tea.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Nickel is an essential participant of metabolism of plants and some domestic animals. However, even at low concentration, it may have a general toxic effect on human organism, causing nosopharynx, lung disease, malignant tumors, and dermatological problems [1,2]. Nickel enters waters from dissolution of rocks and soils, biological cycles, atmospheric fallout, especially from industrial processes and waste disposal [1]. These facts explain the importance of monitoring nickel concentration in natural waters and food samples from public health and environmental point of view. According to the international regulation on water quality, the approved content of nickel in drinking water is 20.0 μg L^{-1} [1]. Thus, determination of nickel in drinking water requires much higher sensitivity than what is achievable with flame atomic absorption spectrometry. Therefore; a preliminary separation and preconcentration prior to its determination could be a good choice. Several methods have been proposed for separation and preconcentration of trace amount of nickel including, liquid–liquid extraction (LLE) [3–6], solid phase extraction (SPE) [7–11], cloud

point extraction (CPE) [12–16] and liquid phase microextraction (LPME) [17–19].

LLE is among the classical pretreatment techniques that have been widely employed in analytical chemistry [19,20]. Although it offers high reproducibility and high sample capacity, it suffers from several limitations, including large volume of organic solvent with toxic properties. Recently, considerable interest has been manifested on using room temperature ionic liquids (RTILs) as the green solvent to replace the traditional volatile organic solvents in a wide range of application [21]. RTILs are organic salts consisting of an organic cation with delocalized charge and organic or inorganic anions that are liquid at room temperature. These ionic solvents possess numerous fascinating properties and are of fundamental interest to modern chemistry and chemical industry. These properties are mainly due to their lack of vapor pressure, high conductivity, high stability, and low viscosity, wide tune ability regarding hydrophobicity, polarity as well as solvent solubility and miscibility [22–25]. Several reports have been appeared in which RTILs have successfully been utilized for extraction of metal ions as chelate of various organic liquids [26–31]; however, only a few of them involve preconcentration of metal ions [30,31] and to the best of our knowledge, there is no report on extraction of nickel with RTILs. Thus, development of an extraction/preconcentration method based on RTILs for determination of trace amount of nickel ion is challenging.

* Corresponding author. Tel.: +98 351 8212667; fax: +98 351 8210644.
 E-mail address: sdadfarnia@yazduni.ac.ir (S. Dadfarnia).

In this study 1-(2-pyridylazo)-2naphthol (PAN), a classical reagent for spectrophotometric determination of transition metal ions [32], was utilized as a ligand for liquid–liquid extraction of nickel with ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6]. The extracted nickel in RTIL was then back-extracted into micro-volume of nitric acid and was determined by flow injection flame atomic absorption spectrometry.

2. Experimental

2.1. Reagents and standard solution

All chemicals used throughout this study were of highest purity available and was at least of analytical reagent grade. The standard solution of nickel (II) (1000 mg L^{-1}) was prepared by dissolving proper amount of Ni(NO$_3$)$_2$·6H$_2$O from Merck (Darmstadt, Germany) in 0.1 mol L^{-1} nitric acid solution. Working solutions were prepared daily by appropriate dilution of stock solution. All solutions were stored in pre-cleaned polypropylene from Nalgene (Lima, Oh, USA) containers. Doubly distilled water was used throughout in sample preparation. 1-Methylimidazole, potassium hexafluorophosphate, 1-cholorobutane, 1-(2-pyridylazo)-2naphthol, nitric acid and ethyl acetate, were obtained from Merck. The samples were filtered through a 0.45 μm membrane filter (25 mm in diameter, Dura pore TM, Millipore) prior to analysis.

2.2. Apparatus

The nickel determination was carried out on a Buck Scientific atomic absorption spectrometer (Model 210 VGP, USA) with a hollow cathode lamp at a wavelength of 232.0 nm using air-acetylene flame. The operating conditions were set as recommended by manufacturer. The single line flow injection system consisting of peristaltic pump (Ismatic, MS-REGLO/8-100, Switzerland), and rotary injection valve (Rheodyne, CA, USA) with a loop of 100 μL capacity was used for effective control of the amount of sample and reproducibility of the measurements. The absorbance time response was monitored on an x-t chart recorder (L-250) and quantitative analysis was based on measurement of the peak height of transient signals. The pH measurements were carried out with a Metrohm pH meter (model 691, Switzerland) using a combined glass calomel electrode. The purity of ionic liquid was confirmed with ^{1}H NMR and ^{13}C NMR spectrums obtained by a Burker 500 MHZ spectrometer.

2.3. Preparation of ionic liquid

The ionic liquid [C_4MIM]PF_6 was prepared as described else where [27,30,31,33]. Briefly, 1-butyl-3-methylimidazolium chloride [C_4MIM][Cl$^-$] was prepared by adding equal amount (0.3 mol) of 1-chlorobutone and 1-methylimidazole to a 250 round bottom flask fitted with reflux condenser. The flask and its content were heated at 80 °C for 24–48 h, until a golden viscous liquid was formed. The viscous liquid was cooled and was washed three times with 50 mL portion of ethyl acetate in a separation funnel. Then, the lower liquid portion [C_4MIM][Cl$^-$] was slowly added to 150 mL potassium hexafluorophosphate (0.3 mol) solution at 4 °C; and the solution was stirred at room temperature for 12 h. A 15 mL dichloromethane was added to the lower liquid portion and the mixture was washed with water until the washing was no longer acidic. The washed RTIL was dried with anhydrous magnesium sulfate. The solvent was removed with rotary evaporation and finally was purged with nitrogen gas. The purity of final product was characterized with ^{1}H NMR and ^{13}C NMR with a Burker 500 MHZ spectrometer. The [C_4MIM]PF_6 was stored in contact with deionized water to equilibrate the water content of RTIL phase.

2.4. Sample preparation

2.4.1. Water samples

The water samples were filtered; the pH was adjusted to ∼7 and was treated according to the given procedure.

2.4.2. Rice flour

Rice flour (7.69 g) was placed in a 100 mL beaker and was dissolved in 7 mL concentrated nitric acid. Then drop wise, 4 mL of hydrogen peroxide (30%, w/v) was added and the solution was heated on a hot plate for 10 min. After cooling to room temperature, the solution was filtered; its pH was adjusted to ∼7, and then was transferred into a 50 mL volumetric flask. Its volume was adjusted with deionized water and was treated according to the given procedure.

2.4.3. Black tea sample

8 mL of 1:1 nitric acid solution was added to 4 g of black tea and was heated at 100 °C for 2 h. Then the solution was cooled to room temperature, filtered and after adjustment of pH to ∼7, it was transferred into a 50 mL volumetric flask, the volume was adjusted with deionized water and was treated according to the given procedure.

2.4.4. Standard reference material

The ore samples were prepared as described else where [34], i.e. proper amount of standard ore 68I-I or BCR No. 288 was weighed into a beaker, 5 mL concentrated nitric acid was added and the mixture was heated. Then 3 mL of hydrogen peroxide was added, and to remove the excess amount of hydrogen peroxide, the mixture was heated to near dryness. Next, ∼10 mL of doubly distilled water was added to the beaker; the solution was filtered and after adjustment of pH to ∼7, it was transferred into a 20 mL volumetric flask, and the volume was adjusted with deionized water and was treated according to the given procedure.

2.5. Procedure

The pH of 10 mL of standard or sample solution containing not more than 5 μg of nickel was adjusted to ∼7 using 0.1 mol L^{-1} nitric acid or ammonium hydroxide and was transferred into a ∼15 mL conical-bottom polypropylene tube containing a stirrer bar. Then, 500 μL of PAN in RTIL (2×10^{-2} mol L^{-1}) was added, the magnetic stirrer was turned on and the solution was mixed for 15 min at 1250 rpm. In this step Ni^{2+} was complexed with PAN and extracted into RTIL. In order to separate the phases, the mixture was centrifuged for 5 min at 3500 rpm and the aqueous phase was removed by decantation. The analyte was then back-extracted into acidified aqueous phase by adding 250 μL of 1.5 mol L^{-1} nitric acid solutions, mixing for 1 min with a vortex, and centrifuging for 3 min at 1500 rpm. Finally, 100 μL aliquot of the resulting solution was introduced into the FAAS by the use of a single line flow injection system.

3. Results and discussion

It is well known that PAN form a 2:1 complex with nickel ion (log $K_{\beta2}$ = 27.5) which is extractable to organic solvents [32]. In the preliminary study it was confirmed that 1-(2-pyridylazo)-2-naphtol (PAN) in ionic liquid [C_4MIM][PF_6] also is capable of extracting nickel from aqueous solution. However, one of the problems in extraction with ionic liquid (IL) in glass vessel is the interaction of IL with the glass, which results in sticking of IL phase onto the wall of the container even after centrifugation at high rpm. This problem was alleviated by Baghdadi and co-workers [35] by addition of non-ionic surfactant to the aqueous phase. However, in this study we used a different approach; a polypropylene centrifuge
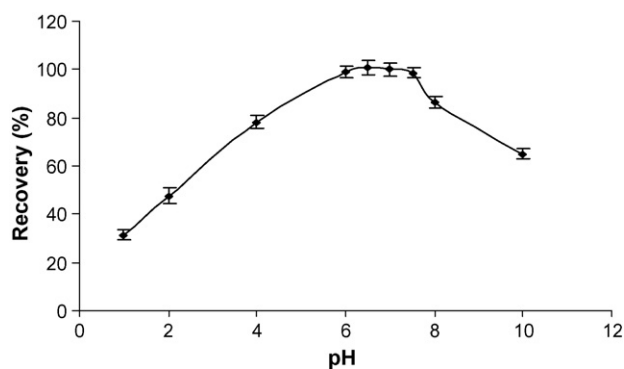
Fig. 1. Effect of pH on nickel extraction. Conditions: sample volume, 10 mL; nickel concentration, 200 µg L^{-1}; PAN concentration, 6.8×10^{-2}; RTIL volume, 500 µL; nitric acid volume, 250 µL.

Fig. 2. Effect of PAN concentration on nickel extraction. Conditions: sample volume, 10 mL; nickel concentration, 200 µg L^{-1}; pH ~7; RTIL volume, 500 µL; nitric acid volume, 250 µL.

tube was employed instead of glass tube. It was observed that with the use of polypropylene or Teflon tube and without addition of any extra chemical, the IL did not stick on the wall of container. So, in order to solve the problem and to eliminate the possibility of contamination by extra chemicals, all the extraction was performed in the polypropylene tube. Furthermore, to establish the best conditions of extraction and analysis, the procedure was optimized by univariable method.

3.1. Effect of pH

The separation of metal ions by RTILs extraction involves prior formation of a complex with sufficient hydrophobicity which can be extracted into small volume of ionic liquid. It is well known that pH of the sample solution plays a unique role on metal-chelate formation and its subsequent extraction. The effect of pH on the complex formation and extraction of nickel ions was studied in the range of 1–10 using nitric acid or ammonium hydroxide. The results illustrated in Fig. 1 reveals that the recovery is nearly constant in the pH range of 6–7. The progressive decrease in extraction of analyte at low pH is due to competition of hydrogen ion with analyte for reaction with PAN, and the decrease in extraction at pH greater than 7 is probably due to precipitation of nickel as nickel hydroxide. A pH of ~7 was selected as optimum value for subsequent work.

3.2. Effect of PAN concentration

The concentration of PAN has effect on the recovery of analyte that was evaluated. The results showed that (Fig. 2) the recovery of nickel increase with an increase in PAN concentration from 3.4×10^{-4} to 1.7×10^{-2} mol L^{-1} and then remains constant up to the 1.0×10^{-1} mol L^{-1}. Thus, the amount of PAN at concentration lower than 1.7×10^{-2} mol L^{-1} is insufficient for formation of a neutral complex with nickel. In this study a concentration of 2.0×10^{-2} mol L^{-1} was employed.

3.3. Influence of extraction time and stirring rate

One important factor influencing the extraction efficiency and speed of analysis is the extraction time. In order to have good precision, sensitivity and high speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between aqueous and RTIL phase and maximize the extraction of analyte. The effect of extraction time was investigated with the time varying from 5 to 40 min at a stirring rate of 1000 rpm. The results showed that the recovery of analyte increase with an increase in extraction time up to 15 min and then remains constant with fur-
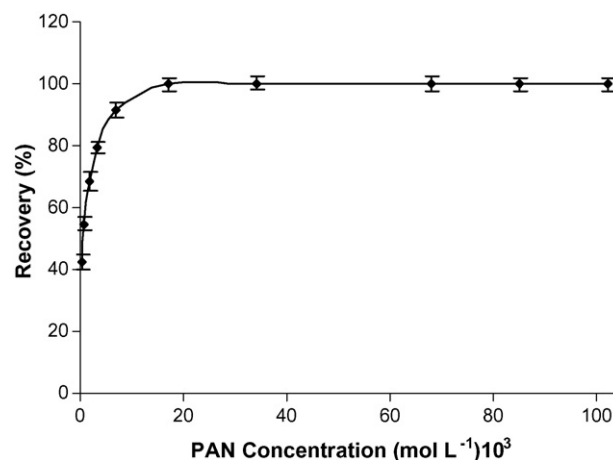
ther increase in extraction time. Thus, an optimum stirring period of 15 min was selected.

Another important factor influenced the extraction speed is stirring rate. A proper stirring rate causes adequate dispersion of IL in aqueous phase resulting in an increase in the interfacial contact of two phases, thereby aqueous phase mass-transfer coefficient and subsequently extraction speed will increase [36]. Hence, the extraction was performed according to the recommended procedure but with different stirring speeds (750–2500 rpm). The results showed that a stirring rate of 1000 rpm was adequate for the prevailing experimental conditions.

3.4. Effect of temperature and ionic strength

The effect of temperature on extraction was studied by varying the temperature between 5 and 70 °C. It was found that the extraction efficiency is constant in the temperature range of 20–50 °C; but a further increase in temperature causes a decrease in recovery. This might be due to increase in solubility of RTIL at high temperature as well as degradation of complex. Thus, the extraction was performed at room temperature for its more convenience.

The effect of ionic strength on extraction of nickel was studied by varying the concentration of NaClO$_4$ within the range of 0–1 mol L^{-1}. The results showed that addition of salt has no significant effect on extraction efficiency. At this stage the amount of nickel remained in the original aqueous phase was determined by graphite furnace atomic absorption spectrometry and was found to be negligible. Thus the extraction was quantitative (>95%).

3.5. Back extraction

In order to recover the ionic liquid and to achieve further preconcentration factor, the RTIL extract was submitted to procedure of back extraction. Fig. 1 demonstrated that, diminishing the media pH (pH < 4) leads to low stability of Ni–PAN complex, causing its dissociation and consequently release of nickel ions to aqueous phase. Therefore, for quantitative back extraction, the concentration of nitric acid solution was optimized. For this purpose, the RTIL extract was back-extracted into 250 µL of nitric acid solution with concentration varying from 0.5 to 4.0 mol L^{-1}. Quantitative back extraction (>95%) was observed when the concentration of nitric acid was at least 1.5 mol L^{-1}. Therefore, 250 µL of 1.5 mol L^{-1} nitric acid solution was chosen for back extraction.

The agitation time for quantitative back extraction of analyte was also studied and it was found that back extraction is very

Table 1
Effect of foreign ions on the recovery of nickel: concentrated volume 10 mL, Ni concentration 200 $\mu g\,L^{-1}$.

Foreign ion	Molar ratio (ion/Ni^{+2})	Ni recovery (%)	Foreign ion	Molar ratio (ion/Ni^{+2})	Ni recovery (%)
NH_4^+	1000	101 ± 3	Zn^{2+}	25	96 ± 2
Ca^{2+}	500	99 ± 4	Cu^{2+}	25	98 ± 2
Mg^{2+}	500	99 ± 4	F^-	1000	100 ± 3
Ba^{2+}	1000	99 ± 3	Br^-	1000	99 ± 3
Ag^+	500	98 ± 3	I^-	1000	101 ± 4
Pb^{2+} [a]	500	99 ± 5	NO_3^-	1000	101 ± 3
Fe^{3+} [a]	250	99 ± 3	CO_3^{2-}	500	100 ± 2
Hg^{2+}	250	98 ± 2	SO_4^{2-}	500	98 ± 3
Cd^{2+}	25	97 ± 4	CH_3COO^-	1000	100 ± 3

[a] In the presence of citrate (0.01 $mol\,L^{-1}$) a molar ratio of 1000 was tolerated.

fast, i.e. in approximately 0.5 min the recovery was completed. An optimum agitation time of 1 min was then chosen.

3.6. Effect of sample volume

The nickel concentration in real samples such as natural waters is usually very low. Thus, the sample volume is one of the most important parameters in development of preconcentration method, since it determines the sensitivity enhancement of the technique. For this purpose, different volumes (5–20 mL) of sample solution containing 2 μg of nickel, under optimum conditions, were subjected to extraction/back extraction procedure. Quantitative extraction was observed when the aqueous volume was between 5 and 10 mL. It was noticed that higher sample volumes partially solubilized the RTIL phase, leading to non-reproducible results. Thus, the solubility of [C_4MIM][PF_6] in aqueous phase limit the magnitude of preconcentration factor. A sample volume of 10 mL was selected for further experiments. Consequently, an enrichment factor of 40 was determined based on consideration of the sample volume (10 mL) and back extraction volume (250 μL). Furthermore, the enhancement factor determined on the basis of the ratio of slope of calibration standard curve with microextraction and without microextraction, was found to be 40.2; thus, extraction/back extraction procedure is quantitative.

3.7. Interference study

The effect of potential interference ions in natural water and food samples on determination of analyte was examined. The study was performed by analyzing 10 mL of 200 $\mu g\,L^{-1}$ of nickel solution containing concomitant ions at different concentration, according to the recommended procedure. The tolerance limit of coexist ions is defined as the largest amount making variation of less than 5% in the recovery of analyte. The results of this investigation are summarized in Table 1, proving that the nickel recovery was almost quantitative in the presence of excessive amount of the possible interfering cations and anions.

3.8. Analytical performance

Under the optimum condition, the calibration graph was constructed by processing standard solutions of nickel according to the given procedure. The linear concentration range was 50–500 $\mu g\,L^{-1}$ with a correlation coefficient of 0.9998. The calibration function was $Y = 0.0073C + 0.0208$, where Y is the peak height and C is the concentration of nickel in $\mu g\,L^{-1}$.

The precision of the method was studied by processing seven replicate solutions at the same day. The relative standard deviation for 50 and 200 $\mu g\,L^{-1}$ nickel was 3.1 and 2.1%, respectively. The limit of detection and quantification based on $3S_b/m$ and $10S_b/m$, (where S_b is standard deviation of the blank signals and m is the slope of calibration curve after extraction) was 12.5 and 41.0 $\mu g\,L^{-1}$, respec-

Table 2
Analytical characteristics of the method.

Linear range ($\mu g\,L^{-1}$)	50–500
Slope	7.3×10^{-3}
Correlation coefficient (r)	0.9998
RSD at 50 $\mu g\,L^{-1}$ (%) ($n = 7$)	3.1
Detection limit ($\mu g\,L^{-1}$)	12.5
Quantification limit ($\mu g\,L^{-1}$)	41.0
Enhancement factor [a]	40.2

[a] Calculated as the slope ratio of the calibration graphs obtained with preconentration of 10 mL solution and without preconcentration.

tively. The analytical characteristics of the method are summarized in Table 2.

3.9. Analysis of real sample

The proposed method was applied to several categories of samples including, tap water, ground water, river water, sea water, rice flour and black tea, with diverse matrix cation and anion concentration. The results are given in Table 3. Reliability was checked either by spiking the sample or comparing the results with data obtained by furnace atomic absorption analysis. As the results showed the recovery of spiked sample is good, and there is satisfactory agreement between the results and data obtained by furnace atomic absorption analysis, suggesting the proposed procedure is reliable for the sample type examined.

Furthermore, the accuracy of the proposed procedure was verified by applying the method to the determination of nickel in two

Table 3
Determination of nickel in real sample.

Sample	Added	Found	Recovery (%)	GFAAS
Rice flour ($\mu g\,g^{-1}$)	–	0.42 ± 0.01	–	0.41 ± 0.01
	0.65	1.05 ± 0.04	96.9	
Black tea ($\mu g\,g^{-1}$)	–	0.34 ± 0.01		0.31 ± 0.01
	1.25	1.58 ± 0.05	99.2	
Tap water ($\mu g\,L^{-1}$)	–	ND[a]		2.56 ± 0.08
	60.0	59.5 ± 2.5	99.2	
	100.0	101.2 ± 3.3	101.2	
Well water ($\mu g\,L^{-1}$)	–	ND[a]		1.90 ± 0.03
	60.0	61.2 ± 3.0	102.0	
	100.0	98.8 ± 2.2	98.8	
River water ($\mu g\,L^{-1}$)	–	ND[a]		3.11 ± 0.08
	60.0	59.9 ± 2.8	99.8	
	100	98.5 ± 2.6	98.5	
Sea water ($\mu g\,L^{-1}$)	–	ND[a]		3.66 ± 0.04
	60.0	60.5 ± 2.9	100.8	
	100	97.2 ± 2.4	97.2	

Results are mean and standard deviation of three independent measurements.
[a] ND: not detected.

Table 4
Determination of nickel in ore reference materials.

Sample	Amount found (μg g^{-1})	Amount accepted (μg g^{-1})
BCR No. 288	4.39 ± 0.48	4.57 ± 0.11
Euro-standard No. 68I-I	156.3 ± 6.8	160 ± 10

Results are mean and standard deviation of three independent measurements.

standard reference ore materials (68I-I and BCR No. 288). Reliability was checked by comparing the data with the accepted values. The results of this investigation, together with the accepted values are given in Table 4. As can be seen, at 95% confidence level there is no significant different between the results and accepted values. Thus, the procedure is reliable for analysis of wide range of samples.

4. Conclusion

It was demonstrated that with the use of polypropylene tube the problem of sticking of IL to the wall of container can be solved; and a novel, simple and selective preconcentration method based on the use of RTILs as extraction solvent has been described for the determination of nickel in various samples. The figure of merit of the proposed method is comparable to the other reported methods [4,5,7–10,12–14,17] and additionally, the method has the advantage of environment-friendly. The present method was successfully applied to separation, preconcentration and final determination of nickel by FI-FAAS in real waters and food samples with good accuracy and precision. Furthermore, it offers an alternative procedure to techniques such as GFAAS and ICP-OES for determination of nickel at μg L^{-1} level in real samples. The main benefits of the system are enhancement of FAAS sensitivity, no use of organic solvent, rejection of matrix constituent, low cost and environment-friendly. Future work will be directed at microextraction of metals with RTILs from different matrices.

References

[1] Guide lines for Drinking Water Quality. Health Criteria and Other Supporting Information, vol. 2, 2nd ed., World Health Organization, Geneva, 1998.
[2] M.M. Greenwood, A. Earnshows, Chemistry of the Elements, Elsevier, Amsterdam, 1988.
[3] B.R. Reddy, D.N. Priya, Chloride leaching and solvent extraction of cadmium, cobalt and nickel from spent nickel–cadmium, batteries using Cyanex 923 and 272, J. Power sources 161 (2006) 1428–1434.
[4] A.M. Haji shabani, S. Dadfarnia, Z. Shahbazi, A.A. Jafari, Extraction-spectrophotometric determination of nickel at microgram level in water and wastewater using 2-[(2-mercaptophenylimino)methyl]phenol, Bull. Chem. Soc. Ethiop. 22 (2008) 323–329.
[5] P.V.R. Bhaskara Sarma, B.R. Reddy, Liquid–liquid extraction of nickel at macro-level concentration from sulphate/chloride solutions using phosphoric acid based extractants, Miner. Eng. 15 (2002) 461–464.
[6] M.B. Arain, T.G. Kazi, M.K. Jamali, H.I. Afridi, N. Jalbani, R.A. Sarfraz, J.A. Baig, M.A. Memon, Time saving modified BCR sequential extraction procedure for the fraction of Cd, Cr, Cu, Ni, Pb and Zn in sediment samples of polluted lake, J. Hazard. Mater. 160 (2008) 235–239.
[7] A.R. Khorrami, H. Naeimi, A.R. Fakhari, Determination of nickel in natural waters by FAAS after sorption on octadecyl silica membrane disks modified with a recently synthesized Schiff's base, Talanta 64 (2004) 13–17.
[8] S. Dadfarnia, A.M. Haji shabani, A.A. Jafari, Z. Saadat, Determination of nickel in water and wastewater at ultratrace level by solid-phase extraction-flame atomic absorption spectrometry, Chem. Anal. (Warsaw) 52 (2007) 791–799.
[9] S.L.C. Ferreira, W.N.L. dos Santos, V.A. Lemos, On-line preconcentration system for nickel determination in food samples by flame atomic absorption spectrometry, Anal. Chim. Acta 445 (2001) 145–154.
[10] I. Narin, M. Soylak, Enrichment and determination of nickel(II), cadmium(II), copper(II), cobalt(II) and lead(II) ions in natural waters, table salts, tea and urine samples as pyrrolydine dithiocarbamate chelates by membrane filtration-flame atomic absorption spectrometry combination, Anal. Chim. Acta 493 (2003) 205–212.
[11] M. Tuzen, M. Soylak, D. Citak, H.S. Ferreira, M.G.A. Korn, M.A. Bezerra, A pre-concentration system for determination of copper and nickel in water and food samples employing flame atomic absorption spectrometry, J. Hazard. Mater. 162 (2009) 1041–1045.
[12] J. Chen, K. Teo, Determination of cobalt and nickel in water samples by flame atomic absorption spectrometry after cloud point extraction, Anal. Chim. Acta 434 (2001) 325–330.
[13] A. Safavi, H. Abdollahi, M.R. Hormozi Nezhad, Cloud point extraction, precon-centration and simultaneous spectrophotometric determination of nickel and cobalt in water samples, Spectrochim. Acta Part A 60 (2004) 2897–2901.
[14] V.A. Lemos, R.S. Franca, B.O. Moreira, Cloud point extraction for Co and Ni determination in water samples by flame atomic absorption spectrometry, J. Sep. Purif. Technol. 54 (2007) 349–354.
[15] M. Ghaedi, A. Shokrollahi, F. Ahmadi, H.R. Rajabi, M. Soylak, Cloud point extraction for the determination of copper, nickel and cobalt ions in environmental samples by flame atomic absorption spectrometry, J. Hazard. Mater. 150 (2008) 533–540.
[16] M. Ghaedi, A. Shokrollahi, K. Niknam, E. Niknam, M. Soylak, Development of efficient method for preconcentration and determination of copper, nickel, zinc and iron ions in environmental samples by combination of cloud point extraction and flame atomic absorption spectrometry, Cent. Eur. J. Chem. 7 (2009) 148–154.
[17] M. Shirani Bidabadi, S. Dadfarnia, A.M. Haji shabani, Solidified float-ing organic drop microextraction (SFODME) for simultaneous separa-tion/preconcentration and determination of cobalt and nickel by graphite furnace atomic absorption spectrometry (GFAAS), J. Hazard. Mater. 166 (2009) 291–296.
[18] H. Jiang, Y. Qin, B. Hu, Dispersive liquid phase microextraction (DLPME) com-bined with graphite furnace atomic absorption spectrometry (GFAAS) for determination of trace Co and Ni in environmental water and rice samples, Talanta 74 (2008) 1160–1165.
[19] N. Yoshikuni, T. Baba, N. Tsunoda, K. Oguma, Aqueous two-phase extraction of nickel dimethylglyoximato complex and its application to spectrophotometric determination of nickel in stainless steel, Talanta 66 (2005) 40–44.
[20] N. Chimpalee, D. Chimpalee, P. Keawpasert, D. Thorburn Burns, Flow injection extraction spectrophotometric determination of nickel using bis(acetylacetone)ethylenediimine, Anal. Chim. Acta 408 (2000) 123–127.
[21] X. Han, D.W. Armstrong, Ionic liquids in separations, Acc. Chem. Res. 40 (2007) 1079–1086.
[22] P. Stepnowski, Solid-phase extraction of room-temperature imidazolium ionic liquids from aqueous environmental samples, Anal. Bioanal. Chem. 381 (2005) 189–193.
[23] F.V. Rantwijk, R.M. Lau, R.A. Sheldon, Biocatalytic transformations in ionic liq-uids, Trends Biotechnol. 21 (2003) 131–138.
[24] W. Liu, L. Cheng, Y. Zhang, H. Wang, M. Yu, The physical properties of aqueous solution of room-temperature ionic liquids based on imidazolium: database and evaluation, J. Mol. Liq. 140 (2008) 68–72.
[25] L. Vidal, E. Psillakis, C.E. Domini, N. Grane, F. Marken, A. Canals, An ionic liquid as a solvent for headspace single drop microextraction of chlorobenzenes from water samples, Anal. Chim. Acta 584 (2007) 189–195.
[26] N. Hirayama, M. Deguchi, H. Kawasumi, T. Honjo, Use of 1-alkyl-3-methylimidazolium hexafluorophosphate room temperature ionic liquids as chelate extraction solvent with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, Talanta 65 (2005) 255–260.
[27] G.T. Wei, Z. Yang, C.J. Chen, Room temperature ionic liquid as a novel medium for liquid/liquid extraction of metal ions, Anal. Chim. Acta 488 (2003) 183–192.
[28] Z. Li, Q. Wei, R. Yuan, Y. Zhou, H. Liu, H. Shan, Q. Song, A new room tempera-ture ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate as a solvent for extraction and preconcentration of mercury with determination by cold vapor atomic absorption spectrometry, Talanta 71 (2007) 68–72.
[29] Z. Li, N. Lu, X. Zhou, Q. Song, Extraction spectrophotometric determina-tion of aluminum in dialysis concentrates with 3,5-ditetbutylsalicylfluorone and ionic liquid 1-butyl-3-trimetylsilylimidazolium hexafluorophosphate, J. Pharm. Biomed. Anal. 43 (2007) 1609–1614.
[30] E.M. Martinis, R.A. Olsina, J.C. Altamirano, R.G. Wuilloud, Sensitive determi-nation of cadmium in water samples by room temperature ionic liquid-based preconcentration and electrothermal atomic absorption spectrometry, Anal. Chim. Acta 628 (2008) 41–48.
[31] Z. Li, Q. Wei, R. Yuan, X. Zhou, H. Liu, H. Shan, Q. Song, A new room tempera-ture ionic liquid 1-butyl-3-trimetylsilylimidazolium hexafluorophosphate as a solvent for extraction and preconcentration of mercury with determination by cold vapor atomic absorption spectrometry, Talanta 71 (2007) 68–72.
[32] Z. Marczenko, Separation and Spectrophotometric Determination of Elements, Ellis Horwood Limited, Chichester, 1986.
[33] A.E. Visser, R.P.S. Swatloski, S.T. Griffin, D.H. Hartman, R.D. Rogers, Liquid/liquid extraction of metal ions in room temperature ionic liquids, Sep. Sci. Technol. 36 (2001) 785–804.
[34] T. Asadoulahi, S. Dadfarnia, A.M. Haji Shabani, Determination of thallium traces by EtAAS after matrix separation, on line preconcentration in a flow injection system, J. Braz. Chem. Soc. 18 (2007) 1353–1359.
[35] M. Baghdadi, F. Shemirani, Cold-induced aggregation microextraction: a novel sample preparation technique based on ionic liquids, Anal. Chim. Acta 613 (2008) 56–63.
[36] L. Li, B. Hu, L. Xia, Z. Jiang, Determination of trace Cd and Pb in environmen-tal and biological samples by ETV-ICP-MS after single-drop microextraction, Talanta 70 (2006) 468–473.