Preconcentration and Determination of Trace Amount of Nickel in Water and Biological Samples by Dispersive Liquid–Liquid Microextraction

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A new, simple and highly sensitive dispersive liquid–liquid microextraction method using a ionic liquid, i.e., 1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) for nickel determination at trace levels in real samples was developed. Nickel was chelated with diethyl dithiocarbamat reagent and extracted into an ionic liquid. Ni was back-extracted from the IL phase with 200 μL of 0.5 mol L^{-1} nitric acid and determined by electrothermal atomic absorption spectrometry (ETAAS). Various parameters such as pH, amount of ionic liquid, eluent type and volume, chelating agent concentration, volume of the sample solution and matrix interference effect on the recovery of the metal ions have been studied. Under the optimum conditions, the enrichment factor 100 was obtained from only 20 mL of sample. The calibration graph was linear in the rage of 20-700 ng L^{-1} of nickel with detection limit of 5 ng L^{-1}. The relative standard deviation (R.S.D.s) for eight replicate measurements of 20 ng L^{-1} of nickel was 5.6%. Validation of the methodology was performed by standard addition method and analysis of certified reference material. The method was successfully applied to the determination of Ni^{+2} in serum and tap water samples.

Keywords: Nickel; Preconcentration; Ionic liquid; Microextraction; Electrothermal atomic absorption spectrometry (ETAAS).

INTRODUCTION

Nickel is a chemical element present in trace amounts in natural water samples, is possible to find very low nickel concentration levels in river waters, in the order of 1.5 μg L^{-1}. 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 processes and waste disposal.[1,2] Nickel was thought be essential to plants and some domestic animals, but not considered to be a metal of biological importance until 1975, when Zerner discovered that urease was a nickel enzyme.[3,4] Nickel is essential constituent in plant urease. Urease-rich legumes such as jack beans and soybeans generally contain high nickel concentrations. The concentration of nickel in the water of rivers and lakes is very low, with the average concentration usually less than 10 μg/L. The highest levels of nickel in drinking water, about 72 μg L^{-1} and EPA recommends that drinking water levels for nickel should not be more than 0.1 mg L^{-1}. Nickel concentrations in human serum taken from 30 individuals not occupationally exposed to nickel ranged from < 0.05 to 1.05 μg L^{-1} with a mean value of 0.34 μg L^{-1}.[5] Tentative reference values for nickel in serum and urine have been proposed: 0.2 μg L^{-1} or lower in serum, and 1-3 μg L^{-1} in urine of healthy adults.[6] 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. Moreover, nickel can cause a skin disorder known as nickel-eczema.[7]

Measurements of the amount of nickel in serum and urine can be used to estimate human exposure to nickel. Therefore, it is necessary and important to develop sensitive methods for determining nickel in environmental and biological samples. Considering the low content of nickel in environmental samples, sensitive analytical techniques are required to obtain low DLs. Spectrophotometric method,[8,9] atomic absorption spectrometry with flame (FAAS),[10,11] chromatography[12] and electrothermal atomization (ETAAS)[13] become the most appropriate techniques for its determina-

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tion, but the detection limits in these methods is not sufficient when the concentrations are too low. Therefore, preconcentration and separation of analyte are needed before measuring. Successful preconcentration can be achieved by various methods, such as liquid–liquid extraction,[14,15] precipitation,[16] solid-phase extraction[17-20] or cloud-point extraction (CPE),[21-23] capillary microextraction,[24] solid phase microextraction,[25] and single-drop microextraction.[26,27]

The development of conventional liquid–liquid extraction (LLE) and solid phase extraction (SPE) methods were limited[28] with respect to disadvantages such as solvent losses, large secondary wastes, a long procedure, and complex equipment. The application of solid phase microextraction (SPME) and liquid phase microextraction (LPME) were developed to remove these disadvantages.[29]

Recently, dispersive liquid–liquid microextraction has been developed as a new mode of liquid-phase microextraction and attracted increasing attention for its simple operation, high enrichment factor, rapidness, and high extraction efficiency. In this extraction procedure, two organic solvents having different characteristics are involved in use, one is hydrophilic which performs as dispersive solvent such as methanol[30] and acetone[31] etc., and the other is hydrophobic which performs as extraction solvent such as chlorobenzene[32] and carbon tetrachloride[33] and this method has been successfully applied to the enrichment of heavy metals.[34,35] Room temperature ionic liquids (RTILs) with negligible vapor pressure and good selective solubility have aroused increasing interests for their promising role as alternative solvents in DLLME.

In the present work, the room temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4MIM][PF_6]$, was employed as a solvent for Ni-DDC complex. DLLME is a miniaturized sample pre-treatment technique. On the other hand, graphite furnace atomic absorption spectrometry (GF AAS) is a micro amount sample analysis technique. Therefore, it makes it perfect when a combination of both DLLME and GF AAS is used. The applicability of the approach has been demonstrated for the determination of nickel in water and biological samples. The effect of various experiment conditions on the extraction of nickel is investigated and discussed in detail.

EXPERIMENTAL

Materials

All chemicals and reagents used in this study were of analytical-reagent grade. Deionized water was used to prepare all solutions. The laboratory glassware was kept in dilute nitric acid at least overnight and subsequently washed with deionized water. Stock solution of nickel (1000 mg L^{-1}) was prepared by dissolving appropriate quantity of $Ni(NO_3)_2 \cdot 6H_2O$ (Merck) in slightly acidified distilled water and a working solution was prepared by appropriate dilution. Acetate (6) buffer was used to adjust the sample pH. The chelating agent, 0.5% (m/v) Sodium diethyldithiocarbamate solution was prepared by dissolving the appropriate amount of NaDDC (Merck) in water. Serum sample was purchased from Sigma–Aldrich (Germany). Ultrapure water was obtained from a Millipore Continental Water System (Institute of Petroleum Industry, Iran). The ionic liquids of 1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) was purchased from Sigma Aldrich (USA).

Apparatus

A GBC 932-AUS model GF3000 atomic absorption spectrometer with deuterium background correction and a pyrolytic graphite tube atomizer, equipped with furnace auto-sampler and a circulating cooling unit, were employed throughout measurements. A nickel electrodeless discharge lamp (EDL) was used as light source operated at 4 mA. The slit was set at 0.2 nm, while the wavelength was set at 341.5 nm resonance line. Two preheating/drying steps were necessary for gradual drying of the organic solvent. Argon 99.996% was used as purge and protective gas. Integrated absorbance (peak height) was used exclusively for signal evaluation. The pH values were measured with a Metrohm pH-meter (Model: E-632, Switzerland) supplied with a glass-combined electrode.

Sample preparation

A sample of serum was maintained at -20 °C in a cleaned plastic tube with a colorless stopper. The urine was collected in a disposable plastic bag, and a subsample (5-20 mL) was poured into a 50 mL plastic container. We tested the plastic containers for nickel leakage by leaching with 1% nitric acid; no detectable nickel contamination occurred. After sampling, the urine specimens were kept frozen at -20 °C until analysis. To prevent any risk of laboratory-acquired infection and to redissolve urine precipitates, all urine samples were heated for 1 hr at 95 °C in a laboratory oven prior to analysis.

For tap water samples collection, domestic water was allowed to run for 20 min and approximately a volume of 1000 mL was collected in a beaker. To recover any nickel

adsorbed to the inner surface of the sample containers, we added 0.5 mL 65% ultrapure nitric acid to each 25-mL tap water sample 24 hr before the nickel measurements were performed.

Recommended procedure

In the pre-concentration procedure of nickel, 0.1 g $[C_4MIM][PF_6]$ was used as extraction solvent and added into a centrifuge tube tube. 1 mL of % 0.5 sodium diethyl dithiocarbamate (NaDDC) solution as chelating agent, 1 mL of acetate buffer solution (pH = 6) and 20 mL of solution containing 20-700 ng L^{-1} of nickel was added to the working solution. Triton X-100 was an emulsifier and it is an anti-sticking agent, therefore in order to raise the efficiency of the extraction procedure, 100 μL of Triton X-100 (1%) was added to solution. Then the sample solutions were heated in a water bath with the temperature controlled at 55 °C. The IL was dissolved completely and would entirely mix with the working solutions in order to make the chelate complex migrate into the IL phase. The mixture was shaken for 4 min. Then it was cooled and the solution became turbid. After that the solution was centrifuged for 6 min at 35000 rpm. The upper aqueous phase was removed with a syringe, and the residue was dissolved in 200 μL of 1.0 mol L^{-1} nitric acid and it was shaken for 60 s. 20 μL of the final solution was also injected into graphite furnace and the amount of nickel was determined. Blank solutions were analyzed in the same manner as standard and sample solutions.

RESULTS AND DISCUSSION

For higher sensitivity, selectivity and precision for metal determination with the DLLME method, the effect of the main parameters, like the type of disperser and extraction solvent, sample, sample acidity, amount of chelating agent, and extraction time, were studied and optimized thoroughly. All analyses were carried out in triplicate.

Optimization of ETAAS conditions

In order to decreases the possibility of chemical interference and reduces the magnitude of the background signal, the pyrolysis and atomization temperatures should be optimized. Here, these parameters were studied using 40 ng L^{-1} nickel solutions submitted to the DLLME procedure. It was found that at the pyrolysis temperature of 900 °C, the maximum absorbance was achieved. At lower pyrolysis temperature, the background signal was high, which is probably due to the vaporization of excess DDC and/or ionic liquid itself at the atomization step. This causes a significant signal suppression, which resulted in the low absorbance values for low pyrolysis temperatures. Increasing pyrolysis temperature above 900 °C leads to loss of analyte and hence decreases analytical signal. Therefore, 900 °C was selected as the optimized pyrolysis temperature for the determination of nickel.

Table 1. The graphite furnace temperature program for Ni determination

Step	Hold time (s)	Ramp time (s)	Temperature (°C)	Argon flow rate (mL min^{-1})
Drying	10	20	120	300
Pyrolysis	72	50	900	300
Atomization	2	1	2400	0
Cleaning	5	1	2600	300

The effect of pyrolysis time on the absorbance of Ni was also investigated. The results showed that the absorbance was increased with increasing pyrolysis time up to 72 s and no appreciable improvements were observed for longer times. As a result, a pyrolysis time of 72 s was chosen. The atomization temperature was similarly optimized. According to the results, the signal was reached a maximum at about 2400 °C, and then decreased with the further increasing of temperature. So, the atomization temperature of 2400 °C was selected for the further experiments.

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 3-12. The results illustrated in Fig. 1 reveals that the recovery is nearly constant in the pH range of 6-8 and under this condition nickel is soluble. The progressive decrease in extraction of analyte at low pH is due to competition of hydrogen ion with analyte for reaction with DDC, and the decrease in extraction at pH greater than 10 is probably due to precipitation of nickel as nickel hydroxide. A pH of 6 was selected as optimum value for subsequent work.

Effect of the NaDDC concentration

Concentration is a critical variable to be optimized in

extraction methods based on a chelating agent such as NaDDC. Thus, it is highly important to establish the minimal reagent concentration that leads to total complex formation while achieving the highest extraction. The results are shown in Fig. 2. The concentration of NaDDC was increased until the total extraction of nickel was obtained. The extraction efficiency was stable when the NaDDC concentration was higher than 7.0×10^{-6} mol L^{-1}. Therefore, the concentration of 7.0×10^{-6} mol L^{-1} NaDDC was chosen for the further studies.

Effect of the extraction solvent

The variation of extraction efficiency upon RTIL amount was examined within the range of 0.05-0.2 g. It was observed that the extraction efficiency of the system was remarkably affected by the RTIL amount. Quantitative extraction was observed for a RTIL amount higher than 0.1 g. No significant changes were observed on the extraction efficiency for higher RTIL amounts. Therefore, in order to achieve a suitable preconcentration, 0.1 g RTIL was chosen as optimum value (Fig. 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 IL phase and maximize the extraction of analyte. The effect of shaking time was investigated with the time varying from 1 to 10 min. The results showed that 4 min shaking time and 6 min centrifugation time at 3500 rpm were as optimum since complete separation and the recovery were occurred.

Effect of sample volume

Sample volume is one of the most important parameter to be studied when real samples are analyzed by a preconcentration technique, since it conditions the sensitivity enhancement of the method. The effect of sample volume was examined in a range of 10-50 mL for 40 ng L^{-1} Ni^{2+}. It was found that the analyte could be recovered quantita-

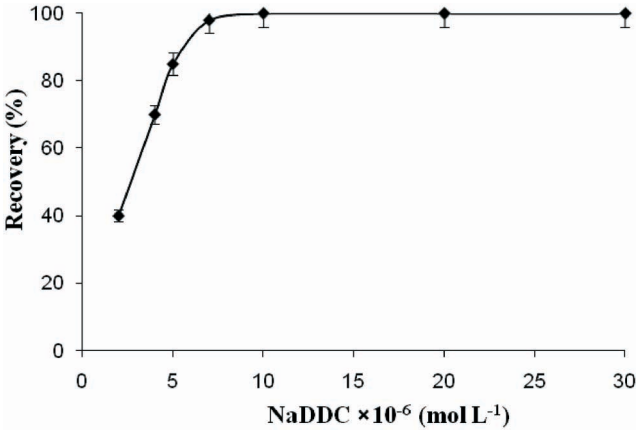

Fig. 2. Effect of NaDDC concentration on the recovery. Conditions: Concentration of nickel: 40 ng L^{-1}; amount of ionic liquid: 0.1 g; extraction time: 10 min; pH = 6; centrifugation rate: 3500 rpm; sample volume: 20 mL; N = 3.

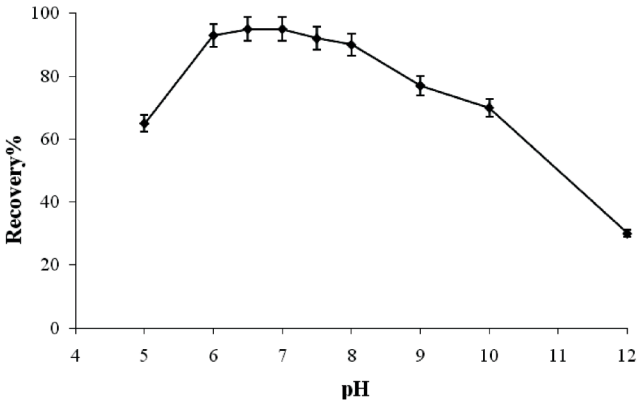

Fig. 1. Effect of samples pH on the recovery. Conditions: Concentration of nickel: 40 ng L^{-1}; amount of ionic liquid: 0.1 g; extraction time: 10 min; centrifugation rate: 3500 rpm; sample volume: 20 mL; N = 3.

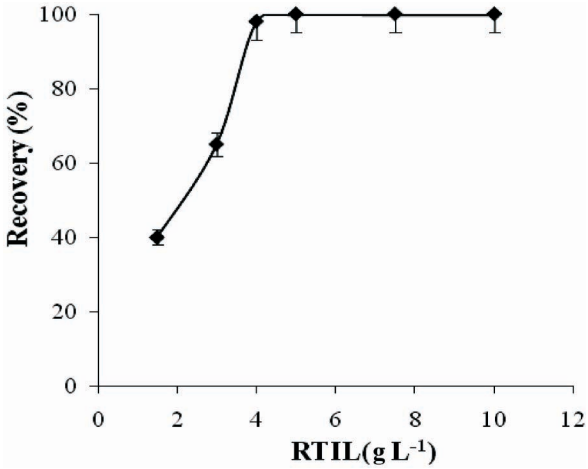

Fig. 3. Effect of amount of ionic liquid on the recovery. Conditions: Concentration of nickel: 40 ng L^{-1}; extraction time: 10 min; pH = 6; centrifugation rate: 3500 rpm; sample volume: 20 mL; N = 3.

tively when up to 20 mL of the sample solution was used. At higher a volume the recoveries are decreased (Fig. 4). It was also noticed that higher sample volumes partially solubilized the RTIL phase, leading to non-reproducible results. Therefore sample volume of 20 mL was selected for further experiments and the enrichment factor (EF) 100 was achieved.

Effect of eluent solvent

1-Butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$) has high viscosity, so direct automatic injection of nickel into the ETAAS furnace was not possible, therefore back-extraction of Ni^{+2} ion with an acidic aqueous solution was needed. Therefore diminishing of the media pH (pH < 2) leads to low stability conditions of the Ni-DDC complex, yielding its dissociation and further releasing of Ni^{2+} ion into the aqueous phase. Different mineral acids such as HCl, HNO_3 and $HClO_4$ were studied for Ni^{2+} back-extraction from the RTIL phase into a minimum aqueous volume. The study showed that 200 μL of 1 mol L^{-1} HNO_3 was the best eluent to quantitative extracts nickel from the RTIL phase.

Analytical performance

Performance characteristics of the method were obtained by processing standard solution of nickel and are summarized in Table 2. Under the optimized conditions, the calibration graph was linear from 20 to 700 ng L^{-1} of nickel. The equation of calibration graph was $H = 0.0124C + 0.005$ (where H is the peak height and C is the concentration of nickel (ng L^{-1}) in aqueous phase) with the correlation coefficient of 0.9997. The limit of detection (LOD) of the proposed method for the determination of nickel was studied under the optimal experimental conditions. The LOD was calculated as LOD = kS_b/m, where k is equal to 3 according to the desired confidence level (95%), S_b is the standard deviation of the blank signal and m is the slope of the analytical curve. The LOD was found to be 5.0 ng L^{-1}. The reproducibility of the proposed method for the extraction and determination of 20 ng L^{-1} nickel from 20 mL water was investigated and for 8 replicate measurements a R.S.D. of 5.6% was obtained.

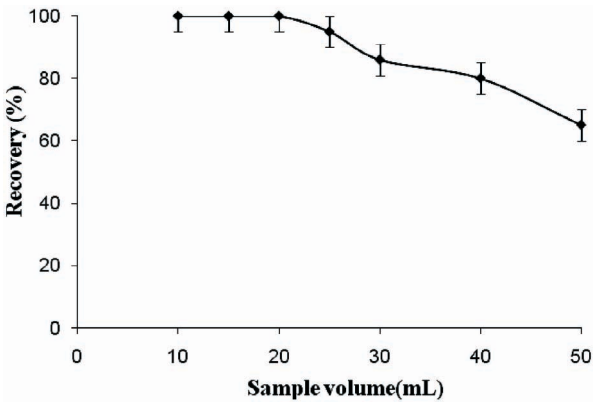

Fig. 4. Effect of sample volume on the recovery. Conditions: Concentration of nickel: 40 ng L^{-1}; amount of ionic liquid: 0.1 g; extraction time: 10 min; pH = 6; centrifugation rate: 3500 rpm; N = 3.

Table 2. Analytical characteristic of the method

Dynamic range	20-700 ng L^{-1}
Correlation coefficient (R^2)	0.9997
Limit of detection	5 ng L^{-1}
R. S. D (%) (n = 8)	5.6 (at 20 ng L^{-1})
Enrichment factor	100

Interference studies

The effect of concomitant ions regularly found in water samples was evaluated. Analytical ET-AAS is very specific technique and low sensitive to interferences. Then, the interferences effects occurring in this procedure are mainly related to the extraction during the preconcentration step applied to the target samples. Considering the samples of interest, and the most probable metal ions reported the effect of potential interfering ions on the determination of nickel was investigated. For this study, different amounts of ionic species tested were added to a 20 mL of 20 ng L^{-1} solution of Ni^{2+} and the general procedure was followed. The results showed that many ions such as, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sr^{2+}, Fe^{2+}, Cr^{3+}, Co^{2+}, Al^{3+}, V^{3+} and As^{5+} could be tolerated up to at least 20 μg L^{-1}. A contaminant ion was considered to interfere if it resulted in an analytical signal variation of ± 5%. The ions normally present in water such as Na^{+}, Ca^{2+}, Mg^{2+} do not interfere under the experimental conditions used. Thus, they are not extracted from the aqueous solution. Furthermore, their contribution to the ionic strength of the system is insignificant and does not affect the extraction efficiency.

Method validation

In order to demonstrate the accuracy of the proposed method, a recovery study was performed evaluating any

matrix interferences and/or possible analyte losses during the sample pre-treatment of different certified reference materials. The certified values and the obtained analytical results are presented in Table 3. Metal contents established by the present procedure agree well with the certified value. Results indicate the applicability of the developed procedure in nickel determination free of interference. To test the applicability of the procedure developed, it was applied to the extraction and determination of nickel content from different samples: tap water, serum and urine. All the samples were treatment and analyzed following the procedure described before. The average concentration of Ni(II) found was taken as a base value. Then, increasing quantities of nickel were added to the other aliquots of sample and the analyte was determined by the recommended method. As shown in Table 4, analyte recoveries were all around 100%.

CONCLUSIONS

A simple, precise and accurate method was developed for selective separation, preconcentration and determination of nickel from various complex matrices. In this method we used the dispersive liquid-liquid microextraction method with room temperature ionic liquid for the determination of trace amount of nickel in tap water, serum and urine samples. RTILs are receiving an upsurge of interest as green solvents; primarily as replacements for conventional media in chemical processes and clean industrial technology with significant cost and environmental benefits. The results of this work show the possibility of using the NaDDC-[C_4MIM][PF_6] system for nickel preconcentration, since quantitative extraction (98%) and a preconcentration factor of 100 were achieved. The method applied provides good precision with relative standard deviations lower than 6% and high accuracy obtained with the quantitative recoveries of spiked analyte. Thus, it may be concluded that the method is an effective approach in preconcentration and selective separation of nickel from the complex matrices including tap waters, serum and urine samples.

Table 3. Analytical results of nickel determination in certified reference material

Sample (CRM)-LGC	Certified (ng L^{-1})	Added (ng L^{-1})	Found[a] (ng L^{-1})	Recovery (%)
SeroB1-lyophilised human blood	20	50	68 ± 0.4	97.1

[a] Mean value ± standard deviation based on three replicate measurements.

Table 4. Analytical results of nickel determination in real samples

Sample	Added (ng L^{-1})	Found (ng L^{-1})[a]	Recovery (%)
Tap water	-----	20 ± 0.5	-----
	10	29 ± 0.4	97
	20	38 ± 0.8	95
Serum	-----	33 ± 0.5	-----
	10	42 ± 0.9	97
	15	46 ± 0.7	96
	25	59 ± 0.6	101
Urine	-----	53 ± 0.6	-----
	10	62 ± 0.4	98

[a] Mean value ± standard deviation based on three replicate measurements.

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