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

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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 $[C_4MIM][PF_6]$, 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 $\mu g\,L^{-1}$, 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.

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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 $\mu g\,L^{-1}$ [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.

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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 $Ni(NO_3)_2 \cdot 6H_2O$ 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 ^1H 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 elsewhere [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 ^1H 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 $K_{\beta 2}$ = 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