ISSN : 0974-7419 Volume 14 Issue 2

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 14(2) 2014 [55-60]

Differential pulse polarographic determination of ultra trace nickel in natural waters after solid phase extraction

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ABSTRACT

A highly selective and sensitive anodic stripping differential pulse polarographic method for determination of ultra trace amounts of Ni^{2+} ions in water samples is proposed. The method is based on the separation and preconcentration of Ni^{2+} on an octadecyl bonded silica membrane disk modified by a recently synthesized Schiff base, 2-((E)-(2-(2-(pyridine-2-yl) ethylthio) ethylimino) methyl)-4-bromophenol (PYTABr) at pH=7. The retained nickel on the membrane was eluted with 10 ml 0.1 M HNO_3 and determined by anodic stripping differential pulse polarography. Extraction efficiency, influence of sample volume and eluent flow rates, amount of ligand, amount of eluent for elution of Ni^{2+} ions from membrane disk, pH, breakthrough volume and limit of detection have been evaluated. The effect of foreign ions on the percent recovery of heavy metal ions has also been studied. The limit of detection of proposed method for Ni^{2+} was found to be 3.2ng. L^{-1} and also an enrichment factor of 200 were obtained. The maximum capacity of the membrane disks modified by 5 mg of PYTABr was found to be 325±13.31 μg Ni^{2+}.

The proposed method has been applied to the determination of nickel in several water samples with satisfactory results.

KEYWORDS

Nickel (II);
SPE;
Preconcentration;
Shiff base;
Stripping voltammetry.

INTRODUCTION

The determination of heavy metal ions, such as nickel, in environmental and biological samples is very importance and can hardly be overemphasized because they have undoubtedly a serious potential hazard to the human organism. Nickel was long thought to be essential to plants and some domestic animals[1], but not considered to be a metal of biological importance until 1975, when Zerner discovered that urease was a nickel enzyme[2-3]. It is known that inhalation of nickel and its compounds can lead to serious problems, including nasopharynx, lung and dermatological diseases and malignant tumors[4-5]. So, separation of toxic Ni(II) is of intense current interest in research and environmental cleanup.

Essentiality of nickel to man does not yet seem to have been demonstrated. More attention has been focused on the toxicity of nickel in low concentration, such as the fact that nickel can cause allergic reactions and that certain nickel compounds are carcinogenic[6]. Nickel is one of the essential micronutrients for plants, animals, and humans, but is toxic at elevated concentrations[7-8]. Compared with other transition metals, nickel is a moderately toxic element[9,10]. For example, nickel can cause a skin disorder known as nickel-eczema[11]. Therefore, the accurate and sensitive determination of nickel in environmental samples is very important.

The main sources of nickel in aquatic systems are from dissolution of rocks and soils, biological cycles, atmospheric fallout, and especially industrial processes and water disposal[12]. The maximum recommended concentration of nickel ion in drinking water for livestock is 2.5mg. L^{-1}[13]. The upper human drinking water consumption limits are evens less. The development of reliable, yet affordable, analytical approaches for the determination of Ni^{2+} in low concentration levels seem worthwhile.

The traditional preconcentration and separation methods for metal ions are liquid–liquid extraction, coprecipitation, and ion-exchange, etc. These methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems[14]. Nowadays, the SPE is being widely utilized for preconcentration or separation of metals due to the following advantages. These include[15]: (1) higher enrichment factors; (2) absence of emulsion; (3) safety with respect to hazardous samples; (4) minimal costs due to low consumption of reagents; (5) flexibility; (6) ease of automation.

Anodic stripping differential pulse polarography is a sensitive technique for the determination of trace amount Ni^{2+} in aqueous media. This technique reduces consumption and exposure to solvent, disposal costs, and extraction time. Octadecyl bonded silica (ODBS) membrane disks have been utilized for the extraction and analysis of many different organic and environmental matrices[16,17]. Moreover, these membrane disks modified by suitable ligands are successfully used for the separation and sensitive determination of metal ions[18,19].

The Schiff bases as poly dentate ligands are known to form very stable complexes with transition metal ions[20]. In the present work, we have developed an anodic stripping differential pulse polarographic method for determination trace amounts of Ni^{2+} ions from aqueous media using ODBS membrane disks modified with a newly synthesized Schiff base, 2-((E)-(2-(2-(pyridine-2-yl)-ethylthio)ethylamine)methyl)-4-bromophenol (PYTABr) (Figure 1).

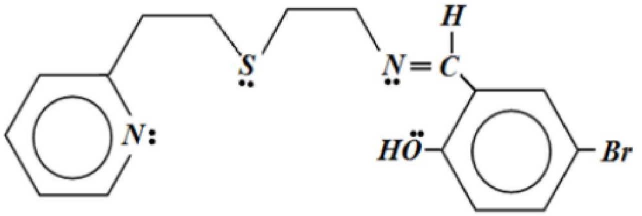

Figure1 : Chemical structure of PYTABr ligand

EXPERIMENTAL

Standard and buffer solutions

Dissolve 0.2000 g of high purity nickel in 10 ml concentrated nitric acid, dilute with doubly distilled water to volume in a 1000 ml calibration flask and mixed. Working solutions were prepared by appropriate dilution of the stock solution in doubly distilled water.

Phosphate buffer solution (pH = 7) have prepared by dissolve 0.375 g of potassium dihydrogene phosphate and 0.556 g of disodium hydrogen phosphate in doubly distilled water and dilute to 100 ml in a calibrated flask. All other reagents were of analytical grade reagents.

Apparatus

Voltammetric measurements were taken with a Metrohm 757 VA comp trace, with a three electrode system consisting of a hanging mercury drop electrode (HMDE) as the working electrode, an Ag/AgCl reference electrode and platinum counter electrode. The operating parameters were set as recommended by the manufacturer. The pH was determined with a seven multi model Metrohm pH meter with a combined glass-calomel electrode.

Filteration

Extractions were performed with Empore membrane disks (47 mm diameter and 0.5 mm thick) containing ODBS (8 mm particles, 6 nm pore size) from 3M. The typical composition of the disks was 90% w/w ODBS and 10% w/w PTFE fibers. The disks were used in conjunction with a standard S&S 47 mm filtration apparatus connected to a vacuum. In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be done before its use.

Thus, after placing the membrane disk in the filtration apparatus, 10 mL methanol was poured onto the disk and immediately drawn through the disk by applying a slight vacuum to remove all contaminants arising from the manufacturing process and the environment. After all of the solvent has passed through the disk, passing air through it for a few minutes dried it. This procedure is especially important for the disks, which are used for the first time. After drying the disk, a solution of 5 mg PYTABr in 3 ml Acetonitril was introduced onto the disk and allowed to penetrate inside the solid phase completely.

Then the modified disk was washed and preconditioned by passing a 10 mL portion of buffer solution (pH = 7) to prewet the surface of the disk prior to the extraction of Ni^{2+} ion from aqueous samples. In order to ensure complete wetting of the disk with the buffer solution it is preferable to leave extra buffer above the disk rather than to allow any air to contact the surface of the disk.

Extraction, elution and determination

The general procedure for the extraction of Ni^{2+} ion on a membrane disk was as follows: 100 mL of the sample solution containing 2 mL of phosphate buffer (pH = 7) and 10μg Ni^{2+} was passed through the modified membrane, at 20 $mL.min^{-1}$ flow rate. The disk was dried completely by passing air through it. After the extraction, a 25×200 mm test tube was then placed under the extraction funnel. The nickel ion were stripped from the modified disk using 2×5 mL of 0.1 M nitric acid at 5 $mL.min^{-1}$ flow rate and nickel concentration was determined by anodic stripping differential pulse polarography.

For extraction of water samples, a 1000 ml aliquot was first passed through a filter paper to remove suspended solids. Then the filtrate was passed through an ODBS membrane disk without PYTABr to remove organic compounds that may be present in the water and then complete the determination as recommended procedure.

Anodic stripping differential pulse polarography

In the present work, the differential pulse polarogram for nickel was obtained in nitric acid medium as supporting electrolyte. A sample solution was transferred into polarographic cell, after the removal of dissolved oxygen by passing purified nitrogen gas for 3 min., the polarograms were recorded by sweeping the potential from -1.2 to -0.1 V versus reference electrode. Nickel was deposited on a hanging mercury drop electrode at -0.70 V for 90 s, while stirring the solution. The amalgamate nickel was stripped by differential pulse polarography by scanning of potential of the electrode a scan rate of 0.0132 $V.s^{-1}$ and pulse amplitude of 0.04 mV.

RESULTS AND DISCUSSION

Choice of eluent

In order to choose a proper eluent for the retained Ni^{2+} ion after extraction of 10 μg of nickel in a 100 ml buffered solution by the modified disks, the nickel ion were stripped with 2×5 mL of different concentrations of various mineral acids, and the results are listed in TABLE 1. Results showed that all acids could afford the quantitative elution of Ni^{2+} from the modified disk. Subsequent quantitative elution of the complex was carried out with 0.1 M HNO_3 solution. The reason for choice of nitric acid as eluent was that nitrate ion is reported to be a more acceptable matrix for voltammetric experiments than chloride and sulfate ions.

TABLE 1 : Percent recovery of Ni^{2+} from modified membrane disk using different stripping solutions

eluent	Concentration		
	0.1	0.5	1.0
HCl	77.9	75.4	73.0
H_2SO_4	66.0	61.0	66.2
HNO_3	100.2	69.9	94.0

Effect of pH

The influence of the pH of aqueous sample on the recovery of 10μg of Ni^{2+} from 100 ml solution was studied in the pH range 2 - 8. The pH was adjusted by using 0.01 M of either nitric acid or sodium hydroxide solutions. The results obtained are shown in Figure 2. Maximum and constant retention of Ni^{2+} ion by the modified membrane disk was obtained in the pH range 6 – 7, therefore, the pH 7 was chosen. Higher pH values (>8) were not tested because of the possibility of the hydrolysis of ODBS in the disks. Addition of 1-3 ml phosphate buffer was sufficient for pH adjustment.

Hence, an addition of 2 mL was chosen.

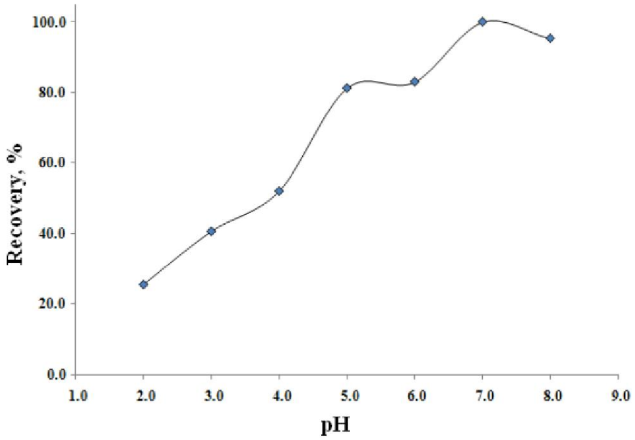

Figure 2 : Effect of pH on the extraction of Ni^{2+} by the modified membrane disk.

Effect of flow rates

The flow rates effect of the sample and stripping solutions on the retention and recovery of Ni^{2+} ion was investigated. It was found that, in the range of 5-35 mL.min$^{™1}$, the retention of nickel by the membrane disk was not considerably affected by the sample solution flow rate. Similar results for the extraction of organic and inorganic[21,22] materials by ODBS disks have been reported in the literature. The flow rate of sample was maintained at 20 mL.min$^{™1}$ through the experiment. Quantitative stripping of nickel ion from the disk achieved in a flow rate range of 1-10 mL.min$^{™1}$, using 2×5 ml of 0.1 M HNO_3 as a stripping solution. At higher flow rates, a large volume of eluent was necessary for the quantitative stripping of Ni^{2+} ion. Hence, subsequent experiments were carried out with a flow rate of 5 mL.min$^{™1}$.

Effect of ligand amount

In order o investigate the optimum amount of ligand on the quantitative extraction of nickel by the membrane disk; extraction of 10μg of Ni^{2+} from 100 mL solution under optimal conditions was conducted by varying the amounts of ligand from 1 to 6 mg. In all cases, the extraction of nickel was found to be quantitative. Hence, subsequent SPE experiments were carried out with 5 mg of the ligand (Figure 3).

Analytical performance

Breakthrough volume

The measurement of breakthrough volume is important in solid phase extraction, because breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 10μg nickel in 100, 300, 700, 1000, 1500, and 2000 mL of water and the recommended procedure was followed. In all cases, the extraction by modified disk was found to be quantitative. Thus the breakthrough volume for the method should be greater than 2000 mL. Consequently, by considering the final elution volume of 10 mL and the sample solution volume of 2000 mL, an enrichment factor of 200 was easily available.

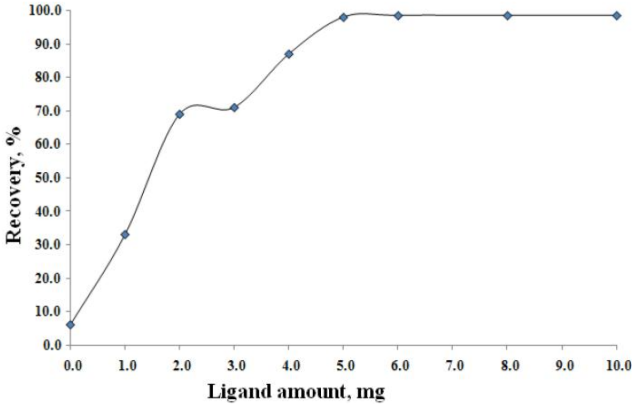

Figure 3 : Effect of ligand amount

Sorption capacity

The maximum capacity of the disk modified by 5 mg PYTABr was determined by passing 50 mL portions of an aqueous solution (pH = 7) containing 500μg Ni^{2+} through the disk, followed by determination of the retained Ni^{2+} ions using polarograph. The maximum capacity of the disk obtained from three replicate measurements was 325(±13.31) μg of nickel on the disk.

Limit of detection

The limit of detection (LOD) of the proposed method for the determination of nickel was studied under the optimal experimental conditions. The LOD based on 3σ of the blank, is 3.2ng.L^{-1}. The reproducibility of the proposed method for the extraction and determination of 10μg nickel from 100 ml water was also studied. The results obtained on 10 replicate measurements revealed a RSD of 2.61%.

Effect of diverse ions on sorption of nickel

In order to investigate the selective separation and determination of nickel ion from binary mixtures with diverse metal ions, a 100mL aliquot solution containing 10µg Ni^{2+} and milligram amounts of other cations was taken and recommended procedure was followed. The results are summarized in TABLE 2. The result show that the nickel ion in the binary mixture are retained almost completely by modified membrane disk, even in presence of up to about 100 mg of the diverse ions. It is interesting to note that retention of other cations by the disk is negligible and they can be separated completely from the nickel ion.

TABLE 2 : Effect of diverse ions on the recovery of 10µg of nickel ion.

Ion	Amount taken(mg)	Recovery, %
Na^+	100	97.3
K^+	100	98.8
Ca^{2+}	40	96
Mg^{2+}	40	98.6
Cu^{2+}	10	98.6
Mn^{2+}	5	98.1
Fe^{3+}	5	97.3
Co^{2+}	2	97.8
Zn^{2+}	2	98.2

TABLE 3 : Recovery of nickel added to 1000 ml of different water samples (pH = 7.0)

sample	Ni^{2+} added(g)	Ni^{2+} determined (g L^{-1})	%Recovery
Tap water	0	1.5	-
	5	6.2	94
	10	11.4	99
Agricultural water	0	3.17	-
	5	8.22	101.9
	10	13.06	98.9
River water	0	1.12	-
	5	6.09	99.4
	10	11.01	98.9
Synthetic sample (K^+,Mg^{2+},Ca^{2+},Fe^{3+})	0	-	Nd
	5	4.73	93.2
	10	9.74	93.9

Values in parenthesis are RDS$_s$ based on three replicate analysis; nd : not determined

Analysis of water samples

To test the applicability of the procedure developed, it was applied to the extraction and determination of nickel content from different water samples. Tap water and river water (Qazvin), agricultural water sample, and synthetic sample were analyzed (TABLE 3). As seen, the result of all samples analysis shows that, in all cases, the nickel recovery is quantitative.

CONCLUSION

Results presented in this work well demonstrate the tremendous possibilities offered by the solid phase extraction of trace amounts of Ni^{2+} in water samples using octadecyl-bonded silica membrane disks modified by a newly synthesized Schiff base, 2- ((E) - (2 (2- (pyridine -2 - yl) - ethylthio) ethylamine) methyl) - 4bromophenol (PYTABr) and its determination by anodic stripping differential pulse polarographic method. The method developed is a precise and accurate alternative to conventional procedures for determining nickel in water samples. In conclusion, the developed SPE method has been successfully used on a routine basis and allows the quantization in water samples. It opens exciting possibilities for the determination of nickel in other samples and by other techniques, which some studies on this direction are now in progress in our laboratory.

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