



Original scientific paper

## Monitoring of nickel(II) in biological samples using 4-(2-hydroxy-phenylethamino)benzene-1,3-diol by extractive differential pulse polarography

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### Abstract

A novel analytical reagent, 4-(2-hydroxyphenylethamino)benzene-1,3-diol was synthesized for determination of nickel(II) in biological samples and plant materials by extractive differential pulse polarography. The analysis of nickel(II) was carried out by extracting the nickel(II)-(4-(2-hydroxyphenylethamino)benzene-1,3-diol) complex from chloroform prior to injecting into the instrument. The electrochemical behavior of nickel(II) complex was studied under optimum parameters like effect of pH, pulse amplitude, scan rate and choice of solvent. The calibration curve was constructed in the concentration range of 0.05-42  $\mu\text{g mL}^{-1}$  at pH 4.0 (acetate buffer) with a correlation coefficient of 0.992, respectively. Interference of diverse ions was also investigated during the analysis of nickel(II) to optimize the conditions. The accuracy and validity of the proposed method were checked by the analysis of Certified Reference Materials which is distributed by the National Institute of Standard Technology

### Keywords

Monitoring, nickel(II), Extractive differential pulse polarography

### Introduction

Nickel(II) exposure into environment of more than 0.05 mg/kg has a toxic effect on human beings and animals [1,2]. Nickel(II) has a wide range of applications including but not limited to batteries, welding rods and wires, electronic equipment, pigment for paints, ceramics, consumer products, steel, magnets, and it can be the source of several diseases. Considering these toxicological considerations, monitoring of nickel(II) is of great importance in the field of the human health or environment and it is highly desirable to develop analytical methods at trace level.

Various analytical methods have been proposed for the monitoring of nickel(II) in environmental matrices such as spectrophotometry [3,4], X-ray fluorescence spectrophotometry

[5], atomic absorption spectrometry [6], inductively coupled plasma atomic emission spectrometry [7,8], inductively coupled plasma mass spectrometry [9], voltammetry [10,11] and chromatography [12]. Most of these techniques, however, are either very expensive, suffer from many interferences or require highly skilled technicians. On the other hand, differential pulse polarography (DPP) is an old but a conventional approach in trace analysis. In addition, the concentration of nickel is generally at very low level in environmental samples and it is not possible to determine in a simple complex sample concentration below the quantification limit of the instrument used. Hence, we have developed a simple, economic sensitive differential pulse polarography method, after extracting the metal complex from chloroform in biological samples and plant materials. The metal complex was formed by interaction of nickel(II) with newly synthesized analytical reagent 4-(2-hydroxyphenylethamino)benzene-1,3-diol at ordinary laboratory conditions. The various parameters have been evaluated. The developed method can be employed for efficient determination of nickel(II) at ppm levels. The results of analysis obtained were compared with those obtained by the well knowing method with certified values of nickel(II). The proposed method is found free from various interferences and successfully applied for determination of nickel (II) in biological and plant materials.

## Experimental

### Apparatus

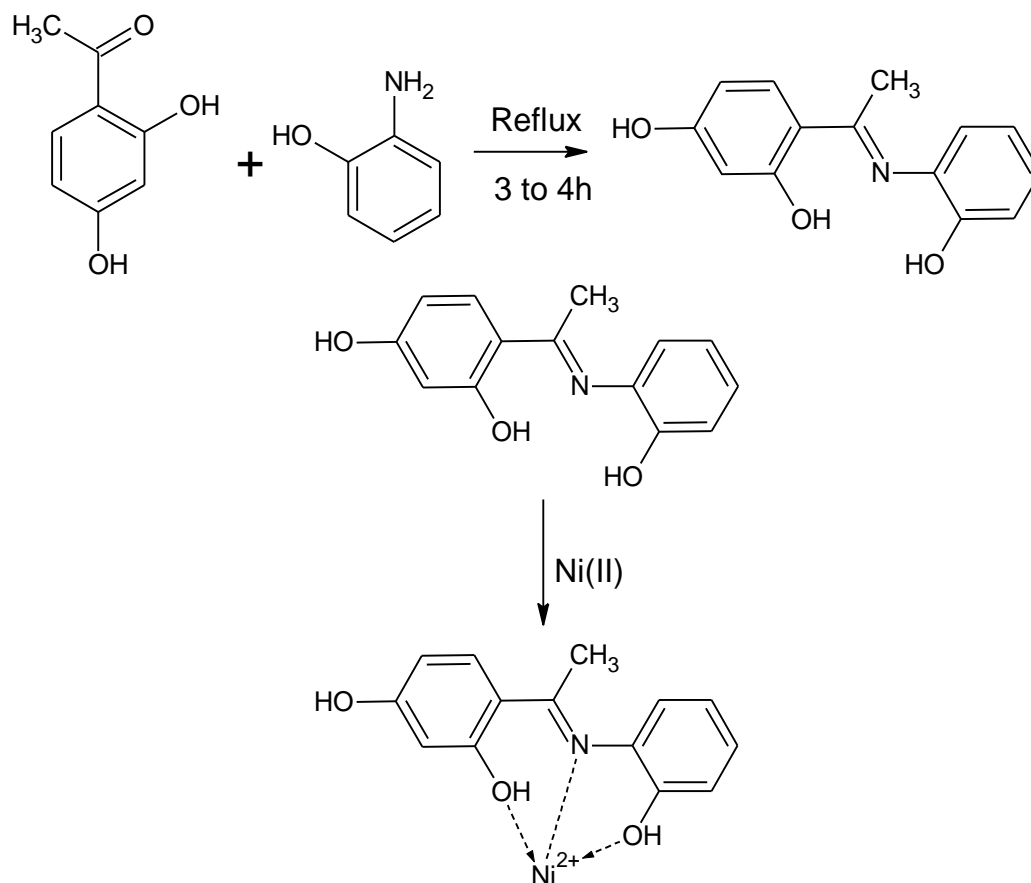
An Elico CL-362 model polarographic analyzer was used for differential pulse polarography (DPP) measurements and the three-electrode system consisted of a hanging mercury drop working electrode, Ag/AgCl/KCl reference electrode and a platinum wire as the auxiliary electrode. The entire system was outfitted with the LX 300<sup>+</sup> X-Y recorder. Cyclic voltammetric measurements were carried out by the Metrohm 757 VA Computrace Model AFRDE 4 potentiostat and MSRX speed control unit supplied from Pine Instrument Company (USA) coupled with digital electronics 200X-y/t recorder. An Elico Li-129 Model glass-calomel combined electrode (Purchased from Elico Ltd, Chennai, India) was employed for measuring pH values. All experiments were performed at 25±1 °C.

### Reagents

Analytical reagent grade chemicals and doubly distilled water were used throughout the experiments. 2,4-dihydroxy acetophenone, 2-amino phenol, organic solvents, HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, CH<sub>3</sub>COOH, C<sub>2</sub>H<sub>3</sub>NaO<sub>2</sub> were purchased from Merck Chemicals. A stock solution of nickel(II) (0.01 M) was prepared by dissolving 2.377 g of NiCl<sub>2</sub> 6H<sub>2</sub>O in double distilled water in 100 mL volumetric flask. The working standard solution was freshly prepared by diluting the stock solution with double distilled water at the time of analysis. A stock solution of 0.001 M solution of 4-2-HPEDB-1,3,D was prepared by dissolving an appropriate amount of the reagent in 100 mL of methanol. The working solution was prepared by its appropriate dilution with the same solvent. Acetate buffer solutions of pH values ranging from 3.0–11.0 were prepared as appropriate ratios of 0.1 M acetic acid and 0.1 M sodium acetate (13.6 g/L).

### Synthesis of 4-(2-hydroxyphenylethamino)benzene-1,3-diol (4-2-HPEDB-,3,D)

The equimolar ratio of 2,4-dihydroxy acetophenone (1.0 g) and 2-aminophenol (1.0 g) in methanol mixture was refluxed for three to four hours and the contents were cooled at room temperature creating an orange-red color precipitate. The resulting precipitate was filtered (Whatman filter paper No. 44) and washed with 50 mL ethanol. The crude solid was recrystallized from aqueous ethanol and dried on CaCl<sub>2</sub>, with a Yield=97 % and M.P: 115-120 °C. Infrared absorption spectrum gave the following peaks (cm<sup>-1</sup>, KBr pellet): 3375.3 (O-H), 2900 (C-H), 1601 (C=N) and 1465.9 and 1280 (C-O, O-H). The synthesis of analytical reagent and the metal complexation with the reagent are shown in the Scheme 1.



**Scheme 1.** Synthesis and complexation of 4-2-HPEDB-1,3-D with nickel(II)

### General procedure

The aliquot of the working standard solution (0.001 M) containing 1–100  $\mu\text{L}$  (0.2377 g) of metal ion was taken into 25 mL volumetric flask what was followed by addition of the solution containing 5 mL of acetate buffer solution (pH 4.0) and 2 mL of reagent (soluble in methanol) into the mixture. The mixture was shaken with 5 mL portions of chloroform for 30 s and allowed to stand for 5–10 min. The organic layer was collected and transferred into the polarographic cell, diluted with 9 mL of acetate buffer and then deoxygenated with nitrogen gas for 10 min. After recording the polarogram, a small increment (0.2 mL) of standard solution was added to the cell, treated for one min and the polarogram was again recorded under similar conditions. In the present study, the greatest precision was obtained at pH 4.0 having the correlation factor of 0.992 and RSD 0.7 % with a drop time of 2 sec, pulse amplitude of 50 mV, scan rate of 12  $\text{mV s}^{-1}$  and the applied potential of  $-615.0$  mV.

### Sample collection

Tirupati, city located in the south of India was chosen as the study area for the sample analysis. It is a rapidly growing city which is widely known at the global level. The arrival of approximately 50,000-60,000 pilgrims per day to visit the Lord Balaji Temple (Tirumala) is mainly responsible for threatening the natural beauty of this holy town. At the same time, several small and medium scale industries are situated in the suburban fringes of Tirupati town. For this reason, this holy pilgrim center has been chosen as the potential collection area for the present study. The biological and plant samples were collected from different locations of the study area in and around Tirupati. All necessary and possible precautions were taken at various stages starting from sample containers, sample collection and storage, processing and analyzing the samples.

### Application

The hair samples were washed with acetone two to three times in a beaker with continuous stirring and dried in an electric oven at 70 °C for four hours. 2.0 g of the sample was weighed and taken in a beaker. Then, the (1:1) mixture of nitric acid and perchloric acid was added and the mixture was heated on a hot plate. The solution was evaporated to near dryness. The ash was taken up with 5 mL of HCl (35.5 %) and evaporated to dryness. The residue was taken up in 2 mL HCl (35.5 %) then filtered and made up to 25 mL with water. Suitable volumes of these solutions were taken for determination of nickel(II) as described above and the results are shown in Table 1.

**Table 1.** Determination of nickel(II) in biological sample

Sample	Certified values	Reported method [18]	R.S.D, % (n=5) <sup>a</sup>	Present method Extractive-DPP	R.S.D, % (n=5) <sup>a</sup>
NIES No.5 Human hair: Pb(6.0), Cd(0.20), Sb(0.07), Zn(169), Al(240), Sc(0.05), Fe(225), Mg(208), Hg(4.4), Co(0.10), Rb(0.19), K(34), Mn(5.2), Cu(16.3), Ti(22), Ca(728), Cr(1.4), Ba(2.2), Se(1.4), Na(26), Sr(2.3).	1.80	1.90	0.12	1.96	0.65

<sup>a</sup>Mean values for five determinations

### Analysis of plant material

The freshly collected *Pisum sativum* (Hulls), *Mangifera indica*, *Eucalyptus*, *Azadirachta indica* leaves (5.0 g each) samples were placed in a 250 mL beaker, and a solution of concentrated H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> 1:1 (v/v) (10 mL) was added. This mixture was heated until the solution was clear. The solution was filtered (Whatman filter paper No 44) off and concentrated in a porcelain bowl up to 5 mL, then cooled and diluted to 50 mL with deionized double-distilled water. The general procedure was then applied to 1 mL of this solution and the obtained results were presented in Table 2. In addition, plant tissues like *Umbilicaria muhlenbergii* has been examined in detail followed by the reference procedure [13]. The obtained results were compared with the reported method as shown in Table 3.

**Table 2.** Determination of nickel(II) in plant material

Samples <sup>a</sup>	AAS method [19]	R.S.D, % (n=5) <sup>b</sup>	Present method	R.S.D, % (n=5) <sup>b</sup>
<i>Pisum sativum</i> (Hulls)	2.060	0.003	2.065	0.068
<i>Mangifera indica</i> leaves	2.150	0.004	2.153	0.072
<i>Eucalyptus</i> leaves	1.038	0.002	1.044	0.013
<i>Azadirachta indica</i> leaves	1.481	0.005	1.489	0.015

<sup>a</sup> Samples collected from Acharya N. G. Ranga Agricultural college Tirupati, A.P, India;

<sup>b</sup> Mean values for five determinations

The accuracy and precision of the present method were validated by analyzing the Certified Reference Materials (CRM's) which was distributed by the National Institute of Standard Technology (NIST) of Rice Flour (NIES-CRM-10A), Wheat Flour (ARC/CL-WF), and Rye Bread Flour (CSRM-12-2-05). Inter calibration was performed by using above materials and the analytical results obtained from the present method strongly agreed with the Certified Reference Materials (CRM's) and the data were mentioned in Table 5.

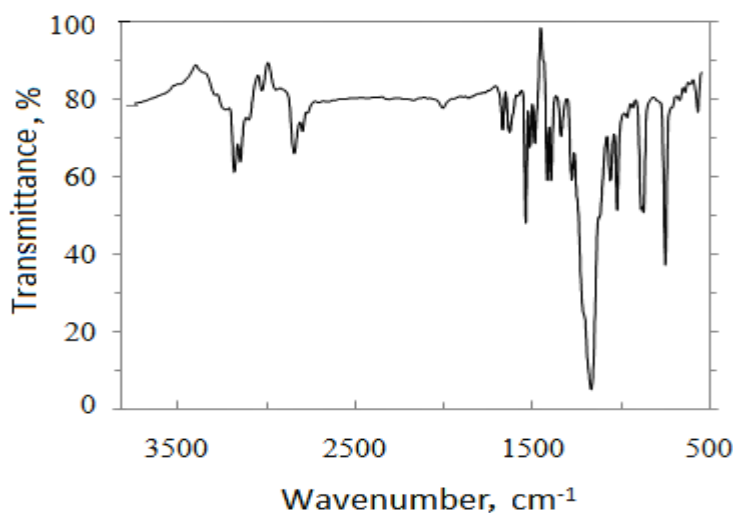
**Table 3.** Determination of nickel(II) in plant tissues (*Umbilicaria muhlenbergii*) by differential pulse polarography.

Samples	Nickel(II) content of zone, $\mu\text{g/g}$	
	Proposed method	Reported method(DPP) [13]
Set 1	$12 \pm 2$	$13 \pm 3^a$
Set 2	$14 \pm 6$	$12 \pm 5^a$
Set 3	$792 \pm 50$	$790 \pm 60$
Set 4	$635 \pm 40$	$640 \pm 50$

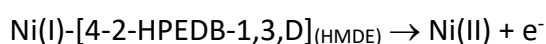
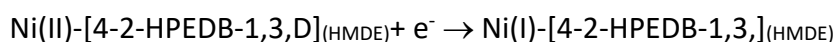
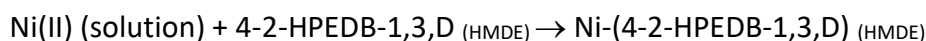
<sup>a</sup>DPP+DMG analysis

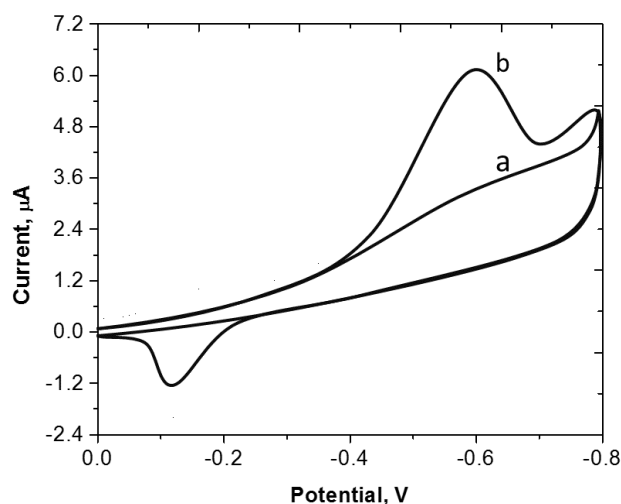
## Results and discussion

The analytical reagent 4-2-HPEDB-1,3,D is a ligand having chelating functional groups that form a complex with Ni(II) ions at pH 4.0 (acetate buffer). Figure 1 shows the typical FTIR spectrum of Ni(II)-(4-2-HPEDB-1,3,D) complex. In the FTIR spectra of the complex, a strong peak was observed in the region of  $1610\text{--}1640\text{ cm}^{-1}$ , which is ascribed to involvement of nitrogen donor atoms of azomethine ( $-\text{C}=\text{N}-$ ) in coordination to the Ni(II) ions [14]. The band at  $524\text{ cm}^{-1}$  observed for the Ni(II)-(4-2-HPEDB-1,3,D) complex is assigned to  $\nu(\text{M}-\text{O})$ . The stretching vibration of the free ligands  $\nu(\text{O}-\text{H})$ ,  $3430\text{--}3464\text{ cm}^{-1}$  was not observed, suggesting deprotonation of hydroxyl groups and formation of Ni-O band [15]. The bands observed for the complexes between  $720\text{--}620$  and  $564\text{--}495\text{ cm}^{-1}$  were metal sensitive and are assigned to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  [16], respectively.

**Figure 1.** FTIR spectra of Ni(II)- [4-2-HPEDB-1,3-D] complex

Cyclic voltammetry is widely used for the characterization of electrochemically active systems. Figure 2 shows the cyclic voltammogram of nickel(II)-[4-2-HPEDB-1,3,D] system at a scan rate of  $12\text{ mV s}^{-1}$  in the acetate buffer (pH 4.0). In the forward scan, the cathodic peak potential ( $E_{\text{cp}}$ ) observed at  $-0.62\text{ V}$  corresponds to reduction of nickel(II)-4-2-HPEDB-1,3,D complex. The anodic peak potential ( $E_{\text{ap}}$ ) is observed at  $-0.12\text{ V}$  and corresponds to oxidation of nickel(II)-[4-2-HPEDB-1,3,D] complex generated in the anodic step. The anodic and cathodic peak potential difference ( $\Delta E$ ) is  $-0.50\text{ V}$ . The possible electrode mechanism can be described as follows:





**Figure 2.** Cyclic voltammogram of (a) Ni(II) and (b) Ni(II)-[4-2-HPEDB-1,3-D] complex at HMDE, acetate buffer (pH 4.0), scan rate  $50 \text{ mV s}^{-1}$

### Differential pulse polarographic studies

#### *Effect of pH, choice of solvent and scan rate*

The effect of pH is one of the important parameter for the investigation of nickel(II) and [Ni-(4-2-HPEDB-1,3,D)] complex by differential pulse polarography [17]. The pH studied varied in the range of 2.0 to 10.0 for [Ni-(4-2-HPEDB-1,3,D)] complex. The maximum peak current was obtained with pH 4.0 at peak potential  $-615 \text{ mV}$  as shown in Figure 3. When pH was increased from 2.0 to 10.0 at constant potential, the concentration of metal complex decreased. Therefore, the acetate buffer of pH 4.0 was suitable for determination of nickel(II) for better sensitivity and selectivity in further investigations. The extraction of the nickel(II)-[4-2-HPEDB-1,3,D] complex was tested in various organic solvents, such as toluene, benzene, n-butanol, dimethyl formaldehyde, carbon tetrachloride, cyclohexane and chloroform. Among the various solvents studied, the chloroform was selected as the most suitable for extraction of nickel(II)-[4-2-HPEDB-1,3,D] complex. This was because of its maximum peak current and greater extraction ability, due to polarity of complex. In addition, the scan rate was also changed from 4 to  $18 \text{ mV s}^{-1}$ . The peak current values increased with increasing scan rate up to  $12 \text{ mV s}^{-1}$  and after that the peak current decreased. Therefore, the scan rate of  $12 \text{ mV s}^{-1}$  was selected for further studies.

#### *Effect of foreign ions*

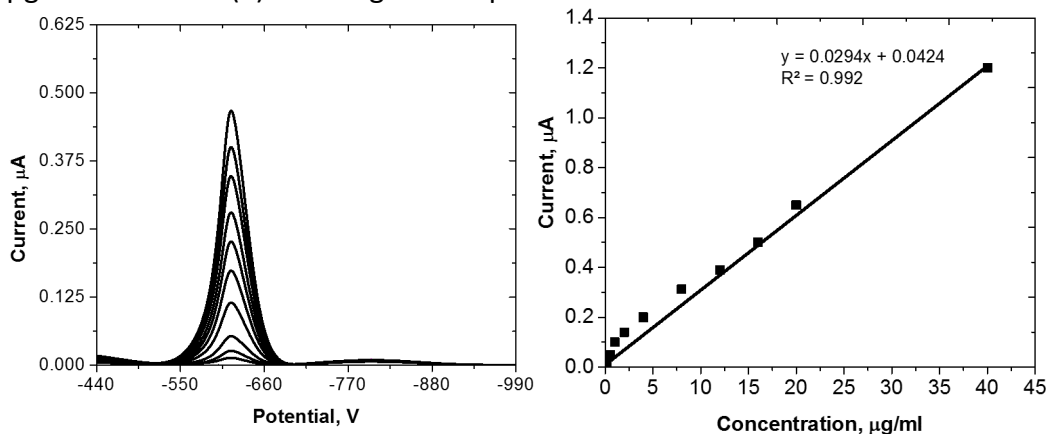
The selectivity of the proposed method was enhanced by the study of diverse ions for determination of nickel(II) in biological samples, plant materials and the results are shown in Table 4. Foreign ions were added to the solution containing  $10 \text{ µg mL}^{-1}$  of nickel(II) and measurements were taken under optimized conditions. Many of diverse ions were tolerated up to the maximum level by using suitable masking agents with the error of  $\pm 2 \%$  during the analysis of nickel(II). Though, some of the ions could be masked by addition of a sufficient amount of EDTA solution. Low concentrations of  $\text{As}^{3+}$  at  $40 \text{ °C}$  was also used to reduce the chromium ions. In addition,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  interference was eliminated by prior extraction with KI/Isobutyl methyl ketone. Sodium, potassium, chlorides, nitrites, sulfates, bicarbonates, phosphates and other remaining ions do not interfere with determination of trace metals up to  $50 \text{ µg mL}^{-1}$ . Almost all the results were quantified in the presence of diverse ions to elevate the feasibility and selectivity of the proposed method at appropriate amounts of nickel(II) solution, followed by the general procedure.

**Table 4.** Tolerable limits of diverse ions in determination of nickel(II) with error of  $\pm 2\%$ 

Diverse ions	Tolerable limit, $\mu\text{g mL}^{-1}$
$\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{NO}_3^-$	60,000
$\text{Al}^{3+}$ , $\text{PO}_4^{3-}$ , $\text{NO}_2^-$ , $\text{ClO}_4^-$ , $\text{SO}_4^{2-}$ ,	40,000
$\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , B(III), $\text{ClO}_3^-$ , $\text{BrO}_3^-$ ,	30,000
$\text{Mn}^{2+}$ , $\text{Fe}^{3+}$ , Ce(IV), Mo(VI),	20,000
V(V), Ti(IV), Cr(VI), Bi(III), U(IV), Cr(VI), $\text{Ba}^{2+}$	3,000
$\text{Cu}^{2+}$ , $\text{Pd}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ , $\text{La}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Cl}^-$ , Zr(IV)	1,000
$\text{Pb}^{2+}$ , Bi(III), $\text{Hg}^{2+}$ , $\text{Ag}^+$ , Th(IV), $\text{Sb}^{3+}$ , Sn(IV),	500
$\text{Au}^{3+}$ , Te(IV), Se(IV),	250
$\text{Co}^{2+}$	100

#### Calibration, detection limit and precision

The calibration curve was constructed based on the general procedure under optimized conditions at the concentration range of  $0.05\text{--}42\ \mu\text{g mL}^{-1}$  with the correlation coefficient of 0.992. The detection limit was found to be  $0.15\ \mu\text{g mL}^{-1}$  of the final solution by taking five individual replicates of nickel(II) solution which gives the relative standard deviation of 0.7%. Typical calibration curve is shown in Figure 3b that is drawn based on the S.D. (standard deviation) values. The Method of Quantification (MOQ) value, calculated based on the calibration curve was found to be  $7.940\ \mu\text{g mL}^{-1}$  for nickel(II) in biological samples.



**Figure 3.** (left) Differential pulse polarogram of nickel(II), peak at  $-615.0\ \text{mV}$ , acetate buffer (pH 4.0), pulse amplitude  $50\ \text{mV}$ , scan rate  $50\ \text{mV s}^{-1}$ ; (right) Calibration curve for nickel(II)

The present method was successfully applied for determination of nickel(II) using the simple chloroform extraction procedure prior to DPP in biological samples, plant materials and the results are shown in Tables 1, 2 and 3. The validity of the present method was checked by analyzing the CRM's and the results are shown in Table 5. In addition, the obtained results are compared to several analytical reagents synthesized for the determination of nickel(II) in various environmental samples, presented in Table 6. The developed method shows good sensitivity in terms of solvent medium, techniques used for the determination of nickel(II) ion, concentration range and detection limits.

**Table 5.** Determination of nickel(II) in Certified Reference Material (CRM's)

Sample	Standard values	Present method	RSD, % (n=5) <sup>b</sup>
Rice Flour (NIES-CRM-10A)	0.19	0.187	1.33
Wheat Flour (ARC/CL-WF)	0.153	0.155	0.62
Rye bread Flour (CSRM-12-2-05)	0.234	0.230	0.8

<sup>a</sup> CRM's distributed by NIST National Institute of Standard Technology [NIST (USA)]

<sup>b</sup> Mean values for five determinations

**Table 6.** Comparison of reagents for the determination of nickel(II) with other methods

Reagents	Solvent/medium	Techniques	Concentration range	Limit of detection	Ref.
1-pyridylazo-2-naphthol	Amberlite XAD-resin	ICP-AES	0.10-275 $\mu\text{g L}^{-1}$	0.20 $\mu\text{g mL}^{-1}$	[8]
HNO <sub>3</sub>	Surfactant Triton X-100	ICP-MS	up to 2.0 $\mu\text{g L}^{-1}$	0.11 $\mu\text{g L}^{-1}$	[20]
1-phenyl (3-methyl-3-benzoyl)5-pyrozolone	Sufactant Triton X-100	GFAAS	up to 100 $\text{ng mL}^{-1}$	0.12 $\text{ng mL}^{-1}$	[21]
1-(2-Pyridilazo)-2-naphthol	-	FAAS	-	2.60 $\mu\text{g L}^{-1}$	[22]
2,(2-Quinolylazo) dimethyl dimethylaminoaniline(QADEAA)	sodium dodecyl sulfonate (SDS)	Spectro-photometry	0.01-0.4 $\mu\text{g mL}^{-1}$	0.20 $\mu\text{g mL}^{-1}$	[23]
5- Bromo-2- hydroxyl -3-methoxybenzaldehyde-4-hydroxy benzoichydrazone	DMF	Spectro-photometry	0.117 to 2.64 $\mu\text{g mL}^{-1}$	0.016 $\mu\text{g mL}^{-1}$	[24]
2-pyridylazo 2-resorcinol (PAR)	Acetate buffer	HPLC	up to 50 $\mu\text{L}$	-	[25]
2-(2-Quinolylazo)-5-dimethylaminoaniline QADMAA	sodium dodecyl sulfonate (SDS)	Spectro-photometry	0.01-0.6 $\mu\text{g mL}^{-1}$	0.20 $\mu\text{g mL}^{-1}$	[26]
4-(2-hydroxy phenyl ethaminodiol), benzene-1.3-diol	Acetate buffer	Extractive-DPP	0.05-42 $\mu\text{g mL}^{-1}$	0.15 $\mu\text{g mL}^{-1}$	Present Work

## Conclusions

A simple, sensitive, rapid, and eco-friendly solvent extractive differential pulse polarography method was designed for determination of nickel(II) in biological samples and plant materials. The preconcentration method following chloroform extraction procedure has been established. A new analytical reagent 4-2-HPEDB-1,3,D has been synthesized, which can be able to form stable complexes with nickel (II). The selective functional group of -C=N- in the complex, gives a good response and is easily reduced at the electrode surface. The reagent also suppresses the interference of diverse ions such as cations, anions, and other salts by a judicial use of masking agents.

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