

## Polarographic Interaction of Nickel (II) with Ammonium Piperidine-1-Carbodithioate: Application to Environmental Samples

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Rec date: Jan 21, 2014; Acc date: Mar 10, 2014; Pub date: Mar 12, 2014

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### Abstract

This paper describes the interaction of nickel (II) with ammonium piperidine-1-carbodithioate (APC) using Direct Current (DC) polarography (DCP) & differential pulse polarography (DPP) at the Dropping Mercury Electrode (DME) in  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  buffer medium at pH 6.0. The polarograms shows a predominant peak for nickel (II)-APC at -1.30 V vs SCE, indicating the production of catalytic hydrogen wave (CHW) due to electrostatic interactions between APC and nickel (II). The interactions were characterized with UV-visible spectrophotometer, FT-IR and cyclic voltammetric techniques. The developed method was applied successfully to determine the nickel (II) levels in leafy vegetables and biological samples with acceptable recoveries.

**Keywords:** Direct Current Polarography (DCP); Differential Pulse Polarography (DPP); Nickel (II); Ammonium Piperidine-1-Carbodithioate (APC); Interaction; Environmental samples

### Introduction

Carbodithioates, a group of small organic molecules with a strong chelating ability towards inorganic species that have been extensively been used in the agricultural industry for more than eighty decades. In recent years their applications have not only become apparent as pesticides and fungicides, but also widely used as vulcanization accelerators in the rubber industry [1]. Moreover, carbodithioates are of biological importance due to their antibacterial, antituberculosis and antifungal properties. The insolubility of metal salts (with the exception of sodium and other alkali and alkaline earth metals) and the capacity of the carbodithioates to form stable metal-complexes are mainly responsible for the extensive use of this class of compounds as superior ligands. Furthermore, carbodithioates exhibit strong binding properties with a number of transition metal ions resulting in stable colored complexes [2]. Nickel is ubiquitous in the environment and an essential metal for animal nutrition, and consequently it is probably essential to humans. Nickel is a relatively non-toxic element; however, certain nickel compounds have been proven to be carcinogenic. The main sources of nickel in aquatic systems include dissolution of rocks and soils, biological cycles, atmospheric fallout, and most importantly industrial processes and water disposal [3].

Over toxicity of nickel may cause skin disorder known as "Nickel-eczema" [4] and other occupational disease [5] especially to workers who handle nickel on regular basis. This skin disorder has also been reported by Cempel and Nikel [6] to appear in people who have great sensitivity to nickel, mostly women, and can be caused by wearing of jewellery made of nickel alloys [6]. While the medical diagnosis is currently established through nickel determination in blood and urine, other studies [7,8] show that disease incidence increased in patients

who consume foods rich in nickel, such as oats, nuts, beans and chocolate. Hence, an appropriate knowledge of the nickel content in foods could be of a great interest for the dietary control of nickel-eczema patients. Several analytical techniques such as FAAS [9-13], GFAAS [14-16], ETAAS [17], AFS [18], UV-vis spectrophotometry [19-24] and ICP-OES [25,26] have been proposed for the analysis of nickel (II), but most of these require expensive equipments and time consuming sample preparation procedures. However, the electrochemical analysis of trace amounts of nickel (II) require relatively inexpensive equipment but presents certain difficulties due to their irreversible reduction behavior [27,28] of nickel. Therefore it is needless to say, it has successfully been accomplished using a variety of electro-analytical techniques such as stripping & voltammetric analysis [29-34] including polarography [35].

In this paper, electrochemical and spectrophotometry data are reported on the interaction between nickel(II) and APC, obtained by applying cyclic voltammetry (CV), differential pulse polarography (DPP), FT-IR and UV-visible spectrophotometry. After interaction, the electrochemical behaviour of the complex is studied at DME in presence of  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  medium at pH 6.0 with the view of attaining catalytic hydrogen wave which ensures the credibility of the method for the determination of nickel (II) in selected leafy vegetables and biological samples.

### Experimental

#### Chemicals

All the experiments were performed at 25°C using freshly prepared solutions. Double distilled mercury and double distilled water were used throughout the experiment. The dissolved oxygen in the solutions was removed by passing a 99.99% pure nitrogen gas through the measuring solution in an electrochemical cell for 10-15 minutes. Standard metal ion solution was prepared taking 0.004050 g L<sup>-1</sup> of

NiCl<sub>2</sub>.6H<sub>2</sub>O to get 1 µg mL<sup>-1</sup> and adding few milliliters of acid corresponding to the anions of the salts to suppress the hydrolysis. Ammonium Chloride (1 M) (S.D Fine Chemicals, India) was prepared by dissolving 53.49 g of ammonium chloride (Analytical grade) in 1 L with double distilled water. Carbon disulphide and piperidine were also purchased from Merck Chemicals, India.

## Reagents

A 5% ammonium hydroxide and 1 % HCl (S.D Fine Chemicals, India) used for pH adjustments were prepared from AnalaR chemicals. Potassium iodate (S.D Fine Chemicals, India) and sodium sulphite (S.D Fine Chemicals, India) were also prepared in double distilled deionised water using Analytical grade samples. Triton X-100 is prepared in w/v basis by weighing 0.2 g and dissolving it to 100 mL with double distilled water Gelatin (Difco laboratories, USA) was prepared by weighing accurately 0.1250 g and dissolving to 25 mL with doubly distilled water. APC was synthesized according to procedure reported in literature [1,36-43].

## Instrumentation

The current-voltage curves were recorded using a DC Polarographic analyzer, model CL-357 coupled with model LR-101 strip chart recorder manufactured by Elico Private Ltd (Hyderabad, India). Effects of mercury height on polarographic currents were studied using DC recording polarograph model CL-25 of Elico Pvt Ltd, Hyderabad. DPP & Cyclic voltammetric studies were performed with a 797 VA Computrace (Metrohm, Herisau, Switzerland). All pH measurements ranging from 2 to 10 were done using pH meter, model LI-120 (Elico Pvt. Limited, India). An IR spectrum was obtained using a Varian 800 FT-IR Scimitar Series supplied by SMM Instruments [Durban, South Africa (SA)].

## Electrochemical measurements

A measured volume of the NH<sub>4</sub>Cl-NH<sub>4</sub>OH buffer and APC solution at optimum pH were made in a 100 mL in beaker with distilled water and then adequate amount was transferred into the electrochemical cell followed by addition of the required sample or standard nickel (II) solution. The dissolved oxygen was expelled by bubbling pure nitrogen through the analyte solution for 15 min. Polarograms of the solution were recorded using DC/DP polarography at -1.30 V vs SCE in ammonium chloride-ammonium hydroxide medium. APC or simple metal ions [nickel (II)] in the medium do not give any current signal at the potential mentioned.

## Real sample preparation

To test the validity of the proposed method, different samples of environmental importance were collected and processed for the analysis of nickel (II) after interaction with APC in the presence of NH<sub>4</sub>Cl-NH<sub>4</sub>OH medium. The evolved catalytic hydrogen currents were determined using DC/DPP.

## Vegetable samples

5.0 g of *Hibiscus cannabinus* (Gongura), *Celosia argentea* (gurugaku), *Spinacia oleracea* (palaku), *Amaranthus graecizans* (Sirraku) and *Alternanthera sessilis* (ponagantaku) samples were collected from the local market. The collected samples were digested by dry ashing method followed by dissolution to 25 mL with double

distilled water. The metal ions that are commonly associated with nickel (II) are included in the preparation of the standards. Aliquots of the above sample solution were taken into a beaker and the quantitative experimental conditions were maintained as already described. The polarograms were recorded after filtering the precipitates of interfering ions and after spiking the solution with a known amount of nickel (II).

## Milk samples

A 100 mL sample of milk was added drop wise into a crucible and heated to 450 -500°C for 1 hr to remove moisture and evaporate it without frothing. The obtained dark ash was dissolved in 3 mL of concentrated HNO<sub>3</sub> and evaporated, and again dissolved in the 3 mL of dilute HNO<sub>3</sub>. The sample was filtered and the filtrate was made up to the mark in a 25 mL volumetric flask with deionized water. Required volume of the sample was used for the analysis of nickel (II) using aforesaid procedure.

## Blood samples

Blood samples obtained from local sources were digested by mixing 30 mL of sample, 10 mL of deionised water, 18 mL concentrated HNO<sub>3</sub> and 5 mL of 30% H<sub>2</sub>O<sub>2</sub> in a 100 mL beaker. The mixture was heated while stirring until the volume decreased to half than filtered. The filtrate was made up to a 250 mL volumetric flask with deionized water for the analysis of nickel (II) using the aforesaid procedure.

## Results and Discussion

### Electrochemical behavior of nickel (II)-APC complex

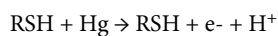
**Cyclic voltammetric studies:** Cyclic voltammetric studies have been performed to illustrate and validate the promising mechanism between nickel (II) and APC in aqueous solution using hanging mercury dropping electrode (HMDE) with a scan rate of 0.09 mV/sec. Figure 1A shows cyclic voltammogram of APC in a 0.4 M NH<sub>4</sub>Cl-NH<sub>4</sub>OH electrolyte solution of pH 6.0. On the other hand Figure 1B shows cyclic voltammogram of nickel (II)-APC complex. In the case of APC, two predominant reversible peaks at E<sub>1/2</sub> of - 0.48 V and - 0.68 V, while Figure 1B shows only one reversible peak at E<sub>1/2</sub> = -0.5. The shift in potential and disappearing of the first peak confirms that there are interactions between nickel (II) and APC. Based on this investigation, praise worthy mechanism is proposed as follows: The sulphur atoms of APC involves in the co-ordination of nickel (II).

**DC/DPP studies:** In this methodology, nickel (II) forms a complex with APC, which subsequently absorb onto the DME/HMDE working electrodes during the deposition step. During the polarographic scan, nickel(II)-APC [Ni<sup>+2</sup>-APC]ads complex is reduced to [Ni<sup>0</sup>-APC]ads which undergoes protonation by accepting proton from the solution [Ni<sup>0</sup>-APCH<sup>+</sup>]ads in the adsorbed state, followed by the reduction to liberate hydrogen in presence of mercury electrode, as shown in equations 1-3 below [1,36]:



M = Nickel (II), RS = Carbodithioates

Therefore, oxidation of APC at the HMDE is represented as which was in agreement with the earlier reports in the literature [1,36,44].



RS = Carbodithioates

The typical DC/DPP polarograms recorded at  $E_{1/2} = -1.30$  V for nickel (II)-APC complex system are shown in Figure 2A and 2B.

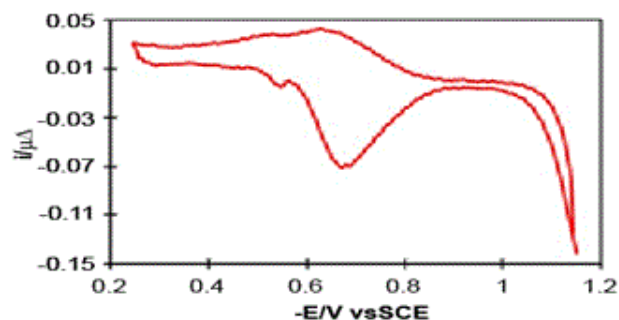
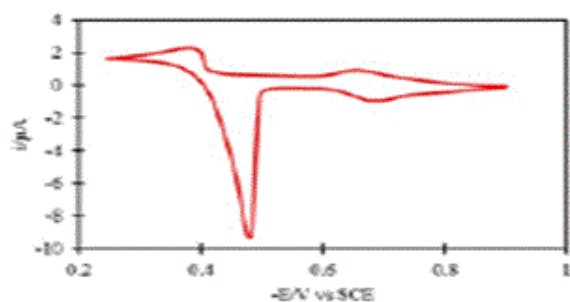


Figure 1: Cyclic voltammograms for (A) 2.0 mM APC (B) 2.0 mM APC + 2.0  $\mu\text{g mL}^{-1}$  nickel (II) in 0.3 M  $\text{NH}_4\text{OH-NH}_4\text{OH}$  at pH 6.0.

### Spectrophotometric studies on nickel (II)-APC complex

**UV-Visible studies:** UV-visible spectrophotometric techniques have often been used to study the interaction mechanism between metal and ligand [1,35-43]. Figure 3 shows the UV spectra of nickel (II) and APC before and after their interaction. The spectrums of this figure depict that before the interaction of nickel (II) with APC, there is less or no absorption while after the interactions, a sharp absorption peak is observed at about 230 nm confirming the interaction. Therefore, it could be concluded that nickel (II) interacts with APC and both the results of electrochemical studies and UV-Vis spectrophotometry are in agreement in this regard.

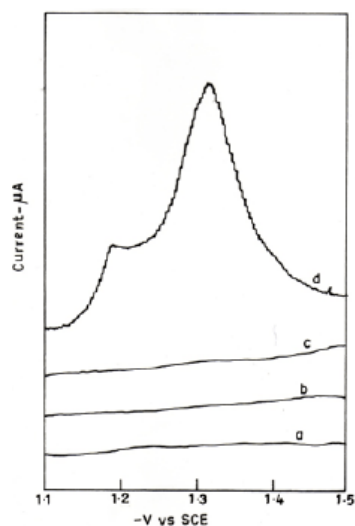


Figure 2A: Polarographic curve of nickel (II) in  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  medium in the presence of APC (a) 0.4 M  $\text{NH}_4\text{Cl}$ , pH  $\sim 6.0$  (b) a + 2.0 mM APC (c) a + 2.0  $\mu\text{g mL}^{-1}$  Nickel (II) (d) b + 2.0  $\mu\text{g mL}^{-1}$  nickel (II).

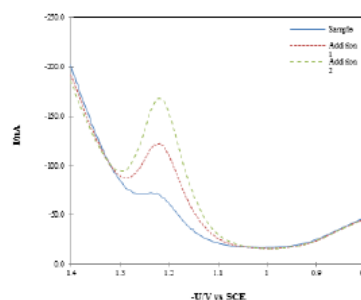


Figure 2B: Obtained DPP curves of nickel (II) in  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  medium in the presence of APC using standard addition method [Conditions:-Current range: 100  $\mu\text{A}$ , Scan rate: 6 mV/S, Pulse amplitude: 50 mV, Drop time: 1 Sec, Nickel (II): 2.0  $\mu\text{g mL}^{-1}$ ].

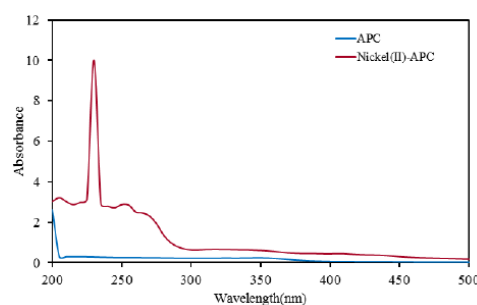


Figure 3: Absorption spectra of before and after interaction of nickel (II) with APC [Conditions: APC= 2.0 mM, Nickel (II) = 2.0  $\mu\text{g mL}^{-1}$ ].

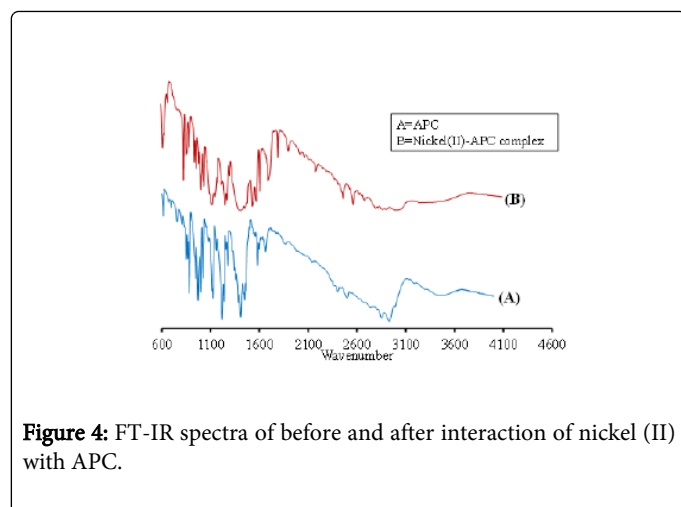


Figure 4: FT-IR spectra of before and after interaction of nickel (II) with APC.

### FT-IR studies

In Figure 4, the IR spectra of the pure APC and nickel (II)-APC complex system are shown. Here, a single band of strong intensity was observed in the range  $1022-1001\text{ cm}^{-1}$  which may be attributed to  $\nu(\text{C-S})$  vibration. A negative shift of  $83-28\text{ cm}^{-1}$  in comparison to the corresponding band in the free ligand indicates that the APC coordinates with the nickel (II) through sulphur atoms. The presence of an only C-S band can be due to the greatest contribution of the resonance form  $(\text{RN}+\text{CS}^{2-})$  in the adducts and the complex, thus suggesting symmetrical bidentate binding of the carbodithioates moiety.

### Optimization of analytical parameters

**Effect of pH:** pH plays vital role in the interaction of nickel (II) with APC and their catalytic hydrogen waves production from the complex. The effect of pH ranging from 5.0 to 10.0 on solutions containing  $2.0\text{ }\mu\text{g mL}^{-1}$  of nickel (II) in 0.4 M buffer solution was tested. With increasing pH, the height of the CHW increased, after attaining a maximum peak current at pH 6.0, the wave height decreased with further increase in pH. The maximum wave heights of the polarograms are selected as optimum pH for further studies as shown in Figure 5.

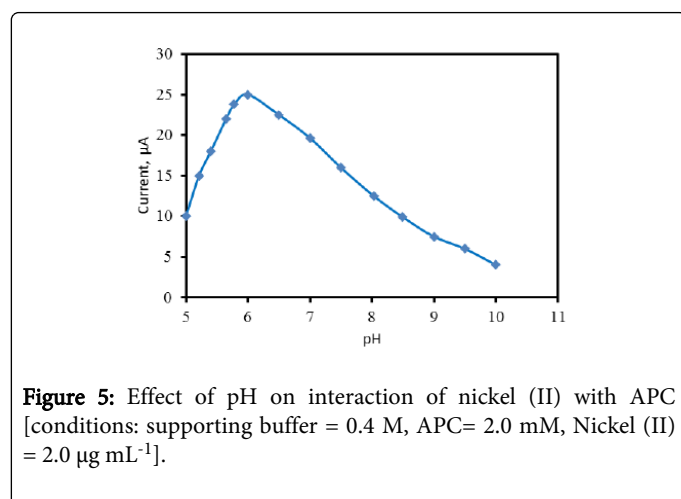


Figure 5: Effect of pH on interaction of nickel (II) with APC [conditions: supporting buffer = 0.4 M, APC= 2.0 mM, Nickel (II) =  $2.0\text{ }\mu\text{g mL}^{-1}$ ].

### Effect of buffer concentration

The effect of  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  (buffer) was studied in the range of 0.1 to 0.8 M on the nature of current-voltage curves at DME/HMDE obtained after interaction of nickel (II) with APC, keeping the nickel (II) ion concentration at  $2.0\text{ }\mu\text{g mL}^{-1}$  and APC at 2.0 mM. The polarograms were well defined in  $\text{NH}_4\text{Cl-NH}_4\text{OH}$  of 0.4 M and the peak height is decreased beyond this concentration as shown in Figure 6.

### Effect of APC concentration

The solution of nickel (II) and ammonium chloride containing fixed quantities of  $2.0\text{ }\mu\text{g mL}^{-1}$  and 0.4 M respectively and an APC concentration varied from 0.5 to 6.0 mM, while the pH of the solution was maintained at 6.0. The peak current does not vary linearly with concentration of APC which was a typical characteristic nature of catalytic hydrogen wave (Figure 7). From the results it is observed that the wave height increased linearly with increase in APC concentration up to 2.0 mM. With further increase in APC concentration, the independence of the wave height from the concentration is unveiled as, it become relatively stable after 2.0 mM. The concentration of the APC was fixed at maximum wave height for quantitative studies. The peak potential of the catalytic wave shifted more towards a negative potential upon increasing the APC concentration, until maximum current response was observed and remained constant beyond the respective concentrations. Plot of  $[\text{APC}]/i_p$  Vs  $[\text{APC}]$  was a straight line (Figure 8) and confirms that adsorption phenomenon was involved in the electrode reaction process.

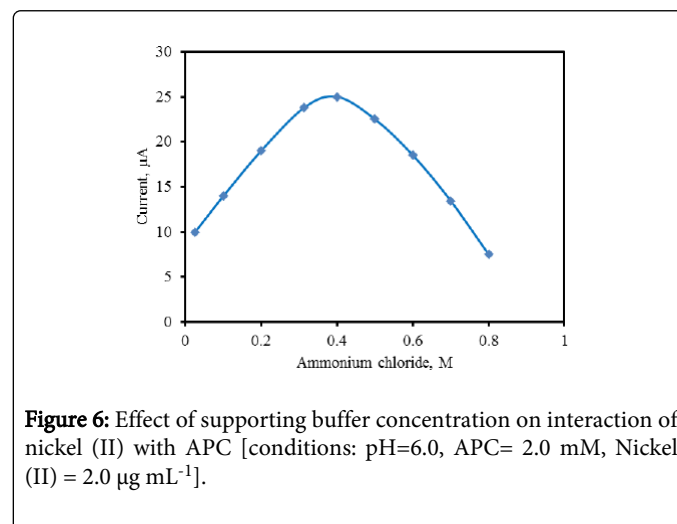
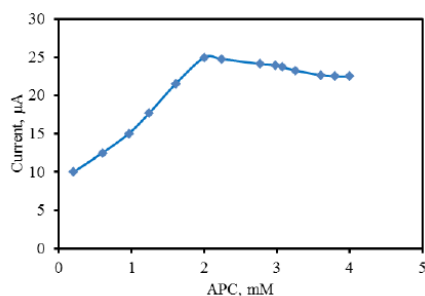


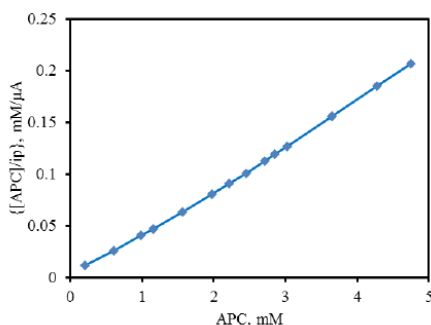
Figure 6: Effect of supporting buffer concentration on interaction of nickel (II) with APC [conditions: pH=6.0, APC= 2.0 mM, Nickel (II) =  $2.0\text{ }\mu\text{g mL}^{-1}$ ].



**Figure 7:** Effect of APC concentration on interaction of nickel (II) with APC [conditions: pH=6.0, Supporting buffer=0.4 M, Nickel (II) = 2.0  $\mu\text{g mL}^{-1}$ ].

### Effect of nickel (II) concentration

At fixed concentrations of APC at 2.0 mM, buffer at 0.4 M and pH at 6, the metal ion concentration was varied between 0.5 to 6.0  $\mu\text{g mL}^{-1}$  and its proportionality to the peak current was studied. The results obtained are shown in Figure 9. The peak current increased linearly with nickel (II) concentration in the range 0.5 to 6.0  $\mu\text{g mL}^{-1}$ . The method suggests that the quantification of trace and ultra-trace levels of nickel (II) was possible in unknown samples. No changes were observed in the shape of the wave throughout the selected range of nickel (II) concentration.

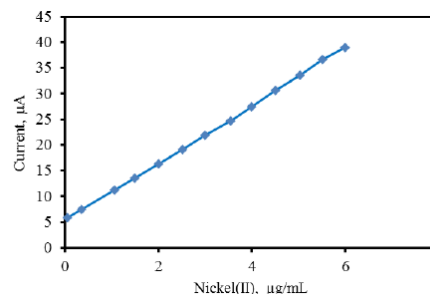


**Figure 8:** Langmuir adsorption isotherm plot after interaction of nickel (II) with APC [conditions:- pH=6.0, Supporting buffer=0.4 M, APC=2.0 mM, Nickel=2.0  $\mu\text{g mL}^{-1}$ ].

### Foreign ion effect

Different metal ions and salts were added individually to a 20 mg of nickel (II) solution and analysis was carried out as per to the aforesaid electrochemical measurements procedure. The tolerance limit was set as  $\pm 2\%$  error in the peak current for the determination of nickel (II). Among all the metal ions examined, most could be tolerated up to 1 mg, except for 35 mg of copper (II), 40 mg of aluminum (III) and 20 mg of iron (III) ions. However, these could easily be masked by addition of 0.5 g sodium fluoride, 7 mg of trisodium citrate for aluminum (III) & iron (III), 0.1 g of thiourea and 0.1 g of  $\text{Na}_2\text{S}_2\text{O}_3$  for copper (II). Among the salts (anions) examined, most could be well

tolerated to above mg levels, except for 15 mg of EDTA. The results obtained are depicted in Table 1. Accordingly the developed method is highly selective and may be successfully applied for the determination of nickel (II) in leafy vegetables and biological samples.



**Figure 9:** Effect of nickel (II) concentration on interaction of nickel (II) with APC [conditions: pH=6.0, Supporting buffer=0.4 M, APC=2.0 mM].

### Method validation

The analytical method was validated considering different validation parameters including selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), accuracy, precision (inter-day precision & intra-day precision) and stability for the analysis of nickel (II).

A linear trend between the peak current and nickel (II) concentration is observed in the range of 0.1-7.0  $\text{mg L}^{-1}$  with the regression co-efficient of 0.998. The coefficient of determination ( $r^2$ ) obtained from the regression line was 0.999. The electrochemical methodology described in this paper was based on a calibration curve for quantitative analysis, and the corresponding limit of detection (LOD) and limit of quantification (LOQ) are determined and found to be 0.25 and 1.59  $\text{mg L}^{-1}$  respectively.

The accuracy of the developed method was performed using synthetic samples as shown in Tables 2,3. Synthetic samples were prepared with known amounts of standard solutions (0.2, 0.4, 0.6, 0.8, 1.0 and 1.2  $\mu\text{g mL}^{-1}$ ). It is evident in tables 2 and 3 that the method had good accuracy, which was in the range of 92.10-99.57 % within the concentration range investigated for the determination of nickel (II) in various water systems. The precision of the method was also validated based on the relative standard deviation (RSD) measuring repeatability ( $n=5$ ) at different concentrations. The % RSD values were less than 2% and illustrated a good precision of the analytical method (Tables 2 and 3). In addition to the accuracy results which confirmed the selectivity of the method, %RSD values were lower than 1.89%, confirming a good precision of this method for the analysis of nickel (II). The stability of pure APC and nickel (II)-APC complex were determined by storing the samples at room temperature and in refrigerator for one to seven days. The results of stored sample solutions are analyzed and compared with those of a freshly prepared standard at each time interval. No degradation in the APC and nickel (II)-APC was observed during from day one to day five. After day five,  $\pm 0.5/0.7\%$  decrement in the absorbance and peak current were observed, which indicated the stability of the complex and samples can be stored for at least one week prior to analysis.



Ions	Tolerance limits (mg)
Pb <sup>+2</sup>	15
Co <sup>+2</sup>	0.5
Os <sup>+8</sup>	0.7
Cu <sup>+2</sup>	15, 0.40
Ag <sup>+1</sup>	10
Mo <sup>+6</sup>	5.0
Cr <sup>+6</sup>	7.0
Hg <sup>+2</sup>	0.5
V <sup>+5</sup>	2.0
Fe <sup>+3</sup>	0.00030, 0.30 <sup>**</sup>
Ru <sup>+3</sup>	1.5
Zn <sup>+2</sup>	5.0
Sb <sup>+3</sup>	7.0
Cu <sup>+2</sup>	0.00025, 0.20 <sup>*</sup>
Al <sup>+3</sup>	0.00030, 5.0 <sup>**</sup>
Bi <sup>+3</sup> , Rh <sup>+3</sup>	0.5
Cd <sup>+2</sup>	9
U <sup>+6</sup> , Cr <sup>+3</sup>	3.0
Ga <sup>+3</sup> , Se <sup>+6</sup>	2.0
KI, NaF	500
Na <sub>2</sub> EDTA	0.0002
KSCN	20
CaCl <sub>2</sub> , Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	150
K <sub>2</sub> SO <sub>4</sub>	250
CH <sub>3</sub> COONa.3H <sub>2</sub> O	750
KNO <sub>3</sub> , NH <sub>4</sub> Cl	1000
KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> .4H <sub>2</sub> O	45
Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	15
*Masked with 0.5 g NaF and 10 mg trisodium citrate **Masked with 0.3 g thiourea and 0.1 g Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	

**Table 1:** Effect of foreign ions on the determination of nickel (II) in various water samples

### Analytical applications

To test the validity of the proposed method, various leafy vegetables and biological samples were collected for the determination of nickel (II) after complexation with APC in the presence of NH<sub>4</sub>Cl-NH<sub>4</sub>OH medium by evolution of peak current in DC/DPP analysis.

The results obtained by this method are further supported by DPP method. The developed method is compared with the DPP method in terms of Student's 't'-test and Variance ratio 'F'-test as shown in Table 2. The analytical data summarized in Tables 2 and 3 suggest that the percentage of nickel (II) recovery ranges from 92.10 to 99.57% with R.S.D (%) = 1.05. The optimization of various parameters for the interaction nickel (II) with APC in the presence of NH<sub>4</sub>Cl-NH<sub>4</sub>OH medium is found to be sensitive, selective, specific, reliable and rapid,

hence may be successfully applied for the analysis of nickel (II) in leafy vegetables and biological samples.

Sample <sup>a</sup> Scientific/Local name	DCP method		DPP method		t-test <sup>*</sup>	f-test <sup>**</sup>
	Ni(II), µg mL <sup>-1</sup>	Recovery (%) ± RSD <sup>b</sup>	Ni(II), µg mL <sup>-1</sup>	Recovery(%) ± RSD <sup>b</sup>		
<i>Hibiscus cannabinus</i> / gongura	1.048	96.40 ± 1.62	1.052	96.80 ± 1.70	1.62	0.25
<i>Celosia argentea</i> / gurugaku	1.102	97.55 ± 1.39	1.100	97.40 ± 1.54	1.19	0.12
<i>Spinacia oleracea</i> / palaku	1.258	98.00 ± 1.55	1.250	97.98 ± 1.62	1.26	0.79
<i>Amaranthus graecizans</i> / Sirraku	0.951	99.10 ± 1.20	1.027	99.25 ± 1.40	1.82	0.20
<i>Alternanthera sessilis</i> / ponagantaku	1.209	98.80 ± 1.86	1.210	99.10 ± 1.15	1.40	0.46

Conditions: pH=6.0, Supporting buffer=0.4 M, APC=2.0 mM <sup>a</sup>5 mL of the concentrated sample is used, <sup>b</sup>Relative Standard Deviation (n=6), <sup>\*</sup>1% level of significance, <sup>\*\*</sup>5% level of significance. All samples were spiked with 0.5 µg mL<sup>-1</sup> nickel (II) standard

**Table 2:** Analysis of nickel (II) after interaction with APC in leafy vegetable samples

Samples	DCP method			DPP method		t-test <sup>*</sup>	f-test <sup>**</sup>
	Ni(II) Added, µg mL <sup>-1</sup>	Ni(II), Found µg mL <sup>-1</sup>	Recovery (%) ± RSD <sup>b</sup>	Ni(II), Found µg mL <sup>-1</sup>	Recovery(%) ± RSD <sup>b</sup>		
Milk samples							
1	0.2	0.250	92.55 ± 1.50	0.263	95.75 ± 1.45	1.48	0.23
2	0.4	0.437	93.40 ± 1.62	0.440	93.20 ± 1.20	1.26	0.10
3	0.6	0.690	99.50 ± 1.33	0.690	99.50 ± 1.30	1.19	0.37
4	0.8	0.866	98.15 ± 1.05	0.872	98.55 ± 1.73	1.56	0.55
5	1.0	1.055	98.82 ± 1.20	1.100	99.00 ± 1.55	1.37	0.62
6	1.2	1.284	99.57 ± 1.73	1.290	99.70 ± 1.10	1.94	0.40
Blood samples							
1	0.2	0.246	94.66 ± 1.27	0.248	94.80 ± 1.48	1.29	0.24
2	0.4	0.444	92.10 ± 1.49	0.438	94.75 ± 1.35	1.53	0.18
3	0.6	0.682	98.50 ± 1.66	0.690	99.00 ± 1.26	1.48	0.36
4	0.8	0.873	98.75 ± 1.50	0.875	98.80 ± 1.57	1.24	0.12
5	1.0	1.140	94.00 ± 1.35	1.155	95.55 ± 1.62	1.67	0.47
6	1.2	1.238	97.15 ± 1.73	1.243	98.60 ± 1.70	1.70	0.50

Conditions:- pH=6.0, Supporting buffer=0.4 M, APC=2.0 mM <sup>a</sup>5 mL of the concentrated sample is used, <sup>b</sup>Relative Standard Deviation (n=6), <sup>\*</sup>1% level of significance, <sup>\*\*</sup>5% level of significance

**Table 3:** Analysis of nickel (II) after interaction with APC in biological samples

## Conclusions

This paper described the interaction of nickel (II) with APC by electrochemical, UV-visible spectroscopic and FT-IR techniques. From the electrochemical studies by supported with UV-vis and FI-IR studies, it was concluded that there is one electron reaction between nickel (II) and APC with a highly stable complex. The optimized parameters lead to the development of analytical techniques for the determination of nickel (II) in trace and ultratrace levels in various water systems. The present method is highly sensitive, selectivity, accurate and precise for the analysis of nickel (II). The limit of detection of the developed method is superior when compared with already reported methods. The CHW method developed is free from interferences of many commonly associated metal ions with nickel (II) which usually requires separation techniques and therefore reported here can be placed among the most sensitive and rapid methods of analysis of environmental samples.

## Acknowledgement

S Kanchi is highly grateful to the Durban University of Technology for the financial support to carry out this work.

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