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# Sensitive Determination of Nickel (II) using Catalytic Hydrogen Wave in the Presence of Dithiocarbamates at DME

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#### **Abstract**

Two new ligands, ammonium 2,6-dimethylmorpholine dithiocarbamate and ammonium 3-methylpiperidine dithiocarbamate were synthesized for the determination of nickel (II) in various environmental samples. The method was based on chelation of nickel (II) with ADMM-DTC/AMP-DTC in presence of NH<sub>4</sub>OH at pH 6.4 to produce catalytic hydrogen currents at -1.30V and -1.41 V vs SCE respectively and prior detected by DC polarography at Dropping Mercury Electrode (DME). Optimized polarographic conditions were established by studying effect of pH, supporting electrolyte, ligand and metal ion concentrations and effect of adverse ions on peak height to improve the sensitivity, selectivity and detection limits of the present method. The present technique was successfully applied for the analysis of nickel (II) in different matrices with recoveries ranging from 97.00 - 99.00% and the results obtained were comparable with the differential pulse polarography.

**Keywords:** DC polarography; Catalytic Hydrogen Current (CHC) technique; Nickel (II); Ammonium 2,6-Dimethylmorpholine Dithiocarbamates (ADMM-DTC); Ammonium 3-methylpiperidine Dithiocarbamates (AMP-DTC); Differential Pulse Polarography (DPP)

#### Introduction

Nickel is naturally available in the form of ores like Gernirite, Magnesium nickel silicate of variable composition. The important oxidation state of nickel is +2. It is a metal ion appearing together in a wide variety of samples of the food industry, in the manufacture of alloys, the production of heat-resistant steels and it is present in small amounts in soils, plants and animal tissues. Nickel is used in ceramic industry and batteries which are in convincing to the environment. A dietary deficiency of nickel, leads to various pathological manifestations. Compared with other transition metals, nickel is moderately toxic element, and still at low concentration produces a general toxic effect on the human organism, causing nasopharynx and lung diseases, malignant tumours and dermatological disease [1]. Nickel enters waters from dissolution of industrial processes and waste disposal [2]. The average concentration of nickel in domestic water supplies is 4.8 μg L<sup>-1</sup> as reported by United State Public Health Service. Daily intake of this metal in human diet is about 0.3 to 0.6 mg/day. Higher average levels of nickel (II) occur in foods because of contamination during processing and during cooking in nickel-plated utensils. Cigarette smoking causes lung cancer due to nickel carbonyl produced.

Several analytical techniques have been reported for the determination of trace level nickel (II), which includes Atomic Absorption Spectrometry [3-6], Inductive Coupled Plasma Optical/Emission Spectrometry [7-9], X-ray Fluorescence Spectrometry [10] and Voltammetry [11]. However, electrochemical instrumentation is comparatively inexpensive and equally sensitive and selective for parts per million to billion level nickel (II) found in various environmental and agricultural samples including foodstuffs. Catalytic hydrogen wave technique was earlier developed in our laboratories [12-14] for the determination of nickel (II) in drinking water samples and agricultural samples using D.C. polarography. Therefore, it is very important to develop sensitive, rapid and economical method for quantitative determination of its trace amount in various samples of environmental importance.

The preliminary work on polarographic behaviour of nickel (II) in the presence of two dithiocarbamates (ADMM-DTC/AMP-DTC)

in ammonium chloride-ammonium hydroxide medium revealed that a nickel (II) reduction wave is followed by a catalytic wave. Dithiocarbamates (ADMM-DTC/AMP-DTC) or simple metal ions in the medium do not give any peak current at the potentials of catalytic hydrogen currents (CHC; -1.30 V and -1.40 V vs SCE). Typical current-voltage curves of nickel (II)-dithiocarbamate complexes were shown in the Figures 1a and 1b.

## Experimental

#### Materials and method

**Instrumentation:** The current-voltage curves were recorded using a DC/DPP polarographic analyzer, model *CL-357/CL-362* 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. All pH measurements were made using pH meter, model *LI-120* (Elico Pvt. Limited, India) with combined electrode of pH range 2-14.

**Reagents:** All reagents were of analytical grade and deionized doubly distilled water was used for preparation of all solutions. 2,6-dimethylmorpholine, 3-methylpiperidine, carbon disulphide, ammonium chloride, and ammonia solution were purchased from S.D. Fine chemicals, Mumbai, India. Standard solution of nickel (II) [1  $\mu$ g mL<sup>-1</sup>) was prepared by weighing 4.050 g of NiCl<sub>2</sub>.6H<sub>2</sub>O (S.D.Fine chemicals, Mumbai, India) and dissolved in deionized doubly distilled water in 1000 mL standard flask.

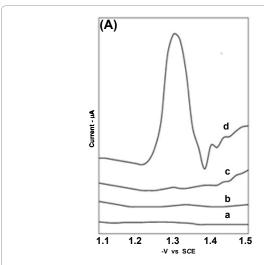
ADMM-DTC (0.01 M) was prepared by weighing 0.208 g of

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**Figure 1a:** Polarographic curve of nickel (II) in  $\mathrm{NH_4Cl\text{-}NH_4OH}$  medium in the presence of ADMM-DTC (a) 0.4 M  $\mathrm{NH_4Cl}$ , pH~6.4 (b) a+2.6 mM ADMM-DTC (c) a+4.0 ppm nickel (II) (d) b+4.0 ppm nickel (II).

ADMM-DTC and dissolved in 100 mL deionized doubly distilled water. AMP-DTC (0.01 M) was prepared by weighing 0.192 g of AMP-DTC and dissolved in 100 mL deionized doubly distilled water. Freshly prepared solution was stored in dark colored bottle. Stock solutions of ADMM-DTC, AMP-DTC and NH $_4$ Cl were prepared by appropriate addition of reagents and chemicals in 250 mL standard flask and stored in dark place.

**Synthesis of ADMM-DTC and AMP-DTC:** Carbon disulphide (40 g) was slowly added to a solution of 2,6-dimethylmorpholine/3-methylpiperidine (45 g) in 25 mL of deionized doubly distilled water at 5°C with constant stirring, followed by ammonium hydroxide. The product (Scheme 1a, 1b in supplementary material) was warmed to room temperature and washed repeatedly two or three times with purified acetone. The reaction product was purified by recrystallization in acetone [15-21]. The purified compounds have melting points of 176-182°C (ADMM-DTC) and 192-195°C (AMP-DTC) at 740 mm pressure.

General procedure: A measured volume of the NH $_4$ Cl, supporting electrolyte, and ligands (ADMM-DTC/AMP-DTC) were added to the electro-active species[nickel (II)], maintaining the optimum pH and the solution was made up to 100 mL in a standard flask with de-ionized doubly distilled water and then transferred to the polarographic cell. The dissolved oxygen was expelled by bubbling pure nitrogen through the analyte solution for 15 min. Polarograms of the solutions was recorded using DC polarography.

## **Results and Discussion**

Various optimal conditions developed for the determination of nickel (II) at DME are reported below.

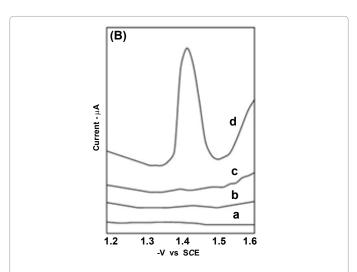
### Optimization of experimental parameters

Effect of pH: The polarogram of 4.0 ppm nickel (II), 2.6 mM ADMM-DTC and 3.2 mM AMP-DTC in ammonium chloride medium (0.4 M ADMM-DTC, 0.3 M AMP-DTC) were recorded in the pH range 0.5 to 10.0 maintain 0.002 % Triton X-100. Precipitations of nickel (II)-dithiocarbamates were not formed within the pH range of study. The wavelength increased upto pH 6.4 in case of both ADMM-DTC and AMP-DTC and the peak potentials shifted towards more

negative values with increase in pH. With further increase in pH the wavelength decreased. Hence, the pH where the wave has maximum height was fixed as the optimum value for all other studies as shown in Figure 2.

Effect of supporting electrolyte concentration: The effect of supporting electrolyte concentration on the peak current was investigated by employing the solution containing 4.0 ppm nickel (II), 2.6 mM ADMM-DTC and 3.2 mM AMP-DTC. The concentration of ammonium chloride was changed in the range of 0.05 M to 6.0 M and the polarograms were recorded maintaining pH of the solution at 6.4 for both ADMM-DTC/AMP-DTC as shown in Figure 3. The peak height increased with ammonium chloride concentration up to 0.4 M in case of ADMM-DTC and 0.3 M for AMP-DTC. With further increase in concentration the wavelength decreased. Therefore, the concentration of ammonium chloride was fixed at the maximum wave height value for all the studies. The peak potential shifted slightly towards positive potential with ammonium chloride concentration.

Effect of reagent concentration: The influence of dithiocarbamates on the polarographic characteristics of nickel (II)-dithiocarbamate complexes were studied using 4.0 ppm nickel (II) ion in 0.4 M and 0.3 M ammonium chloride for ADMM-DTC and AMP-DTC respectively



**Figure 1b:** Polarographic curve of nickel (II) in  $NH_4CI-NH_4OH$  medium in the presence of AMP-DTC (a) 0.3 M  $NH_4CI$ ,  $pH\sim6.4$  (b) a+3.2 mM AMP-DTC (c) a+4.0 ppm nickel (II) (d) b+4.0 ppm nickel (II).

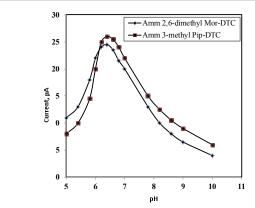


Figure 2: Effect of pH for the determination of nickel (II) with ADMM-DTC and AMP-DTC.

maintaining the pH 6.4. The dithiocarbamates concentration was varied in the range 0.2 mM to 4.0 mM. The peak current increases with dithiocarbamates concentration and tends to a limiting value similar in the form to the Langmuir adsorption isotherm (Figures 4 and 5). The reagent concentration at maximum wave height was fixed for all the studies as 2.6 mM for ADMM-DTC and 3.2 mM for AMP-DTC. The peak potential shifted to more negative potential with increase in dithiocarbamate concentration and beyond the optimum concentration the peak potential as well as height remained constant.

Effect of mercury pressure: The effect of the height of the mercury column on the nickel (II) dithiocarbamate complexes was studied maintaining the optimum conditions as already fixed. The catalytic current decreased with the increase in the height of the mercury column and  $i_c \sqrt{h}$  values decreased, whereas nickel reduction wave increased with pressure following diffusion controlled nature and  $i_c \sqrt{h}$  were constant as tabulated in Table 1.

**Effect of maximum suppressor:** For a solution containing nickel (II) 4.0 ppm, dithiocarbamates 2.6 mM (ADMM-DTC) and 3.2 mM (AMP-DTC) at pH 6.4 for both ADMM-DTC and AMP-DTC, gelatine

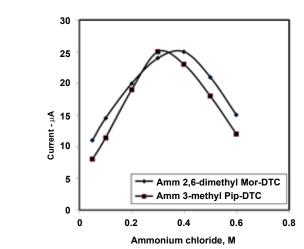


Figure 3: Effect of supporting electrolyte for the determination of nickel (II) with ADMM-DTC and AMP-DTC.

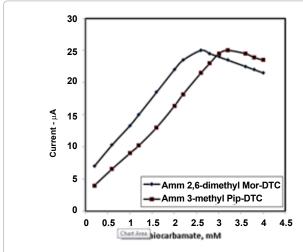
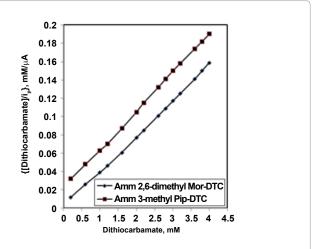


Figure 4: Effect of reagent concentration for the determination of nickel (II) with ADMM-DTC and AMP-DTC.



**Figure 5:** Langmuir adsorption isotherm plot for the determination of nickel (II) with ADMM-DTC and AMP-DTC.

	ADMM-DTC		AMP-DTC		
Height of the mercury column, cm	Current, µA	$i_c \sqrt{h}$	Current, µA	$i_c \sqrt{h}$	
21	25.50	5.548	24.50	4.357	
26	24.75	4.967	21.00	3.578	
31	24.50	4.251	19.50	3.024	
36	23.50	3.746	18.75	2.843	

Table 1: Effect of mercury pressure for the determination of nickel (II) with ADMM-DTC and AMP-DTC.

in the range 0.005 to 0.001% and Triton X-100 0.002 to 0.004% were added and the effect was studied. It was found that the nickel (II) reduction wave was suppressed slightly by adding gelatine and the catalytic wave was reduced to about 10% up to 0.005% gelatine and the decrease was small above this concentration. The peak potential shifted towards less negative potentials. Triton X-100 has no effect on nickel (II) reduction as well as on the catalytic peak current and peak potential. However, the presence of Trition X-100 improves the catalytic wave to a well-defined and a symmetrical one with a clear base line. 0.002% Triton X-100 was therefore maintained for all studies as represented in Table 2.

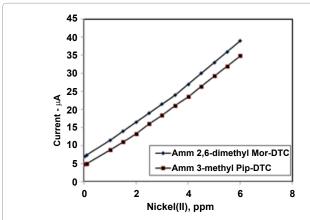
Effect of temperature: The current-voltage curves for the system containing 4.0 ppm nickel (II), 2.6 mM ADMM-DTC, 0.4 M NH $_4$ Cl at pH 6.4 and 3.2 mM AMP-DTC, 0.3 M NH $_4$ Cl at pH 6.4 in the presence of 0.002% Triton X-100 were recorded at various temperatures from 20 to 50°C. It was found that with increase in temperature, the catalytic wave height increases and the temperature coefficient values gradually decreases up to 35°C. Above 35°C the current,  $i_c$  became completely temperature independent.

Effect of nickel (II) on peak current: The effect of nickel (II) ion in the range 0.05 to 6.0 ppm was studied on the peak current in the presence of optimum concentrations of dithiocarbamate and ammonium chloride at fixed pHs and Triton X-100. The current-voltage curves show that the peak height increased linearly with the metal ion concentration in the range 0.05 ppm to 6.0 ppm with ADMM-DTC and 0.05 to 6.0 ppm with AMP-DTC. The results obtained were shown in Figure 6. The nickel (II) reduction wave also increases with increase in metal concentration without any shift in peak potential and the catalytic wave increases linearly with nickel (II) concentration.

Effect of Foreign Ions: Various metal ions commonly associated

Maximum Summanau 9/	Current, µA						
Maximum Suppressor, %	ADMM-DTC	AMP-DTC					
Gelatin							
0.000	25.00	24.00					
0.002	23.50	21.60					
0.004	19.90	19.50					
Triton X-100	·						
0.00	25.00	24.00					
0.005	25.00	24.00					
0.010	25.00	24.00					

**Table 2:** Effect of maximum suppressors for the determination of nickel (II) with ADMM-DTC and AMP-DTC.



**Figure 6:** Effect of nickel (II) on peak current for the determination of nickel (II) with ADMM-DTC and AMP-DTC.

with nickel like iron (II), copper (II), chromium (VI), zinc(II), molybdenum (VI) and aluminium (III) have been used in the present study to evaluate the change that occur in the catalytic wave of nickel (II)-dithiocarbamate system. The concentration of nickel (II) was maintained at 4.0 ppm and 100-fold excess of foreign ions were added. Of all the metal ions studied iron (II) and copper (II) form precipitates with dithiocarbamate in the conditions where nickel (II)dithiocarbamate complex gives a catalytic wave. Aluminium (III) does not interfere whereas chromium (VI) gives catalytic current with peak potentials at -1.56 V and -1.65 V vs SCE and suggests that a simultaneous determination of nickel (II) & chromium (VI) was possible without any separation or adding masking agents. Zinc (II) interferes in the determination of nickel (II) but was masked by adding 5 mL of 2% sodium tartrate solution. Molybdenum (VI) severely interferes by increasing the wave height of nickel (II) and shifting the peak potential towards more negative values. Selenium (IV), telurium (IV), cerium (IV) and tin (II) also do not interfere up to 100 fold excess with the nickel (II)-dithiocarbamate system.

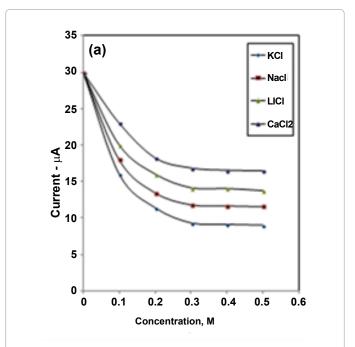
Anions such as fluoride, bromide, iodide, tartrate, sulphate, thiosulphate, phosphate, carbonate, oxalate, nitrite, and nitrate do not interfere with the catalytic current of nickel (II)-dithiocarbamate complexes. Perchlorate and thiocyanate interfere with the wave by reducing the wave height nearly 40% and EDTA interferes severely by completely suppressing the nickel (II) catalytic wave.

Effect of indifferent cations: The effect of neutral salts on the nickel (II)-dithiocarbamate system, catalytic waves has been studied by adding several concentrations of different chlorides of sodium, potassium, lithium, and calcium keeping the value of the quantitative experimental conditions in the solution constant. The catalytic hydrogen current

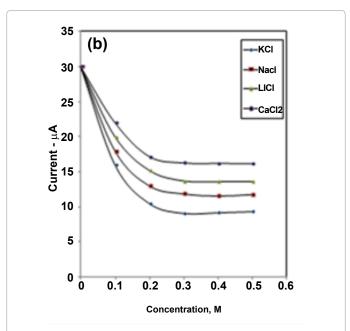
(CHC) had the lowest level to KCl, increasing consecutively for NaCl and LiCl, and presenting the highest level for CaCl<sub>2</sub> (Figures 7a and 7b). The peak potential was shifted towards less negative potential in all cases.

## **Analytical Applications**

The method is extended to the analysis of trace quantities of nickel in various water samples, agricultural materials. One litre of the water samples collected from Industrial estate and around Amararaja



**Figure 7a:** Effect of indifferent ions on ADMM-DTC-nickel (II) complex at Dropping Mercury Electrode (DME) for the determination of nickel (II).



**Figure 7b:** Effect of indifferent ions on AMP-DTC-nickel (II) complex at Dropping Mercury Electrode (DME) for the determination of nickel (II).

batteries (Tirupati town, Chittoor Dt.) was preconcentrated to 100 mL. 5 g of *Hibiscus cannabinus* (Gongura), *Rumex vesicarius* (Chukkaku) and 10 g of *Phaeolus vulgaris* (Beans), *Pisum sativum* (Peas) samples are digested by dry ash method and made upto 25 mL with deionized doubly distilled water.

The amount of nickel (II) present in the samples is determined by referring its current to the calibration curve drawn with standard solutions of nickel (II). The amount of metal ion obtained by catalytic polarographic method was further supported by DPP method. The results in Tables 3 and 4 reveals that the various water samples analyzed contain traces of nickel (II) within the tolerance limits and

the percentage recovery values obtained with the two ligands were comparable and in good agreement with DPP data as shown in Figures 8a and 8b. The nickel content present in agricultural materials, *Hibiscus cannabinus* (Gongura), *Rumex vesicarius* (Chukkaku), *Phaeolus vulgaris* (Bean) and *Pisum sativum* (Peas) show that the values were in agreement with the standard values reported (Tables 5 and 6).

These observations indicates that the proposed catalytic method for the determination of nickel (II) using two dithiocarbamates(ADMM-DTC/AMP-DTC) in ammonium chloride-ammonium hydroxide medium may be successfully applied to the various environmental samples.

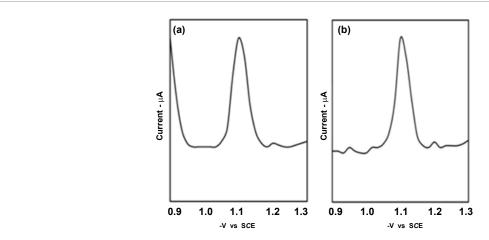


Figure 8: DPP curve for the determination of nickel (II) in  $NH_4CI-NH_4OH$  medium in the presence of (a) ADMM-DTC (b) AMP-DTC, Conditions: Current Range : 100  $\mu$ A, Scan Rate : 6 m V/S, Pulse Amplitude : 50 mV, Drop time : 1 Sec, Nickel (II) : 0.001 ppm.

	Ni(II) added, ppm	CHC method	(DC polarography)	DPP method ADMM-DTC		
Sample		AD	MM-DTC			
		Ni(II) found, ppm	Recovery(%) ± R.S.D <sup>b</sup>	Ni(II) found, ppm	Recovery(%) ± R.S.Db	
	1.0	1.08	99.00 ± 2.45	1.05	97.95 ± 2.15	
	1.2	1.21	97.99 ± 2.95	1.28	98.95 ± 2.15	
I	1.6	1.63	98.75 ± 2.50	1.64	99.37 ± 2.74	
	1.8	1.90	98.88 ± 2.89	1.91	99.44 ± 2.80	
	2.0	2.15	99.95 ± 2.63	2.10	99.50 ± 2.89	
	1.0	1.08	98.95 ± 2.35	1.02	97.00 ± 2.35	
II	1.2	1.28	99.00 ± 2.74	1.29	99.56 ± 2.72	
	1.6	1.76	99.44 ± 2.80	1.75	98.00 ± 2.74	
	1.8	1.86	97.70 ± 2.98	1.95	98.00 ± 2.58	
	2.0	2.09	100.00 ± 2.56	2.05	98.99 ± 2.48	

I-Industrial Estate; II-Amararaja Batteries, <sup>a</sup>Five millilitres of the Concentrated sample is used, <sup>b</sup>Relative standard deviation (n=6)

Table 3: Determination of nickel (II) with ADMM-DTC in water samples collected around Tirupati, Chittoor District, A.P., India using Catalytic Hydrogen Current (CHC) technique.

		CHCmethod	(DC polarography)	DPP method		
Sample <sup>a</sup> scientific/Local name	Ni(II) added, ppm	ADMM-DTC		ADMM-DTC		
		Ni(II) found, ppm	Recovery(%) ± R.S.Db	Ni(II) found, ppm	Recovery(%) ± R.S.Db	
Vegetables						
Pisum sativum/Peas	1.0	1.14	98.80 ± 2.55	1.13	97.75 ± 2.35	
Phaeolus vulgaris /Bean	1.0	1.12	100.15 ± 2.15	1.10	98.90 ± 2.70	
Leafy vegetables						
Rumex vesicarius/Chukkaku	1.0	1.05	99.15 ± 2.45	1.05	99.25 ± 2.87	
Hibiscus cannabinus/Gongura	1.0	1.06	98.75 ± 2.95	1.04	97.36 ± 2.53	

I-Industrial Estate; II-Amararaja Batteries, <sup>a</sup>Five millilitres of the concentrated of sample is used <sup>b</sup>Relative standard deviation (n=6)

Table 4: Determination of nickel (II) with AMP-DTC in water samples collected around Tirupati, Chittoor District, A.P., India using Catalytic Hydrogen Current (CHC) technique.

		CHCmethod (DC polarography)		DPP method			
Sample <sup>a</sup> scientific/Local name	Ni(II) added, ppm	AD	MM-DTC	ADMM-DTC			
		Ni(II) found, ppm	Recovery(%) ± R.S.Db	Ni(II) found, ppm	Recovery(%) ± R.S.Db		
Vegetables							
Pisum sativum/Peas	1.0	1.14	98.80 ± 2.55	1.13	97.75 ± 2.35		
Phaeolus vulgaris /Bean	1.0	1.12	100.15 ± 2.15	1.10	98.90 ± 2.70		
Leafy vegetables							
Rumex vesicarius/Chukkaku	1.0	1.05	99.15 ± 2.45	1.05	99.25 ± 2.87		
Hibiscus cannabinus/Gongura	1.0	1.06	98.75 ± 2.95	1.04	97.36 ± 2.53		

<sup>&</sup>lt;sup>a</sup>Five millilitres of the concentrated sample is used, <sup>b</sup>Relative standard deviation(n=6)

Table 5: Determination of nickel (II) with ADMM-DTC in agricultural samples around Tirupati, Chittoor District, A.P., India using Catalytic Hydrogen Current (CHC) technique.

		CHC method (DC polarography)		DPP method	
Sample <sup>a</sup> scientific/Local name	Ni(II) added, ppm	Al	MP-DTC	AMP-DTC	
		Ni(II) found, ppm	Recovery(%) ± R.S.Db	Ni(II) found, ppm	Recovery(%) ± R.S.Db
Vegetables					
Pisum sativum/Peas	1.0	1.17	99.62 ± 2.55	1.15	98.95 ± 2.35
Phaeolus vulgaris /Bean	1.0	1.09	98.15 ± 2.15	1.10	98.90 ± 2.15
Leafy vegetables					
Rumex vesicarius/Chukkaku	1.0	1.05	99.15 ± 2.16	1.05	99.25 ± 2.63
Hibiscus cannabinus/Gongura	1.0	1.03	97.05 ± 2.55	1.04	97.46 ± 2.29

<sup>&</sup>lt;sup>a</sup>Five millilitres of the concentrated sample is used, <sup>b</sup>Relative standard deviation(n=6)

Table 6: Determination of nickel (II) with AMP-DTC in agricultural samples around Tirupati, Chittoor District, A.P., India using catalytic hydrogen current (CHC) technique.

## **Conclusions**

The present developed CHC technique is novel, reliable and highly sensitive for the determination of nickel (II) in real samples such as drinking water samples and agricultural materials. The limit of determination of the developed method was superior when compared with already reported methods of these laboratories. The nickel (II)-dithiocarbamate complexes were more stable and thereby more catalytic activity. The developed method was distinct in terms of sensitivity and selectivity towards nickel (II) present in various environmental matrices.

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