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Novel Dithiocarbamates for Electrochemical Detection of Nickel(II) in Environmental Samples

T. NIRANJAN[1], SUVARDHAN KANCHI[2], KRISHNA BISETTY[2] and N. VENKATASUBBA NAIDU[1,*]

[1]Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, India
[2]Department of Chemistry, Durban University of Technology, Durban 4000, South Africa

*Corresponding author: E-mail: nvsn69@gmail.com

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Ammonium 4-phenylpiperazine-1-dithiocarbamate (Amm 4-PP-DTC) and ammonium 4-benzylpiperidine-1-dithiocarbamate (Amm 4-BP-DTC) were synthesized for the determination of nickel(II) using catalytic hydrogen currents (CHC's) technique with DC Polarography. The method was based on the chelation of nickel(II) with Amm 4-PP-DTC/ Amm 4-BP-DTC in presence of NH_4OH at pH 6.8 to produce catalytic hydrogen current at -1.50V and -1.41 V *vs.* SCE respectively. Optimized polarographic conditions were established by studying effect of pH, supporting electrolyte (NH_4Cl), ligands and metal ion concentration and effect of adverse ions on peak height to improve the sensitivity, selectivity and detection limits of the present method. This technique is successfully applied for the analysis of nickel(II) in different matrices with recoveries ranging from 96.0-99.0 % and the results obtained were comparable with the atomic absorption spectroscopy.

Keywords: DC polarography, Catalytic hydrogen current technique, Nickel(II), Ammonium 4-arylpiperazine-1-dithiocarbamate.

INTRODUCTION

Nickel is a naturally occurring, lustrous, silvery-white metallic element. It is mainly available in gernirite, magnesium nickel silicate of different composition in the form of ores. Nickel is an important element, because it forms alloys with several other elements and also useful in making corrosive-resistant alloys such as Monel, Inconel and the Hastelloys. Nickel plating is often used to coat other metals for protection and used in the manufacture of ceramics, Edison storage battery.

The absorption of nickel is dependent on its physico-chemical form, with water soluble forms being more readily absorbed. The metabolism of nickel involves conversion to various chemical forms and binding to various ligands[1]. Nickel in large dose (< 0.5 g), some forms of nickel may be acutely toxic to human when taken orally[2,3]. The toxic effect of oral exposure to nickel usually involve the kidney defects with some evidence form animals studies showing a possible developmental/ reproductive toxicity effect[1,4]. Even though nickel is moderately toxic, still low concentration effects on human system causing dermatological, lung disease and malignant tumours[5]. Mainly nickel enters into water system from the industrial processes and waste disposals[6]. According to U.S. Public Health Service, the average concentration of nickel in domestic water is 4.8 µg/L and the daily intake is about 0.3 to 0.6 mg/day. Higher average levels of Ni(II) occur in foods because of contamination during processing and cooking in nickel-plated utensils.

Therefore, it is important to develop sensitive, rapid and economical method for the quantitative determination of trace amounts of nickel in various samples of environmental importance. Several analytical techniques such as AAS[7-10], ICP-AES[11-13] and XRF[14,15] for the determination of nickel was reviewed. However, electrochemical instrumentation is comparatively economical, sensitive and selective for the analysis of Ni(II) in trace and ultra-trace levels in various environmental and agricultural samples. Catalytic hydrogen current's technique was earlier developed in our laboratory for the determination of Ni(II) in drinking water samples and agricultural samples using D.C. Polarography[16-19].

The preliminary work on polarographic behaviour of Ni(II) with ammonium 4-phenylpiperazine-1-dithiocarbamate (Amm 4-PP-DTC) and ammonium 4-benzylpiperidine-1-dithiocarbamate (Amm 4-BP-DTC) in ammonium chloride-ammonium hydroxide medium revealed that a nickel reduction wave is followed by a catalytic wave. Dithiocarbamates (Amm 4-PP-DTC and Amm 4-BP-DTC) or simple metal ions in the medium do not give any peak current at the potentials of catalytic hydrogen current's (CHC; -1.50 V and -1.41 V *vs.* SCE) and the current-voltage curves of Ni(II)-dithiocarbamate complexes are shown in the Fig. 1a and 1b.

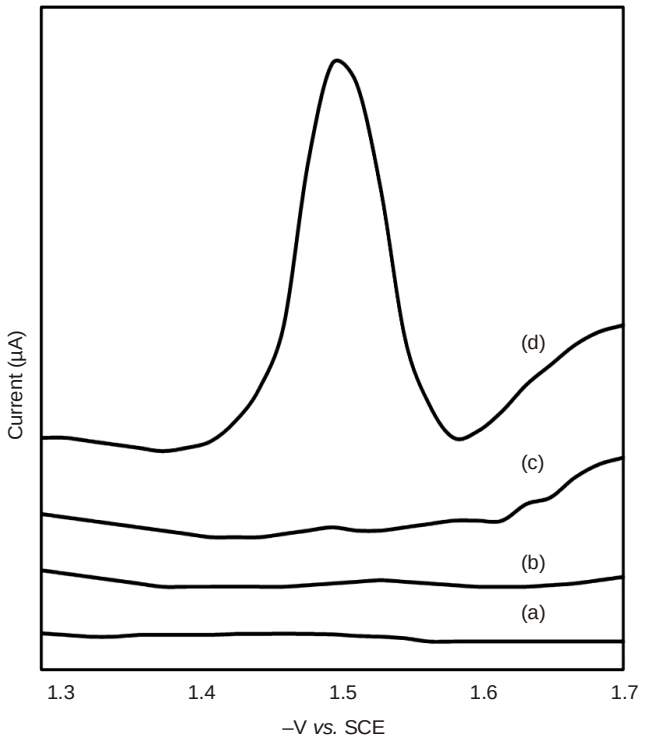


Fig. 1a. Polarographic curve of Ni(II) in NH_4Cl-NH_4OH medium in the presence of Amm 4-PP-DTC (a)0.3 M NH_4Cl, pH~6.8 (b) a+3.6 mM Amm 4-PP-DTC (c) a+3.0 ppm Ni(II) (d) b+3.0 ppm Ni(II)

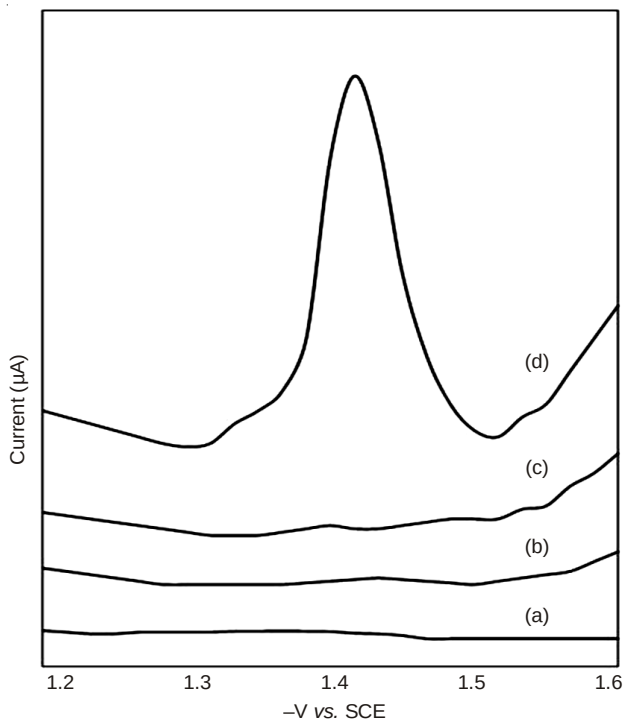


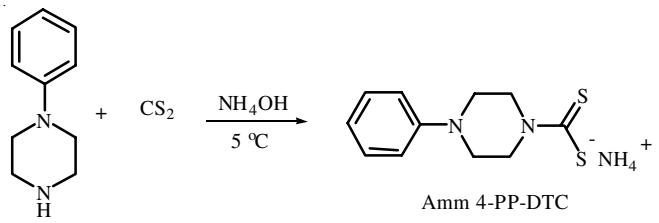
Fig. 1b. Polarographic curve of Ni(II) in NH_4Cl-NH_4OH medium in the presence of Amm 4-BP-DTC (a) 0.4 M NH_4Cl, pH~6.8 (b) a+3.8 mM Amm 4-BP-DTC (c) a+3.0 ppm Ni(II) (d) b+3.0 ppm Ni(II)

EXPERIMENTAL

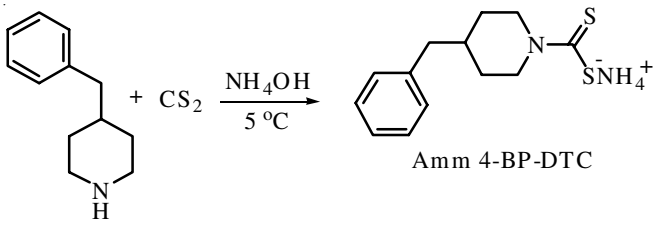
The current-voltage curves are recorded using a DC polarographic analyzer, model CL-357 coupled with model LR-101 strip chart recorder manufactured by Elico Private Ltd. (Hyderabad, India). Effects of mercury height on polarographic currents are studied using D.C. recording polarograph model CL-25 of Elico Pvt. Ltd., Hyderabad, India. The Shimadzu AA 6300 spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths (resonance line) using an air acetylene flame was used. The instrumental parameters were those recommended by the manufacturer.

All reagents were of analytical grade and deionized double distilled water was used for the preparation of all solutions. 1-Phenylpiperazine, 4-benzylpiperidine, carbon disulphide, ammonium chloride and ammonia solution were purchased from S.D. Fine chemicals, Mumbai, India. Standard solution of Ni(II) (1 μg/mL) was prepared by weighing 4.050 g of $NiCl_2 \cdot 6H_2O$ (S.D. Fine chemicals, Mumbai, India) and dissolved in deionized double distilled water and made up to the mark in 1 L standard flask. Amm 4-PP-DTC (0.01 M) was prepared by weighing 2.55 g of Amm 4-PP-DTC and dissolved in 100 mL deionized double distilled water. Amm 4-BP-DTC (0.01 M) was prepared by weighing 2.67 g of Amm 4-BP-DTC and dissolved in 100 mL deionized double distilled water. Freshly prepared solution was stored in dark coloured bottle. Stock solutions of Amm 4-PP-DTC, Amm 4-BP-DTC and NH_4Cl were prepared by appropriate dilutions in 250 mL standard flask and stored in dark place.

Synthesis of Amm 4-PP-DTC and Amm 4-BP-DTC: Carbon disulphide (40 g) was slowly added to a solution of 1-phenylpiperazine/4-benzylpiperidine (45 g) in 25 mL of deionized double distilled water at 5 °C with constant stirring, followed by ammonium hydroxide. The product (**Schemes I** and **II**) was warmed to room temperature and washed repeatedly two to three times with purified acetone. The reaction product was purified by recrystallization in acetone[20-26]. The purified compounds have melting points of 194-199 °C (Amm 4-PP-DTC) and 207-213 °C (Amm 4-PP-DTC) at 740 mm pressure.



Scheme-I: Synthesis of Amm 4-PP-DTC



Scheme-II: Synthesis of Amm 4-BP-DTC

General procedure: A measured volume of the NH_4Cl, supporting electrolyte and ligands (Amm 4-PP-DTC and Amm 4-BP-DTC) were added to the electro-active species [Ni(II)],

maintaining the optimum pH and the solution was made up to 100 mL in a standard flask with deionized double 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 were recorded using DC Polarography.

RESULTS AND DISCUSSION

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

Effect of pH: The polarogram of 4 ppm Ni(II), 3.6 mM Amm 4-PP-DTC and 3.8 mM Amm 4-BP-DTC in ammonium chloride medium (0.3/0.4 M for Amm 4-PP-DTC/Amm 4-BP-DTC) are recorded in the pH range 0.5-10.0. Precipitations of Ni(II)-dithiocarbamate were not formed at any pH. The peak current increased upto pH 6.8 in case of both Amm 4-PP-DTC/ Amm 4-BP-DTC and the peak potentials shifted towards more negative values with the increase in pH. Further, increase in pH, the peak current decreases. Hence, the pH = 7 where the peak has maximum height was fixed as the optimum value for all other studies. The results are shown in Fig. 2.

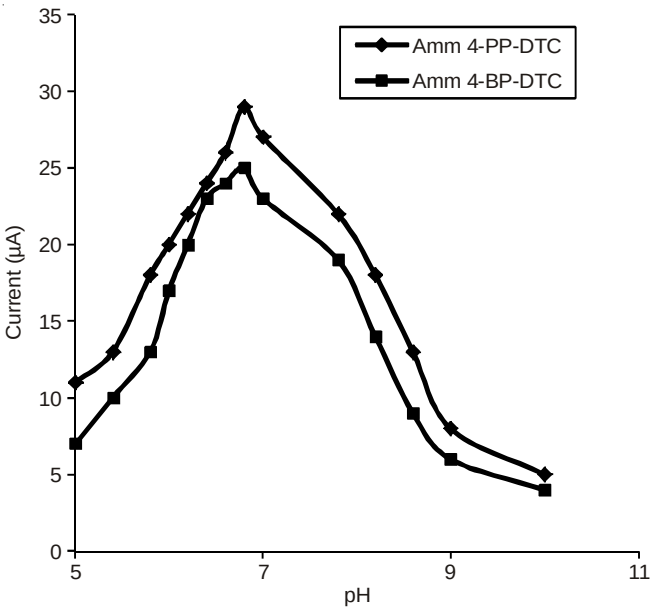


Fig. 2. Effect of pH for the determination of Ni(II) with Amm 4-PP-DTC and Amm 4-BP-DTC

Effect of supporting electrolyte concentration: The effect of supporting electrolyte concentration on the peak current is investigated by employing the solution containing 4.0 ppm Ni(II) and 3.6/3.8 Amm 4-PP-DTC/Amm 4-BP-DTC respectively. The concentration of ammonium chloride was changed in the range of 0.05 - 6.0 M and the polarograms were recorded maintaining pH of the solution at 6.8 (Fig. 3). The peak height was increased with ammonium chloride concen-tration upto 0.3 and 0.4 M in case of Amm 4-PP-DTC/Amm 4-BP-DTC respectively. With further increase in concentration, the peak height also decreases. The concentration of ammonium chloride was therefore fixed at the maximum peak height value. The peak potential shifted slightly towards positive potential with ammonium chloride concentration.

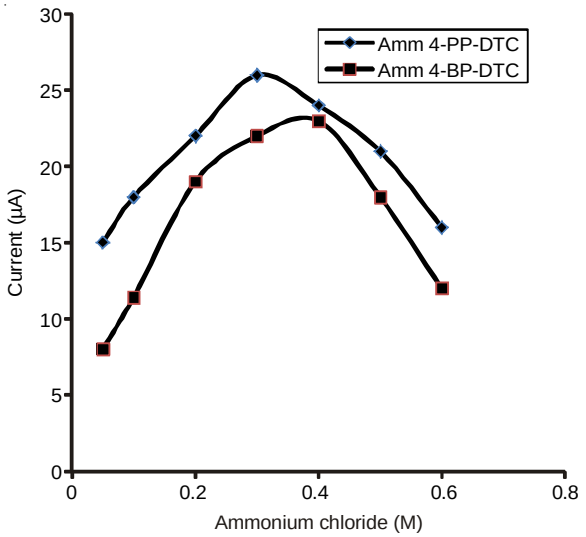


Fig. 3. Effect of supporting electrolyte for the determination of Ni(II) with Amm 4-PP-DTC and Amm 4-BP-DTC

Effect of reagent concentration: The influence of dithiocarbamate on the polarographic characteristics of Ni(II)-dithiocarbamate complexes were studied using 4 ppm Ni(II) ion in 0.3/0.4 M ammonium chloride for Amm 4-PP-DTC/Amm 4-BP-DTC respectively at pH 6.8. The dithiocarbamates concentrations were varied in the range of 0.2-5.0 mM. The peak current increases with dithiocarbamate concentration and tends to a limiting value similar in the form to the Langmuir adsorption isotherm (Figs. 4 and 5). The reagent concentration at maximum wave height was fixed as 3.6 and 3.8 mM for Amm 4-PP-DTC and Amm 4-BP-DTC respectively. The peak potential shifted to more negative potential with increase in dithiocarbamates concentration and beyond the optimum concentration, the peak potential, as well as height remained constant.

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

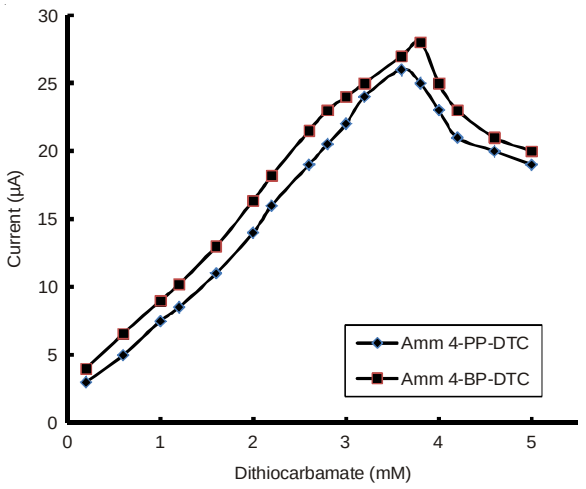


Fig. 4. Effect of reagent concentration for the determination of Ni(II) with Amm 4-PP-DTC and Amm 4-BP-DTC

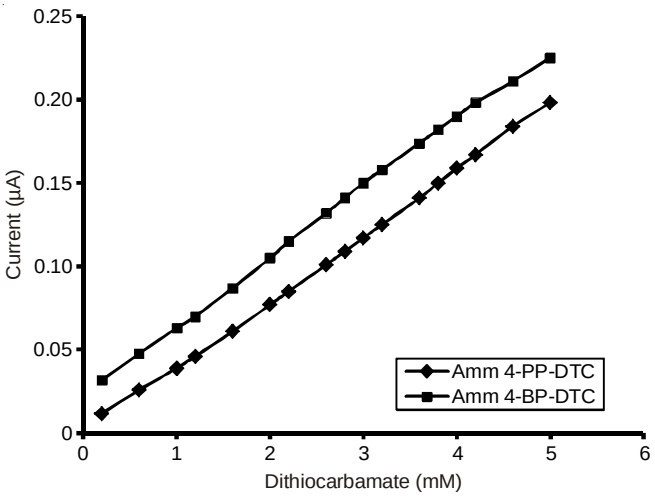


Fig. 5. Langmuir adsorption isotherm plot for the determination of Ni(II) with Amm 4-PP-DTC and Amm 4-BP-DTC

TABLE-1
EFFECT OF MERCURY PRESSURE FOR THE DETERMINATION OF Ni(II) WITH Amm 4-PP-DTC AND Amm 4-PP-DTC

Height of the mercury column (cm)	Amm 4-PP-DTC		Amm 4-BP-DTC	
	Current (μA)	$i_C/\sqrt{h}$	Current (μA)	$i_C/\sqrt{h}$
22	25.60	5.598	24.40	4.367
27	24.75	4.979	21.60	3.598
32	24.60	4.271	19.70	3.034
37	23.40	3.726	18.55	2.893

Effect of maximum suppressor: For a solution containing 4 ppm Ni(II), dithiocarbamate 3.6/3.8 Amm 4-PP-DTC/Amm 4-BP-DTC at pH 6.8 with gelatine in the range 0.005-0.001 % and 0.002-0.004 % Triton X-100 were added and the effect was studied.

It was found that Ni(II) reduction wave was suppressed slightly by adding gelatine and the catalytic wave reduced to about 10 % upto 0.005 % of gelatine. The peak potential shifted towards less negative potentials.

Triton X-100 has no effect on Ni(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 symmetrically one with a clear base line. 0.002 % of Triton X-100 was therefore, maintained for all studies and the results were tabulated in Table-2.

TABLE-2
EFFECT OF MAXIMUM SUPPRESSORS FOR THE DETERMINATION OF Ni(II) WITH Amm 4-PP-DTC AND Amm 4-BP-DTC

Maximum suppressor (%)	Current (μA)	
	Amm 4-PP-DTC	Amm 4-BP-DTC
Gelatin		
0.000	24.00	23.00
0.002	22.70	20.60
0.004	18.70	18.30
Triton X-100		
0.00	24.00	23.00
0.005	24.00	23.00
0.010	24.00	23.00

Effect of temperature: The current-voltage curves for the system containing 4 ppm Ni(II), 3.6 mM Amm 4-PP-DTC, 0.3 M NH_4Cl at pH 6.8 and 3.8 mM Amm 4-BP-DTC, 0.4 M NH_4Cl at pH 6.8 in the presence of 0.002 % Triton X-100 were recorded at various temperatures from 20-50 °C. It was found that with increase in temperature the catalytic wave height increases and the temperature coefficient values have gradually drops down upto 35 °C. Above 35 °C the current, i_C become completely temperature independent.

Effect of nickel(II) on peak current: The effect of Ni(II) in the range of 0.05-6.0 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 shows that the peak height increases linearly with the Ni(II) concentration and the obtained results were illustrated in Fig. 6.

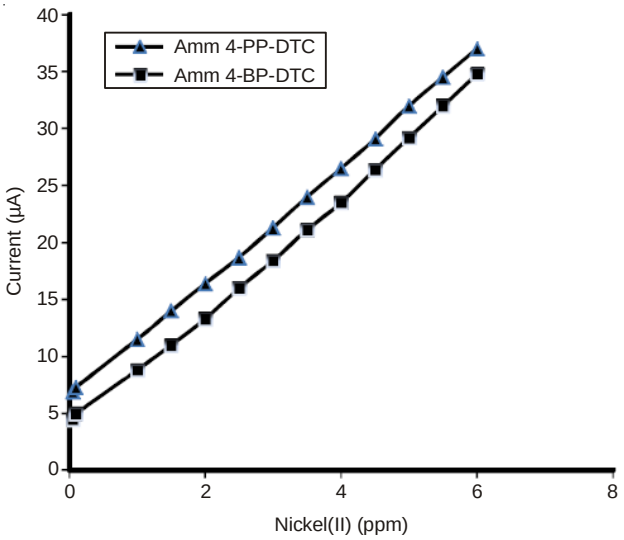


Fig. 6. Effect of nickel(II) on peak current for the determination of Ni(II) with Amm 4-PP-DTC and Amm 4-BP-DTC

The Ni(II) reduction wave also increases with increase in Ni(II) concentration without any shift in peak potential. The catalytic wave also increases linearly with Ni(II) concentration.

Effect of foreign ions: Various metal ions commonly associated with Ni(II) like Fe(II), Cu(II), Cr(VI), Zn(II), Mo(VI) and Al(III) have been used in the present study to evaluate the change that occur in the catalytic wave of Ni(II)-dithiocarbamate system. The concentration of Ni(II) was maintained at 4 ppm and 100-fold excess of foreign ions were added. Of all the metal ions studied Fe(II) and Cu(II) form precipitates with dithiocarbamates in the conditions where Ni(II)-dithiocarbamate complex gives a catalytic wave. Aluminium(III) does not interfere whereas Cr(VI) gives catalytic current with peak potentials at -1.56 V and -1.65 V *vs.* SCE and suggests that a simultaneous determination of Ni(II) and Cr (VI) is possible without any separation or adding masking agents. Zn(II) interferes in the determination of Ni(II), but it was masked by adding 5 mL of 2 % sodium tartrate solution. Mo (VI) severely interferes by increasing the wave height of Ni(II) and the peak potential shifts towards more negative values. Se(IV), Th(IV), Ce(IV) and Sn(II) also do not interfere upto 100-fold excess with the Ni(II)-dithiocarbamtes system.

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

Effect of indifferent cations: The effect of neutral salts on Ni(II)-dithiocarbamate 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 increase in ionic strength due to the addition of neutral salts results in a continuous decrease in catalytic current and also in wave height in the presence of sodium chloride was little less to that of potassium chloride and the decrease was more for lithium chloride and much more for calcium chloride (Fig. 7a and 7b). The peak potential shifts towards less negative potential in all cases.

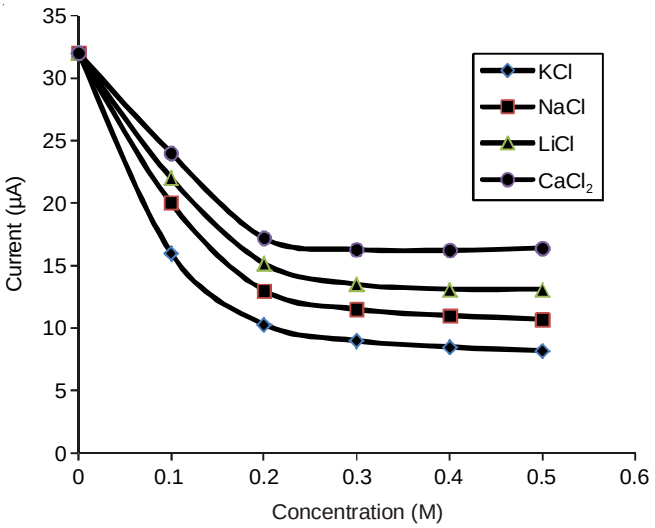


Fig. 7a. Effect of indifferent ions on Ni(II)-Amm 4-PP-DTC complex at (DME) for the determination of Ni(II)

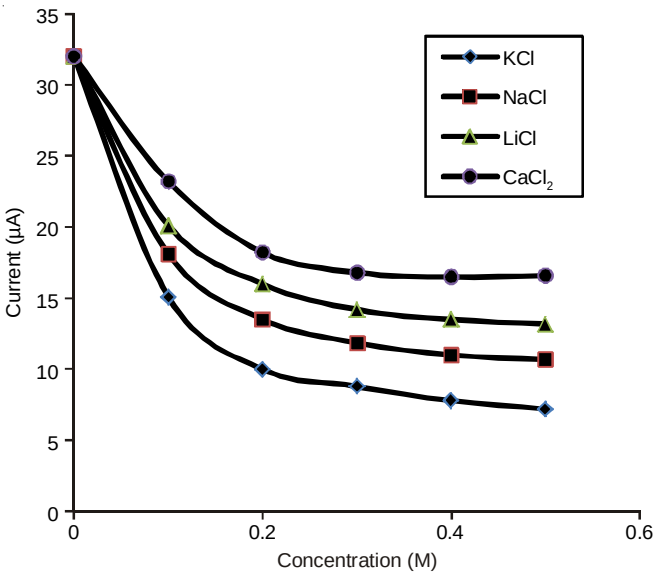


Fig. 7b. Effect of indifferent ions on Ni(II)-Amm 4-BP-DTC complex at (DME) for the determination of Ni(II)

Application of the catalytic hydrogen current method to real samples: The method was extended to the analysis of trace quantities of Ni(II) in various waters and agricultural materials.

Drinking water samples: 1 L of the water samples collected from industrial estate and around Amararaja batteries (Tirupati town, India) were preconcentrated to 100 mL.

Agricultural materials: 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 triple distilled water.

The amount of Ni(II) present in the samples was determined by referring its current to the calibration curve drawn with standard solutions of Ni(II). The amount of Ni(II) obtained by catalytic polarographic method was further supported by AAS method. The results in Tables 3 and 4 reveals that the

TABLE-3
DETERMINATION OF Ni(II) WITH Amm 4-PP-DTC IN WATER SAMPLES COLLECTED AROUND TIRUPATI, INDIA USING CATALYTIC HYDROGEN CURRENT (CHC) TECHNIQUE

Sample[a]	Ni(II) added (ppm)	CHC Method (DC polarography)		AAS Method	
		Amm 4-PP-DTC		Amm 4-PP-DTC	
		Ni(II) found (ppm)	Recovery (%) ± R.S.D.[b]	Ni(II) found (ppm)	Recovery (%) ± R.S.D.[b]
I	1.0	1.07	98.93±2.43	1.05	98.95±2.15
	1.2	1.18	98.82±2.75	1.28	98.72±2.15
	1.6	1.61	98.39±2.47	1.64	98.36±2.74
	1.8	1.80	98.20±2.82	1.91	99.09±2.80
	2.0	2.13	99.87±2.59	2.10	97.90±2.89
II	1.0	1.05	98.95±2.32	1.02	98.98±2.35
	1.2	1.24	98.76±2.72	1.29	98.71±2.72
	1.6	1.69	99.31±2.60	1.75	98.25±2.74
	1.8	1.82	98.18±2.96	1.95	98.05±2.58
	2.0	2.07	97.93±2.54	2.05	97.95±2.48

I: Industrial estate; II: Amararaja Batteries, [a]5 mL of the concentrated sample is used; [b]Relative standard deviation (n = 6)

TABLE-4
DETERMINATION OF Ni(II) WITH Amm 4-BP-DTC IN WATER SAMPLES COLLECTED AROUND TIRUPATI, INDIA USING CATALYTIC HYDROGEN CURRENT (CHC) TECHNIQUE

Sample[a]	Ni(II) added (ppm)	CHC Method (DC polarography)		AAS Method	
		Amm 4-BP-DTC		Amm 4-BP-DTC	
		Ni(II) found (ppm)	Recovery (%) ± R.S.D.[b]	Ni(II) found (ppm)	Recovery (%) ± R.S.D.[b]
I	1.0	1.08	98.92±2.52	1.04	98.96±2.15
	1.2	1.24	98.76±2.58	1.24	98.76±2.35
	1.6	1.63	98.37±2.35	1.64	99.36±2.84
	1.8	1.91	98.09±2.86	1.92	98.08±2.85
	2.0	2.13	97.87±2.69	2.14	97.86±2.89
II	1.0	1.06	98.94±2.36	1.02	98.98±2.35
	1.2	1.18	98.82±2.34	1.29	98.71±2.72
	1.6	1.72	98.28±2.61	1.74	98.26±2.64
	1.8	1.87	98.13±2.89	1.95	98.05±2.50
	2.0	2.08	97.92±2.35	2.05	97.95±2.35

I: Industrial estate; II: Amararaja Batteries, [a]5 mL of the concentrated of sample is used; [b]Relative standard deviation (n = 6)

TABLE-5
DETERMINATION OF Ni(II) WITH Amm 4-PP-DTC IN AGRICULTURAL SAMPLES AROUND TIRUPATI, INDIA USING CATALYTIC HYDROGEN CURRENT TECHNIQUE

Sample[a] Scientific/Local name	Ni(II) added (ppm)	CHC Method (DC polarography) Amm 4-PP-DTC		AAS Method Amm 4-PP-DTC	
		Ni(II) found (ppm)	Recovery (%) ± R.S.D.[b]	Ni(II) found (ppm)	Recovery (%) ± R.S.D.[b]
Vegetables					
Pisum sativum/Peas	1.0	1.12	98.88 ± 2.570	1.13	98.87 ± 2.12
Phaseolus vulgaris/Bean	1.0	1.10	98.90 ± 2.152	1.10	98.90 ± 2.23
Leafy vegetables					
Rumex vesicarius/Chukkaku	1.0	1.02	98.98 ± 2.40	1.05	98.95 ± 2.08
Hibiscus cannabinus/Gongura	1.0	1.08	98.92 ± 2.99	1.04	98.96 ± 2.45

[a]5 mL of concentrated sample is used; [b]Relative standard deviation (n = 6)

TABLE-6
DETERMINATION OF Ni(II) WITH Amm 4-BP-DTC IN AGRICULTURAL SAMPLES AROUND TIRUPATI, INDIA USING CATALYTIC HYDROGEN CURRENT TECHNIQUE

Sample[a] Scientific/Local name	Ni(II) added (ppm)	CHC Method (DC polarography) Amm 4-PP-DTC		AAS Method Amm 4-BP-DTC	
		Ni(II) found (ppm)	Recovery (%) ± R.S.D.[b]	Ni(II) found (ppm)	Recovery (%) ± R.S.D.[b]
Vegetables					
Pisum sativum/Peas	1.0	1.18	98.82 ± 2.57	1.15	98.85 ± 2.81
Phaseolus vulgaris/Bean	1.0	1.08	98.92 ± 2.17	1.10	98.90 ± 2.12
Leafy vegetables					
Rumex vesicarius/Chukkaku	1.0	1.04	98.96 ± 2.18	1.05	98.95 ± 2.18
Hibiscus cannabinus/Gongura	1.0	1.01	98.99 ± 2.57	1.04	98.96 ± 2.15

[a]5 mL of concentrated sample is used; [b]Relative standard deviation (n = 6)

various water samples analyzed contain traces of Ni(II) are within the tolerance limits and the percentage recovery values obtained with the two ligands are comparable and in good agreement with AAS method. The Ni(II) content present in agricultural materials, *Hibiscus cannabinus* (Gongura), *Rumex vesicarius* (Chukkaku), *Phaeolus vulgaris* (Bean) and *Pisum sativum* (Peas) showed that the values were in agreement with the standard values (Tables 5 and 6).

These observations indicate that the catalytic hydrogen current method proposed for Ni(II) using Amm 4-PP-DTC and Amm 4-BP-DTC in ammonium chloride-ammonium hydroxide medium may be successfully applied for the determination of low concentration of Ni(II) present in waters and agricultural materials.

Conclusion

The present developed catalytic hydrogen current technique is reliable and highly sensitive for the determination of Ni(II) in real samples such as drinking water samples and agricultural materials. The limit of determination of the developed method is superior when compared with already reported methods in this laboratory. The method has added an advantage over reported methods owing to it is: (i) More stable complexes with dithiocarbamates and thereby more catalytic activity. (ii) Distinct in terms of sensitivity and selectivity towards Ni(II) present in various environmental matrices. (iii) Obtained results are comparable with AAS method.

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