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Ni(II)-ammonium morpholine dithiocarbamate complex studies with polarography at DME by catalytic hydrogen currents in various environmental samples

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ABSTRACT

This paper deals with the simple, sensitive catalytic hydrogen polarographic method for the determination of Ni(II) with Amm Morpholine dithiocarbamate (Amm Mor-DTC) in various water samples and agricultural materials. The method was based on the catalytic hydrogen wave of Amm Mor-DTC-Ni(II) complex in the presence of $\text{NH}_4\text{Cl-NH}_4\text{OH}$ medium at pH 6.0 and produce a catalytic hydrogen wave at -1.30 V vs SCE. Various parameters such as effect of pH, $\text{NH}_4\text{Cl-NH}_4\text{OH}$, Amm Mor-DTC, metal ion concentration and foreign ion effect on peak height were investigated to enhance the sensitivity of the present method. The obtained results were in good agreement with differential pulse polarographic method in terms of terms of Student's 't'-test and Variance ratio 'F'-test. The proposed method was applied for the determination of Ni(II) in various water samples and agricultural materials. © 2011 Trade Science Inc. - INDIA

KEYWORDS

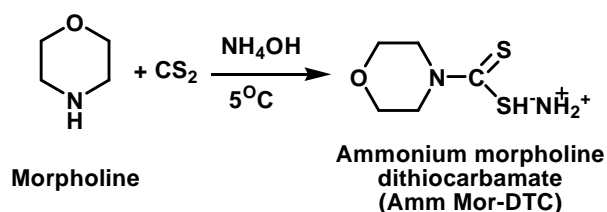
D.C.Polarography;
Differential pulse polarography (DPP);
Catalytic hydrogen waves;
Nickel (II)-ammonium morpholine dithiocarbamate- (Amm Mor-DTC);
Water samples;
Agricultural materials.

INTRODUCTION

Industrially and biologically nickel was having great importance^[1,2]. In nature nickel mainly available in combination with arsenic, antimony and sulphur. Electroplating, nickel based batteries, steel and ceramic industries were the common sources to enter nickel into environment and nickel was also used as a catalyst and coinage element in olden days. Several analytical methods were employed such as Spectrophotometry^[3], Neutron activation analysis^[4], Inductively coupled plasma atomic emission spectrophotometry^[5,6], Stripping and Voltammetric analysis^[7-9], Polarography^[10-12] Atomic absorption spectrometry^[13] and X-ray fluorescence^[14]. The above reported methods are commercial, time con-

suming and requires special instrumentally skilled analyst for analysis except spectrophotometry and polarography.

In view of this and speedy growth of analytical field for monitoring the trace and toxic metals, there was an increasing need to develop facile, rapid, sensitive and selective, economically advantageous (low reagent con-



Scheme 1: Synthesis of ammonium morpholine dithiocarbamate (Amm Mor-DTC)

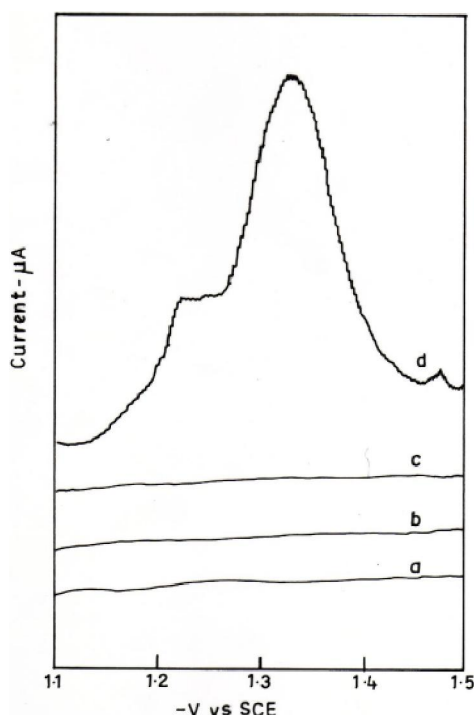


Figure 1 : Polarographic curve of Nickel(II) in $\text{NH}_4\text{Cl-NH}_4\text{OH}$ medium in the presence of Amm Mor-DTC. (a) $0.3 \text{ M NH}_4\text{Cl}$, $\text{pH} \sim 6.0$, (b) a + $3.0 \text{ mM Amm Mor-DTC}$, (c) a + 4.0 ppm Ni(II) (d) b + 4.0 ppm Ni(II)

sumption), provides reproducible results in statistical importance (elimination of subjective analytical errors and foreign species) and useful analytical tool for quantification of sample in a variety of real natural samples at low detection levels for series of analysis for the determination of toxic species in various environmental matrices. By keeping this in view d.c polarography was selected due to its presence in every ordinary laboratories and synthesized a novel small, simple, selective, economical and eco-friendly ligand for the analysis of Ni(II) in the present study.

EXPERIMENTAL

Materials and apparatus

All reagents were of analytical grade and deionized doubly distilled water was used for preparation of all solutions.

Morpholine hydrochloride, carbon disulphide, potassium chromate, ammonium chloride and ammonia were purchased from S.D Fine Chemicals, Mumbai, India. A d.c recording polarograph, differential pulse polarography and pH meter with models CL-358, CL-

362 and Li-120 were used for polarogram recordings and pH measurements respectively.

Ammonium Morpholine dithiocarbamate was synthesized by slight modifications in the reported method^[12] in our laboratory and recrystallized in acetone as shown in Scheme 1.

Stock solutions of Ammonium Morpholine dithiocarbamate, NH_4Cl and potassium chromate were prepared by appropriate addition of reagents and chemicals in 250 ml standard flask and stored in dark place.

Experimental procedure

A measured volume of the $\text{NH}_4\text{Cl-NH}_4\text{OH}$ buffer and ligand was added to the required of the electroactive species, maintaining the optimum pH and the solution is made up to 100 ml in beaker with deionized 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. Polarogram of the solution was recorded using d.c polarography at -1.30 V as shown in figure 1.

RESULTS AND DISCUSSION

Effect of pH

The polarogram of $4.0 \text{ ppm nickel(II)}$, $3.0 \text{ mM Amm Mor-DTC}$ in ammonium chloride medium (0.3 M for Amm Mor-DTC) was recorded in the pH range 5.0 to 10.0 maintaining 0.002% Triton X-100. Precipitations of Ni(II)-Amm Mor-DTC was not formed at any pH . The wave length increased up to $\text{pH} 6.0$ and the peak potentials shifted towards more negative values with increase in pH . With further increase in pH the wave length decreased. Hence, the pH where the wave has maximum height was fixed as the optimum value for all other studies. The results obtained are summarized 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 Ni(II) and $3.0 \text{ mM Amm Mor-DTC}$. The concentration of ammonium chloride was changed in the range of 0.05 M to 0.6 M and the polarogram was recorded maintaining pH of the solution at 6.0 Amm Mor-DTC. The results were given in

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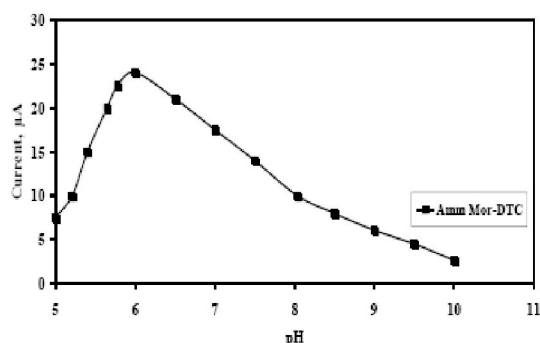


Figure 2 : Effect of pH on Ni(II)-Amm Mor-DTC complex system

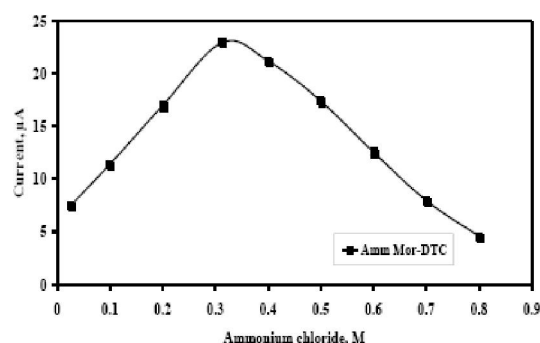


Figure 3 : Effect of Supporting Electrolyte on Ni(II)-Amm Mor-DTC complex system

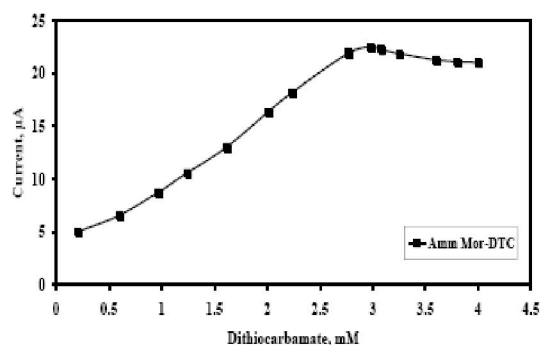


Figure 4 : Effect of reagent concentration on Ni(II)-amm mor-DTC complex system

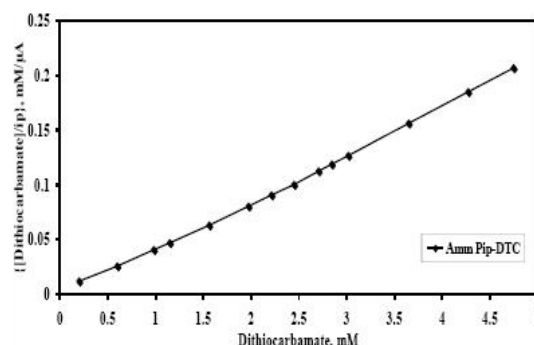


Figure 5 : Langmuir adsorption isotherm plot of Ni(II)-amm mor-DTC complex system

figure 3. The peak height increased with ammonium chloride concentration up to 0.3 M for Amm Mor-DTC. With further increase in concentration the wave length decreased. The concentration of ammonium chloride was therefore fixed at the maximum wave height value. The peak potential shifted slightly towards positive potential with ammonium chloride concentration.

Effect of reagent concentration

The influence of Amm Mor-DTC on the polarographic characteristics of Ni(II)-Amm Mor-DTC complex was studied using 4.0 ppm Ni(II) ion in 0.3 M ammonium chloride for Amm Mor-DTC maintaining pH 6.0. The Amm Mor-DTC concentration was varied in the range 0.2 mM to 4.0 mM. The peak current increased with Amm Mor-DTC concentration and tends to a limiting value similar in the form to the Langmuir adsorption isotherm (Figure 4 & 5).

The reagent concentration at maximum wave height is fixed for all studies as 3.0 mM for Amm Mor-DTC. The peak potential shifted to more negative potential with increase in Amm Mor-DTC 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 Ni(II) Amm Mor-DTC 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/v_h values also decreased, whereas nickel reduction wave increased with pressure following diffusion controlled nature and i_d/v_h was constant (TABLE 1).

Effect of maximum suppressor

For a solution containing Ni(II) 4.0 ppm and Amm Mor-DTC (3.0 mM) at pH 6.0, gelatin in the range 0.005 to 0.01% and Triton X-100 0.002 to 0.004 % are added and the effect was studied.

It was found that the Ni(II) reduction wave was suppressed slightly by adding gelatin and the catalytic wave was reduced to about 10% up to 0.005 % gelatin and the decrease was small above this concentration. The peak potential shifted towards less negative potentials.

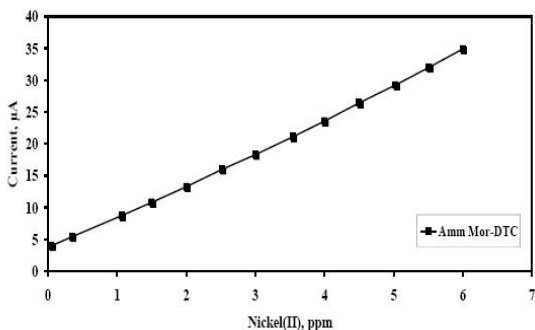


Figure 6 : Effect of Nickel (II) on Peak Current of Ni(II)-Amm Mor-DTC complex system

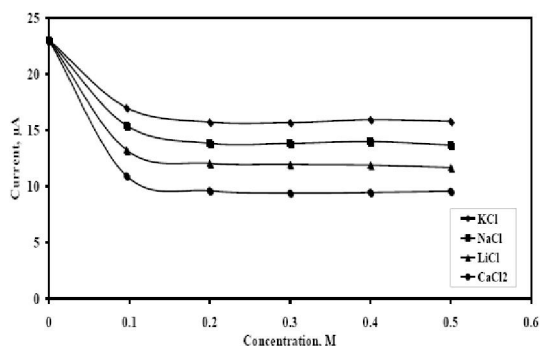


Figure 7 : Effect of Indifferent Ions on Ni(II)-Amm Mor-DTC complex system

Triton X-100 has no effect on Ni(II) reduction as well as on the catalytic peak current and peak potential. But the presence of Triton 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. The results are given in TABLE 2.

Effect of temperature

The current-voltage curves for the system containing 4.0 ppm Ni(II), 3.0 mM Amm Mor-DTC and 0.3 M NH_4Cl at pH 6.0 in the presence of 0.002% Triton X-100 are recorded at various temperatures from 20 to 50°C.

It is found that with increase in temperature the catalytic wave height increased and the temperature coefficient values have gradually fallen down 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 ion in the range 0.05 to 6.0 ppm is studied on the peak current in the presence of

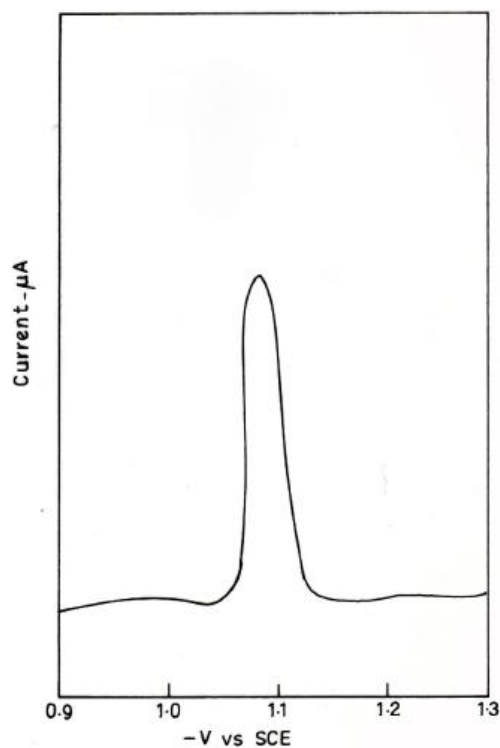


Figure 8 : Differential Pulse Polarographic curve of Nickel (II) in $\text{NH}_4\text{Cl-NH}_4\text{OH}$ medium in the presence of Amm Mor-DTC. Current Range : 100 μA Scanrate : 6 mV/S, Pulse Amplitude : 50 mV Droptime : 1 Sec, Manganese(II) : 0.001 ppm

optimum concentrations of Amm Mor-DTC and ammonium chloride at fixed pH 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 with Amm Mor-DTC. The results obtained were presented in figure 6.

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

Effect of foreign ions

Various metal ions commonly associated with nickel like Fe(II), Cu(II), Cr(VI), Zn(II), Mo(VI) & Al(III) have been used in the present study to evaluate the changes that occur in the catalytic wave of Ni(II)-Amm Mor-DTC system. The concentration of Ni(II) was maintained at 4.0 ppm and 100 fold excess of foreign ions are added. Of all the metal ions studied Fe(II) and Cu(II) form precipitates with dithiocarbamate in the conditions where Ni(II)-Amm Mor-DTC complex gives a catalytic wave. Al(III) does not interfere whereas

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TABLE 1 : Effect of mercury pressure on Ni(II)-Amm Mor-DTC complex

System		Amm mor-DTC	
Ni(II), ppm		4.0	
NH ₄ Cl, M		0.3	
Dithiocarbamate, mM		3.0	
pH		6.0	
S. No	Height of the mercury column, cm	Amm mor-DTC	
		Current, μ A	I _c /h
1	21	24.00	4.357
2	26	21.00	3.578
3	31	19.00	3.024
4	36	18.75	2.843

TABLE 2 : Effect of maximum suppressors on Ni(II)-amm mor-DTC complex

System		Amm mor-DTC	
Ni(II), ppm		4.0	
NH ₄ Cl, M		0.3	
Dithiocarbamate, mM		3.0	
pH		6.0	
S. No	Maximum suppressor, %	Current, μ A	
		Amm mor-DTC	
A. Gelatin			
1	0.000	24.00	
2	0.005	21.60	
3	0.010	19.44	
B. Triton X-100			
1	0.000	24.00	
2	0.002	24.00	
3	0.004	24.00	

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) & Cr(VI) was possible without any separation or adding masking agents. Zn(II) interferes in the determination of Ni(II) but was masked by adding 5 ml of 2 % sodium tartrate solution. Mo(VI) severely interferes by increasing the wave height of Ni(II) and shifting the peak potential towards more negative values. Se(IV), Te(IV), Ce(IV) and Sn(II) also do not interfere up to 100 fold excess with the nickel-Amm Mor-DTC system.

Anions such as fluoride, bromide, iodide, tartrate, sulphate, thiosulphate, phosphate, carbonate, oxalate, nitrite and nitrate do not interfere with the catalytic cur-

rent of Ni(II)-Amm Mor-DTC. Perchlorate and thiocyanate interfere with the wave by reducing the wave height nearly 40 % and EDTA interferes severely by completely suppressing the nickel catalytic wave.

Effect of indifferent cations

The effect of neutral salts on the Ni(II)-Amm Mor-DTC 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 resulted in a continuous decrease of catalytic current and the decrease of wave height in the presence of sodium chloride was little less to that of potassium chloride and the decrease is more for lithium chloride and much more for calcium chloride (Figure 7). The peak potential was shifted towards less negative potential in all cases.

Application of the catalytic method to real samples

The method was extended to the analysis of trace quantities of nickel in various water samples, agricultural materials and synthetic mixtures. The samples are prepared adapting the procedure given in chapter III.

Water samples

One litre of the water samples collected from Industrial estate and around Amararaja batteries (Tirupati town, Chittoor Dt.) are 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 up to 25 ml with double distilled water.

The amount of nickel present in the samples is determined by referring its current to the calibration curve drawn with standard solutions of Ni(II). The amount of metal ion obtained by catalytic polarographic method was further supported by differential pulse polarographic method. The results in TABLE 3 & 4 reveals that the various water samples analyzed contain traces of nickel within the tolerance limits and the percentage recovery values obtained with Amm Mor-DTC was comparable and in good agreement with

TABLE 3 : Determination of Ni(II) with Amm Mor-DTC in water samples around Tirupati, Chittoor District, A.P.INDIA

I. Industrial estate		II. Amararaja batteries					
Amm Mor-DTC		Amm Mor-DTC					
NH ₄ Cl, M		0.3					
Dithiocarbamate, mM		3.0					
Triton X-100%		0.002					
pH		6.0					
Sample ^a	Ni(II) Added, ppm	Catalytic hydrogen current method(DC)				DPP method	
		Amm Mor-DTC				Amm Mor-DTC	
		Ni(II) Found, ppm	Recovery(%)±R.S.D ^b	t-test*	f-test**	Ni(II) Found, ppm	Recovery(%)±R.S.D ^b
I	1.0	1.08	97.00±2.21	2.44	0.56	1.10	99.00±2.63
	1.2	1.33	98.33±2.45	1.62	0.21	1.34	99.16±2.72
	1.6	1.66	98.12±2.41	1.30	0.09	1.68	99.37±2.74
	1.8	1.84	98.33±2.45	1.49	0.16	1.86	99.44±2.80
	2.0	2.07	99.50±2.89	1.08	0.07	2.07	99.50±2.89
II	1.0	1.10	97.00±2.21	1.56	0.19	1.11	98.00±2.39
	1.2	1.33	98.33±2.45	1.75	0.38	1.34	99.16±2.72
	1.6	1.65	99.32±2.74	1.18	0.05	1.66	100.00±2.98
	1.8	1.92	100.00±2.98	1.00	0.02	1.92	100.00±2.98
	2.0	2.05	99.00±2.63	1.05	0.03	2.09	99.50±2.89

^a5 ml of the concentrated sample is used, ^bRelative standard deviation(n=6), *1% level of significance, **5% level of significance

TABLE 4 : Determination of Ni(II) with Amm Mor-DTC in agricultural samples around Tirupati, Chittoor District, A.P.INDIA

System		Amm Mor-DTC						
NH ₄ Cl, M		0.3						
Dithiocarbamate, mM		3.0						
Triton X-100%		0.002						
pH		6.0						
Sample ^a Scientific/ Local name	Ni(II) Added, ppm	Catalytic hydrogen current method(DC)				DPP method		
		Amm mor-DTC				Amm mor-DTC		
		Ni(II) Found, ppm	Recovery(%)±R.S.D ^b	t-test*	f-test**	Ni(II) Found, ppm	Recovery(%)±R.S.D ^b	
Leafy vegetables								
Hibiscus cannabinus/ Gongura		1.0	1.04	99.00±2.75	1.03	0.09	1.04	99.00±2.75
Rumex vesicarius/ Chukkaku		1.0	1.07	98.00±2.60	1.25	0.39	1.08	99.00±2.75
Vegetables								
Phaeolus vulgaris/Bean		1.0	1.02	99.00±2.75	1.20	0.26	1.13	100.00±2.90
Pisum sativum/Peas		1.0	1.18	99.00±2.75	1.36	0.55	1.19	100.00±2.90

^a5 ml of the concentrated sample is used, ^bRelative Standard Deviation(n=6), *1% level of significance, **5% level of significance

differential pulse polarography data and the typical differential pulse polarographic curve was shown in figure 8. The nickel content present in agricultural materials, Hibiscus cannabinus (Gongura), Rumex vesicarius(Chukkaku), Phaeolus vulgaris (Bean) and Pisum sativum (Peas) show that the values are in

agreement with the standard values reported^[15] (TABLE 3 & 4).

CONCLUSIONS

The developed method was simple, rapid, selec-

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tive and reproducible for the determination of Ni(II) in various environmental samples. The ligand synthesized in present investigation is selective towards the Ni(II), enhanced the detection limits up to ppb levels. The present method was free from interfering effect which indicates the sensitivity of the method and the obtained results were in good agreement with the DPP method.

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