RESEARCH ARTICLE

Dithiocarbamates as Selective Ligands for Polarographic Study of Manganese(II) at DME

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Abstract: Two new ligands, ammonium 2,6-dimethyl morpholine dithiocarbamate (ADMM-DTC) and ammonium 3-methyl piperdine dithiocarbamate (AMP-DTC) were synthesized in the laboratory. The method was based on chelation of manganese(II) with ADMM-DTC/AMP-DTC in the presence of NH_4OH at pH 6.2 and 6.8 to produce catalytic hydrogen currents at -0.72 V and -0.62 V *vs*. SCE respectively and prior detected by D.C poarography. Optimized polarographic conditions were established by studying effect of pH, supporting electrolyte (NH_4Cl), 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. This technique is successfully applied for the analysis of manganese(II) in different matrices with recoveries ranging from 97 – 99% and the results obtained were comparable with the differential pulse polarography (DPP).

Introduction

Manganese is a trace element, which plays a significant role in metabolism of man, animals and plants. Manganese is commonly found throughout most aquatic environments. Manganese has several oxidation states. The most stable and important one is the divalent state, Mn(II) that forms a series of complexes with number of chelating agents. The average daily intake of adult is 2.2-2.7 mg of manganese. Bowen[1] found normal human blood to have an average of 24±8 mg. Manganese deficiency has been observed in man with a vitamin K deficiency[2]. Haemoglobin levels do not appear to be significantly affected by lack of manganese[3,4]. Manganese toxicity is a serious constraint to crop cultivation since it is taken-up by plants and can easily be passed into the food chain again causing symptoms of Parkinson's disease. The impairment in mucopolysaccharide synthesis associated with manganese deficiency has been related to the activation of glycosyl transferases by this element[5].

The analysis of manganese in biological and environmental samples is usually performed using radio-analytical and absorption spectrophotometric methods. These instruments

are not available in all laboratories due to sophisticated conditions required and cost involved. An alternative method is therefore developed for trace analysis of manganese(II) using simple D.C. polarograph available in most of the laboratories utilizing the catalytic hydrogen currents of manganese-dthiocarbamate complexes in NH_4Cl medium. The method is applied for the analysis of Mn(II) in soil, agricultural and environmental samples[6,]. It is enviable to develop a simple, sensitive, selective, rapid and cost effective method for the determination of manganese(II) in different matrices by synthesizing ADMM-DTC and AMP-DTC that gives catalytic hydrogen currents with the metal at DME. The results of this method is reported here which is more sensitive than our earlier reported ones.

Experimental

The current-voltage curves are recorded using a D.C.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.

Differential pulse polarograph

The current-voltage curves are recorded using polarographic analyzer, model CL-362 coupled with optional printer manufactured by Elico Private Limited (Hyderabad, India). All pH measurements are made using pH meter, model LI-120(Elico Pvt. Limited, India) with combined electrode of pH range 0-13.

Reagents

All reagents were of analytical grade and deionized doubly distilled water was used for preparation of all solutions. 2,6-Dimethyl morpholine, 3-methyl Piperidine, carbon disulphide, ammonium chloride and ammonia solution were purchased from S.D. Fine Chemicals, Mumbai, India and used in the present investigation. Standard solution of cobalt (1 μgmL^{-1}) was prepared by weighing 3.074 g of $MnSO_4.7H_2O$ (SD. Fine Chemicals, Mumbai, India) and dissolved in de-ionized doubly distilled water and made up to the mark in 1,000 mL standard flask.

ADMM-DTC (0.01 M) was prepared by weighing 0.208 g of ADMM-DTC and dissolved in 100 mL de-ionized doubly distilled water. AMP-DTC (0.01 M) was prepared by weighing 0.192 g of AMP-DTC and dissolved in 100 mL de-ionized doubly distilled water. Freshly prepared solution was stored in dark colored bottle. Stock solutions of ADMM-DTC, AMP-DTC and NH_4Cl were prepared by appropriate addition of reagents and chemicals in 250 mL standard flask and stored in dark place.

Synthesis of ammonium 2,6-dimethyl morpholine dithiocarbamate (ADMM-DTC) and ammonium 3-methyl piperidine dithiocarbamate (AMP-DTC)

Carbon disulphide (40 g) was slowly added to a solution of 2,6-dimethyl morpholine/ 3-methyl piperidine (45 g) in 25 mL of de-ionized doubly distilled water at 5 ^oC with constant stirring, followed by ammonium hydroxide. The product (Scheme 1 and 2) was warmed to room temperature and washed repeatedly two to three times with purified acetone. The reaction product was purified by recrystallization in acetone[7-10]. The purified compounds have melting points of 176-182 ^oC (Amm 2,6-dimethyl Mor-DTC) and 192-195 ^oC (Amm 3-methyl Pip-DTC) at 740 mm pressure.
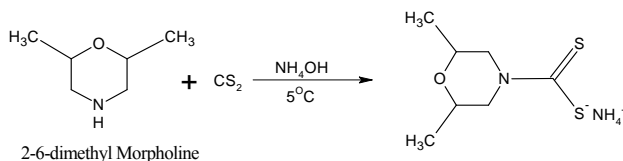
Scheme 1. Synthesis of ammonium 2-6-dimethyl morpholine dithiocarbamate (ADMM-DTC)
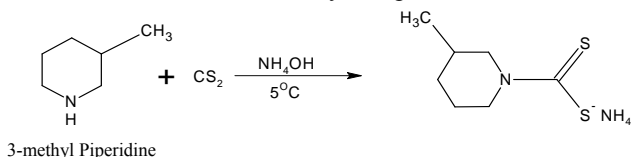
Scheme 2. Synthesis of ammonium 3-methyl piperidine dithiocarbamate (AMP-DTC)

Procedure

General procedure for the determination of manganese(II) with catalytic hydrogen current technique at dropping mercury electrode using dithiocarbamates (Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC).

A measured volume of the NH_4Cl, supporting electrolyte and ligands (ADMM-DTC and AMP-DTC) were added to the electroactive species [Mn(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 D.C Polarography. Dithiocarbamates (ADMM-DTC and AMP-DTC) or simple metal ions in the medium do not give any peak current at the potentials of catalytic hydrogen currents (CHC;-0.72 V and -0.62 V *vs*. SCE). Typical current-voltage curves at DME in the quantitative experimental conditions are presented in Figure 1a-b.
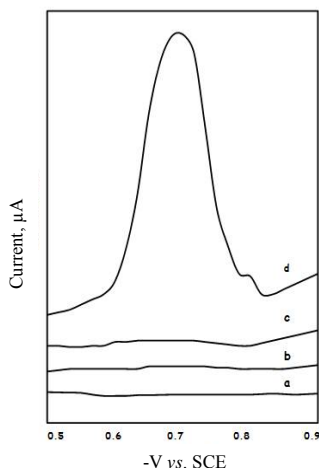
Figure 1a. Polarographic curve of Manganese(II) in NH_4Cl-NH_4OH medium in the presence of Amm 2,6-dimethyl Mor-DTC (a)0.3 M NH_4Cl,pH~6.2 (b) a+3.8 mM Amm 2,6-dimethyl Mor-DTC (c)a+ 3.0 ppm Mn(II) (d) b+3.0 ppm Mn(II)
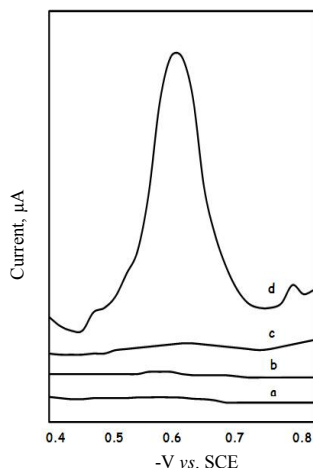
Figure 1b. Polarographic curve of Manganese(II) in NH_4Cl-NH_4OH medium in the presence of Amm 3-methyl Pip-DTC (a) 0.4 M NH_4Cl, pH~6.8 (b) a+3.8 mM Amm 3-methyl Pip-DTC (c) a+3.0 ppm Mn(II) (d) b+3.0 ppm Mn(II)

Results and Discussion

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

Effect of pH

The effect of pH on solutions containing 3.0 ppm of manganese(II) ion in 0.5 M ammonium chloride was studied, using 3.0 mM of ADMM-DTC/AMP-DTC as complexing agents, varying the pH from 5.0 to 10.0 adjusting with ammonium hydroxide. With increasing pH, the height of the catalytic wave increased and after attaining a maximum peak current [pH 6.2 (ADMM-DTC) and 6.8 (AMP-DTC)] the wave height decreased with further increase in pH. The maximum wave height of the polarograms was selected as optimum pH, which was maintained in all other studies. The results are graphically presented in Figure 2.
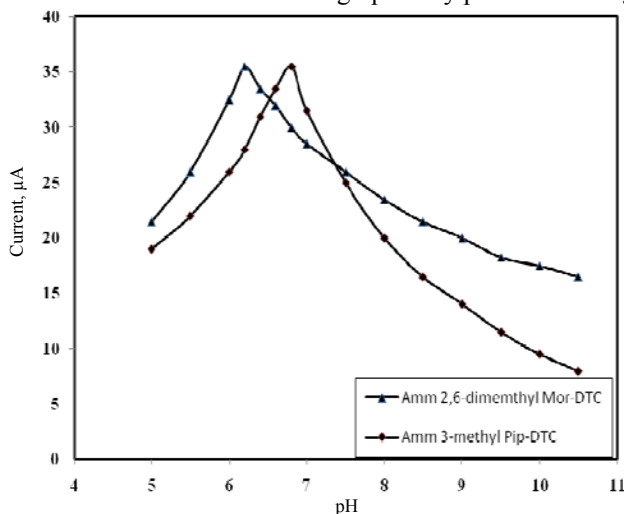

Figure 2. Effect of pH for the determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC

Effect of supporting electrolyte concentration

The effect of ammonium chloride in the range of 0.1 to 0.6 M on the nature of current-voltage curves at dropping mercury electrode (DME), keeping the Mn(II) concentration at 3.0 ppm and dithiocarbamate concentration at 3.0 mM (ADMM-DTC)/(AMP-DTC) and adjusting the pH to 6.2(ADMM-DTC) or 6.8 (AMP-DTC). The polarogram are well defined in NH$_4$Cl of 0.3 M for ADMM-DTC and 0.4 M for AMP-DTC. The peak height decreased beyond this concentration and therefore, 0.3 M for ADMM-DTC and 0.4 M for AMP-DTC concentration was maintained for further studies and the results obtained are given in Figure 3.

Effect of reagent concentration

Series of solutions containing 3.0 ppm of manganese(II), 0.3 M and 0.4 M ammonium chloride for ADMM-DTC and AMP-DTC respectively with 2.0 to 6.0 mM dithiocarbamates (ADMM-DTC and AMP-DTC) were polarographed, maintaining the pH of the solution at 6.2 in case of ADMM-DTC and 6.8 for AMP-DTC. The peak current does not vary linearly with all concentrations of ligand, which is a typical characteristic nature of catalytic waves, and the results obtained are represented graphically in Figure 4. From the results, it is seen

that the wave height increased linearly with dithiocarbamate concentration up to 3.8 mM for both ADMM-DTC and AMP-DTC. With further increase in dithiocarbamate concentration, the wave height was independent of concentration indicating that the complex was stable. Therefore, the concentration of the ligands where the maximum wave height obtained is fixed for quantitative studies. The peak potential of the catalytic wave shifted towards more negative potentials on increasing the dithiocarbamate concentration, up to the maximum concentration reported above and remained constant beyond these concentrations. Plot of {[Dithiocarbamate] / i_p} *vs.* [Dithiocarbamate] was a straight line (Figure 5) and confirms that adsorption phenomenon was involved in the electrode reaction process.
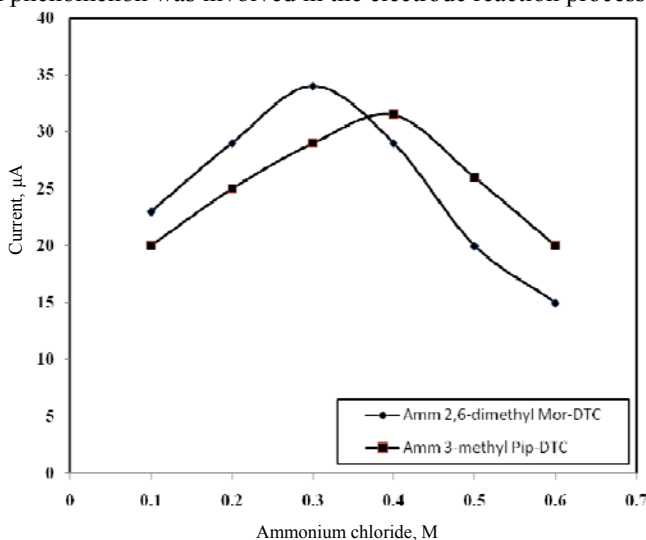

Figure 3. Effect of supporting electrolyte for the determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC
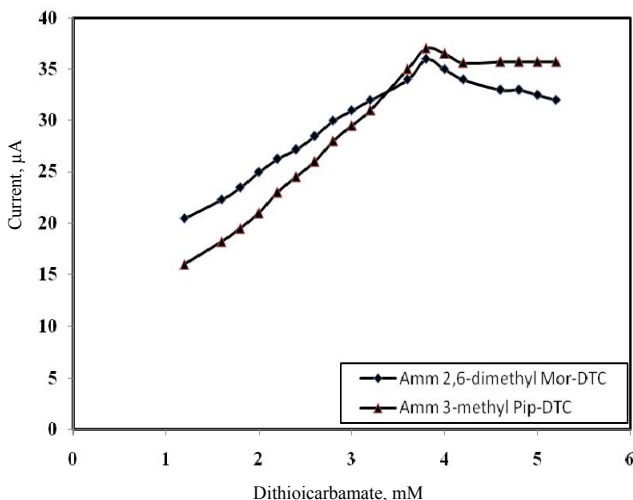

Figure 4. Effect of reagent concentration for the determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC
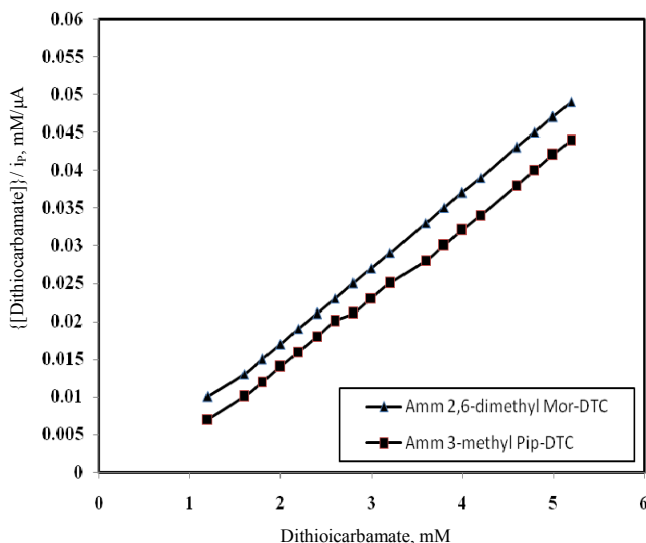
Figure 5. Langmuir adsorption isotherm plot for the determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC

Effect of mercury pressure

The effect of the height of the mercury column on the polarograms of manganese(II)3.0 ppm in quantitative experimental conditions was investigated and found that the catalytic current as well as $i_C/\sqrt{h}$ decreased with the height of the mercury column indicating that the current is catalytic in nature and the experimental observations are recorded in Table 1.

Table 1. Effect of mercury pressure for the determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC

Height of the mercury column, cm	Amm 2,6-dimethyl Mor-DTC		Amm 3-methyl Pip-DTC	
	Current, µA	$i_C/\sqrt{h}$	current, µA	$i_C/\sqrt{h}$
21	37.00	1020	36.00	1010
26	36.50	978	33.50	965
31	35.75	850	31.75	850
36	35.25	758	30.25	775

Effect of maximum suppressor

The effect of surface active substances, gelatine in the range 0.005 to 0.01% and Triton X-100, of 0.002 to 0.004% on the catalytic wave height was studied maintaining the fixed analytical concentrations developed for two dithiocarbamates (ADMM-DTC and AMP-DTC). The analytical data obtained are presented in Table 2. The catalytic wave decreases sharply up to 0.005% gelatine concentration and further increase in concentration of the surface-active material suppresses the wave further by only about 2%. The peak potential shifted towards positive potentials and the catalytic peak became round shaped. The suppression of the catalytic wave with 0.002 to 0.005% triton x-100 was small when compared to gelatine. The peak potential shifted towards positive potentials in this case also.

Table 2. Effect of maximum suppressors for the determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC

S. No	Maximum suppressor, %	Current, µA	
		Amm 2,6-dimehtyl Mor-DTC	Amm 3-methyl Pip-DTC
Gelatin			
1	0.000	36.00	35.50
2	0.005	25.50	25.25
3	0.010	24.50	25.00
Triton x-100			
1	0.000	36.00	35.00
2	0.002	25.25	25.50
3	0.004	24.50	25.00

Effect of temperature

The current-voltage curve of the systems with the two dithiocarbamates (ADMM-DTC and AMP-DTC) were recorded at various temperatures, *i.e*., 15 to 45 ^{o}C and found that with increase in temperature, the wave height increased and temperature coefficient values decreased gradually. The current, i_c became completely temperature independent above 30 ^{o}C.

Effect of manganese(II) concentration on peak current

At fixed concentration of dithiocarbamate, (3.8 mM ADMM-DTC and AMP-DTC) and (0.3 M for Amm 2,6-dimethyl Mor-DTC and 0.4 M for Amm 3-methyl Pip-DTC) ammonium chloride adjusting the pH to 6.2 and 6.8, respectively the metal ion concentration was varied between 0.05 to 6.0 ppm and its effect on the current-voltage curve was studied. The peak current increased linearly with manganese(II) concentration in the range 0.05 to 4.0 ppm in case of both dithiocarbamates (ADMM-DTC and AMP-DTC). However, the sensitivity of the method was more with AMP-DTC compared to ADMM-DTC because of strong complex of manganese(II) with AMP-DTC and increased catalytic activity. The calibration plot is shown if Figure 6. The method suggests that the determination of micro-amount of manganese(II) is possible in unknown samples. It was observed that there was no change in the shape of the wave throughout the manganese(II) concentration range studied.
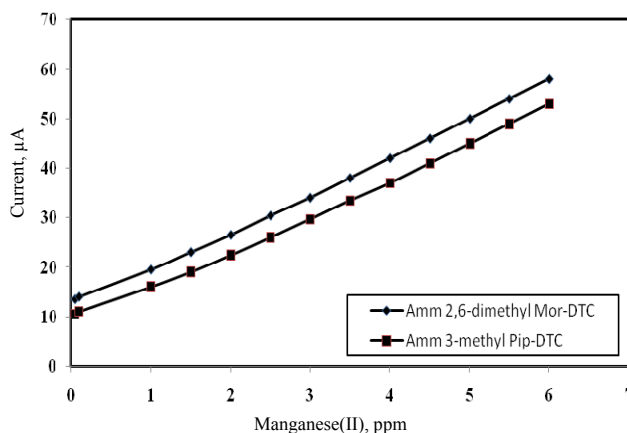
Figure 6. Effect of manganese(II) on peak current for the determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC

Effect of foreign ions

The effect of transition metal ions like Co(II), Ni(II), Cu(II), Fe(II) and Cr(VI) which are commonly associated with manganese(II), on the nature and height of the catalytic wave of manganese was studied using 3.0 ppm manganese in the quantitative experimental conditions developed. These metal ions do not interfere with manganese(II) due to its specific conditions. Ni(II) gets precipitated below pH 9.0 and Fe(II) at pH 8.0 and above which can be filtered off. Cr(VI) does not interfere even when present up to 100-fold excess as its peak potential was negative to that of manganese(II). The other metal ions such as cadmium(II), mercury(II), vanadium(V), magnesium(II), lead(II),aluminium(III), silver(I), uranium(VI), selenium(IV), tellurium(IV), cerium(IV), tin(IV), do not interferes with Mn(II) even in 100 fold excess and Zn(II) up to 20 ppm. The only metal ion, molybdenum(VI) interferes seriously by increasing the wave height and shifting the peak potential of the manganese(II) catalytic wave. Anions such as fluoride, bromide, iodide, tartrate, sulfate, thiosulfate, perchlorate, carbonate, thiocyanate and phosphate do not interfere with manganese(II) catalytic wave. Oxalate, citrate and EDTA interfere by completely suppressing the manganese catalytic wave, whereas nitrite and nitrate interfere by increasing the catalytic wave height.

Effect of indifferent cations

The effect of neutral salt and replacement of monovalent cation with divalent cation leads to changes both in the height and in the potential location of the catalytic wave. The concentration of NH_4Cl in the solution was kept constant and several amounts of different chlorides were added to the polarographed solutions of 3.0-ppm Mn(II) in fixed concentrations of dithiocarbamates (ADMM-DTC and AMP-DTC) at corresponding pH values. Three alkali chlorides potassium, sodium and lithium and bivalent cation, calcium were used. With increase in concentration of chlorides, the wave height decreased continuously and the decrease of wave height in sodium chloride is slightly less to that of potassium chloride. The decrease is more for lithium chloride and much more for calcium chloride as shown in Figure 7a and b.
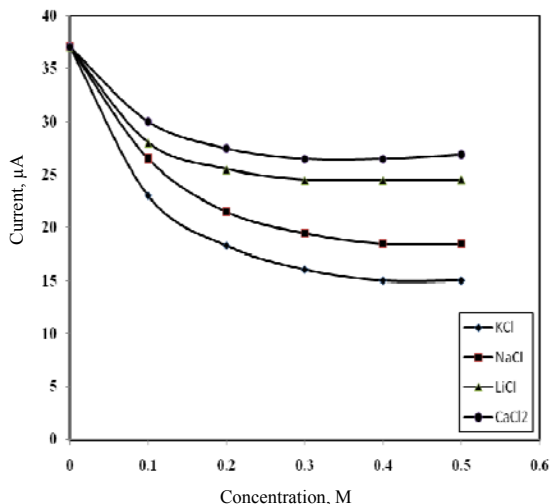

Figure 7a. Effect of indifferent ions on Amm 2,6-dimethyl Mor-DTC-manganese(II) complex at dropping mercury electrode(DME) for the determination of manganese(II) in various water samples and leafy vegetables using catalytic hydrogen current(CHC) technique

Figure 7b. Effect of indifferent ions on Amm 3-methyl Pip-DTC-manganese(II) complex at dropping mercury electrode(DME) for the determination of manganese(II) in various water samples and leafy vegetables using catalytic hydrogen current(CHC) technique
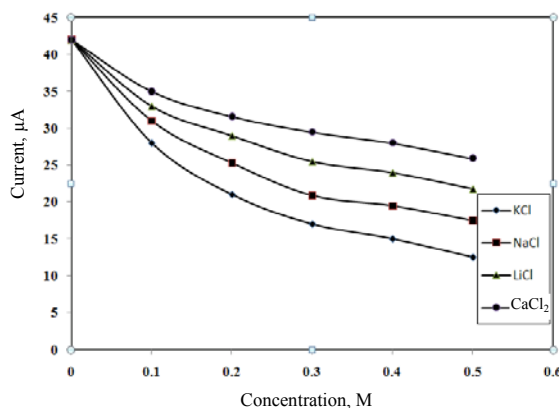
Methods of evaluation

The present CHC technique is critically evaluated with regard to reproducibility, accuracy and detection limits for analysis of manganese(II) in various water samples, vegetable samples.

Reproducibility

To test reproducibility of the CHC technique for Mn(II), six repetitive analysis of each sample were run. A % R.S.D in the range of 2.25 to 2.97 was obtained as shown in Tables 3-6.

Accuracy

The accuracy of the present CHC technique was evaluated by comparing the results with those obtained by the other methods already reported in these laboratories and also with the differential pulse polarography (DPP) method. The analytical data presented in Tables 3-6 shows that the present CHC technique is more sensitive than the earlier reported methods of these laboratories.

Table 3. Determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC in drinking water samples collected around Tirupati, Chittoor District, A.P. India using catalytic hydrogen current (CHC) technique

Sample[a]	Mn(II) added, ppm	CHC method (DC Polarography)		DPP method	
		Amm 2,6-dimethyl Mor-DTC		Amm 2,6-dimethyl Mor-DTC	
		Mn(II) found, ppm	Recovery % ±R.S.D[b]	Mn(II) found, ppm	Recovery % ±R.S.D[b]
	0.2	0.315	99.00±2.55	0.310	98.50±2.54
	0.4	0.520	98.75±2.67	0.520	98.75±2.56
I	0.6	0.730	98.33±2.33	0.725	98.16±2.53
	0.8	0.895	99.37±2.41	0.905	99.75±2.57
	1.0	1.210	100.00±2.88	1.190	99.00±2.99
	0.2	0.299	98.50±2.55	0.299	100.00±2.99
	0.4	0.474	97.50±2.40	0.425	97.50±2.53
II	0.6	0.696	99.33±2.38	0.690	98.66±2.61
	0.8	0.950	99.75±2.66	0.946	99.00±2.48
	1.0	1.115	98.00±2.57	1.190	100.00±2.57

***I** Industrial Estate; **II** Amara raja Batteries, [a]Five millilitres of the concentrated sample is used, [b]Relative standard deviation (n=6)*

Table 4. Determination of manganese(II) with Amm 3-methyl Pip-DTC in Drinking Water Samples collected around Tirupati, Chittoor District, A.P. India using catalytic hydrogen current (CHC) technique

Sample[a]	Mn(II) added, ppm	CHC method (DC Polarography)		DPP method	
		Amm 3-methyl Pip-DTC		Amm 3-methyl Pip-DTC	
		Mn(II) found, ppm	Recovery % ±R.S.D[b]	Mn(II) found, ppm	Recovery % ±R.S.D[b]
	0.2	0.310	98.25±2.45	0.301	97.50±2.54
	0.4	0.517	98.25±2.57	0.517	98.25±2.56
I	0.6	0.710	98.0±2.23	0.715	98.50±2.53
	0.8	0.885	99.30±2.61	0.878	99.25±2.57
	1.0	1.200	99.75±2.98	1.190	99.50±2.69
	0.2	0.279	99.50±2.55	0.290	100.00±2.49
	0.4	0.450	97.50±2.30	0.402	97.50±2.50
II	0.6	0.700	98.33±2.58	0.680	99.75±2.55
	0.8	0.950	99.75±2.26	0.936	99.00±2.50
	1.0	1.150	100.00±2.47	1.150	100.00±2.97

I Industrial Estate; II Amara raja Batteries, [a]Five millilitres of the concentrated sample is used, [b]Relative standard deviation (n=6)

Table 5. Determination of manganese(II) with Amm 2,6-dimethyl Mor-DTC in leafy vegetables and medicinal plant samples around Tirupati, Chittoor District, A.P. India using catalytic hydrogen current (CHC) technique

Sample[a]	Mn(II) Added, ppm	CHC method (DC Polarography)		DPP method	
		Amm 2,6-dimethyl Mor-DTC		Amm 3-methyl Pip-DTC	
		Mn(II) found, ppm	Recovery % ±R.S.D[b]	Mn(II) found, ppm	Recovery, % ±R.S.D[b]
Leafy Vegetables *Ammaranthyus graecizans/ Sirraku*	3.0	3.09	99.00±2.25	3.00	98.50±2.54
Ammaranthus cruentus/ Thottakura	3.0	3.04	98.25±2.42	3.05	98.75±2.44
Medicinal Plants					
Calotropis gigantean/ Thella gilleddu	3.0	3.03	98.50±2.54	3.09	99.00±2.39
Cassia auriculate/ Thangeddu	3.0	3.11	99.75±2.30	3.12	100.00±2.92

[a]Five millilitres of the concentrated sample is used, [b]Relative standard deviation (n=6)

Table 6. Determination of manganese(II) with Amm 3-methyl Pip-DTC in leafy vegetables and medicinal Plant samples around Tirupati, Chittoor District, A.P. India using catalytic hydrogen current (CHC) technique

Sample[a]	Mn(II) Added, ppm	CHC method (DC Polarography)		DPP method	
		Amm 3-methyl Pip-DTC		Amm 3-methyl Pip-DTC	
		Mn(II) found, ppm	Recovery % ±R.S.D[b]	Mn(II) found, ppm	Recovery % ±R.S.D[b]
Leafy Vegetables					
Ammaranthyus graecizans/ Sirraku	3.0	3.07	99.00±2.25	3.01	98.00±2.54
Ammaranthus cruentus/ Thottakura	3.0	3.04	98.00±2.42	3.05	98.50±2.34
Medicinal Plants					
Calotropis gigantean/ Thella gilleddu	3.0	3.10	98.50±2.54	3.09	98.00±2.35
Cassia auriculate/ Thangeddu	3.0	3.11	98.70±2.30	3.12	100.00±2.62

[a]Five millilitres of the concentrated sample is used, [b]Relative standard deviation (n=6)

Detection limits

This technique was applied for the determination of manganese(II) at DME in various water samples, vegetable samples using newly synthesized Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC up to 0.001 ppm levels.

Applications

The CHC technique developed is applied for the determination of traces of manganese(II) in various water samples and vegetable samples.

Analysis of manganese(II) in various water samples

One liter of the water samples collected from Industrial Estate and Amararaja batteries (Tirupati town, Chittor Dt.) are preconcentrated and analyzed.

Analysis of manganese(II) in leafy vegetable samples

3.5 g of Leafy vegetable samples and medicinal plant (leaves) samples were collected from local sources and digested by dry ash method[11]. The mass was made up to 100 mL with triple distilled water. Aliquots of the above solution are taken and polarographed using conditions developed. The results obtained by this method are further supported by DPP method and typical polarogram is shown in Figure 8a and 8b.
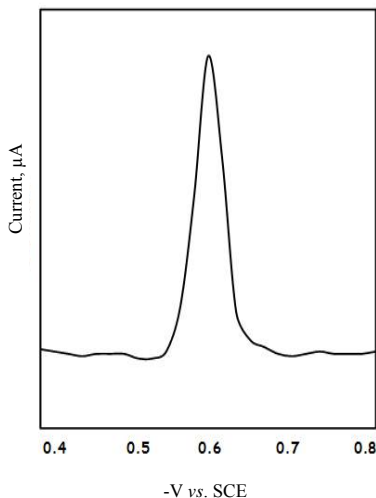
-V *vs.* SCE

-V *vs.* SCE

Figure 8a. Differential pulse polarographic curve for the determination of manganese(II) in NH_4Cl-NH_4OH medium in the presence of Amm 2,6-dimethyl Mor-DTC. Current Range: 100 μA, Scan rate: 6 m V/S, Pulse Amplitude: 50 mV, Drop time: 1 Sec, Manganese(II): 0.001 ppm

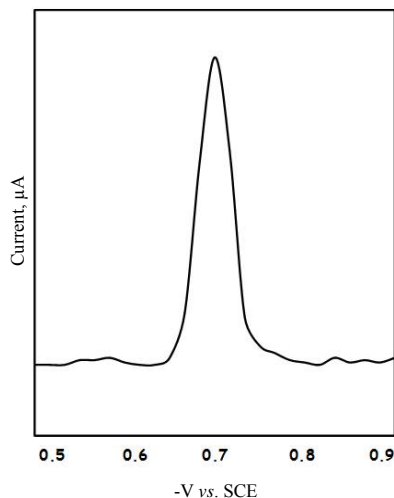**Figure 8b.** Differential pulse polarographic curve for the determination of manganese(II) in NH_4Cl-NH_4Cl medium in the presence of Amm 3-methyl Pip-DTC. Current range: 100 μA, Scan rate: 6 m V/S, Pulse amplitude: 50 mV, Drop time: 1Sec, Manganese(II): 0.001 ppm

Conclusion

The polarographic reduction of manganese(II) in aqueous solution in the presence of dithiocarbamate exhibits a catalytic wave as a function of concentration of supporting electrolyte, dithiocarbamate, pH, metal ion. These effects are studied to establish the catalytic character of the complex. The graph of the catalytic current as a function of the concentration of dithiocarbamate shows that the peak current does not vary linearly with the concentration of dithiocarbamate, which is typical of Brdicka catalytic hydrogen waves[12]. It is assumed that the dithiocarbamate complexes with metal ions involve adsorption process and can be described by a Langmuir adsorption isotherm[13] and the plot of C_L / i_p *vs.* C_L should be linear. Such a plot is found with manganese complexes of dithiocarbamates studied as shown in Figure 5. The decrease of catalytic peak current with increase in mercury column height also suggests that the wave is kinetically controlled[14].

Effect of ionic strength of indifferent cations explains the adsorption process. The presence of an indifferent electrolyte diminishes the peak height and this effect is correlated with the adsorption and catalytic nature of manganese-dithiocarbamate complexes on mercury, which is characteristic of catalytic surface reactions[15,16].

It is known that the surface catalytic currents are almost independent of temperature, and these currents increase at high temperatures, which is a deviation from purely kinetic behaviour. This is because an increase of the rate constant of protonation of the catalyst is compensated by a decrease in its adsorptivity on the electrode surface[17].

References

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