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# The polarographic study of Cobalt(II)-dithiocarbamate complexes at DME

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**ABSTRACT**

Cobalt is a naturally occurring element in the earth's crust. It is a very small part of our environment and very small amounts are needed for many animals and humans to stay healthy. Cobalt poisoning can occur when exposed to large amounts of cobalt. The aim of this study was to develop a facile, rapid, robust, sensitive and selective methodology for the determination of cobalt(II). 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 cobalt(II) with ADMM-DTC/AMP-DTC in presence of $NH_4OH$ at pH 7.2 and 8.2 to produce catalytic hydrogen currents at -1.28 V and -1.38 V vs SCE respectively and prior detected by D.C polarography. Optimized polarogaphic conditions were established by studying effect of pH, supporting electrolyte ($NH_4Cl$), ligand & 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 cobalt(II) in different matrices with recoveries ranging from 93- 98 % and the results obtained were comparable with the differential pulse polarography (DPP).

**Keywords** D.C Polarography . Catalytic hydrogen current (CHC) technique . Cobalt(II) . Ammonium 2,6-dimethyl Morpholine dithiocarbamate (ADMM-DTC) . Ammonium 3-methyl Piperidine dithiocarbamate (AMP-DTC). Differential pulse polarography (DPP)

## INTRODUCTION

Cobalt is an important trace element that has a vital role in human metabolic system. The quantitative determination of trace amounts of cobalt plays an important role in the field of environmental analysis, process control, and medicine [1-3]. Toxicological effects of cobalt include vasodilation, flushing, and cardiomyopathy in humans and animals [4]. Cobalt is an integral part of vitamin $B_{12}$ which is needed by humans. In 1926, the disease "Pernicious Anaemia" was considered incurable and normally fatal, was controlled by incorporating large amounts of raw or lightly cooked liver in the diet which contains vitamin $B_{12}$. Deficiency of vitamin $B_{12}$ affects the normal blood cell formation and the nervous system is seriously affected with, sometimes, degeneration of nerve fibers in the spinal cord and peripheral nerves. The average concentration of cobalt in domestic water supplies is 2.2 µg l$^{-1}$ as reported by U.S. Public Health Service. The daily intake of this metal in human diet is about 5 µg/day and toxic effects of cobalt have not been reported much and are possible only when cobalt compounds have been deliberately added during food processing or used in high doses therapeutically for the treatment of

"Anaemia" and "Goitre" which is the side effect of cobalt therapy [5, 6].

In view of the importance of cobalt(II) in diverse fields and particularly for its active role in various metabolic activities of living systems including man, various analytical methods such as HR-ICP-MS [7], FASS [8-14], ETAAS [15], GFAAS [16], ICP-MS [17], ICP-OES [18], spectrophotometry [19-24], and voltammetric technique [25-26] were reported for its determination in trace amounts in various environmental samples. The above-reported instruments are sophisticated which are not available in ordinary laboratories and the methodologies [23, 25] are also tedious and time consuming for the determination of trace and ultra-trace amounts of cobalt(II) in various matrices of environmental importance. The catalytic hydrogen waves of Co(II)-thiocompound complexes at dropping mercury electrode (DME) were reported earlier for its analysis in water samples, agricultural materials and pharmaceutical samples from these laboratories [27-29] which is simple and the instruments used is available in most laboratories. It is enviable to develop a simple, sensitive, selective, rapid and cost effective method for the determination of cobalt(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. The results are compared with differential pulse polarography.

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## MATERIAL AND METHODS

### Instrumentation

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 polarography model CL-25 of Elico Pvt Ltd, Hyderabad. The current-voltage curves with DPP 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. All reagents were of analytical grade and deionized double distilled water was used for preparation of all solutions. 2,6-dimethyl Morphonline,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(II) [1.0 µg ml$^{-1}$] was prepared by weighing 4.050 g of $CoCl_2.6H_2O$ (Merck Chemicals, Mumbai, India) and dissolved in deionized double distilled water and made up to the mark in 1000 ml standard flask. ADMM -DTC (0.01 M) was prepared by weighing 0.208 g in 100 ml deionized double distilled water. AMP-DTC (0.01 M) was prepared by weighing 0.192 g in 100 ml deionized double 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.

## MATERIALS

### Synthesis of ADMM-DTC and AMP-DTC

Carbon disulphide (40 g) was slowly added to a solution of 2,6-dimethyl morphloline/ 3-methyl piperidine (45 g) in 25 ml of deionized double distilled water at 5°C with constant stirring, followed by ammonium hydroxide. The Product (scheme 1a and b) was warmed to room temperature and washed repeatedly two to three times with purified acetone. The reaction product was purified by recrystallization in acetone [30-37]. The purified compounds have melting points of 176-182°C (ADMM-DTC) and 192-195°C (AMP-DTC) at 740 mm pressure.
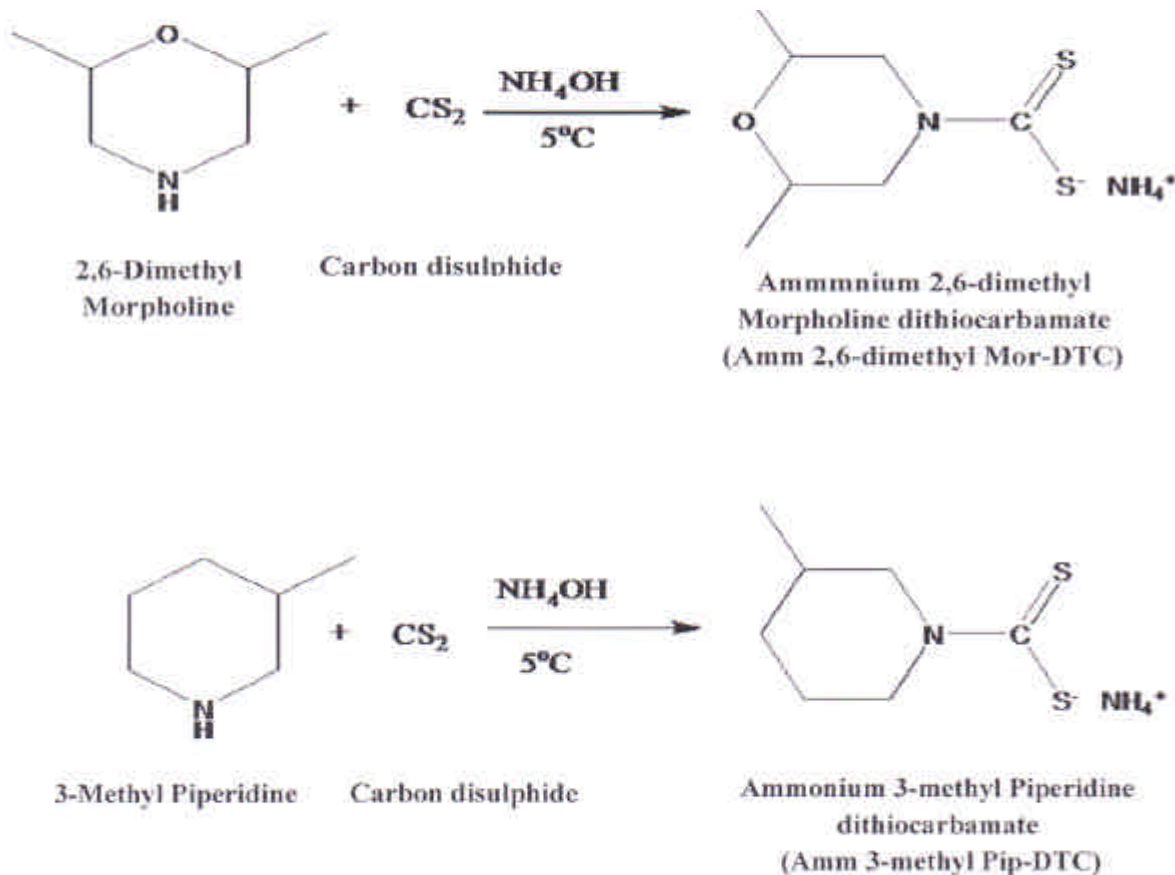




**Scheme. 1a & b. Synthesis of Ammonium 2,6-dimethyl Morpholine dithiocarbamate and Ammonium 3-methyl Piperidine dithiocarbamate**

## General procedure

A measured volume of the $NH_4Cl$, supporting electrolyte and ligands (ADMM-DTC and AMP-DTC) were added to the electro-active species[Co(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 solution 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 (CHCs; -1.28 V and -1.38 V vs SCE). The typical current-voltage curves at DME in the quantitative experimental conditions are presented in Fig. 1a-b.
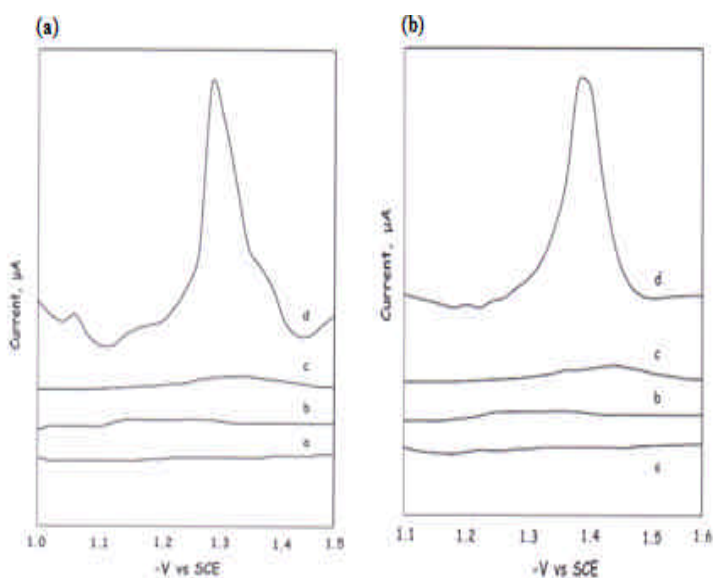


**Fig.1 Polarographic curve of Cobalt(II) in $NH_4Cl$-$NH_4OH$ medium in the presence of (A) Amm 2,6-dimethyl Mor-DTC (a)0.5 M $NH_4Cl$,pH~8.2 (b) a+3.0mM Amm 2,6-dimethyl Mor-DTC (c)a+3.0ppm Co(II) (d) b+ 3.0ppm Co(II) & (B) Amm 3-methyl Pip-DTC (a)0.5 M $NH_4Cl$, pH~7.8 (b)a+3.0 mM Amm 3-methyl Pip-DTC (c)a+3.0 ppm Co(II) (d)b+3.0 ppm Co(II)**

## RESULTS AND DISCUSSION

### Effect of pH

The effect of pH on solutions containing 3.0 ppm of cobalt(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 8.2 (ADMM-DTC) and 7.8 (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 Fig. 2.
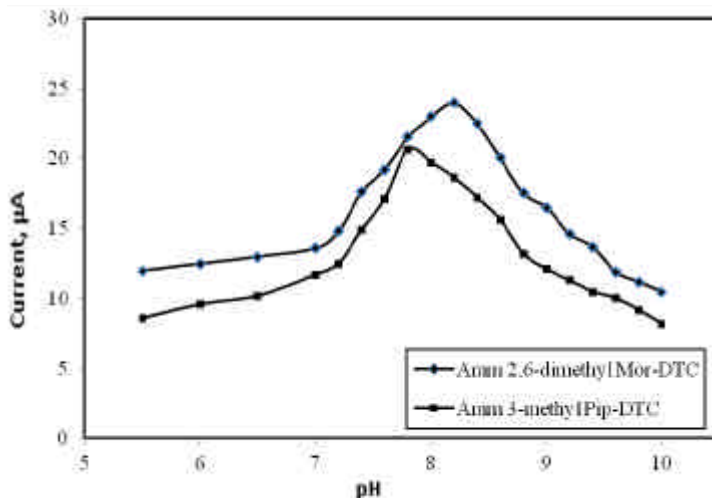


**Fig. 2. Effect of pH for the determination of cobalt(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC**

### 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 cobalt(II) concentration at 3.0 ppm and dithiocarbamate concentration at 3.0 mM (ADMM-DTC)/(AMP-DTC) and adjusting the pH to 8.2 (ADMM-DTC) or 7.8 (AMP-DTC). The polarograms are well defined in $NH_4Cl$ of 0.5 M with both ADMM-DTC and AMP-DTC and the wave heights increased up to 0.5 M. the peak height decreased beyond this concentration and therefore, 0.5 M concentration was maintained for further studies and the results obtained are given in Fig. 3.
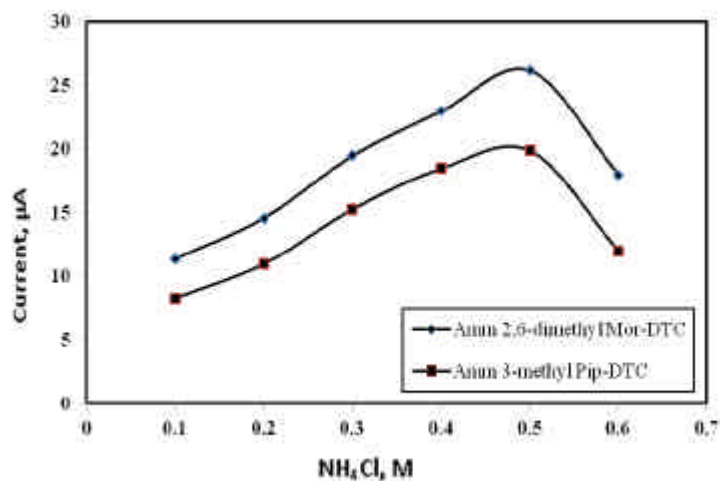


**Fig. 3. Effect of supporting electrolyte for the determination of cobalt(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC**

### Effect of reagent concentration

Series of solutions containing 3.0 ppm of cobalt(II), 0.5 M ammonium chloride with 2.0 to 6.0 mM dithiocarbamates (ADMM-DTC and AMP-

DTC) were polarographed, maintaining the pH of the solution at 8.2 in case of ADMM-DTC and 7.8 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 Fig. 4. From the results it is seen that the wave height increased linearly with dithiocarbamate concentration up to 3.0 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 (Fig. 5) and confirms that adsorption phenomenon was involved in the electrode reaction process.
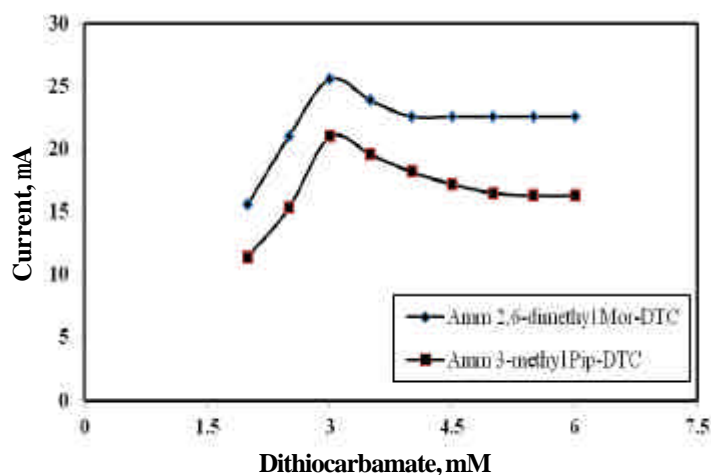


**Fig. 4. Effect of reagent concentration for the determination of cobalt(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC**
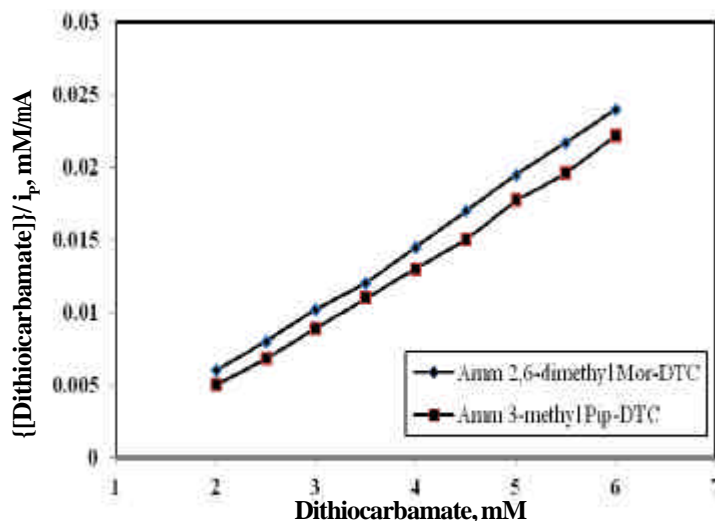


**Fig. 5- Langmuir adsorption isotherm plot for the determination of cobalt(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC**

## Effect of mercury pressure

The effect of the height of the mercury column on the polarograms of cobalt(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 cobalt(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 Current,µA | $i_c/\sqrt{h}$ | Amm 3-methyl Pip-DTC Current,µA | $i_c/\sqrt{h}$ |
|---|---|---|---|---|
| 21 | 27.00 | 6.142 | 24.00 | 5.487 |
| 26 | 26.50 | 4.257 | 23.50 | 3.224 |
| 31 | 26.00 | 3.548 | 22.25 | 2.551 |
| 36 | 25.00 | 2.596 | 21.00 | 1.984 |

## 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 cobalt(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC**

| S.No | Maximum suppressor, % | Current, µA Amm 2,6-dimethyl Mor-DTC | Amm 3-methyl Pip-DTC |
|---|---|---|---|
| **Gelatin** | | | |
| 1 | 0.000 | 25.00 | 24.00 |
| 2 | 0.005 | 21.00 | 21.60 |
| 3 | 0.010 | 18.90 | 19.44 |
| **Triton X-100** | | | |
| 1 | 0.000 | 25.00 | 20.00 |
| 2 | 0.002 | 24.50 | 18.50 |
| 3 | 0.004 | 24.00 | 18.00 |

## Effect of cobalt(II) concentration on peak current

At fixed concentrations of dithiocarbamate, (3.0 mM ADMM-DTC and AMP-DTC) and 0.5 M ammonium chloride adjusting the pH to 8.2 and 7.8, respectively the metal ion concentration was varied between 0.05 to 6.0 ppm and its effect on the current-voltage curves was studied. The peak current increased linearly with cobalt(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 Coblat(II) with AMP-DTC and increased catalytic activity. The calibration plot is shown in Fig. 6. The method suggests that the determination of micro-amount of cobalt(II) is possible in unknown samples. It was observed that there was no change in the shape of the wave throughout the cobalt(II) concentration range studied.
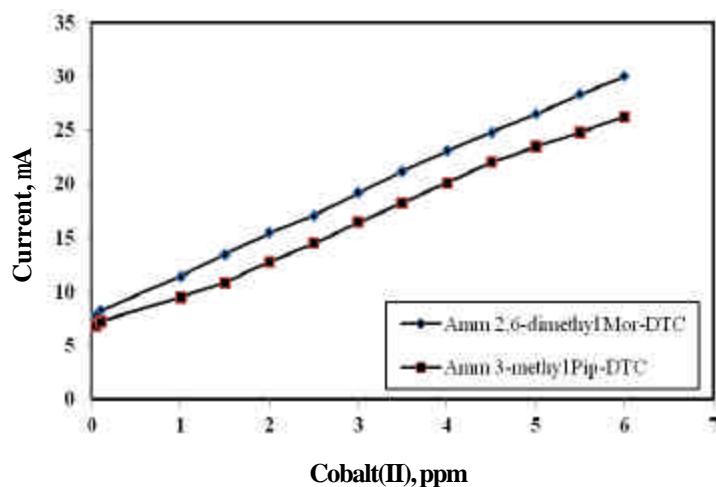


**Fig. 6 Effect of cobalt(II) on peak current for the determination of cobalt(II) with Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC**

### Effect of foreign ions and indifferent cations

The effect of transition metal ions like nickel(II), copper(II), manganese(II), iron(II) and chromium(VI) which are commonly associated with cobalt(II), on the nature and height of the catalytic wave of cobalt was studied using 3.0 ppm cobalt in the quantitative experimental conditions developed. These metal ions do not interfere with cobalt(II) due to its specific conditions. Nickel(II) gets precipitated below pH 9.0 and iron(II) at pH 8.0 and above which can be filtered off. Chromium(VI) does not interfere even when present up to 100-fold excess as its peak potential was negative to that of cobalt(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 cobalt(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 cobalt(II) catalytic wave. Anions such as fluoride, bromide, iodide, tartrate, sulfate, thiosulfate, perchlorate, carbonate, thiocyanate, and phosphate do not interfere with cobalt(II) catalytic wave. Oxalate, citrate, and EDTA interfere by completely suppressing the cobalt catalytic wave, whereas nitrite and nitrate interfere by increasing the catalytic wave height.

The effect of neutral salt and replacement of monovalent cation with divalent cation leads to changes both in the height and 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 cobalt(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 Fig. 7a and b.
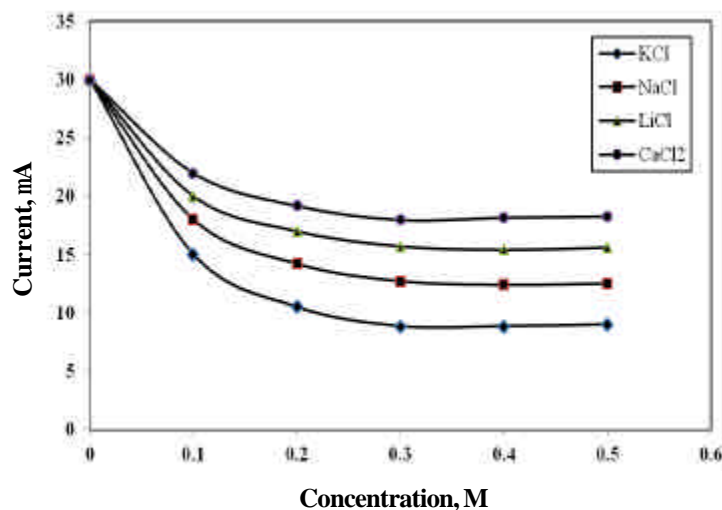


**Fig. 7a. Effect of indifferent ions on Amm 2,6-dimethyl Mor-DTC-cobalt(II) complex at dropping mercury electrode(DME) for the determination of cobalt(II) in various water samples and agricultural materials using catalytic hydrogen current(CHC) technique.**
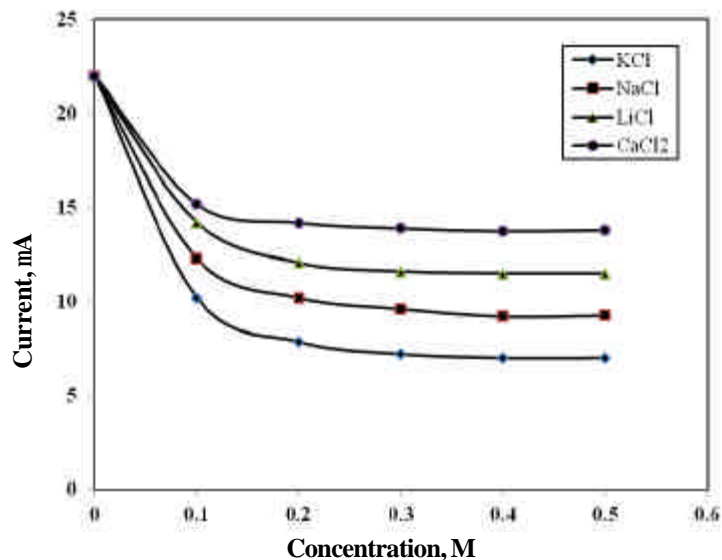


**Fig. 7b. Effect of indifferent ions on Amm 3-methyl Pip-DTC-cobalt(II) complex at dropping mercury electrode (DME) for the determination of cobalt(II) in various water samples and agricultural materials using catalytic hydrogen current(CHC) technique**

**Analytical applications**
The CHC technique developed is applied for the determination of traces of cobalt(II) in water samples, agricultural materials and pharmaceuticals.

**Analysis of cobalt(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 cobalt(II) in agricultural materials**
10 g of *Beeta vulgaris* (beet root), *Ipomoea batatas* (sweet potato), *Brassica rapa* (cabbage), *Raphanus sativus* (radish), *Cucurbita pepo* (pumpkin) and *Daucas carota* (carrot) were cut into small pieces and dried in an oven for 30 min, digested by dry ash method and brought

into solution by dissolving in 25 and 10 ml distilled water, respectively, for two ligands.

The results, in Tables 3-4, indicate that the water samples contain slightly high concentration levels of cobalt(II) whereas the agricultural materials (Tables 5- 6) have microgram quantities of cobalt(II). The results obtained are comparable within two dithiocarbamates (Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC) and also with differential pulse polarography. The typical differential pulse polarographic curves are shown in Fig. 8a-b. The developed method for cobalt(II) in the presence of dithiocarbamates (Amm 2,6-dimethyl Mor-DTC and Amm 3-methyl Pip-DTC) in $NH_4Cl$-$NH_4OH$ medium is found to be sensitive, selective, specific and rapid and may be successfully applied for the analysis of cobalt(II) content in drinking water samples and agricultural materials.

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

| Sample[a] | Co(II) Added, ppm | CHC method (DC Polarography) Amm 2,6-dimethyl Mor-DTC | | DPP method Amm 2,6-dimethyl Mor-DTC | |
|---|---|---|---|---|---|
| | | Co(II) Found, ppm | Recovery(%)± R.S.D[b] | Co(II)Found, ppm | Recovery(%)± R.S.D[b] |
| I | 0.4 | 0.55 | 96.00±1.61 | 0.55 | 96.00±1.62 |
| | 0.8 | 0.94 | 95.00±1.72 | 0.98 | 98.10±1.22 |
| | 1.2 | 1.30 | 75.47±1.30 | 1.35 | 80.25±1.10 |
| | 1.6 | 1.68 | 98.75±2.22 | 1.64 | 96.35±1.70 |
| | 2.0 | 2.14 | 99.15±2.68 | 2.12 | 98.95±2.10 |
| II | 0.4 | 0.58 | 91.35±1.30 | 0.56 | 91.10±1.55 |
| | 0.8 | 1.04 | 92.00±1.51 | 1.00 | 91.55±1.60 |
| | 1.2 | 1.42 | 98.23±1.50 | 1.45 | 98.50±1.40 |
| | 1.6 | 1.68 | 97.50±1.82 | 1.69 | 97.65±1.72 |
| | 2.0 | 2.10 | 99.50±2.52 | 2.10 | 99.50±2.52 |

*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 cobalt(II) with Amm 3-methyl Pip-DTC in water samples collected around Tirupati, Chittoor District. A.P., India using catalytic hydrogen current (CHC) technique**

| Sample[a] | Co(II) Added, ppm | CHC method (DC Polarography) Amm 3-methyl Pip-DTC | | DPP method Amm 3-methyl Pip-DTC | |
|---|---|---|---|---|---|
| | | Co(II) Found,ppm | Recovery (%) ±R.S.D[b] | Co(II)Found, ppm | Recovery (%) ±R.S.D[b] |
| I | 0.4 | 0.50 | 93.00±1.60 | 0.52 | 93.25±152 |
| | 0.8 | 0.95 | 94.10±1.65 | 0.96 | 94.52±1.43 |
| | 1.2 | 1.35 | 95.12±1.70 | 1.40 | 96.10±1.97 |
| | 1.6 | 1.65 | 97.80±1.86 | 1.72 | 98.42±2.50 |
| | 2.0 | 2.12 | 100.00±2.42 | 2.10 | 99.50±2.50 |
| II | 0.4 | 0.60 | 88.20±1.10 | 0.58 | 88.00±2.34 |
| | 0.8 | 0.98 | 96.85±1.56 | 0.99 | 97.15±1.65 |
| | 1.2 | 1.34 | 96.50±1.78 | 1.34 | 96.50±1.05 |
| | 1.6 | 1.68 | 97.10±1.81 | 1.72 | 98.22±1.73 |
| | 2.0 | 2.16 | 100.00±2.32 | 2.10 | 98.85±2.42 |

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

**Table 5: Determination of cobalt(II) with Amm 2,6-dimethyl Mor-DTC in agricultural materials collected around Tirupati,Chittoor District,A.P.,India using catalytic hydrogen current (CHC) technique**

| Sample[a] Scientific/local name | Co(II) Added, ppm | CHC method(DC Polarography) Amm 2,6-dimethyl Mor-DTC | | DPP method Amm2,6-dimethyl Mor-DTC | |
|---|---|---|---|---|---|
| | | Co(II) Found, ppm | Recovery(%)±R.S.D[b] | Co(II) Found, ppm | Recovery (%)±R.S.D[b] |
| *Daucas carota*/Carrot | 1.0 | 1.10 | 98.15±2.00 | 1.08 | 97.10±2.55 |
| *Cucurbita pepo*/Pumpkin | 1.0 | 1.12 | 99.10±2.12 | 1.14 | 100.00±1.20 |
| *Raphanus sativus*/Radish | 1.0 | 1.09 | 100.00±1.65 | 1.07 | 98.56±2.88 |
| *Ipomoea batatas*/Sweet potato | 1.0 | 1.09 | 97.00±2.67 | 1.09 | 97.00±2.67 |
| *Beeta vularis*/Beet root | 1.0 | 1.07 | 99.00±2.10 | 1.10 | 99.50±2.66 |
| *Brassica rapa*/Cabbage | 1.0 | 1.08 | 98.15±2.09 | 1.12 | 100.00±2.87 |

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

**Table 6: Determination of cobalt(II) with Amm 3-methyl Pip-DTC in agricultural materials collected around Tirupati, Chittoor District, A.P., India using catalytic hydrogen current (CHC) technique**

| Sample[a] Scientific/ local Name | Co(II) Added, ppm | CHC method (DC Polarography) Amm 3-methyl Pip-DTC | | DPP method Amm 3-methyl Pip-DTC | |
|---|---|---|---|---|---|
| | | Co(II) Found,ppm | Recovery(%)±R.S.D[b] | Co(II) Found, ppm | Recovery(%)±R.S.D[b] |
| *Daucas carota*/Carrot | 1.0 | 1.05 | 98.00±1.20 | 1.04 | 97.50±1.50 |
| *Cucurbita pepo*/Pumpkin | 1.0 | 1.05 | 100.00±2.63 | 1.05 | 100.00±2.10 |
| *Raphanus sativus*/Radish | 1.0 | 1.06 | 97.25±1.50 | 1.07 | 98.50±2.10 |
| *Ipomoea batatas*/Sweet potato | 1.0 | 1.08 | 99.10±2.67 | 1.08 | 99.15±1.85 |
| *Beeta vularis*/Beet root | 1.0 | 1.09 | 98.20±2.10 | 1.10 | 98.85±2.56 |
| *Brassica rapa*/Cabbage | 1.0 | 1.07 | 97.00±1.90 | 1.08 | 98.56±2.10 |

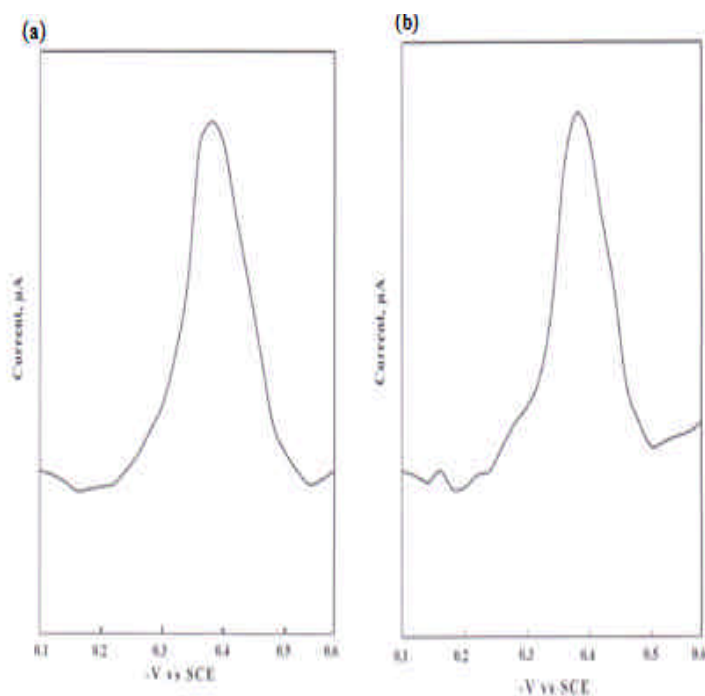[a]*Five millilitres of the concentrated sample is used,* [b]*Relative standard deviation (n=6)*



**Fig. 8a-b. Differential pulse polarographic curve for the determination of cobalt(II) in $NH_4Cl$ –$NH_4OH$ medium in the presence of (a) Amm 2,6-dimethyl Mor-DTC (b) Amm 3-methyl Pip-DTC Conditions: Current Range : 100μA Scan rate : 6 m V/S, Pulse Amplitude : 50 mV, Drop time : 1 Sec, Cobalt(II) : 0.001 ppm**

## CONCLUSION

The present developed CHC technique is novel, reliable and highly sensitive for the determination of cobalt(II) in real samples such as drinking water samples and agricultural materials. The limit of detection of the developed method is superior when compared with already reported methods of these laboratories. The method has added advantages over reported methods owing to it's: (i) More stable complexes with dithiocarbamates and thereby more catalytic activity. (ii) Distinct in terms of sensitivity and selectivity towards cobalt(II) present in various environmental matrices. (iii) The obtained results are comparable with DPP method.

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