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Research Paper

Trace Analysis of Co (II) in Biological and Environmental Samples using Catalytic hydrogen currents at DME

Chemistry

KEYWORDS : Polarographic Catalytic hydrogen waves, Cobalt (II), n-Butyl Amine, Biological samples, Environmental samples

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ABSTRACT

A Catalytic Polarographic method for the determination of Co (II) in trace levels is developed based on the Catalytic currents of Co (II) – amine complexes. The Co(II) – amine complex produces a Catalytic hydrogen wave at peak potential 1.02V VS SCE with n- butyl amine in sodium acetate medium and the current is proportional to Co(II) in the range 1 to 8 ppm. The proposed method is free from interference of many metal ions except Mo (VI). Further, it is simple, sensitive and rapid and is applied for the determination of agricultural products and water samples. The method is first of its kind in the polarographic Analysis.

INTRODUCTION

Catalytic hydrogen waves are due to the presence of certain catalytic substances in the solution, which contribute to the evolution of molecular hydrogen on the mercury electrode with simultaneous consumption of hydrogen ions. The catalytic hydrogen wave is of great practical interest because it has a higher analytical sensitivity than other polarographic waves.

In continuation of our earlier work on catalytic currents at mercury electrode due to complexation of organic thio-compounds and antipyrene with Co(II) ions in ammonium chloride-ammonium hydroxide medium [1-4], a new reagent, n-butyl amine (nBA) is introduced as a complexing agent in sodium acetate medium. Cobalt (II) forms complexes with nBA and gives catalytic hydrogen current at DME. However, amines have not been used so far as a reagent. An attempt has therefore been made with Co (II)-Amine systems. The quantitative experimental conditions have been developed and the details are shown in Table 1.

EXPERIMENTAL

Reagents:

All chemicals used are of analytical reagent grade only. The solutions were prepared in double distilled water and diluted to required strength. 5% NH_4OH and 1% HCl are used for p^H adjustments. Gelatin and Triton X-100 are prepared and diluted as per requirement. N-Butyl amine (S.d. fine-chemicals Ltd., Mumbai) solution is used.

Drinking water samples are obtained by using preconcentration of original samples by simple evaporation. The sample solutions of agricultural materials are prepared by dry ash method [5].

Apparatus

The equipment used is d.c. polarograph model CL-358 coupled with model LR-101 P strip chart recorder supplied by Elico Private Limited (Hyderabad, India). The p^Hmeasurements are made by using p^H meter; model LI-120 (Elico Private Limited) with glass electrode of p^Hrange 0-13. The temperature is maintained at 25 ± 0.2 ^{0}C and the flow of mercury at 2.5 s per drop.

Results and discussion

Polarogram of Cobalt (II)-n-Butyl Amine complex

The catalytic hydrogen waves of Co (II) are recorded in the presence of 0.2 M sodium acetate as supporting electrolyte containing amine as ligand (Fig. 1.).

Effect of pH:

Keeping the concentration of metal ion (4.0 ppm) and amine (0.4 mM) constant in 0.2 M sodium acetate, pH is varied from 6.0 to 9.0 adjusting with ammonium hydroxide. The height of the catalytic wave is maximum at pH 8.0 and decreased beyond these values. The peak potential is shifted towards positive value with increase in pH. Therefore, pH 8.0 is fixed as quantitative parameter.

Effect of supporting electrolyte concentration

With an increase in the concentration of sodium acetate at pH value selected above the height of the Co (II) wave in the presence of 0.4 mM nBA is found to increase upto 0.2 M. with further increase in sodium acetate the wave height started decreasing. Therefore, 0.2 M sodium acetate concentration is maintained for further studies.

The peak potential shifted towards positive value with increase in concentration of sodium acetate throughout the concentration range studied.

Effect of reagent concentration

The concentration of amine is varied from 0.1 mM to 1.0 mM keeping the metal ion and sodium acetate concentration constant at respective pH value selected earlier. The peak height is maximum at 0.3 mM amine concentration and is independent beyond this concentration indicating that the complex gets stabilized.

The peak potential of the catalytic wave shifted towards more negative value on increasing the amine concentration up to optimum concentration and remained constant. The peak current is not varied linearly with all concentrations of ligand, which is characteristic nature of catalytic wave.

The catalytic behavior of cobalt-amine is further supported by the effect of the mercury height on the peak current $i_c/\sqrt{h}$ decreased with the increase of the mercury column indicating that the current is catalytic in nature. The wave height increased with increase in temperature and temperature coefficient values decreased gradually. The surfactant like gelatin suppresses the catalytic wave sharply up to 0.05% and by about 2% beyond and up to maximum permissible concentration. The suppression with Triton X-100 is small when compared to gelatin. The peak potential shifted towards positive values.

Effect of cobalt (II) concentration on peak current

The effect of cobalt ion in the range 1.0 to 8.0 ppm is studied on the peak current in the presence of optimum concentration of amine and sodium acetate at fixed pH. The current-voltage curves show that the peak height increased linearly with the metal ion concentration in the range 1.0 to 8.0 ppm.

Interference Studies:

The effect of various metal ions on the catalytic wave of cobalt is studied. Most of the transition metal ions do not interfere under the conditions developed. The only metal ion, Mo (VI) interferes severely by increasing the wave height and shifting the peak potential of cobalt catalytic wave.

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Anions such as perchlorate and thiocyanate do not interfere with cobalt (II) catalytic wave and EDTA interferes by completely suppressing the cobalt catalytic wave.

Effect of Indifferent cations:
The effect of neutral salts on the cobalt (II)-amine system is studied using lithium, sodium, potassium and calcium chlorides, keeping sodium acetate solution constant at 0.2 M and corresponding p^H values. The wave height decreases continuously and decrease of wave height in sodium chloride is slightly less to that of potassium chloride. The decrease in the height is more with LiCl and is much more with $CaCl_2$. The peak potential is shifted towards less negative potentials with increase in electrolyte concentration.

Application of the catalytic method:
The developed method is applicable to the analysis of water and agricultural samples.

Drinking water samples:
One liter of the samples collected from Kalyani Dam, Bore wells of Tirupati town, Chittoor district, India are preconcentrated to 100ml.

Agricultural materials:
10 g of Daucus carota and Solanum tuberosum is collected from Tirupati town, Chittoor District, are cut into small pieces and dried in a oven for 30 minutes , digested by dry ash method and brought into solution by dissolving in 25 ml and 10 ml distilled water, respectively.

The results obtained by catalytic hydrogen currents are further supported by Atomic Absorption spectrophotometric method given in Table 2 and 3 and the amount obtained is within the tolerance limits.

Conclusions
Cobalt-amine complex is responsible for the generation of catalytic hydrogen waves. The linear dependence of the current on the pH and ligand concentration up to certain values indicates catalytic in nature. Effect of height of the mercury reservoir and temperature co-efficient values are also indicative of catalytic nature of the current at DME due to adsorption of the complex. The method is selective without much interference except Mo (VI) and is also sensitive, rapid and specific compared to diffusion current of Co (II) in classical polarography.

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Table 1: Quantitative experimental conditions for Co (II) determination through Cobalt (II)-Amine catalytic hydrogen waves

Conditions	Optimum values
PH	8.0
CH3COONa, M	0.2
Amine, mM	0.3
Cobalt (II), ppm	1.0 – 7.0

Table 2: Determination of Cobalt (II) in water samples
CH_3COONa, M : 0.2

Amine, mM : 0.3

P^H : 8.0

Sample*	Co (II), ppm added	Co (II), ppm Total found**	Co (II) in the sample, ppm Catalytic method	Co (II) in the sample, ppm DPP method
Kalyani Dam water	0.5 0.5	0.630 0.628	2.60 2.57	2.61
Bore well water	0.5 0.5	0.840 0.843	6.80 6.86	6.80

**5ml of concentrated sample is used.* ** Average of five individual measurements

Table 3: Determination of Cobalt (II) in agricultural materials
CH_3COONa, M : 0.2

Amine, mM : 0.3

P^H : 8.0

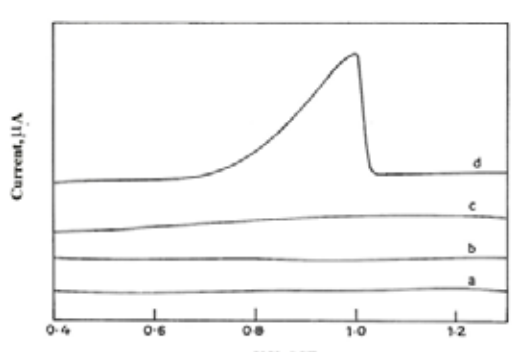
Sample*	Co (II), ppm added	Co (II), ppm Total found**	Co (II) in the sample, ppm Catalytic method	Co (II) in the sample, ppm DPP method
Daucus carota	0.5 0.5	0.70 0.68	0.500 0.450	0.502
Solanum tuberosum	0.5 0.5	1.50 1.48	1.000 0.980	1.050

*1ml of solution is used. ** Average of five individual measurements

The developed method for cobalt (II) in the presence of n-Butyl amine in sodium acetate is found to be sensitive, selective and rapid and may be successfully applied for the analysis of cobalt content in water samples and agricultural materials.

Fig.1. Polarographic curves of Co (II)
a) 0.2 M CH_3COONa, $P^H \sim 8.0$. b) a + 0.4 mM nBA

c) a + 4.0 ppm Co (II) d) b + 4.0 ppm Co (II)



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