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SENSITIVE POLAROGRAPHIC DETERMINATION OF MANGANESE (II) IN SOIL SAMPLES & PLANT MATERIALS USING CATALYTIC HYDROGEN CURRENTS AT DME

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ABSTRACT

A simple and sensitive catalytic polarographic method for the determination of Manganese (II) is developed based on the catalytic currents of Mn (II) - amine complex in the presence of CH_3COONa-NH_4OH medium at pH~ 7.2. The Mn (II) - amine complex produces a catalytic hydrogen wave at -0.36 V Vs SCE with n-butyl amine (nBA) in the presence of CH_3COONa-NH_4OH medium. The proposed method is sensitive with the lowest detection limit up to 0.1 ppm. The developed method is applied for the determination of Manganese (II) in soil samples and Plant materials. The method is first of its kind in the Polarographic Analysis.

Key Words: Polarographic Catalytic Hydrogen Waves, Manganese (II), Nba, Sodium Acetate,Soil Samples And Plant Materials

I. INTRODUCTION

Catalytic hydrogen currents of metal ions with amines have also been suggested but so far there is no reference available on this. In our attempts on catalytic hydrogen currents due to their diagnostic criteria and high sensitive nature, has tried with Mn (II) for the first time. N-butyl amine gives complexes with Mn (II) and is found to give catalytic hydrogen currents at DME at the peak potential -0.36 V Vs SCE in sodium acetate medium at pH 7.2.

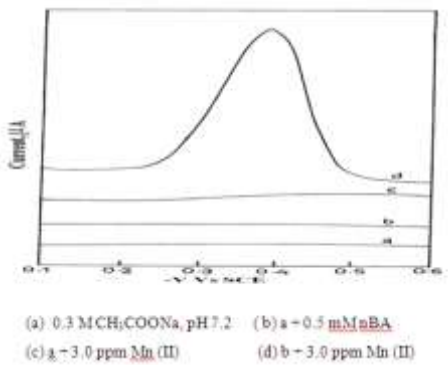
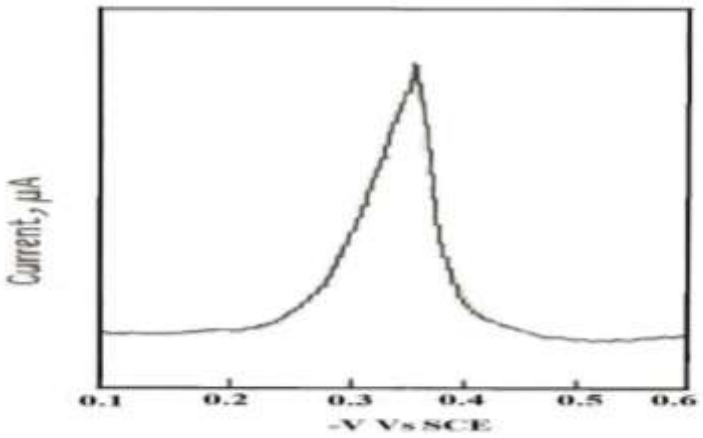


Fig 1: POLAROGRAPHIC CURVES OF Mn (II)



CH_3COONa, M : 0.3 nBA, mM : 0.5

Mn (II), ppm : 0.1 pH : 7.2

Fig 2: TYPICAL DIFFERENTIAL PULSE POLAROGRAM

Table 2: Quantitative experimental conditions for Mn (II) determination through Manganese (II) - Amine catalytic hydrogen waves.

Conditions	nBA
pH	7.2
CH_3COONa, M	0.3
Amine, mM	0.5
Mn (II), ppm	1.0-8.0

II. MATERIALS AND METHODS

2.1 Apparatus

The equipment used is d.c.Polarograph model CL-358 coupled with model LR-101 P strip chart recorder and Differential Pulse Polarography (DPP) model CL-362 coupled with optional printer supplied by Elico Private Limited (Hyderabad, India). The pH measurements are made by using pH meter, model LI-120 (Elico Privte

Limited) with glass electrode of pH range 0-13. The temperature is maintained at 25±0.2^{0}C and the flow of mercury at 2.5 S per drop.

2.2 Reagents

All chemicals used are of analytical reagent grade only. The solutions are prepared in double distilled water and diluted to require strength. 5% ammonium hydroxide and 1% hydrochloric acid is used for pH adjustments. Gelatin and TritonX-100 are prepared and diluted as per requirements. N-butyl amine (S.d.fine-chemicals Ltd.) solution is used.

2.3 Applications

The method developed is applied for the estimation of Mn (II) in soil samples and in plant materials.

a. Soil samples

About 2 g of soil, collected from Agricultural College Farms, Tirupati, is dried, digested by wet digestion method [1] and brought in to solution.

b. Plant materials

1g of oscimum sanctum leaves is dried and digested by dry ash method [2]and brought into solution.

III. RESULTS AND DISCUSSION

3.1 Effect of pH

The concentration of metal ion 3.0 ppm, ligand 0.5 mM/Amine and sodium acetate 0.3 M are fixed and the pH effect is studied from 5.0 to 8.0 adjusting with hydrochloric acid and ammonium hydroxide. A well defined wave is obtained at pH 7.2 with amine. At higher pH values, the wave height is diminished. The pH where the catalytic wave height is maximum and wave is well defined is selected as the optimum pH (7.2) for all other studies. With increase in pH, the peak potential of the catalytic wave shifted towards more negative potentials upto the optimum pH and with further increase in pH the shift in peak potential is small.

3.2 Effect of Supporting Electrolyte

The wave height of the catalytic hydrogen wave is not only dependent on pH but also on the supporting electrolyte capacity. Sodium acetate concentration is varied between 0.1 to 0.8 M maintaining the metal ion concentration at 3.0 ppm, amine concentration at 0.5 mM and adjusting the pH of the solution with ammonium hydroxide to pH 7.2. The wave height is increased upto 0.3 M. 0.3 M sodium acetate is fixed as the analytical concentration of the supporting electrolyte for all the studies. The peak potential of the catalytic wave shifted considerably towards negative potentials with increase in supporting electrolyte concentration.

3.3 Effect of Reagent Concentration

The polarogram of manganese (II)-amine complexes over a wide range of ligand concentration from 0.1to 1.0 mM are recorded maintaining the concentration of manganese (II), sodium acetate and pH at their optimum values as mentioned above. The results reveal that the peak height is maximum where amine concentration is 0.5mM and this concentration is selected as the optimum value for all other studies. The amine concentration shifts the peak potential towards more negative values. The variation of the wave height is a function of amine concentration is not linear and tends to a limiting value, which is a characteristic property of catalytic wave.

The catalytic behavior of iron-amine complex is further supported by the effect of mercury height on the peak current and temperature co-efficient values. The catalytic current decreased with increase in mercury pressure and $i_c/\sqrt{h}$ is found to decrease. The wave height is increased up to 35^0C. The value of temperature co-efficient is less indicating that the current is catalytic in nature.

Gelatin and TritonX-100 suppressed the peak by 20 to 25 up to 0.005 and 0.002% respectively and remained almost constant over and above these concentrations. The shift in peak potential is also small towards negative potentials through the concentration effect studied.

3.4 Effect of Manganese (II) on peak current

In order to obtain concentration range over which the catalytic wave is proportional to the metal ion, Mn (II) is changed from 0.1 – 8.0 ppm in the quantitative experimental conditions and the solutions are polarographed. The peak current increased proportionally with manganese (II) over concentration range 0.1 to 8.0 ppm. The lowest detection limit is 0.1 ppm.

3.5 Effect of Indifferent Cations

The effect of neutral salts on the Mn (II) –amine system is studied using lithium, sodium, potassium and calcium chlorides, keeping phosphate sodium acetate solution constant at 0.3 M and corresponding pH values. The wave height decreased continuously with increase in the concentration of Nacl and Kcl. The decrease in 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.

3.6 Applications of the catalytic method

The method adopted for the analysis of manganese content in soil samples is dried and digested by wet digestion and plant materials by dry ash method. The results obtained by catalytic hydrogen currents are further supported by Differential Pulse Polarographic method given in Table 2.

The results indicate that the soil samples and plant materials grown in the nearby villages of Tirupati town show that the values are in good agreement with the standard values. But within the limits of standard values reported (Table 2).The values obtained with amine are comparable and in good agreement with DPP data.

IV. CONCLUSIONS

The polarographic reduction of manganese (II) in aqueous solution in the presence of amine exhibits a catalytic wave before the metal-aqua complex wave. The linear independence of the current on the pH and ligand concentration up to certain values is catalytic in nature. The decrease of catalytic peak current with increase in mercury column height also suggests that the wave is kinetically controlled. The presence of indifferent electrolyte diminishes the peak height and this effect further confirms the catalytic behavior. The method is sensitive with the detection limit up to 0.1 ppm.

REFERENCES

[1] Purris, E.R. and Peterson, N.K., Soil Sci., 1956, 81, 223.

[2] Scott, W.W. and Furman, N.H., Standard methods of chemical analysis. Sixth Edition, 1963, 1.

Table: 2. Determination of Mn (II) in Soil sample, Tirupati and in oscimum sanctum leaves

	Supporting electrolytes	**Amine, mM**	**pH**
a. nBA	0.3M CH_3COONa	0.5	7.2

Sample*/Amine	**Mn (II) in the Sample, ppm/g**			
	Soil Samples		**Plant materials**	
	Catalytic method	**DPP method**	**Catalytic method**	**DPP method**
a	15.720 15.730 15.720 15.730 15.720 15.715	15.723	9.64 9.64 9.62 9.62 9.63 9.63	9.63
b	15.720 15.730 15.720 15.730	15.722	9.62 9.63 9.64 9.65	9.64

*5 ml of sample solution is used. ** Average of five individuals.

The above tables show that the developed method for the determination of manganese (II) estimation in trace levels is as accurate as other standard methods reported and may be independent alternative analytical quality control technique, in view of simple d.c polarograph involved which is usually available in any ordinary laboratory. The method may be applied successfully for the determination of manganese in soil and plant materials.