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Catalytic Polarographic Determination of Iron (II) in Agricultural Products And Drug Samples

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Abstract: A Catalytic polarographic method for the determination of Iron (II) is developed based on the catalytic currents of Fe (II) –amine complexes. The Fe (II) - amine complex produces a catalytic hydrogen wave at peak potential -1.25V Vs SCE with 2-Mercaptobenzimidazole (2-MBI) in the presence of phosphate medium at pH 7.2. The proposed method is free from interference of many metal ions except Molybdenum (VI) and is sensitive up to 0.1 ppm. The developed method is applied for the determination of iron (II) in agricultural and drug samples. The method is first of its kind in the polarographic Analysis.
Keywords: Polarographic catalytic hydrogen waves, Iron (II), 2-Mercaptobenzimidazole, phosphate supporting electrolyte, agricultural and pharmaceutical samples.

Introduction

Catalytic hydrogen waves due to thio-compounds with xanthates in the presence of Fe (II) at DME have been reported [1,2,3] from the laboratories.

Catalytic hydrogen currents of metal ions with amines have also been suggested [4] 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, 2-Mercaptobenzimidazole as complexing agent in the presence of phosphate supporting electrolyte with Fe (II) is made an attempt for the first time.

2-Mercaptobenzimidazole gives complexes with Fe (II) and is found to give catalytic hydrogen currents at DME at the peak potential -1.25 V Vs SCE in phosphate medium at pH 7.2. Typical current-voltage curves of the iron (II) amine system obtained in phosphate supporting electrolyte is given in Fig:1 and the corresponding Differential Pulse Polarogram curve in Fig: 2.

Experimental

Apparatus

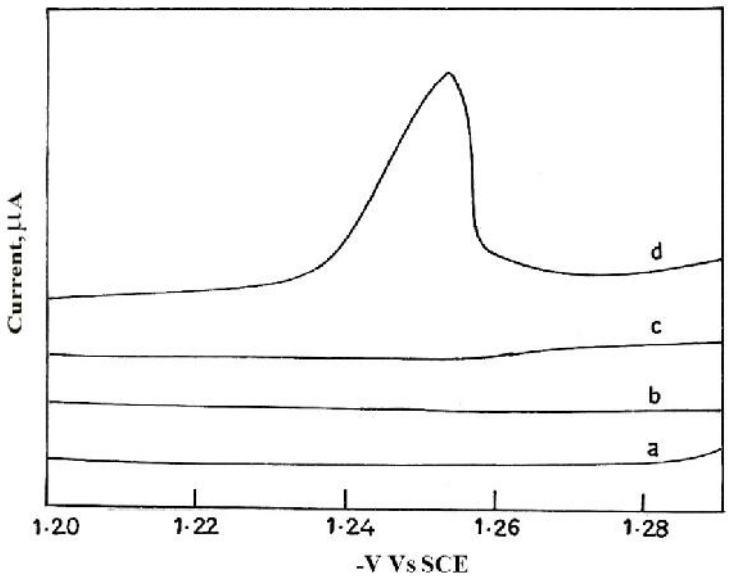
The equipment used is D.C..Polarograph model CL-358 coupled with model LR-101 P strip chart recorder and Differential Pulse Polarography (DPP) model CL-362 coupled with optional printer supplied by Elico Private Limited (Hyderabad, India) is used as supporting technique. The pH measurements are made 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.

Reagents

All chemicals used are of analytical reagent grade (E.Merk, India). 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.

The stock solution of 2-mercaptobenzimidazole is prepared by taking 0.1% w/v in mixed solvents of 60:40 methanol and double distilled water and diluted to required strengths. Phosphate buffer is prepared by mixing potassium dihydrogen phosphate and sodium hydroxide. Dry ash [5]method is used for agricultural products.

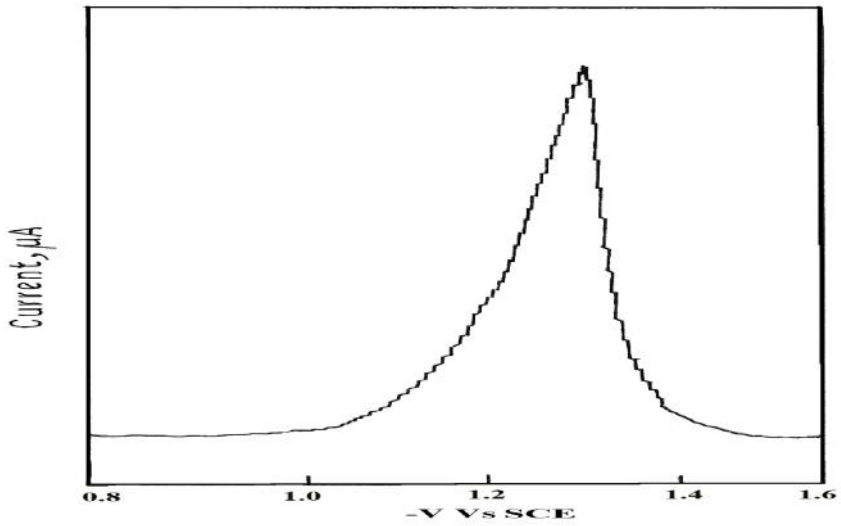
Fig 1: Polarographic Curves of Fe (II)



a) 0.4 M phosphate electrolyte, pH 7.2 b) a + 0.4 mM 2-MBI

c) a + 3.0 ppm Fe (II) d) b + 3.0 ppm Fe (II)

Fig 2: Typical Differential Pulse Polarogram



Phosphate Electrolyte, M : 0.4 Fe (II), ppm : 0.1

2-MBI, mM : 0.4 pH : 7.2

Table 1: Quantitative experimental conditions for Fe (II) determination through Iron (II) -2-Mercaptobenzimidazole catalytic hydrogen waves.

Conditions	Optimum values
pH	7.2
Phosphate supporting electrolyte, M	0.4
Amine, mM	0.4
Iron (II), ppm	1.0-10.0

Preparation of Fe (II) in Agricultural & Pharmaceutical Samples

Agricultural Materials

5g of Amaranth polygonoides (Sirikeerai) and Piper betle (Betle leaves) are collected from Tirupati town, Chittoor District are digested by dry ash method[5] and brought in to solution by dissolving in 500ml double distilled water.

Pharmaceuticals

Feefol and Feonat capsules from E.S. Kayef Limited and Natco Fine Pharmaceuticals Pvt. Ltd. Containing iron in the form of ferrous sulphate have been selected to estimate the iron content in the composition as given by the manufacturers. The capsule is digested and brought into 1 liter solution.

Results And Discussion

Effect of pH

The concentration of metal ion 3.0 ppm, ligand 0.4 mM/Amine and phosphate supporting electrolyte 0.4 M are fixed and the pH effect is studied from 4.0 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.

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. Phosphate buffer concentration is varied between 0.1 to 1.0 M maintaining the metal ion concentration at 3.0 ppm, amine concentration at 0.4 mM and adjusting the pH of the solution with ammonium hydroxide to pH 7.2. The wave height is increased upto 0.4 M. phosphate buffer 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 phosphate buffer concentration.

Effect of Reagent Concentration

The polarogram of iron (II)-amine complexes over a wide range of ligand concentration from 0.1to 0.8mM are recorded maintaining the concentration of iron (II), phosphate electrolyte and pH at their optimum values as mentioned above. The results reveal that the peak height is maximum where amine concentration is 0.4mM 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 as 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 255 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.

Effect of Iron (II) on peak current

In order to obtain concentration range over which the catalytic wave is proportional to the metal ion, Fe (II) is changed from 0.1 – 10.0 ppm in the quantitative experimental conditions and the solutions are polarographed. The peak current increased proportionally with iron (II) over

concentration range 0.1 to 10.0 ppm. The lowest detection limit is 0.1 ppm.

Interference Studies

Zn (II) interferes and is masked by adding 2ml of 2% sodium tartarate solution. Molybdenum (VI) increases the height of the catalytic wave of Fe (II) shifting the peak potential towards more negative value and making the determination of Fe(II) impossible,

Anions such as oxalate and carbonate interfere by suppressing the catalytic wave by 40% where as EDTA interferes severely by suppressing the catalytic wave totally.

Effect of Indifferent Cations

The effect of neutral salts on the iron (II) –amine system is studied using lithium, sodium, potassium and calcium chlorides, keeping phosphate electrolyte solution constant at 0.4 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.

Applications of the catalytic method

The method adopted for the analysis of iron content in leafy vegetables is standard addition method. The results obtained by catalytic hydrogen currents are further supported by Differential Pulse Polarographic method given in Table 2 & 3.

The results indicate that the leafy vegetables grown in the nearby villages of Tirupati town show that iron is present in the samples, but within the limits of standard values reported (Table: 2). Drugs also confirm the manufacturer's values (Table:3).

Table 2: Determination of Iron (II) in agricultural materials

I. Amaranth polygonoides (Sirikeerai)

II. Piper betel (Betle leaves)

Phosphate supporting electrolyte, M: 0.4 Amine, mM: 0.4 pH: 7.2

Sample*	Fe (II), ppm		Fe (II) in the sample, ppm	
	Added	Total found**	Catalytic method	DPP method
Sirikeerai	0.5	1.475	97.50	
	0.5	1.480	98.00	98.30
Piper betel	0.5	1.322	8.22	
	0.5	1.328	8.28	8.32

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

Table 3: Determination of Iron (II) in drugs

I. Feefol E.S.Kayef Limited., India

II. Feonot (Nath Fine Pharmaceuticals Pvt., India)

Phosphate supporting electrolyte, M: 0.4 Amine, mM: 0.4 pH: 7.2

Sample*	Iron in capsule (g)	Fe (II) in the sample**, (g)	
		Catalytic method	DPP method
Feefol (E.S.Kayef Ltd., India)	Ferrous sulphate 0.15	0.1493 0.1492	0.1495
Feonaat (Nath Fine pharmaceuticals pvt., India)	Ferrous sulphate 0.15	0.1419 0.1423	0.1500

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

The above tables show that the developed method for the determination of iron (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 iron in leafy vegetables and pharmaceuticals.

Conclusions

The polarographic reduction of iron (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.

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