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Second Derivative Differential Electrolytic Potentiometry for Oxidation – Reduction Reactions

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ABSTRACT

For the first time, second derivative differential electropotentiometry SDEP is applied for detection of oxidation-reduction reactions, and is utilized for determination of 1-100 ppm iron(II) pure solutions using $5x10^{-3}$*-M cerium ammonium sulfate as an oxidant in 1-M sulfuric acid, and a couple of protected platinum electrodes as an indicating system. No excipient was found to pose any interference, thus rendering the method suitable for determination of iron(II) in pharmaceutical preparations. The results of this study were favorably compared statistically with those obtained with the first derivative differential electropotentiometry FDEP method and direct electropotentiometric EP method.*

Keywords: SDEP, Oxidation titrimetry, Iron(II), Cerium (IV), pharmaceutical preparations.

INTRODUCTION

The technique of direct current SDEP using galvanic cell consists of two protected identical electrodes and measuring the second derivative potential differences ($\frac{\Delta^2 E}{\Delta V^2}$) between them, which produces a sharp symmetrical positive peak followed by a sharp negative peak, the end-point determined at the intercept point of the line between the maximum potential positive value and the minimum potential value with the x-axies. SDEP technique has been applied for the first time to precipitation and acid-base reactions[1] in the same laboratory. We found that this technique has the same advantages of FDEP [2-13],e.g. problems of a salt bridge and reference electrode are eliminated, and the basic technique and apparatus are simple, In addition the location of the end-point using the present method is sharper and easier to define than that of the FDEP, EP and conductimetric method, which requires tedious extrapolation manipulation.

Choice of Redox Reaction

This paper describes the application of the differential potentiometric technique for detection of oxidation reaction where iron (II) is being oxidized with Ce (IV). Iron is the most important element in the biological systems, it provides a fundamental structure for hemoglobin, heme enzymes, and many Co-factors involved in enzyme activity [14,15], playing a significant role in the storage, oxygen and electron transport[16-18].

The deficiency of iron cause anemia [19], and treated with iron salts [20]. However, if iron present in excess, its concentration exceeds the normal level it may become a potential health hazard and accumulates in the heart, liver, and other vital organs [21,22] and puts the organs at risk for serious damage [23]. Some of the iron compounds are suspected to possess carcinogenic activity [15]. The treatment of excess iron with iron salts may produce severe poisoning [20]. Hence, there is a need for iron ion determination in clinical, medicinal, environmental and different industrial samples [24-31].

Presently, various sophisticated techniques are employed [32-49]. However, these methods are disadvantageous in terms of cost and unsuitability for routine analysis. On the other hand, although the EP [1, 50, 51] and potentiometric method with ion selective electrodes [52-59] are simple, cheap, convenient and fast, there are some limitations of these techniques. On solution for these limitations is the use of differential electropotentiometry. We have now developed both the FDEP and SDEP methods for the determination of iron(II), the methods now developed do not suffer from any of the disadvantages associated with the earlier methods.

EXPERIMENTAL SECTION

Apparatus

WTW Instrument model pH DIGI520 D8120 digital potentiometer was used for potentiometric measurements. A bright platinum and a saturated calomel electrode serve as indicator and reference electrodes respectively. The platinum electrodes were Sargent Welch type 30-415 and were cleaned with concentrated sulfuric acid and/or nitric acid, rinsed with distilled deionized water and, placed in the cell. Flawil Magnetic stirrer, model H-9230/SG was used for solutions stirring.

Materials and Reagents

All solutions were prepared with double distilled water from reagent-grade materials and were used as supplied without Further purification. Cerium ammonium sulfate was obtained from Fluka, Switzerland and concentrated sulfuric acid (95-97%) by Riedel de Haen was used for the preparation of Ce(IV) and iron (II) stock solutions in 1-M sulfuric acid. Ferrous ammonium sulfate hexahydrate, Fluka was used to prepare a stock solution of 1000 ppm. Working solutions were prepared from the stock solution by dilutions. Calcium chloride, cadmium chloride, magnesium sulfate, aluminium nitrate, boric, sulfanilic, Tartaric acids, were obtained from BDH, England. Zinc sulfate heptahydrate, citric, and succinic acids were obtained from E.Merck, Germany. Ammonium benzoate was obtained from Fluka.

0.005-M Ce(IV) in 1-M sulfuric acid was prepared by dissolving 0.3162g of hydrous cerium ammonium sulfate in 5.5 ml of concentrated sulfuric acid and 50 ml distilled water in a 100-ml volumetric flask and made up to 100 ml with distilled water.

A 1000 ppm solution of iron(II) was prepared daily by dissolving 0.7022g of ferrous ammoniumsulfate hexahydrate in 5.5 ml concentrated sulfuric acid and 50 ml distilled water in a 100-ml volumetric flask and made up to 100 ml with distilled water, and standardized against a standard solution of dichromate[60]. Other iron(II) solutions were prepared by diluting with distilled water.

A 1000 ppm solutions of various metals using for interference study were prepared by dissolving 0.2769, 0.2303, 0.4952, 0.4397 and 1.390 g of calcium chloride, hydrous cadmium chloride, hydrous magnesium sulfate, zinc sulfate heptahydrate, and hydrous aluminium nitrate respectively in 100 ml distilled water with constant stirring.

A 1000 ppm solution of various organic meterials using for interference study were prepared by dissolving 0.1 g of boric, citric, succinic, sulfanilic, tartaric acids and ammonium benzoate in 100 ml distilled water with constant stirring.

Procedures

(I) Recommend Direct EP method procedure

A 100 ml volume of standard iron(II) solution containing 1-100 mg was transferred to the titration cell. The platinum and calomel electrodes were immersed into the sample solution. The analysis was done by running cerium ammonium sulfate solution from 1-ml micro burette, graduated at 0.001-ml for low concentration solutions, and 10.0-ml micro burett, graduated at 0.01-ml for high concentration solutions slow intervals and constant stirring of the reactions was continued with an electromagnetic stirrer throughout the course of titration. The potential (E mv) were recorded at a stable reading after each addition. The exact volume of the titrant was read from graph plotted between E mv values and titrant volume.

(II) FDEP method procedure

A 100 ml volume of standard iron(II) solution containing 1-100 mg was transferred to the titration cell, which consists of a duplicate platinum electrode assembly. The titration cell is prepared as shown in Fig.1(a).

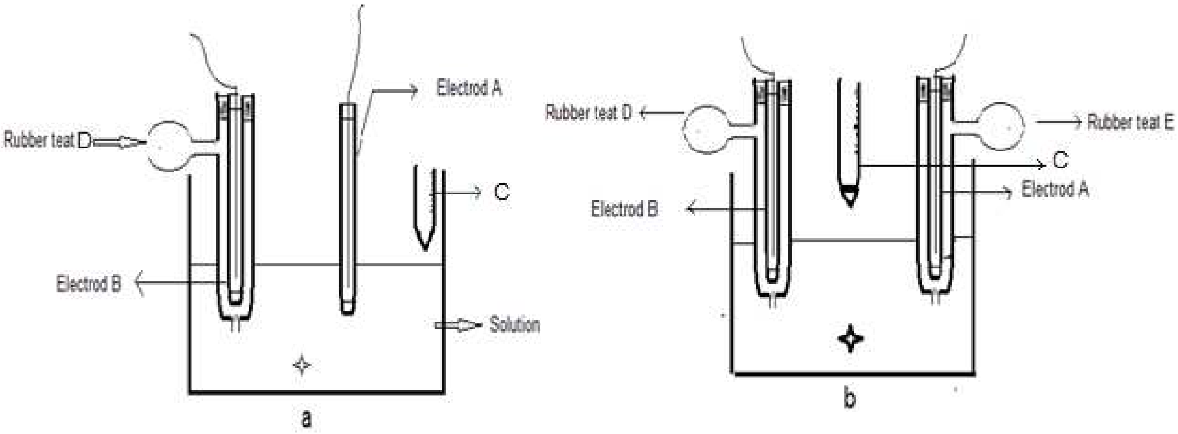

Fig.1: A schematic diagram of a)FDEP b) SDEP cells assembly.

A and B are platinum electrodes immersed in the iron(II) solution, the electrode B is enclosed in a glass jaket with a small orifice at one end. Initially the solution around each platinum electrode will contain iron(II) ions of the same activity and there will be no difference of potential between them.

A small amount, Δv ml, of cerium ammonium sulfate solution is added from the burette C to the iron(II) solution. The solution surrounding electrode A will undergo a decrease in iron(II) ion activity and hence its potential will decrease. The potential of electrode B will, however, remain as before because the solution surrounding this electrode isolated from the bulk of the solution, with the result that there will have been no change in the iron(II) activity. A difference of potential ΔE will thus exist between the two electrodes.

The solution around electrode B is then expelled by means of the rubber teat D. On refilling this compartment all of the solution in the system will be homogeneous and the difference of potential between the electrodes will again be zero. This procedure is then repeated by adding a further small volume, Δv ml of cerium ammonium sulfate solution, and the ΔE value measured. This process is continued until the titration is complete and the full differential curve obtained. The initial addition of the cerium ammonium sulfate can be quite rapid as the end point will be apparent from the increasing ΔE value.

(III) SDEP method procedure

A 100 ml volume of standard iron(II) solution containing 1-100 mg was transferred to the titration cell, which consists of a duplicate platinum electrode assembly. The titration cell is prepared as shown in Fig.1 (b). A and B are platinum electrodes immersed in the iron (II) solution, the electrodes A and B are enclosed in a glass jakets with a small orifice at one end. Initially the solution around each platinum electrode will contain iron (II) ions of the same activity and there will be no difference of potential between the electrodes.

A small amount, Δv ml, of cerium ammonium sulfate solution is added. The solution around electrode A is then expelled by means of the rubber teat D and refilling this compartment. This procedure is then repeated by adding a further small volume, Δv ml of cerium ammonium sulfate solution. The solution around electrode B is then expelled by means of the rubber teat E and refilling this compartment from the mother solution after the second addition, on repeating this process and expelling and refilling of A and B compartments after each addition alternatively, and the Δ^2E value measured. This process is continued until the titration is complete and the full second derivative differential curve obtained. . The initial addition of the cerium ammonium sulfate can be quite rapid as the end point will be apparent from the increasing Δ^2E positive values before the end point and the decreasing Δ^2E value (-ve values) after the end point immediately.

(IV) Procedure for the Determination of Iron (II) in Dosage Forms
Ten tablets containing iron (II) or the contents of 10 capsules were weighted and pulverized. An appropriate amount of the power equivalent to 10 mg of iron (II) was dissolved in about 50 ml of water. It was left for 10 min in the dark to let the gases evaporated and the residue was filtered and washed 3-4 times with water, then was added about 5.5 ml concentrated sulfuric acid. The mixture was made up to the mark with water in a 100-ml volumetric flask. An accurately measured volume of the solution was transferred and continued using the previously stated potentiometric analytical procedures, I,II and III.

RESULTS AND DISCUSSION

The SDEP technique as a detection system has been employed for the first time for the oxidation of iron (II) to iron (III) with cerium (IV) in sulfuric acid media through the following reaction:

$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$, and applied to follow the titration of iron (II) with Ce (IV) in sulfuric acid solution, a differential curves will be obtained and used to locate the end point. The peaks obtained were highly reproducible compared with those obtained with FDEP and direct EP methods, the smoothness, the sharpness and the symmetry of the differential curves depend on the applying of special modified potentiometric procedure (III) indicating the normal behavior of the platinum electrodes which are used as an indicating system without reference electrode and salt bridge, this procedure was found to be suitable for oxidation-reduction reactions, and was employed in this work.

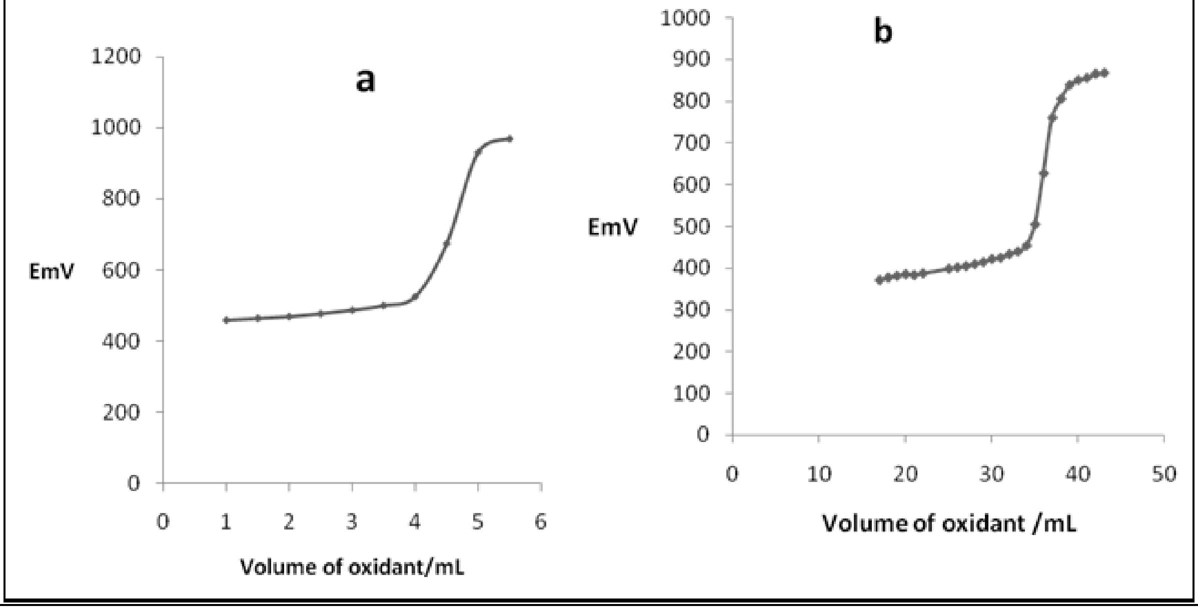

Figure 2. Titration of 100mL of a) 10ppm iron (II) b) 100 ppm iron (II) with 0.005 M ammonium cerium (IV) sulfate using EP method

The applied methods were calibrated by running series of iron (II) standard solutions to examin the response of these methods and also to detect the lowest concentration that can be determined. Iron(II) was determined in the concentration range 1-100 ppm. Results for the determination of iron (II) in pure form are compared with the results obtained by FDEP and EP methods (table 1), and indicate no significant differences between them with respect to accuracy and precision. A set of the titration curves obtained were shown in Figures 2-4.

The results in table 1 indicates the successful applicability of the proposed method, which was simple, easy to detect the end-points, and requires small amount of oxidants.

The results of interference study in table 2 prove that the proposed method suffers no interference from excipients added to iron(II) drug formulations, so this method was applied to the determination of iron (II) in some proprietary drugs as introduced in table 3 , the results obtained were compared with the results of analysis of the same batch of samples with FDEP and EP methods . The statistical calculations indicates high precision with low standard deviation and a reasonable percentage recovery.

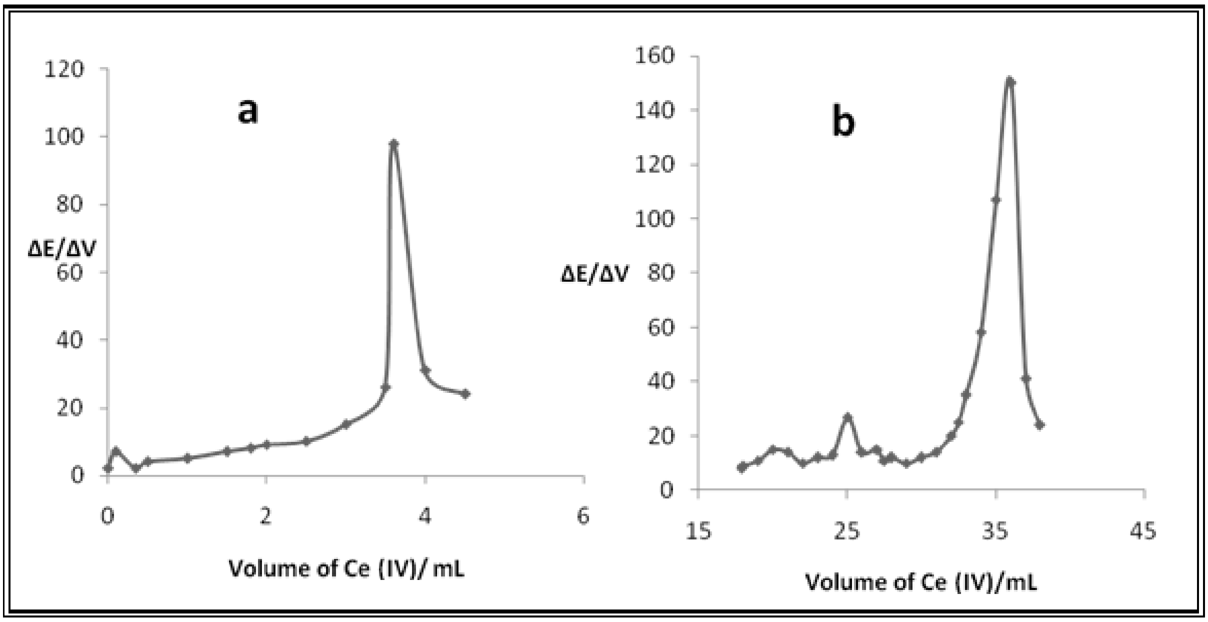

Figure 3. Titration of 100mL of a) 10ppm iron (II) b) 100 ppm iron (II) with 0.005 M ammonium cerium (IV) sulfate using FDEP method

Table 1: Potentiometric analysis of iron (II) standard solutions by application of EP, FDEP and SDEP methods

Amount,µg/ml				**A.E**			**% Recoveries**			**% R.S.D**		
Taken	**Found***			**EP**	**FDEP**	**SDEP**	**EP**	**FDEP**	**SDEP**	**EP**	**FDEP**	**SDEP**
	EP	**FDEP**	**SDEP**									
1	1.0038	0.9843	1.0038	0.0038	-0.0156	0.0038	100.3849	98.4303	100.3849	0.1966	0.9872	0.9834
5	4.997	5.0192	5.0052	-0.0002	0.0192	0.0052	99.3849	100.3849	100.1057	0.0394	0.19669	0.1983
10	10.0175	10.0454	10.0035	0.0175	0.0454	0.0035	100.1755	100.4547	100.0359	0.0985	0.0982	0.0986
20	20.0002	19.9722	20.0002	0.0002	-0.0277	0.0002	100.0010	99.6402	99.9940	0.0093	0.0660	0.0131
30	30.0010	30.0107	29.9968	0.0010	0.0107	-0.0031	100.0033	100.0359	99.9893	0.01316	0.0329	0.0329
50	50.0054	49.9900	49.9926	0.0054	-0.0099	-0.0073	100.0108	99.9800	99.9853	0.0157	0.0197	0.0197
70	69.9972	69.9553	70.0111	-0.0027	-0.0446	0.0111	99.9960	99.9362	100.0159	0.0141	0.0141	0.0141
90	89.9848	90.0463	90.0044	-0.0151	0.0463	0.0044	99.9831	100.0514	100.0049	0.02413	0.0109	0.0109
100	100.0080	99.9731	100.0038	0.00801	-0.0268	0.0038	100.0080	99.9731	100.0038	0.01974	0.0098	0.0059

**average of three determinations*
A.E : Absolute Error ; R.S.D: Relative Standard Deviation

Table 2: Interference study of foreign species in determination of 10 µg/ml of iron (II)

Foreign species & Fold	**Amount found, µg/ml**			**A.E**			**% Recoveries**			**% R.S.D**		
	EP	**FDEP**	**SDEP**	**EP**	**FDEP**	**SDEP**	**EP**	**FDEP**	**SDEP**	**EP**	**FDEP**	**SDEP**
Ca(II) $\frac{1}{2}$	10.0315	10.0454	10.0035	0.0315	0.0454	0.0035	100.3151	100.4547	100.0359	0.0984	0.0982	0.0986
1	10.0343	10.0454	10.0077	0.0343	0.0454	0.0077	100.3430	100.4547	100.0778	0.0590	0.0982	0.0394
Cd(II) $\frac{1}{2}$	10.0259	9.9198	10.0049	0.0259	-0.0801	0.0049	100.2593	99.1982	100.0499	0.0196	0.0995	0.0789
1	10.0021	9.9198	10.0035	0.0021	-0.0801	0.0035	100.0219	99.1982	100.0359	0.0789	0.0995	0.0986
Zn(II) $\frac{1}{2}$	10.0035	10.0454	10.0035	0.0035	0.0454	0.0035	100.0359	100.4547	100.0359	0.0986	0.0982	0.0986
1	9.9756	10.0454	10.0091	-0.0243	0.0454	0.0091	100.7567	100.4547	100.0917	0.0989	0.0982	0.0197
Mg(II) $\frac{1}{2}$	10.2893	9.9198	10.0035	0.2893	-0.0801	0.0035	100.8935	99.1982	100.0359	0.1972	0.0995	0.0986
1	10.4782	9.9198	10.0035	0.4782	-0.0801	0.0035	100.7893	99.1982	100.0359	0.0942	0.0995	0.0986
Al(III) $\frac{1}{2}$	10.0035	10.0454	10.0008	0.0035	0.0454	0.0008	100.0358	100.4547	100.0080	0.0987	0.0982	0.0592
1	10.0102	10.0454	10.0035	0.0102	0.0454	0.0035	100.1025	100.4547	100.0359	0.2013	0.0982	0.0986
Benzoate $\frac{1}{2}$	9.8918	10.0454	10.0063	-0.081	0.0454	0.0063	98.9189	100.4547	100.0638	0.0987	0.0982	0.0591
1	9.1984	10.0454	10.0035	-0.0815	0.0454	0.0035	99.1842	100.4547	100.0359	0.07962	0.0982	0.0986
Boric acid $\frac{1}{2}$	9.9156	9.9198	10.0175	-0.0843	-0.0801	0.0175	99.1561	99.1982	100.1755	0.0401	0.0995	0.1393
1	9.9435	9.9182	10.0189	-0.0564	-0.0801	0.0189	99.4355	99.1982	100.1895	0.0397	0.0995	0.1182
Citric $\frac{1}{2}$	10.1641	10.0454	10.0175	0.1641	0.0454	0.0175	101.6415	100.4547	100.1755	0.3895	0.0982	0.0985
1	10.1571	10.0454	10.0035	0.1571	0.0454	0.0035	101.5717	100.4547	100.0359	0.0971	0.0982	0.0986
Succinic $\frac{1}{2}$	10.0077	10.0454	10.0035	0.0077	0.0454	0.0035	100.0778	100.4547	100.0359	0.0394	0.0982	0.0986
1	10.0035	10.0454	10.0049	0.0035	0.0454	0.0049	100.0353	100.4547	100.0499	0.0986	0.0982	0.11841
sulfamic $\frac{1}{2}$	9.9198	10.0454	10.0035	-0.0801	0.0454	0.0035	99.1982	100.4547	100.0359	0.0995	0.0982	0.0986
1	9.9198	10.0454	10.0063	-0.0801	0.0454	0.0063	99.1982	100.4547	100.0638	0.0995	0.0982	0.0591
Tartaric $\frac{1}{2}$	10.0105	9.9182	10.0035	0.0105	-0.0801	0.0035	100.1057	99.1982	100.0359	0.1970	0.0995	0.0986
1	10.0312	9.9182	10.0091	0.0312	-0.0801	0.0091	100.3124	99.1982	100.0917	0.1025	0.0995	0.0197

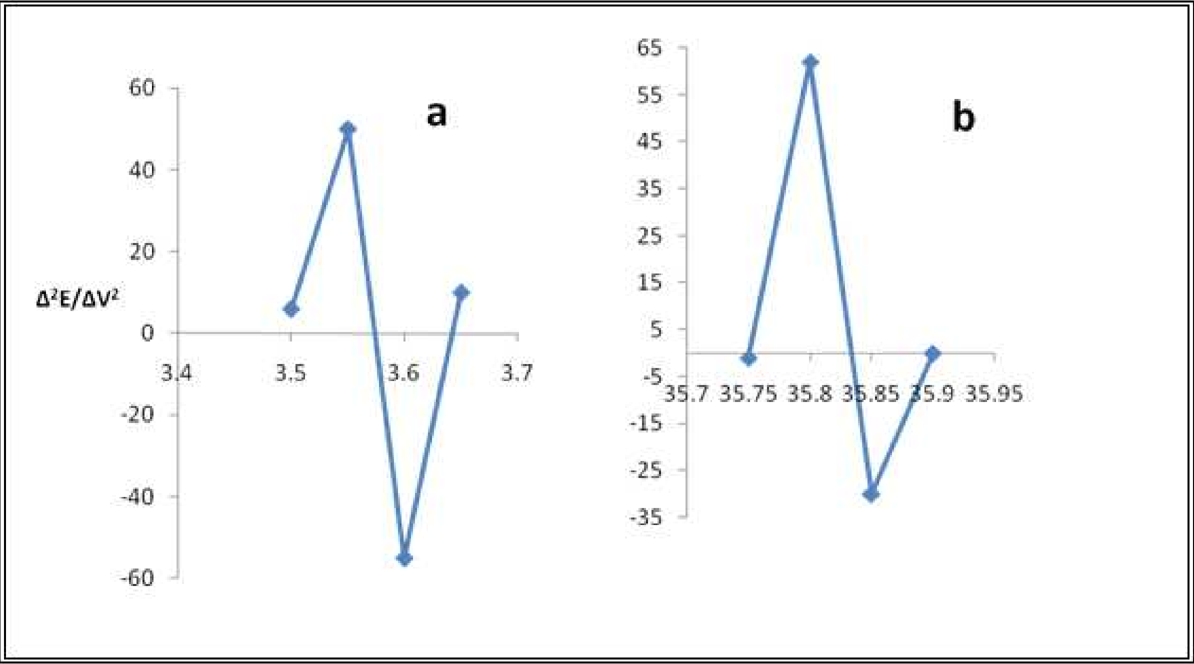

Figure 4. Titration of 100mL of a) 10ppm iron (II) b) 100ppm iron (II) with 0.005M ammonium cerium (IV) sulfate using SDEP method

Table 3 : Determination of 10 µg/ml of iron (II) in some pharmaceutical preparations

Pharmaceutical		**Amount Found ,µg/ml**			**A.E**			**% Recoveries**			**% R.S.D**		
		EP	**FDEP**	**SDEP**	**EP**	**FDEP**	**SDEP**	**EP**	**FDEP**	**SDEP**	**EP**	**FDEP**	**SDEP**
1	Glucofer	10.0454	9.9198	10.0035	0.0454	-0.0801	0.0035	100.4547	99.1982	100.0359	0.0982	0.0995	0.0986
2	Ferronin	9.9896	9.9198	10.0035	-0.0103	-0.0801	0.0035	99.8963	99.1982	100.0359	0.0988	0.0995	0.0986
3	Ferrosam	9.8918	9.9194	10.0035	-0.1081	-0.0815	0.0035	98.9186	99.1842	100.0359	0.0992	0.0796	0.0986
4	Ferrous sulphate	10.0035	9.9198	10.0035	0.0035	-0.0801	0.0035	100.0359	99.1982	100.0359	0.0986	0.0995	0.0986
5	Ferrous sulphate W/ Folic acid	10.2130	10.1990	10.2130	0.2130	0.1990	0.2130	102.1302	101.9405	102.1302	0.0966	0.0967	0.0986
6	Ferro-Fol	10.0943	10.1222	10.1152	0.0943	0.1222	0.1152	100.9434	101.2226	101.1528	0.1956	0.1950	0.0975
7	Feeful	10.0035	10.0454	10.0175	0.0035	0.0454	0.0175	100.0359	100.4547	100.1755	0.0986	0.0982	0.0985
8	Ferocit-TR	9.9477	9.9198	10.0035	-0.0522	-0.0801	0.0035	99.4776	99.1982	100.0359	0.0992	0.0995	0.0986

CONCLUSION

The applicability of a simple and fast SDEP as a detector for oxidation-reduction reactions was investigated successfully and for précis determination of iron (II) in pure form and in its dosage forms. This technique has the advantage over the previously reported methods with respect to specificity and sensitivity, and requires cheaper instrumentation and a simple electric circuit with only two platinum electrodes. The applied method is superior compared with other methods at it is faster and more suitable for routine analysis. In addition the location of the end-point using the present method is sharper and easier to define than that of the FDEP, direct EP, and conductimetric method, which requires tedious extrapolation manipulation.

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