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Spectrophotometric determination of trace amounts of Iron (II) based on its catalytic effect on the reaction of o-Anisidine and Potassium Bromate

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ABSTRACT

A simple and sensitive first order kinetic-spectrophotometric method is proposed for the determination of Iron (II) in nanogram amounts. This method is based on the catalytic effect of Iron (II) on the oxidation of o-anisidine by potassium bromate in acidic medium (HCl). The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of o-anisidine solution at 420 nm by fixed time method (20 minutes). The proposed method allows determination of Iron (II) in the range of 0.501-4.010 µg/ml with good precision and accuracy.The optimization of the operating conditions regarding concentrations of the reagents, temperature and interferences are also investigated. The reaction was found to be first order in o-anisidine, Iron (II) and bromate. The rate of the reaction is found to have an inverse dependence on hydrogen ion concentration. The pseudo-first order rate constants are determined at different temperatures and thermodynamic parameters were evaluated. A possible mechanism has been proposed. The method was applied to the determination of Iron (II) in Pharmaceutical samples. The results obtained were in excellent agreement with the standard methods such as atomic absorption spectrometry. The coefficient of variance and % error were in the range of 0.998 -0.294 and 0.20-0.25 % respectively. The analytical results obtained were satisfactory.

Key Words: iron (II), o-anisidine, potassium bromate, oxidation, kinetic Method

INTRODUCTION

Kinetic methods of analysis have been very frequently used in trace analysis to obtain high sensitivity combined with relatively simple procedure[1]. Vanilin et.al.[2] studied the autovibrational reaction of the oxidation of malonic acid and its analogs with bromate using complex ion as catalyst. Rabio and Epstein[3] made spectrophotometric investigations of the kinetics of oxidation

of hexacyno ferrate (II) by bromate. Mitzner et,al.[4] described a method for the kinetics of oxidation of iron(II) by bromate in perchloric acid medium. Photometric monitoring of the decolourization of tribromo arsenazo due to oxidation by bromate in sulfuric acid medium catalyzed by iron(II) as been utilized by Long and Qie[5]. Smith and Blish[6] were the first to report the bromatometric titration of iron (II) using basic mercuric bromate as the titrant and Bordeaux and naphthol blue black as indicators. Ottaway and Bishop[7] studied the iron (II) –bromate titration using potentiometric and visual indicator methods. Gopala rao and Krishna muthry[8] recommended potentiometric titration of iron (II) with bromate in phosphoric acid media. Rao and Ramana[9] proposed azine dyes as indicators the titration of iron (II). Shokrollahi et,al.[10] studied highly selective and sensitized spectrophotometric determination of iron (III) following potentiometric study. Stoyanova[11] reporting spectrophotometric determination of trace iron by using its catalytic effect on the N-phenylanthranilic acid-potassium periodate reaction. Rapid and sensitive spectrophotometric determination of trace amounts of iron (III) using leuco Xylene cyanol FF was investigated by Kiran kumar and Revanasiddappa[12]. Cai and Xu [13] made an extensive study on simultaneous determination of trace iron and aluminum by catalytic spectrophotometry based on a novel oxidation reaction of xylene cyanol FF. Li Zaijun et.al.[14] carried out investigation on spectrophotometric determination of iron (III)-dimethyldithiocarbamate (ferbam) using 9-(4-carboxyphenyl)-2,3,7-trihydroxyl-6-fluorone. Kass and Ivaska[15] has proposed spectrophotometric determination of iron(III) and total iron by sequential injection analysis technique. Huang et.al.[16] developed a method for simultaneous determination of iron and aluminium by differential kinetic spectrophotometric method and chemometrics. The authors in the present investigation have initiated work on the kinetic method of determination of iron (II) in nanogram amounts, utilizing its catalytic effect on the oxidation of o-anisidine with potassium bromate in acetic acid medium using fixed time method.

EXPERIMENTAL SECTION

Preparation of Reagents

All reagents used were of analytical reagent grade quality. The triply distilled water was used for preparation of all the solution.

O-Anisidine:

1% or 0.0812 M solution of o-anisidine in 2% methanol is prepared from Aldrich USA. The solution is diluted with triply distilled water and stored in the amber colour bottle. Standardization: O-Anisidine was standardized by Spectrophotometric, chromatography or TLC methods[17,18,19].

Potassium Bromate:

A 0.1 mol.dm^{-3} potassium bromate (BDH, AR) solution was prepared by dissolving the requisite amount in triply distilled water and standardized [31].

Iron (II) Solution:

Approximately 0.1 N iron (II) solution is prepared by dissolving ferrous ammonium sulphate (BDH AnalR) in 0.5 N sulphuric acid and standardized with potassium dichromate using diphenyl amine sulphonicacid indicator[20].

Apparatus

A Shimadzu double beam spectrophotmeter (model No.UV140) with 10nm matched quartz cells equipped with thermostat for kinetic measurement was used in this investigation.

Method

The course of the reaction is followed spectrophotometrically by measuring optical density of unreacted o-anisidine at 420nm **[Fig-1]** which is in good agreement with reported values [21]. At this wavelength Beers Law is obeyed in concentration range of substrate and hydrogen ion. All other materials concerned have negligible absorbtion at this wavelength. In all the kinetic runs the ionic strength is maintained constant by the addition of sodium chloride 5.0 ml of 1.62 x 10^{-4} mol.dm^{-3} of o-anisidine was taken in a clean dry 50ml volumetric flask 2.5ml of 2.0x10^{-4} mol.dm^{-3} HCl and 0.1 ml of 1.0x10^{-2} mol.dm^{-3}. Iron (II) were added, and the total volume is made upto 50ml with 2.5-5.0ml of 1.0x 10^{-2} mol.dm^{-3} potassium bromate solution with triply distilled water. A portion of this is transferred into a spectrophotometric cell and absorbance measurements were made at different time intervals.

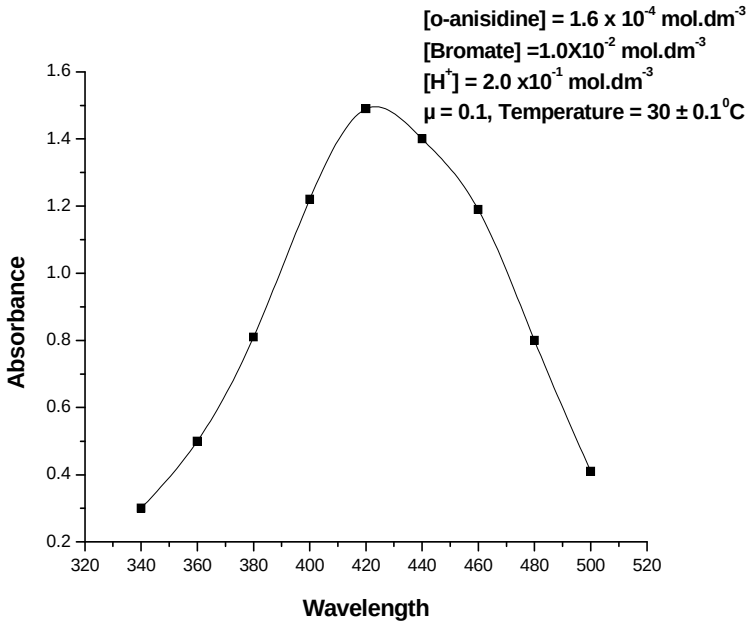

Figure-1: Plot of Absorbance against Wavelength

RESULTS AND DISCUSSION

Dependence of Rate of Reaction on the Concentration of O-Anisidine

Several kinetic runs have been carried out for different concentrations of o-anisidine keeping the concentration of all the other reagents constant. The plots of log of optical density versus time for different initial concentration of o-anisidine were found to be linear, thus this showed that the reaction obeys first order kinetics with respect to concentration of o-anisidine. These straight lines were parallel, further confirming the first order behavior **[Fig-2].** The values of pseudo first order rate constants for different initial concentrations of o-anisidine are tabulated in **Table-1** for the catalyst iron (II).

Dependence of Rate of Reaction on Concentration of Bromate ion

Several kinetic runs were carried out for different concentration of bromate ion keeping the concentration of all other reagents constant. The plot of Logarithm of optical density versus time are found to be straight lines. The pseudo first order rate constants calculated for each concentration of bromate ion are tabulated in **Table-2**. The plots of pseudo first order rate constant versus bromate ion concentration for vanadium(V) were found to be straight line passing through origin **[Fig-3]**. This indicates first order dependence of rate on the concentration of bromate ion.

Table 1 : Dependence of Rate of Reaction on the Concentration of O-Anisidine

S.No	O-Anisidine X 10^4 mol^{-1} dm^{-3}	$K_1X10^3min^{-1}$ [Iron(II)]
1	0.5	3.6
2	1.5	3.6
3	2.4	3.6
4	4.0	3.6
5	6.2	3.6

$[BrO_3^-]$ = 1.0 x 10^{-2} mol/dm^{-3}, [Iron(II)] = 5.0 x 10^{-6} mol.dm^{-3}
$[H^+]$ = 2.0 x 10^{-1} mol.dm^{-3}, μ = 0.1, Temperature = 30 ±0.1 ºC

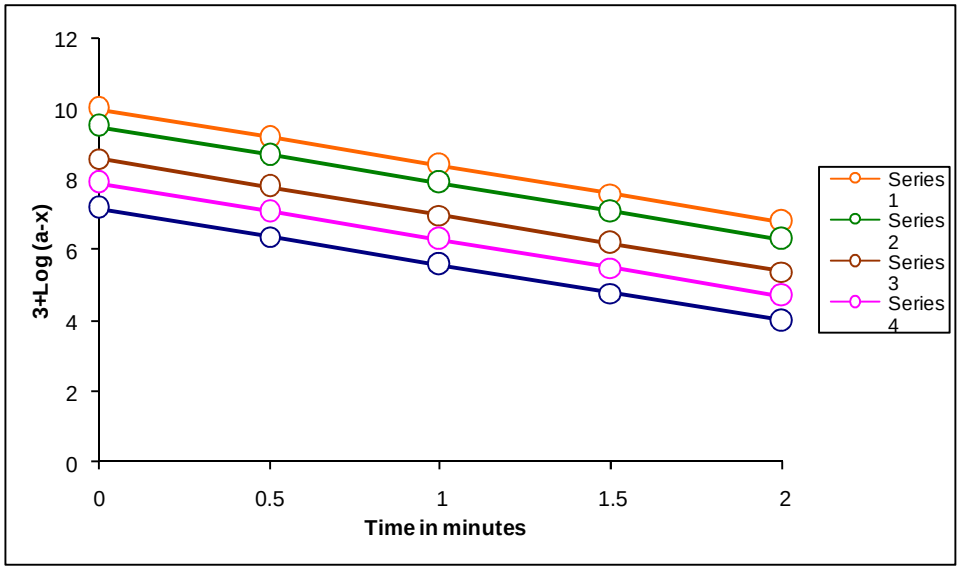

Figure -2: First order Plots for Iron(II) Catalyzed Bromate-O-anisidine Reaction, Variation of [O-anisidine]

Table 2 : Dependence of Rate of Reaction on Concentration of Bromate ion

S.No	$[Bro_3^-]$ X 10^2	K_1X10^3 min^{-1}
1	2.5	3.6
2	3.0	4.6
3	3.5	5.5
4	4.0	6.4
5	5.0	7.7

[O-Anisidine] = 1.62 x10^{-4} mol.dm^{-3}, [Iron (II)] = 5.0 x 10^{-6} mol.dm^{-3},
$[H^+]$ = 2.0 x 10^{-1} mol.dm^{-3}, μ = 0.1, Temperature = 30 ±0.1 ºC

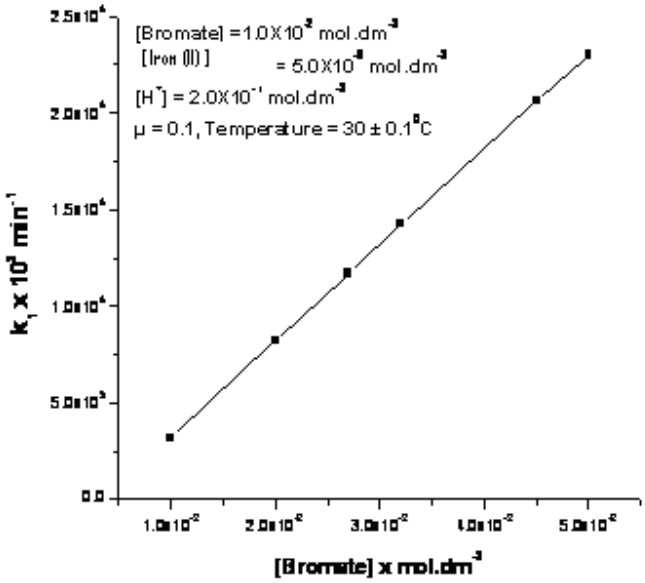

Figure 3: Plot of First Order Rate Constant against [Bromate]

Dependence of Rate of Reaction on the Concentration of Iron (II)

Several kinetic runs were carried out for different concentrations of Iron (II) keeping the concentration of all other reagent constant. The log of absorbance was plotted against time. These straight lines indicating the first order dependence of the rate of the reaction on the concentration of iron (II). **[Fig-4].** The plot of these rate constants versus concentration of iron (II) was found to be a straight line passing through the origin, confirming the absence of uncatalized reaction**.** The pseudo first order rate constants are calculated and tabulated in the **Table-3.**

Table-3: Dependence of Rate of Reaction on the Concentration of Iron(II)

S.No	[Iron(III)]X 10^6	K_1X10^3 min^{-1}
1	0.1	2.3
2	0.2	3.6
3	0.3	5.4
4	0.4	6.4
5	0.5	8.2

[O-Anisidine] = 1.62 x10^{-4} mol.dm^{-3}, [BrO_3^-] = 1.0 x 10^{-2} mol/dm^{-3}
[H^+] = 2.0 x 10^{-1} mol.dm^{-3}, μ = 0.1, Temperature = 30 ±0.1 ºC

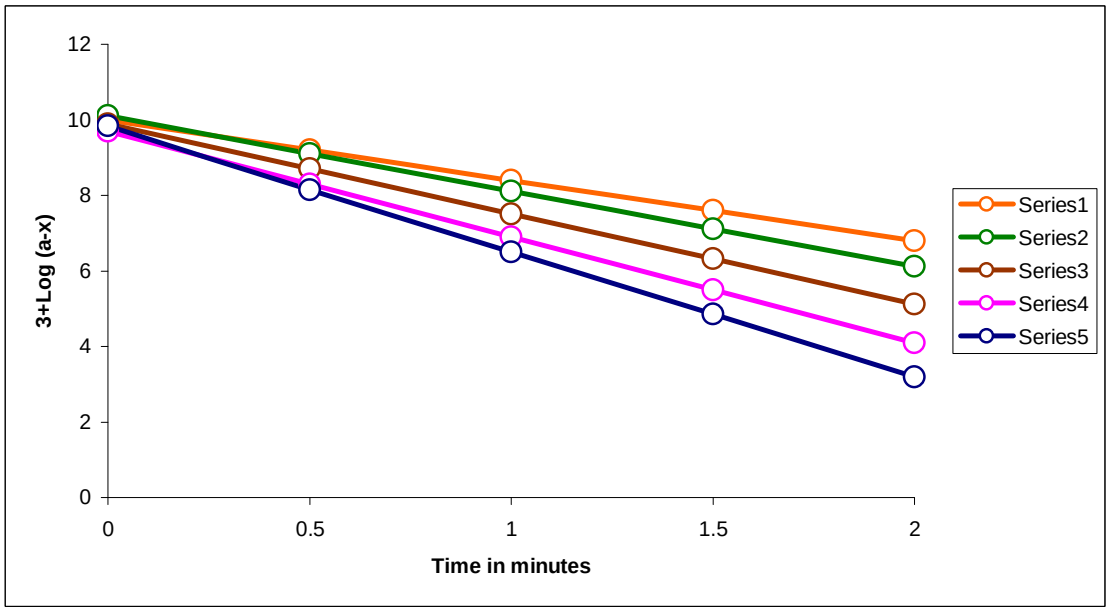

Figure -4: First order Plots for Iron (II) Catalyzed Bromate-O-anisidine Reaction, Variation of [Iron (II)]

Dependence of Rate on Hydrogen ion Concentration

To understand the nature of dependence of the rate of the reaction on hydrogen ion concentration, several kinetic runs were carried out at different concentrations of HCl in the range 1.0 - 3.0x10^{-1}mol.dm^{-3}. The plots of log of absorbance versus time are found to be straight lines. The pseudo first order constants are plotted against reciprocal of hydrogen ion concentration. A straight line passing through origin in obtained in **[Fig-5]** for iron (II) indicating the inverse dependence of rate of the reaction on the hydrogen ion concentration and results are present in **Table-4**.

Determination of Iron (II) by the Catalytic Method

The authors in the present investigation have initiated work on the kinetic method of determination of iron (II) in the nanogram amounts utilizing its catalytic effect on the oxidation of o-anisidine with potassium bromate in the acetic acid medium using the fixed time method.

Table-4: Dependence of Rate on Hydrogen ion Concentration

S.No	[HCl] X 10^{2} mol.dm^{-3}	K_1X10^{3} min^{-1}
1	3.0	10.6
2	4.0	8.5
3	6.0	5.5
4	8.0	4.6
5	10.0	3.6

[O-Anisine] = 1.62 x10^{-4} mol.dm^{-3}, [Iron (II)] = 5.0 x 10^{-6} mol.dm^{-3}, $[BrO_3^-]$ = 1.0 x 10^{-2} mol/dm^{-3}, $[H^+]$ = 2.0 x 10^{-1} mol.dm^{-3} , μ = 0.1, Temperature = 30 ±0.1 ºC

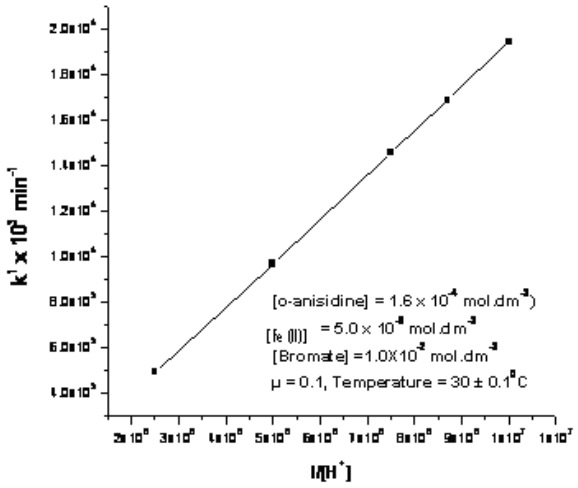

Figure-5: Plot of First Order Rate Constant Against 1/[H^+].

Recommended Procedure:

The authors recommend the following procedure for the determination of the Δx values to the measure the extent of reaction at the end of the twentieth minute. Calculated quantities of o-anisidine and HCl to give an overall concentration of 5.0 x 10^{-6} mol.dm^{-3} and 2.0 x 10^{-1} mol.dm^{-3} respectively are mixed to known volume of iron (II) and total volume is made upto 50ml using triply distilled water. Then calculated quantity of potassium bromate to give an overall concentration of 1.0 x 10^{-2} mol.dm^{-3} was added to reaction mixture, simultaneously starting a stopwatch. Exactly after 20th minute, optical density is measured. The initial optical density of a sample of the reaction mixture without adding potassium bromate is measured. The difference between the optical densities was taken as Δx.

Table-5: Determination of Vanadium (V) by the Catalytic Methods

S,No	Iron(II) in Nanogram/ml	Optical Density at 20th Minute	ΔX
1	0.5	0.623	.0.007
2	1.0	0.614	0.016
3	1.5	0.610	0.020
4	2.0	0.595	0.035
5	3.0	0.583	0.047
6	4.0	0.562	0.068

[O-Anisidine] = 1.62 x 10^{-4} mol.dm^{-3}, [BrO_3^-] = 1.0 x 10^{-2} mol/dm^{-3},
[H^+] = 2.0 x 10^{-1} mol.dm^{-3} μ = 0.1, Temperature = 30 ± 0.1 ºC
Initial optical density = 0.505

Construction of Calibration Curve

The Δx value are determined at different known concentration of iron (II). The results obtained for typical study are given in **Table-5.** The plot of Δx versus iron (II) concentration is a straight line passing through the origin **[Fig-6]** which serves as a calibration curve. Six Δx determinations are made at different initial concentration of iron (II) keeping the concentration of all other reactants constant. Each of the Δx determinations is repeated six times in order to determine the

standard deviation variance and percentage error from Δx values and by using calibration curve, the concentration of iron (II) is determined in each case presented in **Table-6.** By using this data, authors calculated the standard deviation, coefficient of variance and percentage error. The results are presented in **Table -7.**

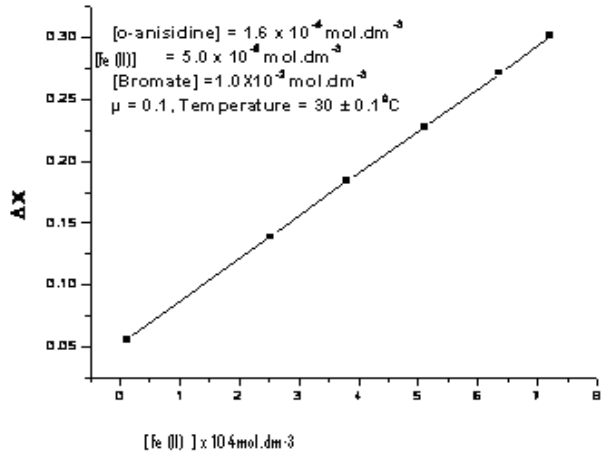

Figure- 6: Calibration Graph for the Kinetic Catalyzed Determination of Iron (II)

Table-6: Replicate Determination of Iron(II)

S.No	Iron(II)Taken Nanogram/ml	Vanadium Found					
		I	II	III	IV	V	VI
1	0.5	0.15	0.12	0.014	0.015	0.013	0.014
2	1.0	0.023	0.023	0.024	0.025	0.026	0.023
3	1.5	0.030	0.030	0.031	0.023	0.031	0.031
4	2.0	0.048	0.049	0.048	0.047	0.046	0.047
5	3.0	0.065	0.065	0.064	0.066	0.064	0.065
6	4.0	0.082	0.081	0.082	0.083	0.081	0.080

[O-Anisidine] = 1.62 x 10-4 mol.dm^{-3}, [BrO_3^-] = 1.0 x 10^{-2} mol/dm^{-3}
[H^+] = 2.0 x 10^{-1} mol.dm^{-3}, Temperature = 30 ±0.1 ºC

Table-7: Statistical Treatment of Results

S.No	Iron (II) Taken in µg/ml	Amount of Iron(II) found µg/ml	Number of Analysis	Coefficient of Variance	% error
1	0.5	0.498	6	0.803	0.40
2	1.0	1.000	6	1.000	NIL
3	1.5	1.502	6	0.399	0.13
4	2.0	1.996	6	0.250	0.20
5	3.0	3.010	6	0.332	0.33
6	4.0	3.995	6	0.200	0.12

[O-Anisidine] = 1.62 x 10^{-4} mol.dm^{-3}, [BrO_3^-] = 1.0 x 10^{-2} mol/dm^{-3},
[H^+] = 2.0 x 10^{-1} mol.dm$^{-3,}$ Temperature = 30 ±0.1 ºC

Interference of Various Ions in the Determination of Vanadium (V)

The interferences of various foreign ions were studied and the results are presented in the **Table-8.** Ions like Na^{+}, Mn^{2+}, Cl^{-} do not have any effect on the extraction of iron, O-Anisidine and bromate complex, when present up to 6,000µg. Ions like Tl^{+}, Zn^{2+}, Cu^{2+}, K^{+}, Cd^{2+}, Th^{4+}, Br^{-} and I^{-} can be tolerated up to 5,000µg. Li^{+},Hg^{2+}, Ni^{2+},Co^{2+}, Cr^{3+} and Se^{4+} do not interfere when present up to 4,000µg. Sr^{2+}, V(IV), EDTA and F^{-} do not have any effect in the determination when present up to 2500 µg.

Table-8: Effect of Various ions on the Determination of Fe (II) Using the Optimum Conditions Reported under Analytical Procedure

S.No	Ions Added	Tolerance Limit µg/ml
1	Na^{+}, Mn^{2+}, Cl^{-}	6,000
2	Tl^{+}, Zn^{2+}, Cu^{2+}, K^{+}, Cd^{2+}, Th^{4+},Br^{-},I^{-}	5,000
3	Li^{+},Hg^{2+}, Ni^{2+},Co^{2+}, Cr^{3+} Se^{4+}, Oxalate	4,000
4	Sr^{2+}, V(IV), EDTA, F^{-}	2,500

[O-Anisidine] = 1.62 x 10^{-4} mol.dm^{-3}, [BrO_3^{-}] = 1.0 x 10^{-2} mol/dm^{-3},
[H^{+}] = 2.0 x 10^{-1} mol.$dm^{-3,}$ Temperature = 30 ± 0.1 ºC

Application of the Developed Method

The developed Kinetic-spectrophotometric method for iron (II) was applied successfully for its determination of food sample and pharmaceutical samples.

Determination of Iron (II) in Pharmaceutical Samples:

The developed Kinetic-spectrophotometric method was applied for the determination of iron (II) in pharmaceutical samples like Fecontin F tablets and Ferrochelate drops. For all these pharmaceutical samples, the metal content was brought into solution by using the standard procedure. The amounts of iron (II) in the pharmaceutical samples were determined by using general procedure. The results obtained are summarized in **Table-9**. The results obtained by the present method are in good agreement with those obtained using thiocyanate method.

Table-9: Determination of Iron (II) in Pharmaceutical Samples

S. No.	Name of the pharmaceutical sample	Citified amount of iron present (mg/mL)	Iron found		Recovery (%)
			By thiocynate method (mg/mL)	By present method *(µg/mL)	
1	Fi contain F tablets	2.0	1.98	1.97	99.4
2	Ferrochelate drops	1.33	1.32	1.32	100

** Average value of true determination*

Determination of Iron (II) Constant in Food Samples:

Determination of iron (II) content in food samples was carried out using the present method. 5g of dried food determinant was weighed and brought to the solution by dry ash method. The result presented in **Table -10** shows that the iron content obtained by the present method was in good agreement with the standard thiocyanate method. The results indicate that iron constant in Amaranth thus (1.172mg) is more when compared to Ragi (0.297mg).

Table-10: Determination of Iron (II) in Food Samples (5g Sample)

S. No.	Name of the food sample	Iron found		Recovery (%)
		By thiocynate method (mg)	By present method *(µg)	
1	Amarantus gangetious (Amaranth)	1.175	1.173	99.8
2	Elensive coracona (Ragi)	0.300	0.298	99.3

** Average value of true determination*

DISCUSSION

The salient kinetic features of kinetic investigation of iron(II) catalyzed oxidation of o-anisidine by bromate ion are:

1. The reaction follows first order kinetics with respect to o-anisidine.
2. The reaction obeys first order kinetics with respect to bromate ion and catalyst iron(II).
3. The rate of the reaction shows inverse dependence on hydrogen ion concentration.
4. Further a plot of the pseudo first order rate constant k_1 versus iron (II) are straight lines passing through the origin which establishes that under these experimental conditions, the uncatalized component is negligibility small.

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