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Determination of Trace Amounts of Total Fe as Fe (II) in Environmental Samples by Catalytic Kinetic Spectrophotometry

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Abstract. The method is based on the selective catalytic effect of iron (II) ions in the presence of 1,10-phenanthroline as an activator, on the oxidation of Coomassie Brillant Blue 2R by bromate. The catalytic reaction was monitored spectrophotometrically at 520 nm by fixed time approach of 3 min. The optimization of the operating conditions are investigated. Obtained optimum conditions: 1.5 mL of Coomassie Brillant Blue 2R (1.0×10^{-4} mol L^{-1}), 0.6 mL of bromate (0.01 mol L^{-1}), 1.5 mL of 1,10-phenanthroline (1.0×10^{-3} mol L^{-1}), reaction temperature 25ºC and time 3 min in pH 2.0 at 520 nm. The proposed method allows quantitatively determination of iron (II) in the range of 0.05-5 mg L^{-1} with a selectivity and quantification limit of 0.0141 and 0.047 mg L^{-1}. The relative standard deviations for five replicate determinations of 0.2 and 3 mg L^{-1} iron (II) are 3.8% and 2.3%, respectively. The method was applied to determination of total iron in some environmental surface waters such as lake, river and well water including pharmaceutical samples used in the treatment of iron deficiency (such as ferrosolanol and maltose) after pre-reduction of iron (III) to iron (II) with sulfite at 40 ºC at pH 4.0, and quantitative percentages of retinas ranging from 98.7-102.7% were obtained by standard attachment-based analysis after wet acid dissolution for possible matrix effect.

Keywords: Iron (II), Coomassie Brillant Blue 2R, 1,10-Phenanthroline, Bromate, Kinetic method

Katalitik Kinetik Spektrofotometri ile Çevresel Örneklerde Eser Miktarlardaki Toplam Fe'nin Fe(II) Olarak Belirlenmesi

Özet. Yöntem, Coomassie Brillant Blue 2R'nin bromat ile oksidasyonuna, aktivatör olarak 1,10-fenantrolin varlığında demir (II) iyonlarının seçici katalitik etkisine dayanır. Katalitik tepkime yaklaşık 3 dakikalık sabitlenmiş-zaman yaklaşımı ile 520 nm'de spektrofotometrik olarak izlenmiştir. Uygulama koşullarının optimizasyonu araştırılmıştır. Elde edilen optimalkoşullar: 1.5 mL Coomassie Brillant Blue 2R (1.0×10^{-4} mol L^{-1}), 0.6 mL bromat (0.01 mol L^{-1}), 1.5 mL 1,10-fenantrolin (1.0×10^{-3} mol L^{-1}), 25 ºC tepkime sıcaklığı and pH 2.0 de, 520 nm'de 3 dakikalık tepkime zamanıdır. Önerilen yöntem, 0.0141 mg L^{-1} ve 0.047 mg L^{-1} lik seçme ve nicelleştirme sınırı ile 0.05-5 mg L^{-1} aralığında demir (II)'nin tayinine izin verir. 0.2 ve 3 mg L^{-1} demir (II)'nin beş tekrarlı analizi için elde edilen bağıl standart sapma değerleri sırasıyla %3.8 ve %2.3 tür. Yöntem, pH 4.0 ve 40 ºC'de sülfit ile demir (III)'ün demir (II)'ye ön indirgenmesi sonrası demir eksikliği tedavisinde kullanılan farmasötik örnekler (ferrosolanol ve maltoz gibi) ve göl, nehir ve kuyu suyu gibi bazı çevresel yüzey sularında toplam demir tayininde uygulanmış, olası örnek matriks etkisi için yaş asitle çözme sonrası standart eklemeye dayanan analizle %98.7-102.7 aralığında değişen kantitatif gerikazanımlar elde edilmiştir.

Anahtar Kelimeler: Fe(II), Coomassie Brillant blue 2R, 1,10-Fenantrolin, Bromat, Kinetik yöntem

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1. INTRODUCTION

Iron is the most abundant elements on Earth, is essential as it maintains good both plants and animals health [1]. The adult human body contains about 4 g of iron, of which about 3 g are in the form of hemoglobin and this level is maintained by absorbing 1 mg of iron per day [2]. Evidence has been presented that at low levels iron is an essential element in the diet, whereas at higher concentrations it is toxic [3]. Iron (II) the preferred nutrient for phytoplankton [4]. Besides, iron (II) is important in the transport and storage of oxygen in animals through the agency of hemoglobine, myoglobine and iron-porphyrine enzymes [5,6]. The main source of iron in natural waters is from the weathering and leaching of rocks and soils [7]. Also, metallic iron and its compounds are used in various industrial processes and may enter natural waters through the discharge of wastes. Thus, iron ion controls the mobility, bioavailability and toxicity of other trace metals in the natural water system [8].

Development of the determination methods for iron in such samples as foodstuffs is important. There are a number of sensitive analytical methods for a highly sensitive method for quantitative analysis of iron speciation in environmental and biomedical studies [9]. These methods include spectrophotometry [10-13], flourimetry [14], flow-injection analysis [15-17], voltammetry [18], chemiluminescence [19], capillary electrophoresis [20], atomic emission and atomic absorption spectrometry [21, 22], and chromatography [23]. Although some of these methods are highly sensitive, they have disadvantages such as the necessity for expensive and sophisticated instrumentation and can only be used to determine iron (III) and/or total iron content.

In the present work, a kinetic procedure proposed for monitoring and determination of iron (II) in presence of 1,10-phenantroline as activator using its catalytic effect on the oxidation of triphenyl methane group dye, Coomassie brilliant blue 2R at pH 2.0 by potassium bromate at 25 ºC. The reaction was monitored spectrophotometrically at wavelength of maximum absorbance of the dye at 520 nm in which the absorbance change between the catalyzed- and uncatalyzed-reactions were measured with fixed time approach of 3 min. The proposed method shows a low detection limit and a wide linear range. Advantages of the proposed method are sensitive, accurate, fast, simple and cheap.

2. MATERIALS and METHODS

2.1. Instrumentation

All absorption measurements at 520 nm were performed using on a double-beam UV-Visible Spectrophotometer (Shimadzu UV-1800 PC, Kyoto, Japan), equipped with the 1.0-cm quartz cells. The pH measurements were made using a pH-2005 digital pH meter equipped with a glass-calomel electrode (pH-2005, JP Selecta, Barcelona, Spain).

2.2. Reagents and solutions

Analytical reagent grade chemicals and twice distilled water were used for preparation of the solutions. Stock solution of iron (II) (Fe (II)) (1000 mg L^{-1}) was prepared by dissolving the appropriate amount of solid $FeSO_4x7H_2O$ (Sigma-Aldrich) in water. All stock standard solutions were stored in polyethylene bottles in a refrigerator at 4 ºC. The working standard solutions were prepared daily by stepwise dilution of the stock solution. A 1.0×10^{-4} mol L^{-1} of Coomassie Brillant Blue (CBB^{+}) solution was prepared daily by dissolving with water. A 1.0×10^{-3} M of 1,10-phenanthroline (1,10-Phen) solution was prepared fresh daily by dissolving a suitable amount of solid reagent (Sigma-Aldrich) in water. The bromate (BrO_3^-) solution of 0.01 mol L^{-1} was prepared by dissolving suitable amount of $KBrO_3$ in 100 mL of

water. The formate buffer solutions at pHs ranging from 1.0 to 4.0 were prepared by mixing HCOOH and HCOONa and adjusting to a suitable pH value by a pH meter. Before starting the experiment, all the containers such as vessels, glassware, pipettes and PTFE bottles were washed first with 10% (w/v) HNO_3 solution, and then with diluted HCl solution (0.1 mol L^{-1}), finally they were rinsed with water.

2.3. General kinetic procedure

The reagent solutions and water were kept at 25 ºC in the thermostatic water bath for fixed-time of 3 min. An appropriate volume of sample or standard solutions in range 0.05-5 mg L^{-1} Fe (II) were added to a 10 mL volumetric flask, and then sequentially 1.5 mL of CBB^+ (1.0×10^{-4} mol L^{-1}), 1.5 mL of 1,10-Phen (1.0×10^{-3} mol L^{-1}) and 0.6 mL of sodium bromate (0.01 mol L^{-1}) solutions and diluted with water to 10 mL. The absorbance change at 520 nm was measured at 30 and 180 s from the initiation of the catalyzed-reaction (ΔA_s). A blank solution (without iron) was prepared and measured in a similar way (ΔA_b). The difference between absorbance changes for the catalyzed- and uncatalyzed-reactions ($\Delta A=\Delta As-\Delta Ab$) was adopted as analytical signal.

2.4. Sample collection, preparation of sample to analysis

Water samples were taken from a local well near Cumhuriyet University in Sivas, Turkey. One milliliter of 1 M HCl was added per 10 mL sample to prevent hydrolysis of iron. The samples were stored in polyethylene containers, and then kept under refrigeration at 4˚C. The samples were filtrated before injection with a 0.45-mm membrane filter before kinetic analysis.

3. DISCUSSION and RESULTS

3.1. Effect of pH and format buffer volume

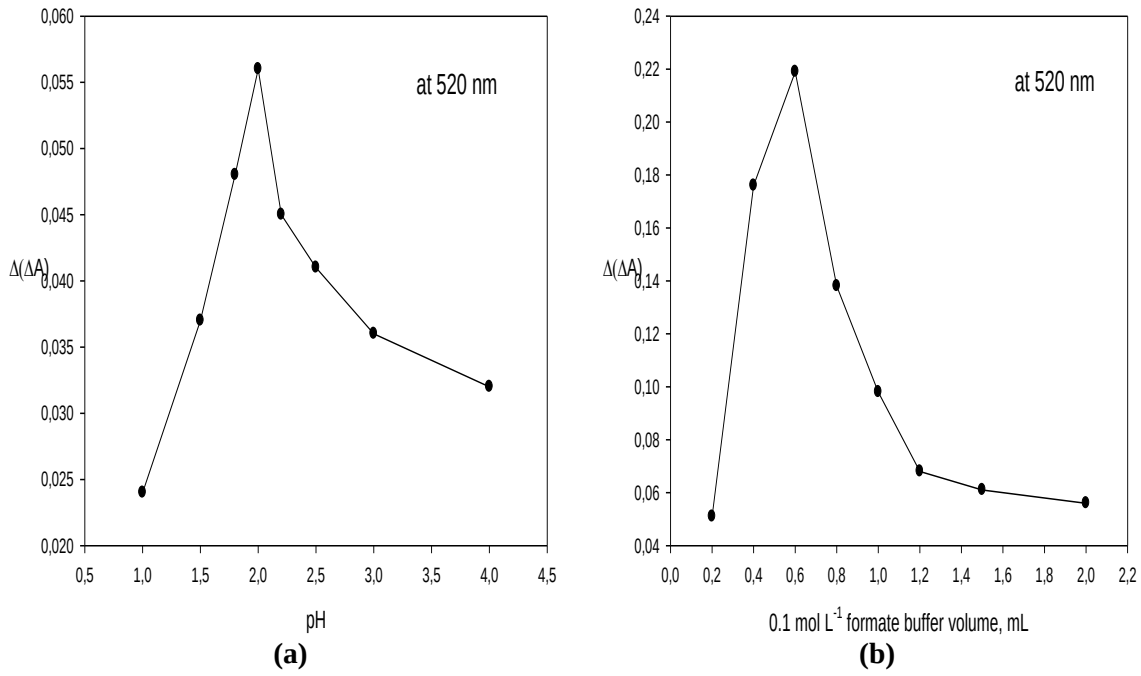

Figure 1 The effect of (a) pH and (b) formate buffer volume of 0.1 mol L^{-1} on analytical signal.

The colour of the dye depends on the acidity of the solution. At a pH of less than 0 the dye has a red colour with an absorption maximum at a wavelength of 470 nm. At a pH of around 1 the dye is green with an absorption maximum at 620 nm and above pH 2 the dye is bright blue with a maximum at 595 nm. At pH 7 the dye has an extinction coefficient of 43,000 $M^{-1}cm^{-1}$ [24]. The CBB^{+} have two sulfonic acid groups that have extremely low pKa's and will normally be negatively charged, thus at a pH of around zero the dye will be a cation with an overall charge of +1 [24]. The pH of the solution is kept acidic throughout the experiment to prevent Fe (II) oxidation. In this study, the effect of pH on the oxidation reaction was investigated in the pH values ranging from 1.0 to 4.0 spectrophotometrically for catalytic measurement of 0.1 mg L^{-1} Fe at 520 nm, as can be seen in Fig. 1(a). From the results obtained, it is clear that the absorbance change linearly increases with increasing pH in the range of 1.0–2.0, and then gradually decreased due to increase in blank signal. Therefore, the best analytical signal was obtained at pH 2.0 for further studies.

In addition, the effect of buffer volume at pH 2.0 was investigated in the range of 0.2–2.0 mL at fixed formate concentration of 0.1 mol L^{-1} in Fig. 1(b), and a buffer volume of 0.6 mL was chosen as optimal value due to give maximum analytical signal.

3.2. Effect of activator volume

The iron complexes of 1,10-phenanthroline (1,10-Phen), pyridine (pyr) and 2,2′-bipyridyl (2,2′-bipyr) are widely used as selective metal binding reagents as promoters and/or activators and model compounds of biologically active substances, due to give stable metal complexes [25-29]. The spectrophotometric measurement of a red-orange complex that forms between Fe (II) and 1,10-phen, is practical, highly sensitive and selective in terms of iron speciation [30].

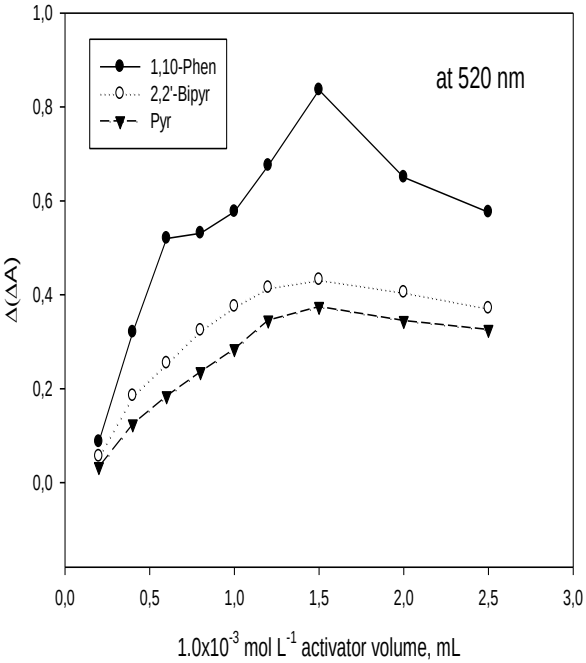

Figure 2. The effect of activator volumes of $1.0x10^{-3}$ mol L^{-1} on analytical signal.

The effect of 1.0 x 10^{-3} mol L^{-1} activator amounts for analytical signal of iron (II) at 0.1 mg L^{-1} were examined in range of 0.25-2.5 mL at 25 ºC in Fig. 2. The optimum volume of standard 1.0 x 10^{-3} mol L^{-1} activator solutions was found to be 1.5 mL with a significant sensitivity difference.

3.3. Effect of Bromate volume

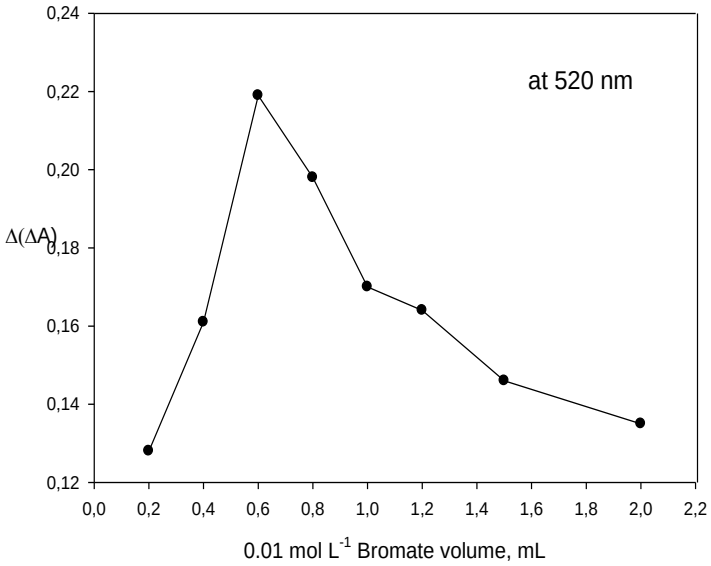

Figure 3. The effect of bromate volume of 0.01 mol L^{-1} on analytical signal.

Dependence of the method sensitivity on the bromate volume at 0.01 mol $L^{-1}$was investigated in the range of 0.2-2.0 mL at 20 ºC. Fig. 3 shows that the reaction rate increases with bromate volume and that analytical signal (ΔA) reaches a maximum value at 0.6 mL, whereas the reaction rate gradually decreases with greater bromate volumes than 0.6 mL. The increase in both ΔA_s and ΔA_b is due to this fact that with increase in bromate concentration, the oxidation ability of bromate increases. According to the results, the bromate volume of 0.6 mL was chosen as the best bromate volume for further studies.

3.4. Effect of the indicator dye volume

The effect of the indicator dye volume, CBB^+ on the oxidation reaction was investigated in the range of 0.2-2.5 mL at 1.0x10^{-4} mol L^{-1} was performed under the optimum conditions. According to the results obtained in Fig. 4, the analytical signal, (ΔA) increase with increase in the CBB^+ volume, and sensitivity increases up to a volume of 1.5 mL, and then it remains constant. Therefore, CBB^+ volume of 0.6 mL was selected as optimal for further studies.

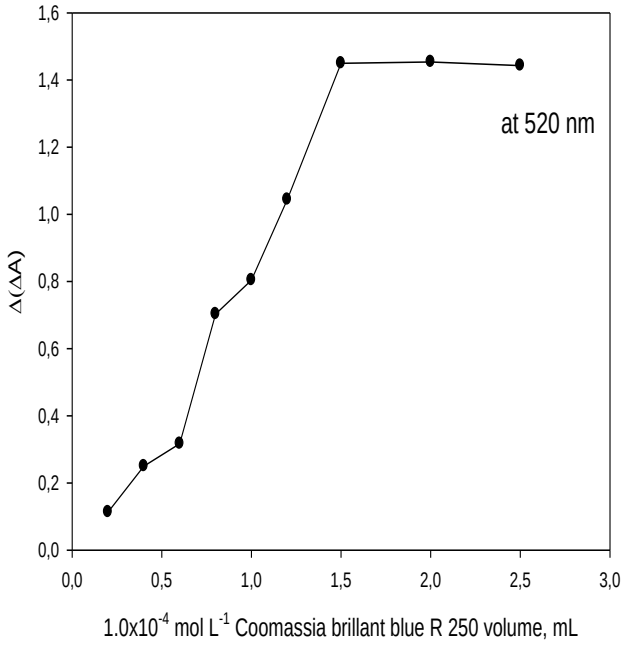

Figure 4. The effect of indicator dye volume, CBC^+ at $1.0x10^{-4}$ mol L^{-1} on analytical signal

3.5. Analytical figures of merit

Under the optimized reagent conditions, as can be seen in Table 1, sequentially the limits of detection and quantification of the method (LOD: $3s_{blank}/m$ and LOQ: $10\ s_{blank}/m$, in which the s_{blank} and m respectively are the standard deviation of ten replicate measurements of sample blank and slope of the calibration curve) of the method for Fe (II) were 14.1 and 47.0 µg L^{-1}, the recovery rates were in range of 98.7-102.7% with a relative standard deviations of 3.8 and 2.3% (0.2 and 3 mg L^{-1}, n: 5), the linear working range was 0.05-1.0 and 0.25-5.0 µg mL^{-1} with a changing calibration sensitivity. The other analytical features are represented in Table 1.

ΔA_1: 0.2971 $C_{Fe(II)}$ (µg mL^{-1}) + 0.0285, R^2: 0.9932

ΔA_2: 0.1370 $C_{Fe(II)}$ (µg mL^{-1}) + 0.0021, R^2: 0.9975

Table 1. Analytical properties of the proposed kinetic spectrophotometric method.

Analytical parameters	Analytical sample, Fe (II)
Regression equation (for N: 5)	ΔA_1: 0.2971 $C_{Fe(II)}$ (µg mL^{-1}) + 0.0285, R^2: 0.9932 ΔA_2: 0.1370 $C_{Fe(II)}$ (µg mL^{-1}) + 0.0021, R^2: 0.9975
Linear range, µg mL^{-1}	0.05-1.0 ve 0.25-5.0
[a]Characteristic concentration of the device, nM	60.3
Limit of detection, LOD (N:12, $3S_b/m$), µg L^{-1}	14.1
Limit of quantification, LOQ (N:12, $10S_b/m$), µg L^{-1}	47
Wavelength (λ_{max}), nm	520
Molar absorptivity L mol^{-1} cm^{-1}	$1.04x10^5$
BSS% (N:5; 0.2 ve 3.0 µg mL^{-1} için)	3.8 ve 2.3

[a]It is the minimum concentration that corresponds to the absorbance change (dA) of 0.001 in the optimum operating conditions of the device.

3.6. The matrix effect

In this study, in order to show the selectivity of the method, the effect of possible interfering anionic and cationic species on the quantitative analysis of Fe (II) (0.1 mg L^{-1}) was tested. The results obtained in this investigation were summarized in Table 2. It is clear that interfering species, which can potentially be found in surface water and pharmaceutical samples with tolerance ratio ranging from 0.3 to 500, did not exhibit a matrix effect in determination of 0.1 mg L^{-1} of Fe (II) by this kinetic approach. Therefore, it can be concluded that the developed method is fairly selective. In a narrow tolerance limit, possible interference of some species can be improved at significant tolerance ratios by using suitable selective masking agents for each interfering species, as can be seen in Table 2.

Table 2. Tolerance levels of foreign ions in the determination of 0.1 μg mL^{-1} of Fe (II).

İnterfering species	Tolerence level, μg mL^{-1}
Acetic acid, tartaric acid, lactic acid, HCO_3^-, *$H_2PO_4^-$, NO_3^-, SO_4^{-2}, Na^+, K^+, NH_4^+, Al^{3+}, Zn^{2+}, Ca^{2+}, Cd^{2+} ,Ce^{3+} and Sr^{2+}	>500
Hydrazine sulfate, triethanolamine, formaldehyde, citric acid, sulfamic acid, As^{3+}, Sb^{3+}, Be^{2+}, Ni^{2+}, Co^{2+}, La^{3+}, Li^+, Mg^{2+}, Mn^{2+}, Pb^{2+}, Tl^+ and Bi^{3+}	125-350
Cl^-, F^-, hydroxyl amine hydrochloride, Tiron, Cu^{2+} and Hg^{2+}	40-120
*N_3^- , Ag^+, Cr^{3+}, Ce^{4+}, *Mn^{7+}, *EDTA, *thiourea, *EDTA, *SCN^-, Fe^{3+} and Sn^{2+}	5-35
*Oxalate, *Br^-, *I^-, *SO_3^{2-}, *$S_2O_5^{2-}$, W^{6+}, Au^{3+}, Pd^{2+} and Sn^{4+}	2-30
[a]NO_2^-, [b]Cr^{6+}, [c]V^{4+}, [c]V^{5+} and [d]Mo^{6+}	0.3-1 (25[a], 35[b], >50[c], 75[d])
[e]Zr^{4+} and [e]Ti^{4+}	0.1-0.3 (> 50[d])

[a]After pretreatment with 0.2 mlLof 100 μg mL^{-1} sulfamic acid

[b]After reduction with 0.2 mL of 100 μg mL^{-1} $NH_2OH.HCl$

[c]After masking with 0.1-0.3 mL of 100 μg mL^{-1} citric acid

[d]After masking with 0.05-0.1 mL of 50 μg mL^{-1} trieathnolamine

[e]After masking with 1.0 mL of 50 μg mL^{-1} NaF

*Ions producing negative interferences either byforming a stable complex with Fe (II) ions or reducing indicatior dye, CBB^+

3.7. Speciation analysis of iron

In order to determine Fe (III) from difference between total Fe and Fe (II) amounts, it was reduced to Fe (II) and was subsequently complexed with 1,10-phen before kinetic analysis. Sulfite was selected as the reducing agent and its concentration for quantitative reduction of Fe (III) to Fe (II) was optimized by extracting 5 mL of Fe (III) at a concentration of 100 μg L^{-1} in the presence of varying amounts of sulfite (0.02–0.2 mol L^{-1}) for 15 min at 40 °C in ultrasonic bath (350 Watt, 40 kHz). The results showed that Fe (III) could be quantitatively reduced when the sulfite concentration was 0.12 mol L^{-1}. Furthermore, the capability of the method for speciation analysis of iron was investigated by processing synthetic model solutions of Fe (III) and Fe (II) according to the given kinetic procedure. The results in Table 3 reveal that the recovery of both species of iron is quantitative; thus the analytical system is capable of speciation of iron.

Table 3. Recovery of Fe (II) and Fe (III) ions from 8 mL of model aqueous solutions at pH 4.0.

Added, μg L^{-1}		Found, μg L^{-1}		[a] Recovery %	
Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)
100	0	101.5 ± 3.0	-	101.5	-
75	25	73.5 ± 3.0	24.0 ± 3.0	98.0	96.0
25	75	24.5 ± 4.0	76.5 ± 4.0	98.0	102.0
50	50	48.5 ± 3.0	48.0 ± 3.0	97.0	96.0
0	100	-	96.5 ± 4.0	-	96.5

[a] The mean and standard deviation of three measurements

3.8. The analytical applications of the method

At initial, the method accuracy was validated by analysis of a certified reference material (CRM); CRM-1643e simulated fresh water-trace elements supplied from NIST as well as recovery studies from spiked samples**.** Clearly, it has been observed that the result found by the present kinetic method is statistically in agreement with the certified value. Moreover, the recovery rates were highly quantitative in range of 99.7-100.8%. The analytical applicability of the proposed method was checked by the quantitation of Fe (II) in pharmaceutical and some environmental water samples. The analysis was also performed as total Fe using three pointed standard addition method around the method determination limit after pre-reduction of Fe (III) to Fe (II) with sulfite at pH 4.0 in ultrasonic bath. In terms of method validation, it can be seen from Table 4(b and c) that the results found by the method are highly compatible with the real Fe (II) contents of the certificated pharmaceutical samples. Also, the recovery studies from spiked samples for different concentration levels in range of 0.2-2.0 mg L^{-1} were conducted. It was found that the recovery rates were quantitative with recoveries ranging from 96.7% to 105% for pharmaceutical samples and ranging from 92% to 99% for Fe (II) and total Fe in environmental waters such as well, river and lake waters.

Table 4(a) The analysis results of certified water samples by means of the proposed kinetic method

Certified environmental water sample	Certified value, μg L^{-1}		Added, μg L^{-1}			*Found, μg L^{-1}		Recovery%		***The statistical t- and F-values
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	**Fe(II)	Total Fe	Fe(III)	Fe(II)	Fe(III)	
NIST-1643e Simulated fresh water-Trace elements	19.62±0.6	-	-	-	19.70±0.18	-	-	-	-	0.275 (0.852)
			5	15	24.65±0.28	39.75±0.34	15.10	99.0	100.7	
			15	5	34.70±0.32	39.74±0.36	5.04	100.5	100.8	
			10	10	29.80±0.30	39.77±0.35	9.97	101.0	99.7	

*The mean value plus its standard deviation of five replicate measurements at 95% confidence level

**The results found by subtracting the amount of Fe(II) from those of total Fe before and after reducing with 1.25 mL of 0.01 moL L^{-1} sulfite with time of 5 min at 40ºC and pH 4.5 formate buffer

***The statistical t- and F-values for 95% confidence level and degree of freedom, 4 are 2.78 and 5.63 respectivel

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Table 4(b). Analysis of pharmaceutical products by the proposed kinetic method.

Sample	Certified value, mg L^{-1}	Fe(II), mg L^{-1}		Fe(III), mg L^{-1}		Total Fe, mg L^{-1}	Recovery%		RSD%	
		Added	Found	Added	Found		Fe(II)	Fe(III)	Fe(II)	Total Fe
Gynoferon draje	0.8	-	0.785±0.03	-	0.00	-	98.13	-	3.82	-
		0.5	1.282±0.04	2.00	2.005	3.287±0.11	99.4	100.25	3.12	3.35
		1.0	1.789±0.05	3.00	2.995	4.784±0.12	100.4	99.83	2.79	2.51
Ferrosanol oral drop	1.2	-	1.16±0.04	-	0.00	-	96.7	-	3.45	-
		0.2	1.37±0.04	2.00	2.02	3.39±0.10	105.0	101.0	2.92	2.95
		2.0	3.15±0.10	1.00	0.97	4.18±0.13	99.5	103.0	3.17	3.11
Maltofer oral solution	0.8	-	0.803±0.03	-	0.00	-	100.4	-	3.73	-
		0.2	1.27±0.04	0.40	0.38	1.68±0.05	105.0	105.0	3.15	2.98
		0.8	1.85±0.05	3.00	3.04	4.93±0.12	98.7	102.3	2.70	2.43

Table 4(c.) Speciative analysis of Fe (II), Fe (III) and total Fe in environmental waters by catalytic kinetic method

Samples	Added (μg L^{-1})		Found by catalytic kinetic method (μg L^{-1}) *			Recovery %	
	Fe(II)	Fe(III)	Fe(II)	Total Fe	Fe(III)**	Fe(II)	Total Fe
Well water	-	-	21.6±0.5	32.4±0.8	10.8	-	-
	5	10	26.2±0.6	47.1±1.3	20.9	92	98
	10	5	31.0±0.8	47.2±1.3	16.2	94	99
Tap water	-	-	14.5±0.3	18.7±0.4	4.2	-	-
	5	15	19.1±0.4	38.5±1.2	19.4	92	97
	15	5	29.0±0.7	38.3±1.2	9.3	97	99
River water	-	-	15.2±0.3	32.5±0.8	17.3	-	-
	5	10	19.7±0.4	47.1±1.3	27.8	90	97
	10	5	24.8±0.5	47.2±1.3	22.7	96	98
Lake water	-	-	16.6±0.3	42.5±1.2	25.9	-	-
	5	10	21.3±0.5	57.1±1.5	30.3	94	97
	10	5	26.1±0.6	57.2±1.5	25.3	95	98

*The mean value and its standard deviation of five replicate measurements at 95% confidence level.

**The results found by subtracting the amount of Fe (II) from those of total Fe after pe-reducing with sodium sulfite at pH 4.0.

***The chemical properties of lake water samples (Hafik, Sivas, Turkey). The mean analysis values obtained by means of thirty replicate measurements: pH: 7.45, total hardness (FS^o) 17.66, total alkalinity 134.67 mg L^{-1}, Ca 58.40 mg L^{-1}, Mg 6.66 mg L^{-1}, Cl^- 34.10 mg L^{-1}, HCO_3^- 134.55 mg L^{-1}

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3.9. Comparison to other reported kinetic methods

A comparison of the presented method with some other reported spectrophotometric determination of iron as Fe (II) determination some samples is given in Table 5. Apparently, the presented method has low LOD (14.1 μg L^{-1}), wide linear range (0.05-1.0 ve 0.25-5.0 μg mL^{-1}), minimum solvent consumption, quantitative recovery (98.7-102.7%).

Table 5. Some spectrophotometric methods reported in the literature for the catalytic–kinetic determination of iron in selected samples.

Reagent	Linear working range, μg L^{-1}	Detection limit μg L^{-1}	References
N-phenylanthranilic acid	2-500	0.88	[31]
m-Acetylchlorophosphonazo	0-100	1.34	[32]
p-acetylarsenazo	0.10-4.0	0.031	[33]
Diphenylamine	1-100	0.52	[34]
2,3-Dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline	1.0-20	280	[35]
Coomassie Brillant Blue 2R	50-1000 and 250-5000	14.1	This study

4. CONCLUSIONS

The results presented clearly demonstrate that catalytic effect of Fe (II) in the presence of 1,10-phen as activator on the oxidation of CBB^{+} by bromate can be used for the determination of trace amounts of Fe (II) at pH 2.0. The proposed kinetic method was found to be accurate, reproductive, sensitive, and selective for only Fe (II) without interference of Fe (III). Also the short time required method is easy to operate, simple, fast, and can be performed with available and cheaper chemicals. Therefore, the proposed method could be applied for pharmaceutical and environmental analyses with satisfactory results.

REFERENCES

[1]. J.D. Lee, *Concise Inorganic Chemistry*, 4rd ed., Chapman & Hall, 1991.
[2]. H.R. Pouretedal, M.H. Keshavars, G.Vanony, *Asian J. Chem.*, 2007, 4969-4976.
[3]. D.L. Tsalev, *Manganese. In: Tsalev DL, editor. Atomic absorption spectrometry in occupational and environmental health practice. Vol. II. Determination of individual elements*. Boca Raton, FL: CRC Press, Inc; 1983.
[4]. J.H. Martin, R.M. Gordon, S.E. Fitzwater, W.W. Broenkow, *Deep-Sea Res*., 1989, 36, 1793-1802.
[5]. D. Nicholls, *The Chemistry of Iron*, Cobalt and Nickel, Pergamon Press, 1973, 979-989.
[6]. B. Jankiewicz, B, Ptaszynski, A. Turek, *Pol. J.Environ.Stud.*, 2002, 11, 745-749.
[7]. J.R. Dojlido, G.A. Best, *Pren. Hall Inc. Englewood*, 1993, 21, 251.
[8]. S. Lunvongsa, M. Oshima, S. Motomizu, *Talanta*, 2006, 68, 969-973.
[9]. K. Hirayama, N. Unohara, *Anal. Chem*., 1988, 60, 2573-2580.
[10]. T. N. Kiran Kumar, H. D. Revanasiddappa, *Anal. Bioanal. Chem.*, 2003, 376, 1126–1130.
[11]. K.S. Patel, A. Shukla, A. Goswami, S.K. Chandavanshi, P. Hoffmann, Fresenius *J. Anal. Chem*., 2001, 369, 530-534.
[12]. M.A. Akl, *Microchem. J*., 2003, 75, 199-209.

[13]. C.D. Stalikas, A.Ch. Pappas, M. I. Karayannis, P.G. Veltsistas, *Microchim. Acta*, 2003, 142, 43–48.
[14]. Z. Zeng, R.A. Jewsbury, *Analyst*, 2000, 125, 1661-1665.
[15]. K. Saitoh, T. Hasebe, N. Teshima, M. Kurihara, T.Kawashima, *Anal. Chim. Acta*, 1998, 376, 247-254.
[16]. S. Lunvongsa, M. Oshima, S. Motomizu, *Talanta*, 2006, 68, 969-973.
[17]. A. Tsuji, N. Teshima, M. Kurihara, S. Nakano, T. Kawashima, *Talanta*, 200,52, 161-167.
[18]. J. Zarebski, *Fresenius J. Anal. Chem*. 1996, 356, 299-302.
[19]. W. Qin, Z.J. Zhang, F.C. Wang, *Fresenius J. Anal. Chem*. 1998, 360, 130-132.
[20]. S. Pozdniskova, A. Padaruskas, *Analyst*, 1998, 123, 1497-1500.
[21]. V. Lazic, R. Fantoni, F. Colao, A. Santagata, A. Morone, V. Spizzichino, *J. Anal. Atom. Spectrom.*, 2004, 19, 429-436.
[22]. P.S. Roldan, I.L. Alcantara, C.C.F. Padilha, *Fuel*, 2005, 84, 305-309.
[23]. S. Osznadowski, A. Pikus, *Talanta*, 2002, 58, 773.
[24]. P.R. Bontchev, *Talanta*, 1970, 17, 499.
[25]. T.S. Lee, I.M. Kolthoff, D.L. Leussing, *J. Am. Chem. Soc*., 1948, 70, 2348–2352.
[26]. J.E. Dickens, F. Basolo, H.M. Neumann, *J. Am. Chem. Soc*., 1957, 79, 1286–1290.
[27]. D.W. Margerum, *J. Am. Chem. Soc*., 1957, 79, 2728–2733.
[28]. B.R. James, J.R. Lyons, R.J.P. Williams, *Biochemistry*. 1962, 1, 379–385.
[29]. G. Nord, B. Pedersen, E. Bjergbakke, *J. Am. Chem. Soc*., 1983, 105, 1913–1919.
[30]. N.Demirhan, F.T. Elmalı, *Turk. J. Chem*, 2003, 27, 315-321.
[31]. A.M. Stoyanova, *Anal. Sci.*, 2008, 24.
[32]. Q.Z. Zhai, L.X. Jin, *Instrum. Sci. Technol.*, 2009, 37, 462–471.
[33]. Q.Z. Zhai, *Bull. Chem. Soc. Ethiop*., 2009, 23, 445-450.
[34]. A. Stoyanova, *J. Univ. Chem. Technol. Metall.*, 2006, 41, 205-210.
[35]. A.S. Amin, A.A. Gouda, *Talanta*, 2008, 76, 1241–1245.