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Original Article

Development of method for extractive spectrophotometric determination of Fe (II) with of 2-[2-(4-chloro benzothiozole) imino]-5- nitro phenol as an analytical reagent

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ABSTRACT

A spectrophotometric method has been developed for the determination of Cu (II) using 2-[2-(4-Chloro Benzothiozole) imino]-5- nitro phenol as an extractive reagent. The reagent forms a coloured complex, which has been quantitatively extracted into n- butanol at PH 8.6. The method obeys Beer's law over a range from 1 to 10 ppm. The Molar absorptivity and Sandell's sensitivity calculated were 0.2602 × 104 LMol-1cm-1 and 0.1507 µg cm-2 respectively. The proposed method is very sensitive and selective. The method has been successfully applied to synthetic and commercial samples.

Key words: Iron, Spectrophotometric determination, n-butanol, 2- [2- (4- Chloro Benzothiozole) imino] -5 – Nitro Phenol.

INTRODUCTION

Iron is the most common element on earth by mass, forming much of earth's outer and inner core. It is the fourth most common element in the Earth's crust. Iron is abundant in biology[1-4]. The color of blood is due to the hemoglobin, an iron-containing protein. As illustrated by hemoglobin, iron is often bound to cofactors, e.g. in hemes. The iron-sulfur clusters are pervasive and include nitrogenase, the enzymes responsible for biological nitrogen fixation. Iron is pervasive, but particularly rich sources of dietary iron include red meat, lentils, beans, poultry, fish, leaf vegetables, watercress, tofu, chickpeas, black-eyed peas, blackstrap molasses, fortified bread, and fortified breakfast cereals. Iron in low amounts is found in molasses, teff, and farina. Iron in meat (heme iron) is more easily absorbed than iron in vegetables[5]. Although some studies suggest that heme/hemoglobin from red meat has effects which may increase the likelihood of colorectal cancer[6,7]. Iron distribution is heavily regulated in mammals, partly because iron ions have a high potential for biological toxicity[8].

Iron is pervasive, but particularly rich sources of dietary iron include red meat, lentils, beans, poultry, fish, leaf vegetables, watercress, tofu, chickpeas, black-eyed peas, blackstrap molasses, fortified bread, and fortified breakfast cereals. Iron in low amounts is found in molasses, teff, and farina. Iron in meat (heme iron) is more easily absorbed than iron in vegetables. Although some studies suggest that heme/hemoglobin from red meat has effects which may increase the likelihood of colorectal cancer,

Several compounds like phenanthroline[9-11], Ferrozine [12-13] are known to react with the metal ions to give coloured complexes and have been employed for the quantitative extraction and spectrophotometric determination[14-16] of metals at trace levels. A number of reagents such as oxime, [17-18] hydrazone, [19,20]semicarbazone, [21] thiosemi carbazone[22], etc have been used for the determination of Iron. However these methods suffer from limitations such as requirement of masking agents, interference of some ions, equillibrium time for superior in sensitivity and selectivity to those reported in the literature, is developed for the extractive spectrophotometric determination of Iron with BIPINP. A close literature survey indicates that BIPINP has far not been employed for analytical studies. The proposed method is free from limitations. The present investigation a novel method for the extractive spectrophotometric determination of iron, which is simple, sensitive, rapid and precise and so far not been employed for either coordination or analytical

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studies. It will be applied for the determination of iron at trace level in synthetic mixtures and alloys.A solvent extraction has grown into one of the most promising method in separation of metal ions at trace level because of its simplicity, rapidity and varsality. In present communication, we describe the extractive spectrophotometric determination of Fe (II) with2- [2- (4- Chloro Benzothiozole) imino] -5 – Nitro Phenol. (CBZTINP)

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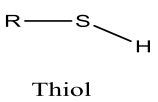
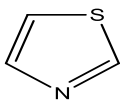
EXPERIMENTAL

The reagent 2- [2- (4- Chloro Benzothiozole) imino] -5 – Nitro Phenol(CBZTINP) was prepared by the given procedure. The stock solution of Iron (II) was prepared by dissolving a weight amount of its ferrous ammonium sulphate in double distilled water containing dilute sulphuric acid, which was diluted to the desired volume with double distilled water and standardized by ophenanthroline. Absorbance and pH measurement were carried out on a Shimadzu UV- Visible 2100 spectrophotometer with 1cm quartz cells and digital pH meter with combined glass electrode respectively.

REACTION



Thiol



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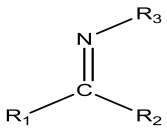
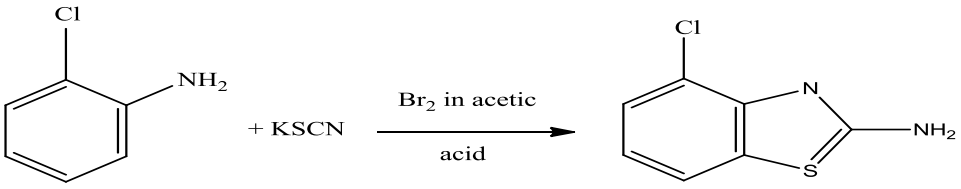
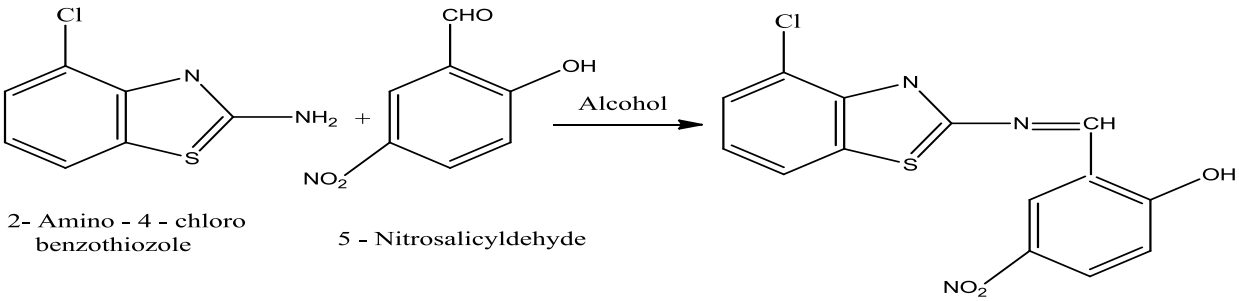


Schiff base



2 - Chloroaniline

2- Amino - 4 - chloro benzothiozole



2- Amino - 4 - chloro benzothiozole

5 - Nitrosalicyldehyde

2 - [2 - (4 - Chlorobenzothiozole) imino] - - nitrophenol

Procedure for the extraction: 1.0 mL of aqueous solution containing 0.1 mg of Iron metal and 1 mL of reagent were mixed in 50 mL beaker. The pH of the solution adjusted to 8.6 with 0.2M boric acid and potassium chloride, keeping the volume 10 mL. The solution was transferred to 100 mL separatory funnel. The beaker was washed twice with n-butanol and transferred to the same funnel. The two phases were shaken for two minutes and allowed to separate. The organic phase was collected in 10 mL measuring flask and made up to the mark with organic solvent, if required. After separation of the two phases, the pH of the aqueous phase was measured and the Fe (II) in each phase was determined by o-phenanthroline.

RESULTS AND DISCUSSION

The reagent CBZTINP forms yellowish brown coloured complex with Fe (II), which was extracted into organic phase. The extraction of Fe (II) froms an aqueous phase by CBZTINP in n-butanol is studied over a wide range experimental condition. The results of various studies are discussed below.

Extraction as a function of pH: The extraction of copper with 2- [2- (4- Chloro Benzothiozole) imino] -5 – Nitro Phenol has been studied over the PH range 1- 10 and was observed that percentage extraction of Fe (II) is maximum at PH 8.6. (Fig.1)

Absorption spectrum: The absorption spectrum of Fe (II): 2- [2- (4- Chloro Benzothiozole) imino] -5 – Nitro Phenol in n-butanol shows the maximum absorption at 480 nm. The absorption due to reagent at this wavelength is nearly negligible. Hence the absorption measurements were carried out at 480 nm.

Influence of diluents: The suitability of diluents was investigated using organic solvents such as chloroform, ethyl acetate, isoamyl alcohol, xylene, hexane, toluene, n-butanol, carbon tetra chloride. The extraction of Fe (II) was quantitative with CBZTINP in n-butanol. Hence, nbutanol was used for further extraction studies as it gave better and quicker phase separation.

Effect of salting out agent: The presence of 0.1M salts of various alkali and alkaline metals does not show any effect over the absorbance value of Fe (II): 2- [2- (4- Chloro Benzothiozole) imino] -5 – Nitro Phenol complex extract. Therefore, no salting out agent was required during the extraction.

Effect of reagent concentration: Various volumes of 0.1% reagent solution were added to the sample solution containing 50µg of iron at respective PH values. The absorbance remained nearly constant when the volume of the reagent solution used was more than 1 mL. Therefore, 1 mL of 0.1 % reagent was chosen for the quantitative determination of the metal.

Effect of equilibrium time and stability of the complex: The study of change in absorbance with variation in equilibrium time extraction of the complex into organic solvent shows that equilibrium time of 60 sec. are sufficient for the quantitative extraction of Iron. The study of stability of colour of the Fe (II): CBZTINP complex with respect to time shows that the absorbance due to extracted species is stable up to 36 hours, after which slight decrease in absorbance is observed. Throughout the experimental work, for practical convenience, the measurements have been carried out within one hour of extraction of iron.

Calibration plot: A calibration plot of absorbance against varying iron concentration and fixed CBZTINP concentration gives linear and reproducible graph in the concentration range 1 to 10 ppm of iron (Table.2). This shows that the Beer's law is obeyed in this range. The Molar absorptivity and Sandell sensitivity were calculated to be is 0.2602 × 104 L mol-1 cm-1 and 0.1507 µg /cm-2 respectively.

Nature of extracted species: The composition of extracted species has been determined by Job's continuous variation method (Fig.4) (Table.1)., Slope ratio method and Mole ratio metho(Fig.3) d. It shows that the composition of Fe (II): CBZTINP complex is 1:2.

Effect of divalent ions and foreign ions: The effect of other ions present in various amount indicated no interference in the spectrophotometric determination of 50 µg of iron. The ions which show interference in the spectrophotometric determination of iron were overcome by using appropriate masking agents (Table 3).

Precision and Accuracy: The precision and accuracy of the developed spectrophotometric method has been studied by analyzing five solutions each containing 50 µg of iron in the aqueous phase. The average of five determinations was 50.0 and variation from mean at 95% confidence limit was ± 0.833.

Applications: The proposed method was successfully applied for the determination of copper from various alloys and synthetic mixtures. The results found to be in good agreement with

those obtained by the standard known method. (Table 4).

CONCLUSION

The proposed method is highly sensitive and selective than the other reported methods for extractive spectrophotometric determination of microgram amounts of iron. It offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and suffers from less interference. It has been successfully applied to the determination of iron at trace level in synthetic mixtures and alloys.

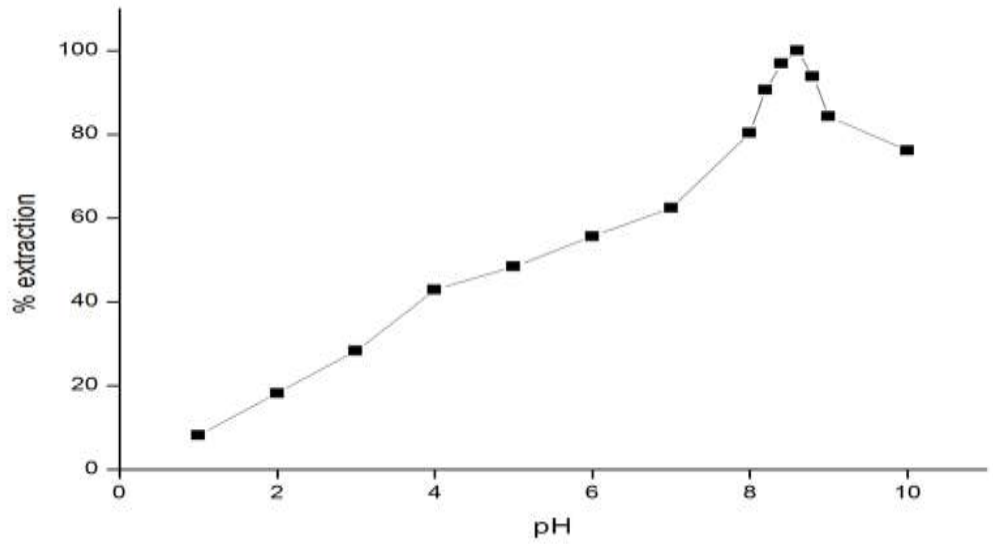


Fig 1: Percentage Extraction as a function of PH

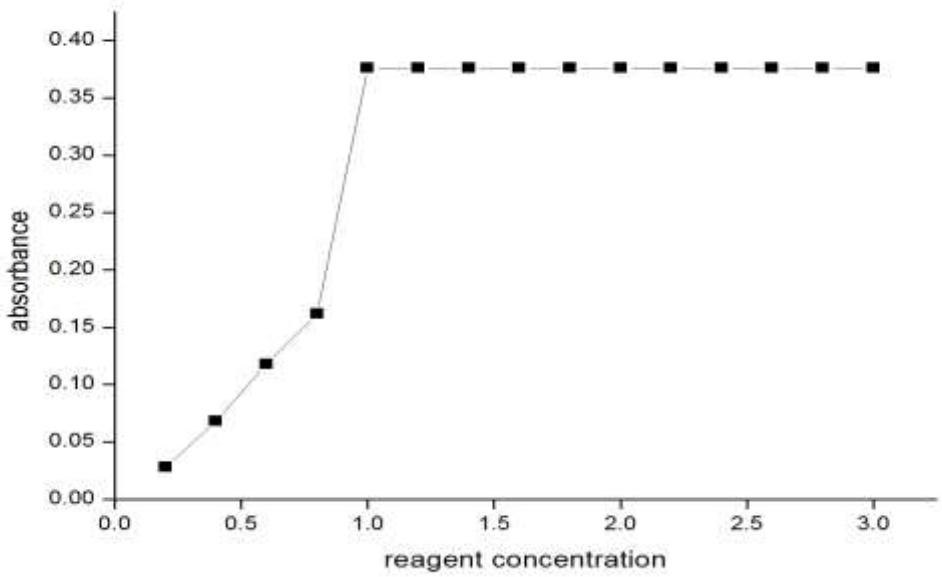


Fig. 2: Effect of reagent concentration

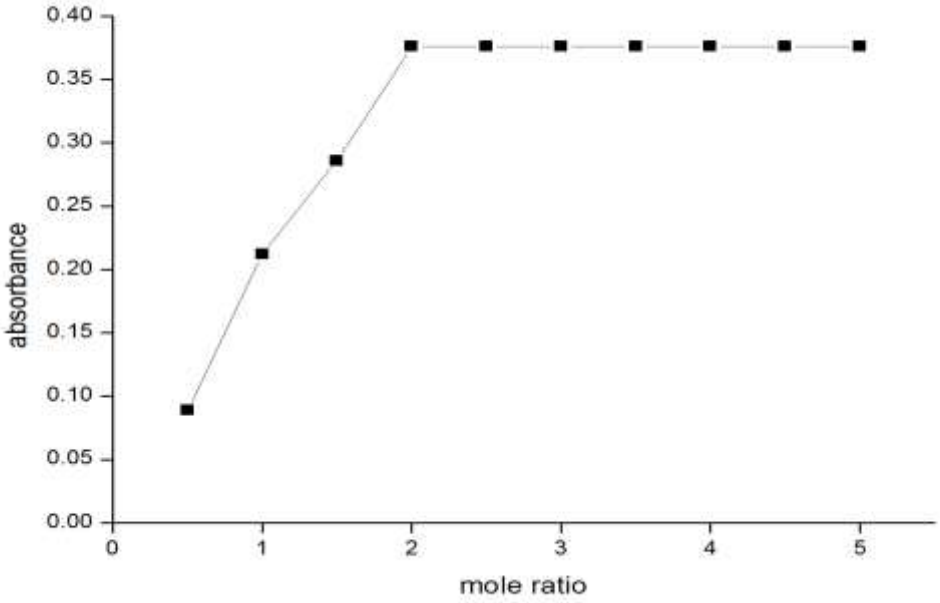


Fig 3: COMPOSITION OF THE EXTRACTED Fe (II): CBZTINP COMPLEX BY MOLE RATIO METHOD

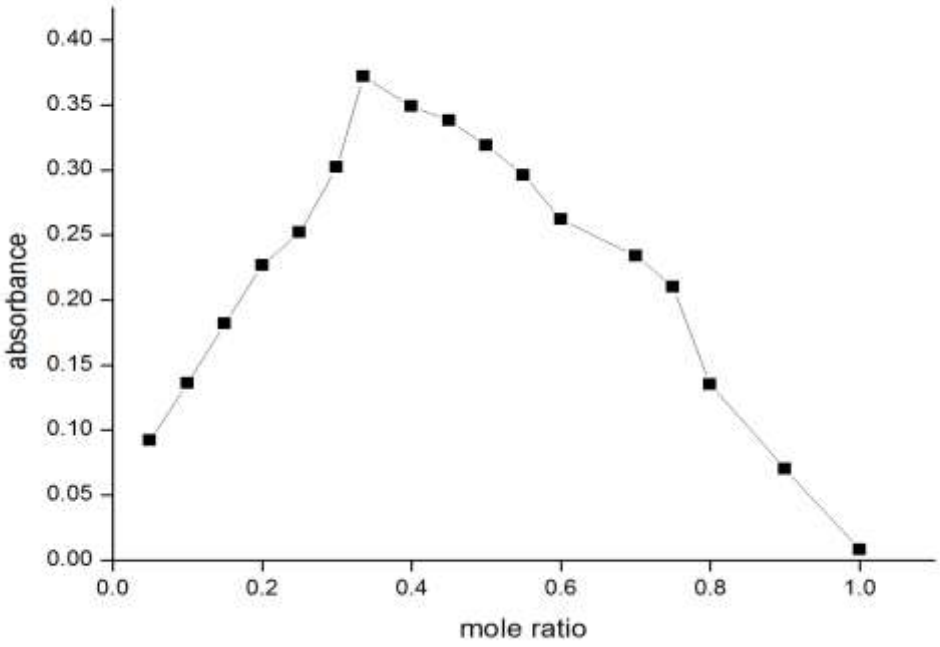


Fig. 4: Job's Continuous variation method

Table1: Job's Continuous variation method

Sr. No.	Volume of Fe (II) in cm^3	Volume of CBZTINP	Mole Fraction [Fe (II)] / [Fe (II)] + [CBZTINP]	Absorbance
1	2.0	0.0	1.00	0.008
2	1.8	0.2	0.90	0.070
3	1.6	0.4	0.80	0.135
4	1.5	0.5	0.75	0.210
5	1.4	0.6	0.70	0.234
6	1.2	0.8	0.60	0.262
7	1.1	0.9	0.55	0.296
8	1.0	1.0	0.50	0.319
9	0.9	1.1	0.45	0.338
10	0.8	1.2	0.40	0.349
11	0.67	1.33	0.335	0.372
12	0.6	1.4	0.30	0.302
13	0.5	1.5	0.25	0.252
14	0.4	1.6	0.20	0.227
15	0.3	1.7	0.15	0.182
16	0.2	1.8	0.10	0.136
17	0.1	1.9	0.05	0.092
18	0.0	2.0	0.00	-----

Table2: Calibration plot of Fe (II): CBZTINP complex

Sr. No.	Concentration of Fe (II) in ppm	Absorbance
1	1	0.059
2	2	0.116
3	3	0.192
4	4	0.252
5	5	0.376
6	6	0.412
7	7	0.498
8	8	0.562
9	9	0.624
10	10	0.752

Table3: STUDY OF THE INTERFERENCE OF SOME ANIONS ON THE ABSORBANCE OF Fe (II): CBZTINP COMPLEX IN N-BUTANOL

Sr. No.	Anion	Amount added (mg)	Absorbance
1	----	-----	0.376
2	Cl^-	18.0	0.376
3	Br^-	18.0	0.376
4	I^-	15.0	0.376
5	F^-	16.0	0.376
6	ClO_3^-	18.0	0.376
7	BrO_3^-	13.0	0.376
8	IO_3^-	11.0	0.376
9	SO_3^{2-}	15.0	0.376
10	SO_4^{2-}	14.0	0.376
11	NO_2^-	8.0	0.376
12	NO_3^-	0.9	0.376
13	PO_4^{3-}	11.0	0.376
14	$S_2O_3^{2-}$	17.0	0.376
15	Acetate	8.0	0.376
16	Urea	8.0	0.376
17	Thiourea	9.0	0.376

Table4: DETERMINATION OF Fe (II) USING CBZTINP FROM REAL SAMPLES

Sr. No.	Sample	Amount of Fe (II)	
		Standard method	**Present method**
1	Alloys 1) Hematite 2) Steel	 35.0 % 67.2 %	 34.98 % 67.18 %
2	Capsule/tablets 1) Austrin 2) Globiro	 32.86 mg 50.0 mg	 32.85 mg 49.97 mg
3	Synthetic mixture 1) Fe (II) + Zn (II) 2) Fe (II) + Mg (II)	 4.99 ppm 4.99 ppm	 4.97 ppm 4.98 ppm

REFERENCES

1. Dlouhy, Adrienne C.; Outten, Caryn E. Metalloprotein, Springer; 2013 Doi: 10.1007/978-94-007-5561-1_8. ISBN 978-94-007. 5560-4-ISSN 1868-0402.
2. Banci Lucia. Metallomics and the Cell, Metal Ions in Life Sciences, 2013. ISBN 978-94-007-5561-1. ISSN 1559-0836.
3. Gereon M. Yee, William B. Tolman, Chapter 5 Transition Metal Complexes and The Activation of Dioxygen. Springer.2015; pp. 131–204. doi: 10.1007/978-3-319-12415-5_5.
4. M.H.Peter, E. Kroneck . Sustaining Life on Planet Earth: Metalloenzymes Mastering Dioxygen and Other Chewy Gases. Metal Ions in Life Sciences 15. ISSN1559-0836, ISBN978-3-319-12914-8.
5. Food Standards Agency – Eat well, be well – Iron deficiency. Eatwell.gov.uk 5 March 2012; Retrieved on 27 June 2012.
6. Sesink, L.A. Aloys. "Red meat and colon cancer: the cytotoxic and hyperproliferative effects of dietary heme". Cancer Research.1999; 59 (22): 5704–9. PMID 10582688.
7. M.Glei, S. Klenow, J. Sauer, U. Wegewitz, K. Richter, B.L. Pool-Zobel, "Hemoglobin and hemin induce DNA damage in human colon tumor cells HT29 clone 19A and in primary humancolonocytes".Mutat.Res.2006;594(1–2)162–171.
8. M.Nanami, T. Ookawara, Y. Otaki, K. Ito,R. Moriguchi, Tumor necrosis factor-α-induced Iron sequestration and oxidative stress in human endothelial cells. Arteriosclerosis, thrombosis, and vascular biology. 2005; 25 (12): 2495–2501.
9. Hiroki Tamura, Katsumi Goto, Takao Yotsuyanagi,Masaichi Nagayama. (1974). Spectrophotometric determination of iron(II) with 1,10-phenanthroline in the presence of large amounts of iron(III) Talanta. 1974; 21(4): 314-331.
10. W.B. Fortune, M.G. Mellon, Determination of Iron with o-Phenanthroline: A Spectrophotometric Study.Ind. Eng. Chem. Anal. Ed.1938; 10 (2): 60–64.
11. J.P. Mehlig, H.R. Hulett, Spectrophotometric Determination of Iron with o-Phenanthroline and with Nitro-o-Phenanthroline .Ind. Eng. Chem. Anal. Ed.1942; 14 (11): 869–871.
12. L. Lawrence, Stookey. Ferrozine---a new spectrophotometric reagent for iron, Anal. Chem.1970; 42 (7): 779–781.

13. M. V. Dawson,J. Samuel . (1990). Spectrophotometric determination of iron and cobalt with Ferrozine and dithizone, Talanta;1990: 37 (12): 1189–1191.
14. M.S. Abu-Bakr, H. Sedaira, E.Y. Hashem(1994). Complexation equilibria andspectrophotometric determination of iron(III) with 1-amino-4-hydroxyanthraquinone. Talanta. 1994; 41(10): 1669-1674.
15. Mohammad Hamidi, Mehdi Vadi. Ionic Strength Dependence of Formation Constants, Protonation and Complexation of Leucine with Iron.RJPBCS.2015; 6(4):1993-2001.
16. M.M. Gibbs. A simple method for the rapid determination of iron in natural waters. Water Research.1979; 13(3): 295–297.
17. J. William Holland, John Bozic, J.T. Gerard. Di-2-Pyridylketoxime, a new reagent for the spectrophotometric determination of iron(II). Analytica Chimica Acta.1968; 43: 417-422.
18. Shigeroku Yamaguchi and Katsuya Uesugi . spectrophotometric determination of iron(III) with 2-hydroxy-1-naphthaldehyde oxime. Analyst.1984; 109 (11): 1393-1395.
19. Tsutomu Nakanishi, Makoto Otomo. Solvent extraction and spectrophotometric determination of iron(II) with di-2-pyridyl ketone benzoylhydrazone. Microchemical Journal.1986; 33(2): 172–178.
20. H. Alexaki-Tzivanidou . Spectrophotometric determination of iron with 2,2'-Dipyridyl-2-pyridylhydrazone.Analytica Chimica Acta.1975; 75(1): 231-234.
21. R.S.Lokhande , R. P. Sonawane . (2012). Synthesis of Hydrazine Carboxamide-2-[(2-Hydroxy-1-Naphthalenyl) Methylene] as an analytical reagent for the Extractive Spectrophotometric determination of Fe (II).RJPBCS.2012; 3(2): 27-33.
22. Francisco Salinas, Juan Carlos Jimenez Sanchez, Teresa Galeano Diaz. (1986). Spectrophotometric determination of iron in wines, foods, and minerals with 5,5-dimethyl-1,2,3-cyclohexanetrione 1,2-dioxime 3-thiosemicarbazone. Anal. Chem.1986; 58 (4), 824–827.