

Second order Derivative Spectrophotometric determination of Fe(II) using 3,4-DihydroxyBenzaldehydeTiosemicarbazone(DHBTSC) in presence of micelle medium

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ABSTRACT

A rapid and sensitive method has been developed for the determination of Fe(II) based on complexation reaction between the metal ion and 3,4,-dihydroxybenzaldehydethiosemicarbazone (DHBTSC) in the presence of non-ionic surfactant Tween-80. The important parameters affecting the analytical procedure were optimized. Absorption maximum for a ternary complex was noted at λ_{\max} 365 nm. The reaction was found to be rapid at room temperature and absorbance remained constant for more than 24h. The method obeys Beer's law in the range 13.96 to 97.73 ng /ml. The apparent molar absorptivity of 4.21×10^5 L mol⁻¹ cm⁻¹ and Sandell's sensitivity 0.013ng/ml. The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of ≥ 100 folds in excess of foreign ions. The method was successfully used in the determination of Iron(II) in Leaf sample. Second order derivative spectrophotometric method were developed at λ_{\max} 485nm for the determination of Iron, which was more sensitive than the zero order method.

Keywords: Spectrophotometric Determination, Iron, 3,4-DHBTSC, Surfactant Tween-80, Leaf sample.

Introduction

Iron is one of the most important transition element in living systems, being vital to both plants and animals. The stunted growth of the former is well known in soils, which are either themselves deficient in iron or in which high alkalinity renders the iron too insoluble to be accessible to the plants. Iron was the first minor element to be recognized as being essential to human being and was used in the treatment of anaemia. The adult human body contains about 4g of iron (i.e., 0.005% of body weight) of which about 3g are in the form of haemoglobin. Proteins involving iron are also present in the human body and its major function is oxygen *transport* and storage. In water samples, iron may occur in true solution either in ferrous or ferric form. Therefore, the determination of iron in environmental samples is important. There are two main forms of iron salts with numerous formulations such as: amino acid chelates, carbonyl iron, polysaccharide iron, combination products and extended release products available globally[1]

The 3D-structures of hydrazones and thiosemicarbazones with multidentate chelating properties bind a large number of metal ions exhibiting a wide spectrum of characteristics. The size of chelate ring, thermodynamic/ kinetic stability, quantum effects of the complexes depend upon side chains/spacers/aromatic heterocyclic rings and medium (aqueous, non_aqueous/aqueous-organic mixtures /micelles/vesicles etc.). The applications of these products are spread in diverse disciplines. Some of the typical tasks include analysis, preparation of non linear optical materials (NLO'S), processes concerned with smart materials and chemico-bio interactions. The impetus to explore the analytical characteristics of newly synthesized thiosemicarbazones and off the shelf hydrazones stem from a perspective of probing into bonding nature of a deeply researched dense domains of ONS donors.

Most of the applications of hydrazones and thiosemicarbazones as chromogenic reagents were carried out in yester year's use water, cosolvent-water mixtures (or) through solvent extraction[2--9] The renaissance brought by green chemistry opened a new path in quantitative estimations through minimizing use of harsh (toxic) solvents. In our research laboratories, during the last three decades, the micelles have been extensively utilized in kinetics of redox/hydrolysis reactions and quantitative estimation of dyes. The small quantity of micelles and thus low toxicity (compared to many solvents) in micro gram/nano gram estimations of metal ions is an accordance with good laboratory practice (GLP) adhering to green chemistry principle (GCP). The continual success of research programs in the synthesis of simple to complex organic compounds for bioactivity studies, electronic structure by computational quantum chemistry and conformational structures of choice in chemical kinetics, an attempt is made now for the synthesis, characterization, chromogenic characteristics and calibration studies of metal organic complexes.

Surfactants are amphiphilic as they contain long hydrophobic alkyl chains (6-18 carbon atoms) and hydrophilic groups. Micelles are aggregates of surfactant monomers. The minimum concentration above which the surfactant molecules form micelle is called critical micelle concentration (CMC) and measured by physico-chemical properties like surface tension, viscosity, refractive index and conductivity. When a surfactant is dissolved in water above cmc, the hydrophilic groups are attracted towards water molecules and thus remain on the surface. The hydrophobic moieties naturally shy away from polar water aggregates and point towards the centre (core) resulting in approximate spherical geometry. The aggregation number (number of monomers) of a micelle is 80-100. The aqueous solutions of surfactants lower interfacial tension and form micelles. The analytical applications concern the usual molecular spectroscopic techniques, in particular, UV-VIS spectrophotometry. The research reports on surfactants dealing with the analytical sciences are extensive. So, the review papers and a few typical research reports [10-19].

The present study was hence planned to suggest a very simple and reasonably good method for determination of mercury ions at low concentration, using the reported reagent. DHBTS as binary complex and sensitizing the reagent with Tween 80 as ternary complex using spectrophotometer which is still frequently used because of its low cost and simplicity.

Experimental

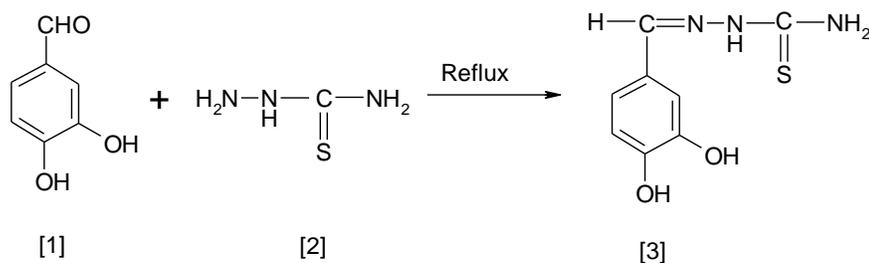
Apparatus

The Absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV -160A) fitted with 1cm Quartz cells and Philips digital pH meter (model L1 613 respectively.)

Reagents and solutions

Preparation of 3,4-di hydroxybenzaldehydethiosemicarbazone(DHBTS):

The Reagent (DHBTS) is prepared by the sah and Daniels procedure. 7 g of 3,4-dihydroxybenzaldehyde [1] was dissolved in 100 mL of methanol and 4.6 g of thiosemicarbazide [2] were dissolved in hot water. The two solutions were taken in 250 mL Erlenmeyer flask and refluxed for 3 hrs. pale yellow colored crystals were separated out on cooling. These crystals were collected by filtration and washed several times with hot water and 50 percent methanol. The product (3,4-dihydroxybenzaldehydethiosemicarbazone) [3] (m.p 221-223⁰c) was recrystallised twice from boiling methanol and dried in vacuum.



All chemicals used were of analytical reagents grade or the highest purity available. Double distilled deionized water, which is non-absorbant under ultraviolet radiation, was used throughout. Glass vassals were cleaned by soaking in acidified solutions of KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$, followed by washing with concentrated HNO_3 and rised several times with deionized water.

Tween-80 solution 1%(v/w)

A 100 mL of Tween-80 solution was prepared by dissolving 1 mL of pure tween-80 in 100 mL of doubly distilled deionized water, sonicated for 15 min and diluted with deionized water when it became transparent.

3,4-Dihydroxybenzaldehydethiosemicarbazone (DHBTS) ($1 \times 10^{-4} \text{mol/dm}^3$)

A 25 mL solution was prepared by dissolving 0.0528 g of recrystallised sample in dimethylformamide and it was suitably diluted to get the required concentration.

Iron (II) standard solution ($1 \times 10^{-2} \text{ mol dm}^{-3}$)

Appropriate quantity of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved in double distilled water containing few drops of con H_2SO_4 and made up to the mark in a 100 mL volumetric flask to obtain ($1 \times 10^{-2} \text{ mol dm}^{-3}$). The resulting solution was standardized with $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Procedure

Direct spectrophotometry

In each of set of different 10 mL volumetric flasks, 5 ml of buffer solution (pH 6.0), 1 mL of DHBTS ($1 \times 10^{-3} \text{ mol/dm}^3$) and various volumes of $1 \times 10^{-6} \text{ mol/dm}^3$ Iron(II) finally added 1 mL of 1% Tween-80 and f solution were taken and made up to the mark with double distilled water. The absorbance was measured at 365nm against the reagent blank. The calibration plot was prepared by plotting the absorbance against the amount of Fe(II).

Second order derivative spectrophotometry

For the above solutions, second order derivative spectra were recorded with a scan speed of fast (nearly 2400 nm min^{-1}); slit width of 1 nm with nine degrees freedom, in the wavelength range 390-510 nm. The derivative amplitude measured at wavelength 435 nm and plotted against amount of Iron(II) to obtain the calibration.

Results and Discussion

Factors affecting the absorbance

The absorption spectra of the Iron (II)-3,4-DHBTS system in a micellar medium were recording using a spectrophotometer. The absorption spectra of the Fe(II)-3,4-DHBTS is a symmetric curve with the maximum absorbance at 365nm and an average molar absorption coefficient of $4.21 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Fig. 1). The reagent blank exhibited negligible absorbance, despite having a wavelength in the same region. In all instances, measurements were made at 365 nm against a reagent blank.

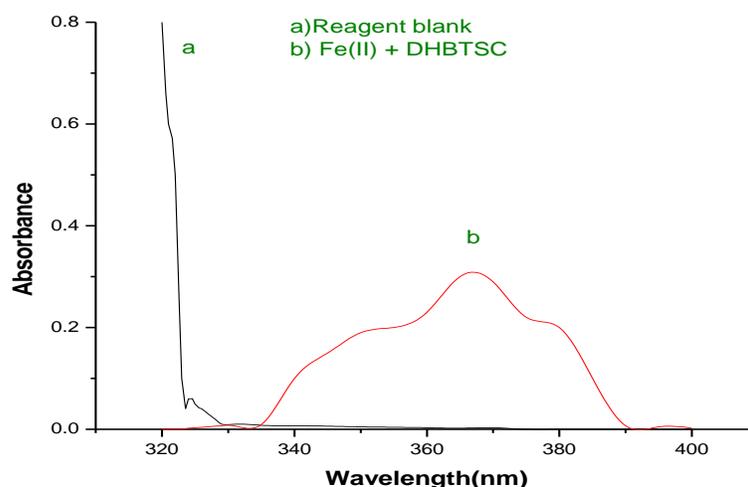


Fig 1: Absorption spectra of Fe(II) complex with DHBTS

Effect of surfactant: The effect of the various surfactants [nonionic {polyoxyethylenedodecylether(Brij-35), Polyoxyethylenesorbitanmonoplamate (Tween-40), Polyoxyethylenesorbitanmonioleate (Tween-80), Triton-X-100}, cationic [cetyltrimethylammoniumbromide(CTAB)] : and anionic { cetylpyridinium chloride (CPC) , sodium dodecyl sulfate SDS } studied. Tween-80 was found to be the best surfactant for the system. In a 1%(V/L) Tween-80 medium however, the maximum absorbance was observed hence, a 1% (V/L) Tween-80 solution was used in the determination procedure.

Different volumes of 1% (V/L) Tween-80 were added to a fixed metal ion concentration, and the absorbance was measured according to the standard procedure. It was observed that 0.7- 2.0 mL of 1% (V/V) Tween-80 produced a constant absorbance of the Fe(II)-chelate (Fig. 2). A greater Excess of Tween-80 were not studied. For all subsequent measurements, 1mL 1% (V/V) Tween-80 was added.

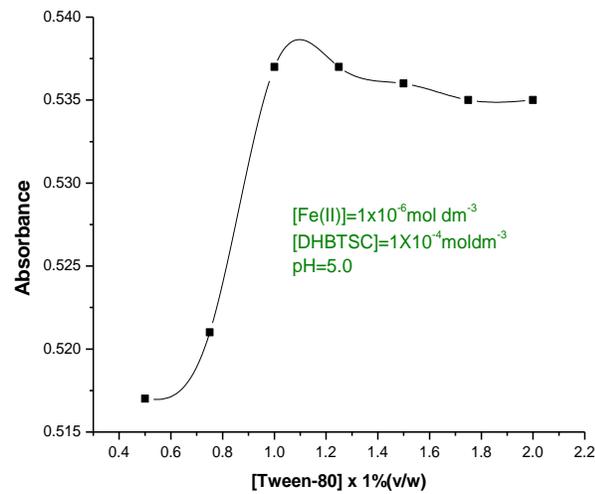


Fig 2: Effect of Tween-80 on Absorbance

Effect of Acidity

The absorbance of the complex reaches a maximum over a pH range of 5.0 to 7.0. The higher pH values may lead to hydrolysis of Fe(II) -3,4-DHBTSC system. The absorbance was at a maximum and constant when a 10 ml of solution (1mgL^{-1} ; path length, 1) contained 1-7 mL (pH5.0) of acidic buffer at room temperature (25 ± 50^0 c). Outside this range of acidity, the absorbance decreased (Fig. 3). For all subsequent measurements 5.0 ml (pH 5.0)acidic buffer was added.

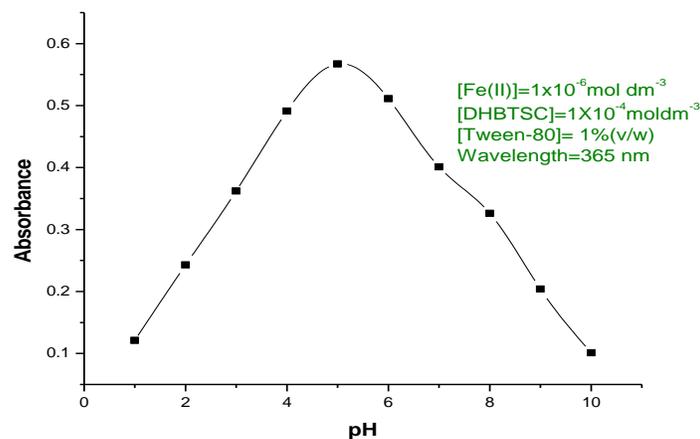


Fig3 : Effect of pH on absorbance

Effect of time

The reaction is very fast. Constant maximum absorbance was obtained just after dilution to volume, and remained strictly unaltered 24h.

Effect of reagent concentration:

Different molar excess of 3,4 –DGBTSC were added to a fixed metal –ion concentration, and the absorbance's were measured according to the standard procedure. It was observed that at 55.84 ng/ml Iron metal(optical path length , 1 cm) reagent molar ratios 1:10 and 1:100 produced a constant absorbance of the Fe(II)-Chelate (*Fig. 4*) . A greater excess of the reagent was not studied. For all subsequent measurement 1mL of $1 \times 10^{-3} \text{ mol/dm}^3$ 3,4 –DGBTSC reagent was added

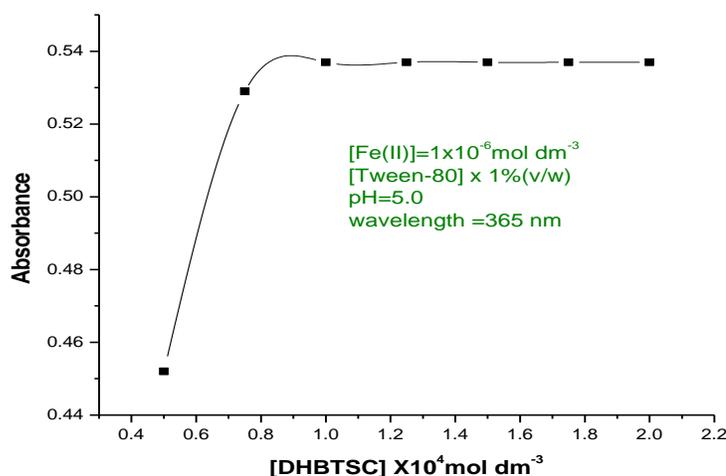


Fig 4: Effect of DGBTSC on Absorbance

Calibration graph (Beers Law and sensitivity)

The Calibration curve for the determination of mercury has been constructed (*Fig. 5*) using the optimum experimental conditions. The straight line calibration curve indicates that Beers' law is obeyed at least over a range of 13.96 to 97.13 ng of Cu(II) per 10 mL. Linear regression analysis of the calibration curve gives a correlation coefficient of 0.9995. The apparent molar absorptivity (ϵ_{370}) calculated from the slope of regression line is $4.21 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. The Sandell's sensitivity (concentration for 0.001 absorbance unit) was found to be 0.013 ng cm^{-2} .

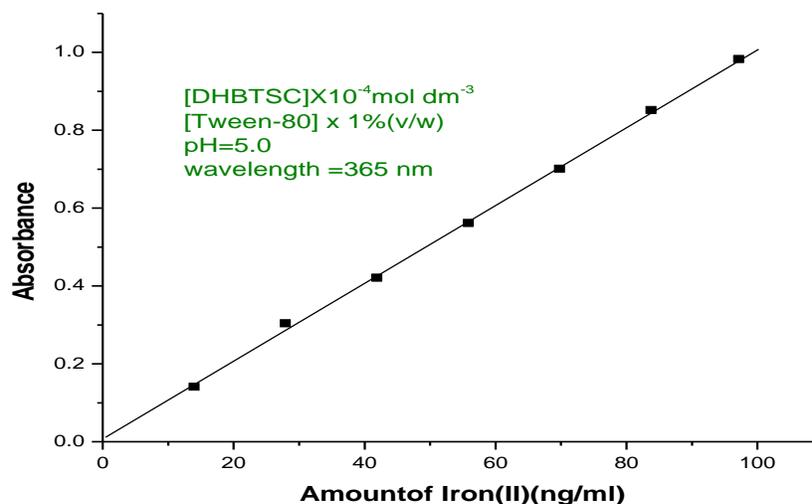


Fig 5: Calibration curve

Effect of foreign ions:

To study the selectivity of the proposed method, the effect of diverse ions on the determination of Fe (II) was investigated by adding a known quantity of the desired ion to a solution containing 55.84ng/mL of Fe(II) which was determined as described in the given procedure. The tolerance limit was defined as the concentration at which the species caused an error of less than $\pm 5\%$. The results obtained are summarized in *Table 1*. Based on the results, most cations and anions did not interfere with the Fe(II) determination even in their presence in the amounts 1000-fold greater than Fe(II). In the absence of a making agent, Cu (II) did not interfere with the Fe(II) determination up to 50-fold concentration of this ion. Interferences caused by Cr^{3+} , Hg^{2+} , and Fe^{3+} could be masked with EDTA ($100 \mu\text{g mL}^{-1}$) up to 100-, 30-, and 80-fold respectively. An advantage of this method is low interference effect of Cu(II) on the determination of Fe(II). The results clearly confirm selectivity of the method.

Table 1: Interference studies

Foreign ion	Tolerance limit(($\mu\text{g/ml}$)	Foreign ion	Tolerance limit(($\mu\text{g/ml}$)
Bromide	800	K(I)	1950
Iodide	635	Pd(II)	1035
Sulphate	480	Ba(II)	685
Nitrate	310	Th(IV)	465
Carbonate	300	Sr(II)	440
Thiosalphate	225	Mn(I)	215
Thiourea	200	Ca(II)	200
Tartarate	200	Ni(II)	170
Chloride	175	Al(III)	135
Fluoride	95	Mg(II)	122
Phosphate	2.5	Cu(II)	120
Oxalate	Interferes	Co(II)	60
Citrate	Interferes	Mo(VI)	50 ^b

Composition of the Metal –Reagent complex

Jobs method of continuous variation (*Fig .6*) and the molar – ratio method were applied to ascertain the stoichiometric composition of the complex. Fe(II) -3,4-DHBTSC(1:1) complex was indicated by both methods. The stability constants was determined by Jobs Method as 0.52×10^7 .

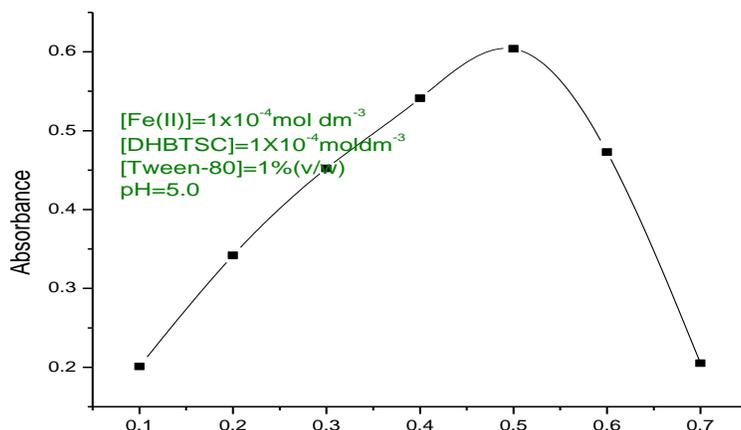


Fig 6 : Job'Curve

Application:

The Present method was successfully applied to the determination of Iron in grape leaf sample.

Determination of Iron in grape leaf sample

The grape leaf samples are freshly collected, cleaned, dried for one hour and powdered in a mortar. By the literature reported wet/dry ashing procedure, aqueous solution of the leaf samples was prepared[20]

To determined the accuracy of the method, a known amount of Iron was determined. 2.0 mL of pre-concentrated water sample was taken in to a 10 mL measuring flask and spiked with known amount of Copper and contents were determined following the general determination procedure. Absorbance was measured after 10 minutes at 382 nm, relative to a blank prepared in the same way except the addition of Iron. The results show a good recovery of Iron (*Table 2.*)

Table 2: Determination of Iron in grape leaf sample

Sample	Amount of iron ($\mu\text{g/ml}$)		Recovery (%)
	APARI value	Present method	
Leaf sample of grape (Vinifera L)	33.70	33.42	99.16

*Average of five determinations

Second order derivative method

The second order derivative curve recorded (*Fig. 7*) for experimental solution showed the derivative amplitude were measured at 435 nm (peak) for different concentrations of Fe(II) and plots were made between the wavelength of Fe(II) and the derivative amplitude. The plots were linear and obeyed Beer's law in the range 13 to 111.68 ng/mL at 435 nm respectively.

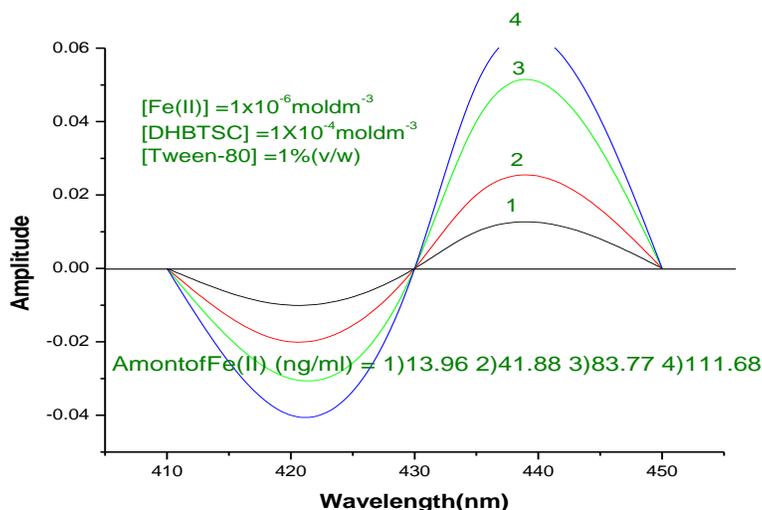


Fig 7: second order derivative spectrum of Fe(II)

Comparison of results

The analytical characteristics of the zero and second order derivative methods in the present investigations for Fe(II) were compared and present in *Table 3*. The results in this table reveal that second order derivative method is more sensitive and selective than the zero order method. The sensitivity of the zero method in the present investigations was compared with those of some reported methods and presented in *Table 4*

Table 3. Comparison of results of Iron(II)

Parameter	Zero order	Second derivative
Analytical wave length(nm)	365	435
Beer`s law range(ng/mL)	13.96- 97.13	13.96 – 111.68
Angular coefficient(m)	0.0189	0.014
Y-ntercept(b)	0.094	0.036
Correlation coefficient(r)	0.9998	0.998
Standared deviation(s)	0..088	0.053

Table 4. Comparison with other methods

Reagent	λ_{\max} (nm)	Molar absorptivity(ϵ) ($L \text{ mol}^{-1} \text{ cm}^{-1}$)	Ref.
antipyrine azo orcinol	461	1.90×10^4	21
sulfosalicylic acid	420	0.5031×10^4	22
1-nitroso-2-naphthol	443	0.50×10^4	23
4-(2-pyridylazo) resorcinol	718	1.1×10^4	24
3,4-Dihydroxy Benzaldehydethiosemicarbazone	365	4.21×10^5	Present work

Conclusion

This method offers several interesting features such as simplicity, rapidity, and low cost besides sensitivity. The number of associated elements does not interfere in the determination. The selectivity of the reagent is also improved by the use of suitable masking agents to suppress the interference of metal ions like Fe(III), Hg(II), and Cr(III). Hence the proposed method is recommended for the determination of Iron (II) with DHBTS in presence of micelles by spectrophotometric method, at minor and trace levels, besides its use for analysis of real samples.

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