



Spectrophotometric Determination of Fe (III), Fe(II) and $S_2O_4^{-2}$ Ions in Aqueous Solutions by using Tetra Sodium Meso – Tetra (P-Sulfophenyl) Porphine as a Ligand

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ABSTRACT

In this paper , the complex reaction of water - Soluble meso -tetra (4-Sulfophenyl) porphyrin (TPPS₄) with Fe(III) ion has been studied in the presence of small amount of hydroxyl amine . The porphyrin was found to be a highly sensitive and highly selective reagent for direct spectrophotometric determination of iron at μg level .The solet band of the complex lay at 394 nm (ϵ : $3.88 \times 10^5 \text{L.M}^{-1}\text{cm}^{-1}$), which is well separated from that of the reagent 432 nm, (ϵ = $2.2 \times 10^5 \text{L.M}^{-1}\text{.Cm}^{-1}$) below PH 2The complex formation is slow at room temperature and PH 5.0 , however , it can be accelerated by heating on boiling water bath and completed within 10 min at 100C° . five determinations of standard solutions containing 0.7 mg /10mL of iron gave a relative standard deviation of $\pm 2.61\%$. Beer's law is obeyed for iron (III) in the range of 0.01-2.0 $\mu\text{g}/10\text{ml}$. The molar ratio of complex is 1:1. This method has been applied to determine iron (III) in water samples with satisfactory results. The complex is highly stable .The interference of many ions and salts have been examined and found to be minimal . Large amounts of rare earth do not interfere with the determination . The complex reaction of Fe (III) TPPS with reducing agent of $\text{Na}_2\text{S}_2\text{O}_4$ was studied as well, it was found the reaction is time dependent ,and the reduction can be completed within 6 min . The solet band of Fe TPPS at PH=12.5 lay at 408 nm but in the presence of sodium dithionite moves to long wave length of 438 nm that assign of Fe(II) TPPS.The reduction was take place at room temperature, however it can be used this reaction to determine the $S_2O_4^{-2}$ ion in aqueous solutions or solids .

Beer's law is obeyed for $S_2O_4^{-2}$ in the range of 0.01-1.85 mg/10ml and the molar absorptivity of Fe (II) TPPS is $3.48 \times 10^5 \text{L.M}^{-1}\text{,Cm}^{-1}$, and ,for $S_2O_4^{-2}$ is $1.47 \times 10^3 \text{L.M}^{-1}\text{,Cm}^{-1}$.Five determinations of standard solutions containing 3.52 mg /10ml of $\text{Na}_2\text{S}_2\text{O}_4$ gave a relative standard deviation of ± 0.315 .The interference of lactose, starch and sodium chloride was found effective.The recovery percentage was in the range of 87.5 -98.29 % and the RSD% in the range of 0.57-1.28 (n=3) .Also in this paper the determination of Fe (II) in Fe (III) TPPS was studied by reduction the Fe(III) TPPS complex at PH 6.5 by using $\text{Na}_2\text{S}_2\text{O}_4$ in the presence of bipyridyl reagent, it has been found the reagent destroy the porphyrin ring and Fe(II) ion come out of ring and react directly with bipyridyl reagent due to steric effect, the amount of Fe (II) equal to the third amount of bipyridyl moles react with Fe(II) ion to form a new red complex of $\text{Fe}(\text{bipy})_3$ with solet band lay at 522nm and (ϵ = $30 \text{L.M}^{-1}\text{.Cm}^{-1}$)Beer's law obeyed for Fe(II) in the range of 0.01-15.6 mg/10ml. Molar ratio was found 3:1 bipyridyl to Fe(II) ion The sensitivity For the 0.001 absorbance sendell's index was 0.00014, 0.087 and 1.8 For Fe(III), $S_2O_4^{-2}$ and Fe(II) respectively . This method can be used to determine the Fe(II) ion in hemoglobin.

Keywords: Tetra (4-sulfophenyl) porphyrin ; Iron spectrophotometry

1. INTRODUCTION

The porphyrins are class of naturally occurring macro cyclic compounds , which play a very important role in the metabolism of living organisms .These have been extensively studied due to their biological importance as well as analytical application[1-3]. Because the porphyrins are the highly sensitive chromo genetic reagents for spectrophotometric determination of several metal ions based on the use of the so-called solet band at 380-500nm[4-6] . Many papers have been published on the mechanism of metal ions in corporation into the porphyrinnucleus[6-8]. Synthetic metaloporphyrin are suitable sensitizers for photodynamic therapy of cancer [9]. TPPS₄ was applied previously as a complexing reagent of many metal ions such as Hg(II),Pb(II),Cd(II),and Zn(II) ions [5,7,10,11] and many

workers have been used water soluble porphyrin to determined trace amount of many transition metals such as Cu,Ni,Pb,Zn,Fe,Cd,Mn and other elements [2,12-17] based on the color complexation . In this work , we report the spectrophotometric study on the reaction between 5,10,15,20-tetra (4-sulfophenyl) porphine (TPPS₄) and Fe(III) with the aim of determining the iron (III), iron(II) ions and the reducing agent $\text{Na}_2\text{S}_2\text{O}_4$ by using the calibration curve method . Bipyridyl ligand was used for determining the Fe(II) ion in Fe(II) TPPS in aqueous solution at PH below 7.0 by destroying the iron(II) TPPS and forming a new Fe(II) (bipy)₃ red complex . Reductive titration of Fe(III) TPPS with a solution of sodium dithionite resulted in the formation of a Fe(II) TPPS complex at high PH was reported too.



2. EXPERIMENTAL SECTION

2.1 Apparatus

Spectrophotometer model 6800 Jenway with 1Cm silica cells was used throughout this research work.

2.2 Materials and Reagents

All reagents used were of analytical grade and were obtained from fluka. Tetra (p-phenyl) porphine (TPP) was prepared by refluxing of 5ml pyrrole with 7.24 ml benzaldehyde 1:1 mole ratio in propanic acid media for two hours [1] after cooling to the room temperature the solution was filtered and the product washed with a minimum quantity of ethanol, a blue crystals of TPP were obtained. Meso-Tetra (p-sulfophenyl) porphine was prepared by mixing 2gm of TPP with 50ml of concentrated sulfuric acid, the mixture was heated on a steam bath for 4-5 hr due to the method was reported by reference[12]

2.3 Standard solutions

Stock solution (10^{-3} M) TPPS4 was prepared by dissolution of 0.308 gm in 250ml of buffer solution (PH=5.0).

1gmol-1 stock solution of Fe (III) was prepared by dissolution (7.0) gm of Ferrous ammonium sulfate in 250 ml

Stock solution (0.012M) bipyridyl was prepared by dissolution of (18.9) gm in (10)ml of buffer solution PH 0.5 .

Stock solution of 0.051M $\text{Na}_2\text{S}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was prepared by dissolution of 90 mg in 10ml buffer solution of NaOH at PH 12.5 . Buffer components were of analytical grade and used without further purification. The acetate buffer was used for PH <5, phosphate buffer for PH 6-8, borate buffer for PH 8-10 ,NaOH solution was used for PH>10.

2.4. Composition of complexes.

2.4.1. Composition of FeTPPS complex

Determination of composition of the forming complex was conducted using mole ratio method. Metal (Fe(III)) was added to 5×10^{-6} M porphyrin solution in the concentration range 10^{-6} - 1.5×10^{-5} M . After 10 min of reaction in the hot water bath ,all the reactants were at PH 5.0 buffer solution, the absorbance at wave length of 394 nm was measured.

2.4.2 Composition of Fe(II)bipy complex

iron(II) concentration in the range 10^{-6} - 1×10^{-5} M was added to 6×10^{-6} M of bipyridyl at PH 6.5 and after a few minutes the absorbance was measured at wavelength of 522nm

2.4.3 Determination of iron (III) ion in tap water .

Tap water samples were just filtered through 0.45um pore size Millipore membrane filter. 1ml of sample was taken in to a calibration flask and 2.5ml of TPPS (10^{-3} M) ,5ml of buffer solution (PH5.0) were added successively. After dilution to the mark (25ml), the absorbance was measured at 394nm against reagent blank.

2.5 Construction of calibration curve for ions .

2.5.1. Calibration curve for Fe(III)

In to a series of ten of 10 ml volumetric flasks containing aliquots of standard Fe(III) ions solutions in the rang of (0.01-2.0) $\mu\text{g} / 10\text{ml}$. To each of these were added 1mlTPPS4 solution(10^{-3} M)After dilution to the mark, the solutions were heated for 10 min in boiling water bath adjusted at 100°C , then cooled and diluted to the mark with distilled water and mixed well . The absorbance of complex was measured at 394nm against reagent blank at pH 5.0, $T=25^\circ\text{C}$.

2.5.2 Calibration Curve of $\text{S}_2\text{O}_4^{-2}$

Into a series of ten of 10ml volumetric flasks containing aliquots of standard $\text{Na}_2\text{S}_2\text{O}_4$ solution (0.01-1.85)mg/10ml .To each of these FeTPPS were added at final concentration of 5.11×10^{-6} M at pH=12.5, $T=25^\circ\text{C}$,after dilution to the mark (10ml) by using distilled water and mixed well for ten min the absorbance was measured at 438nm and 408nm against water blank.

2.5.3 Calibration Curve for Fe (II) ion.

Deferent concentration of bipyridyl in the rang (0.01-0.84)mmoles were placed in series of 10ml volumetric flasks, containing 7.84×10^{-6} M of FeTPPS in the present excess of $\text{Na}_2\text{S}_2\text{O}_4$, then after ten min the absorbance was taken at wave length of 522nm at pH=6.5, $T=25^\circ\text{C}$ against water blank .

3. RESULTS AND DISCUSSION

3.1 Spectrophotometric study of porphyrin

Solution of 3.1×10^{-5} M TPP in chloroform solvent is purple and exhibit six absorption maxima one is soret band at 395nm

($\epsilon = 1.06 \times 10^5 \text{ L.M}^{-1}.\text{cm}^{-1}$), 356 nm as shoulder ($\epsilon = 6.25 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$), 515 nm ($\epsilon = 3.96 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$), 545 nm ($\epsilon = 1.74 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$), 590 nm ($\epsilon = 1.25 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$) and 645 nm ($\epsilon = 1.03 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$). TPPS solution at pH 1.7 exhibit four bands one in soret at 432 nm ($\epsilon = 2.2 \times 10^5 \text{ LM}^{-1}.\text{cm}^{-1}$), 486 nm ($\epsilon = 8.2 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$), 644 nm ($\epsilon = 6.6 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$) and 702 nm ($\epsilon = 3.5 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$), but at high pH=12.5 the spectra shows soret band at 406 nm ($\epsilon = 5 \times 10^4 \text{ LM}^{-1}.\text{cm}^{-1}$), 518 nm ($\epsilon = 6.5 \times 10^3 \text{ LM}^{-1}.\text{cm}^{-1}$), 558 nm ($\epsilon = 3.8 \times 10^3 \text{ LM}^{-1}.\text{cm}^{-1}$) and 650 nm ($\epsilon = 1.45 \times 10^3 \text{ LM}^{-1}.\text{cm}^{-1}$).

TPPS4 has an empirical formula of $\text{C}_{44}\text{H}_{26}\text{N}_4\text{O}_{12}\text{S}_4\text{Na}_4$ with $12\text{H}_2\text{O}$: Analysis. Calc% N= 4.48, S=10.3. Found % N= 4.50, S=10.4

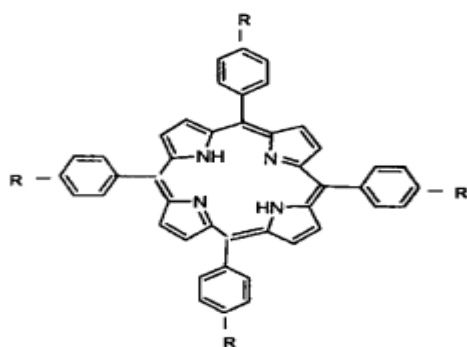


Fig.1 Structure of the porphyrin

R=SO₃H 5, 10, 15, 20- tetrakis (4-sulfonatophenyl) porphyrin, TSPP

FeTPPS spectra shows band at low pH 2.6 as monomer of 394 nm ($\epsilon = 5 \times 10^5 \text{ LM}^{-1}.\text{cm}^{-1}$) and 530 nm ($\epsilon = 1.1 \times 10^5 \text{ LM}^{-1}.\text{cm}^{-1}$), but at high pH about 12.5 shows at 408 nm ($\epsilon = 3 \times 10^5 \text{ LM}^{-1}.\text{cm}^{-1}$) as a soret band of dimer form. Addition of Fe (III) ion to 10^{-5} M of TPPS at pH 5.0 then heated in boiling water bath for 10 min the color change from green to brown with moving the soret band from 432 nm to the 394 nm. The mole ratio is 1:1 of Fe(II) to ligand as shown in figure .2.

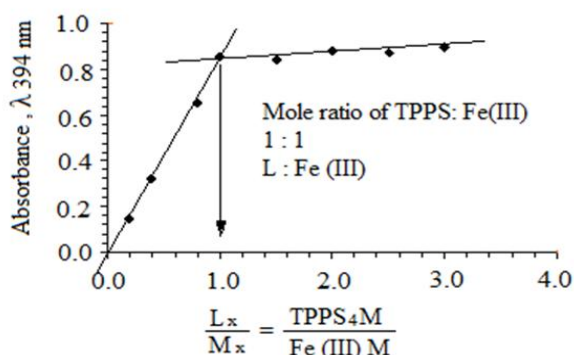


Fig.2: The mole ratio of TPPS₄ / Fe(III)

3.2 Calibration Curve for Fe(III) , S₂O₄⁻² and Fe(II) ions and the interferences

Table.1: shows the analytical and regression parameters , Figure 3,4 and 5 :shows the calibration curve for Fe(III), Fe(II) and S₂O₄⁻² with TPPS₄ ligand. Under the condition employed ,the calibration graphs were linear up to 2.0 μg , 1.85 mg and 15.68 mg per 10 ml for Fe(III) ,S₂O₄⁻² and Fe(II) respectively. The sensitivity for the 0.001 absorbance (Sandell's index) was 0.00014, 0.087 and 1.8 μg Cm⁻² for Fe(III),S₂O₄⁻² and Fe (II) respectively , thus the sensitivity is superior to that obtained previously for porphyrin[8,20,21]. Application of TPPS₄ allowed the determination of small amount of Fe(III) ,S₂O₄⁻² and Fe(II) in aqueous solution or solid materials . The precision of five replicate measurements at 0.7 mg , 3.52 mg and 5.7 mg per 10 ml for Fe(III) , S₂O₄⁻² and Fe(II) concentration level was in the range 0.315-2.16% RSD. The effect of foreign ions was investigated for the determination of Fe(III) and S₂O₄⁻² using TPPS₄ as color reagent see table .2

The method shows a good tolerance to the great excess of alkali and alkaline earth metals. No significant interferences from common inorganic anions, such as chlorids, nitrates and sulfates , were also found for Fe(III) , but not for determination of S₂O₄⁻² ions, it was found the recovery percentage can be affected in the present of interferences such as lactose , starch , and sodium chloride as shown in Figure 6 .The effect of the presence of some heavy metals was examined such as lead and tin and was found caused increasing in the amount of Fe(III) recovery percentage in the range of 2.2 - 2.96%. even they were at similar or smaller level, owing to formation of their complexes with TPPS₄ by metal substitution.

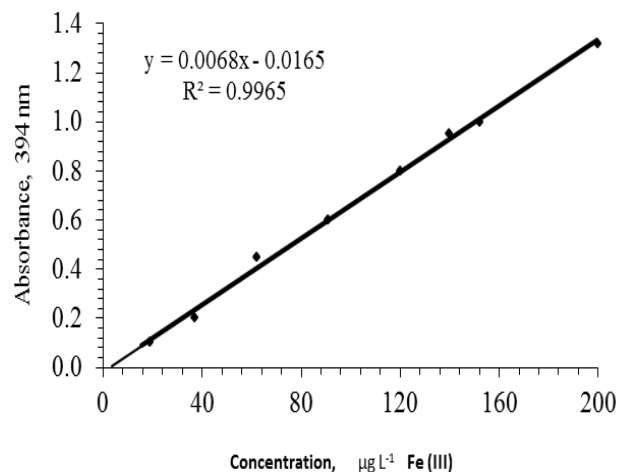


Fig3:The calibration curve of Fe(III)ion

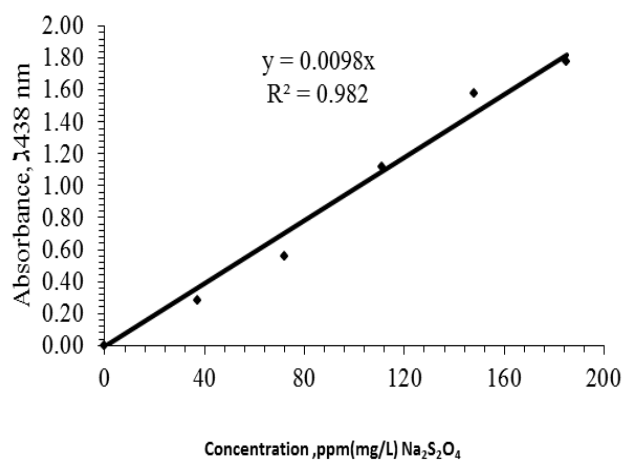


Fig4: The calibration curve of $S_2O_4^{2-}$ ion

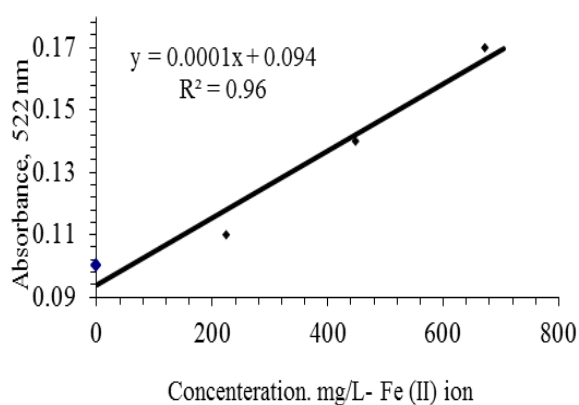


Fig 5: The calibration curve of Fe(II) ion

Table 1: Shows the analytical and regression parameters

| Parameters | Fe(III) ion | $S_2O_4^{2-}$ ion | Fe(II) ion |
|--|--------------------|--------------------|--------------------|
| Beer's law limits($\mu\text{g}/10\text{ml}$) | 0.01-2.0 | 0.01-1.85 mg/10ml | 0.01-15.6 mg/10 ml |
| Molar absorptivity(L.mol ⁻¹ .cm ⁻¹) | 3.88×10^5 | 1.47×10^3 | 30 |
| Sandell,s sensitivity($\mu\text{g ml}^{-2}$) | 0.00014 | 0.087 | 1.8 |
| Average recovery(%) | 98.96 | 99.16 | 99.90 |
| Correlation coefficient | 0.9965 | 0.982 | 0.96 |
| Regression equation Y* | | | |
| Slope.a | 0.0068 | 0.0098 | 0.0001 |
| Intercept.b | -0.0165 | 0.0 | 0.094 |
| RSD% | 2.34 | 0.315 | 1.40 |

* $Y=ax+b$, where x is the concentration of ions

Table.2: shows the effect of foreign ions on determination of Fe(III) and $S_2O_4^{2-}$ ions

| Compound name | λ 394 nm | Cmg Fe(III)/10ml | Recovery % | Interference mg/10ml added | RSD% n=4 | Recovery Increasing % |
|---------------|------------------------|----------------------------------|------------|----------------------------|----------|-----------------------|
| 1 | 2.28 | 4.38 | 100 | Fe(III)=4.38 | -- | -- |
| 1+Zn | 2.289 | 4.40 | 100.4 | Zn=0.59 | 0.99 | 0.4 |
| 1+pb | 2.33 | 4.48 | 102.2 | Pb=0.75 | 1.33 | 2.2 |
| 1+Sn | 2.35 | 4.51 | 102.96 | Sn=0.73 | 0.83 | 2.96 |
| 1+Ni | 2.31 | 4.44 | 101.36 | Ni=0.64 | 1.2 | 1.36 |
| 2 | $\lambda=438\text{nm}$ | $\mu\text{g}/10\text{ml}$ Fe(II) | = | = | n=3 | Recovery decreasing % |
| 2 | 1.76 | 3.13 | 100 | -- | -- | -- |
| 2+Glu | 1.73 | 3.07 | 98.29 | 1.58 | 0.57 | -0.06 |
| 2+La | 1.66 | 2.95 | 94.31 | 1.77 | 0.06 | -0.18 |
| 2+St | 1.67 | 2.97 | 94.88 | 0.15gm/10ml | 1.36 | -0.16 |
| 2+Nacl | 1.54 | 2.79 | 87.5 | 3.15 | 1.28 | -0.40 |



1 = Fe TPPS , 2= Fe(II) TPPS, Glu = glucose , la = lactose , st = starch

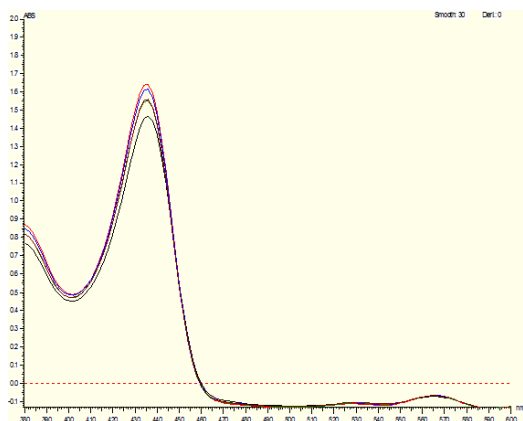


Fig.6: The visible spectra of Fe(II) TPPS in Presence of Glucose , lactose, Starch and sodium chloride at PH 12.5 , λ 438nm.

3.2.1 Analytical application of method for determination of Ferric ion in tap water. The proposed method was applied to the determination of Fe(III) ion in some natural water samples and nutritional supplement. The results are given in table 3 and comparative data obtained by AAS method are also presented. The proposed spectrophotometric method with TPPS₄ allows the sensitive determination of traces of Ferric with quite simple instrumentation.

Table 3: Determination of Ferric ion in tap water

| Sample | proposed method(n=5) | AAS method(n=5) |
|------------------------|----------------------|------------------------|
| Tap water | 1.72±0.1ppm | 1.73±0.04ppm |
| Well water | 0.3±0.01ppm | 0.32±0.01ppm |
| Nutritional Supplement | 2.6±0.1mg per tablet | 2.2±0.05mg per tablet* |

*contain 2.5mg/tablet.

3.2.2 The reduction of FeTPPS with Na₂S₂O₄

Figure 7. Shows changes in visible spectrum of titration Na₂S₂O₄ with FeTPPS 5.11x10⁻⁶ M at high pH=12.5, T=25C^o, it is very clear from spectra that the soret band for FeTPPS

move to long weve length from 408nm to 438nm due to the reduction of iron(III) to the iron (II) porphyrin as shown in this equation.

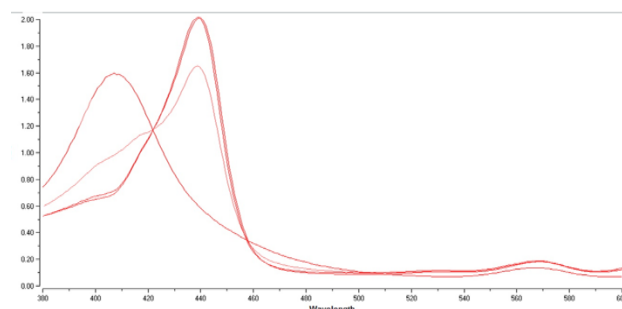
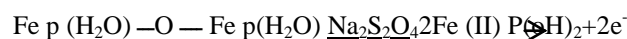


Fig.7: the changes in visible spectrum upon titration Na₂S₂O₄ with Fe TPPS , of 5.11x10⁻⁶ M at PH 12.5 , T= 25 C^o

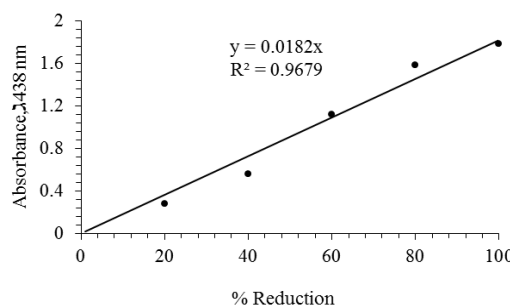


Figure 8: shows the relation between reduction percentage and the absorbance at λ max 438nm

Also it has been found the FeTPPS reduction is time dependent , when 100 µg /10ml of Na₂S₂O₄ was added to the FeTPPS solution at pH=9.5 , the reduction was found completed after 6 min and the progress of absorbance change as shown in figure 9 and 10

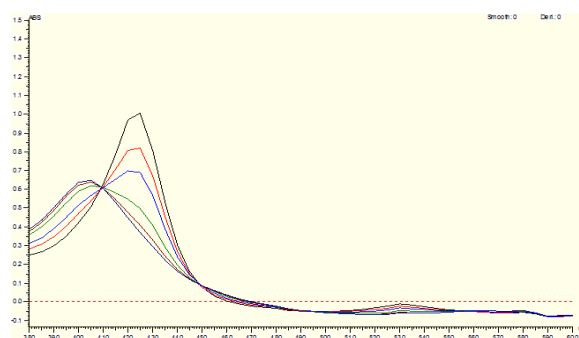


Fig 9 : The absorbance change upon addition 100µg to the FeTPPS at pH=9.5, The λ max of final Fe(II)TPPS complex was at 425nm.

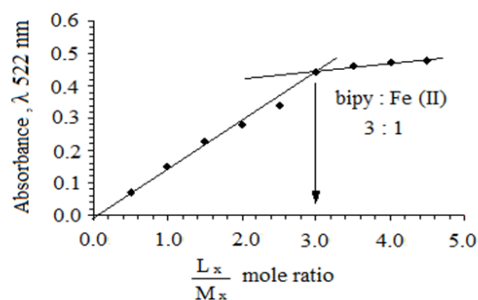
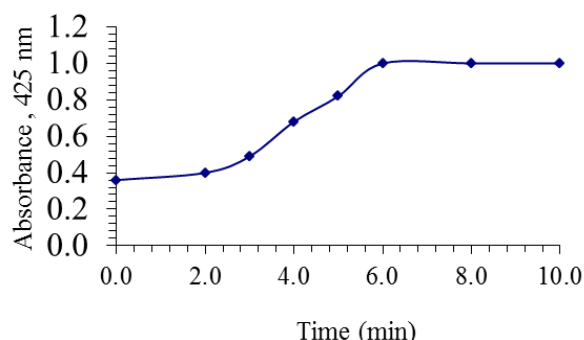


Figure 11

Figure 10: The change in the absorbance of FeTPPS upon addition 100 μ g of Na₂S₂O₄ at pH=9.5, λ_{max} 425nm with time

3.2.3 Reaction FeTPPS with bipyridyl reagent

It has been found there is no reaction between bipyridyl and FeTPPS at high pH > 12.5 in the presence Na₂S₂O₄ as a reducing agent due to the steric effect, but when lowering the pH to the 6.5, the reagent destroy the porphyrin ring, and another red complex form of Fe(bipy)₃, because the Fe(II) ion come out of porphyrin ring in the solution, we used this phenomena for determination of Fe(II) in FeTPPS and may be it is useful to used to determine the Fe(II) ion in protein such as hemoglobin in the same way. The visible spectrum of NH₄FeSO₄ with bipyridyl was found similar to the FeTPPS with Na₂S₂O₄ and bipyridyl with a broad band at 522nm at pH=6.5, T=25C°. The complexing ratio was found 3:1 bipy : Fe(II) as shown in **Figure 11** : shows the mole ratio of bipyridyl with Fe (II) ion. L_x =bipy moles, M_x = Fe(II) ions moles.

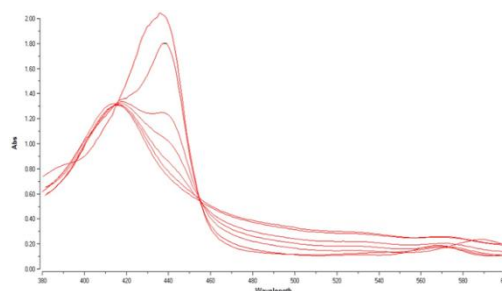


Figure 12: shows destroying the visible spectra, λ_{max} at 425 nm of Fe(II)TPPS with increasing the concentration of bipyridyl in the presence of Na₂S₂O₄ at pH=6.5, T=25C°.

The number of moles of Fe(II) calculated from number of moles of bipyridyl added to the solution and that equal third of it .

The above results indicates that TPPS₄ ligand is very sensitive as a chromogenic reagent, our results are similar to the other workers results using the same porphyrins of TPPS as shown in table 4.

Table 4: Spectrophotometric determination of metal ions with porphyrin reagent

| Metal ion | Reagent | Condition | Absorption Spectra $\lambda_{max}, nm \ \epsilon (x10^5) \ LM^{-1} \ cm^{-1}$ | Range of determination | interference | Refs |
|-----------|-------------------|---------------------------------------|---|----------------------------------|------------------------|------|
| Zn(II) | TPPS ₄ | pH 7.1+ Imidazole+Cd room temp 30 min | 425 , 4.5 | 10-150 ng l ⁻¹ | Mn(II), Co(II), Fe(II) | [16] |
| Pb(II) | TPPS ₄ | pH4+ ascorbic Acid(100.7min) | 411 , 2.2 | - | Cu(II), Hg(II) | [21] |
| Ni(II) | TPPS ₄ | pH8-9+(Cd(II) + imidazole(100°C | 418 , 2.3 | Up to 150 ng l ⁻¹ | | [22] |
| U ion | TPPS ₄ | pH 3.0+NH ₂ OH.HCl | 420 , 2.2 | 0.01-120 μ g l ⁻¹ | | [23] |



| | | | | | | |
|---|--------------------|--|--------------------------|-------------------------------|----------|-----------|
| Cd | T ₄ BPP | pH 10.0 by HPLC | 436 | 0.01 – 120 µg l ⁻¹ | | [1] |
| Hg | T ₄ BPP | 10.0 by HPLC | 449 | 0.01 -120 µg l ⁻¹ | | [12] |
| Fe(III) | TPPS ₄ | PH 5.0+ NH ₄ OH 100C ⁰ 10min | 394 3.88x10 ⁵ | 0.01-200 µg l ⁻¹ | | This work |
| S ₂ O ₄ ⁻² | TPPS ₄ | PH= 12.5 room temp. | 438 1.4x10 ³ | 1.0 – 185 µg l ⁻¹ | La,Gu,St | This work |
| Fe(II) | TPPS ₄ | PH=6.5+Na ₂ S ₂ O ₄ +bipyridyl room temp. | 425,30 | 1.0 – 1560 µg l ⁻¹ | Zn,Cu | This work |

4. CONCLUSION

Porphyrins find many application as a ligand for spectrophotometric determination of cations and anions in analytical chemistry. In this study TPPS₄ used for determination of Fe (III), S₂O₄⁻² and Fe(II) ions by three steps, (1) the stable complex between Fe(III) cations and TPPS₄ enable us to determination the Fe(III) ion in tap water or solid compounds, (2) the reaction of FeTPPS at room temperature with Na₂S₂O₄ as a reducing agent used for determine the S₂O₄⁻² ion in aqueous solution, (3) Reaction of FeTPPS with Na₂S₂O₄ in the presence bipyridyl ligand at pH=6.5 give a new red complex of Fe(bipy)₃ as a result of steric effect and destroying the porphyrin ring, that make Fe(II) ion free in solution to form stable complex, so we used this reaction for determination Fe(II) ion.

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