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# Spectrophotometric Determination of Trace Amounts of Fe(III),Mn(III) and Co(III) Ions by using Tetra(4-BromoPhenyl) Porphyrin as a Ligand in DMF Solvent

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## ABSTRACT

In this paper, the reaction of meso-tetra (4-Bromophenly)porphyrin with Fe(III),Mn(III)andCo(III) ions have been studied in DMF solvent .The porphyrin was found to be a highly sensitive and selective reagent for direct Spectrophotometric determination of these ions at µg level.The soret band of the complexes was found at 416 nm for Fe(III)($\epsilon$ = 6.8 x$10^4$ L.M$^{-1}$.cm$^{-1}$), 466 nm for Mn(III)($\epsilon$ = 1.1x $10^5$ L.M$^{-1}$.cm$^{-1}$) and 418 nm for Co(III) ($\epsilon$ = 1.3 x $10^5$ L.M$^{-1}$.cm$^{-1}$) ,which is well separated from that of the reagent at 416nm ($\epsilon$ = 2.2 x $10^5$ L.M$^{-1}$. cm$^{-1}$), respectively . The complexes formation are slow at room temperature, however , it can be accelerated by heating and completed within 30 min at 100C° except Mn(III) need more than 4 hours refluxing.Four determination of standard solutions containing 0.388 µg/5ml, 0.0798 µg/5ml and 0.092 µg/5ml for Fe(III),Mn(III) and Co(III), gave a relative standard deviation of 0.002% , 0.003% and 0.01%. Beer's law is obeyed in the range of 0.01- 1.1, 0.01-0.1 and 0.01-0.115 µg/5ml, Sandell's index were 0.0008, 0.0005and 0.0004 for the absorbance of 0.001 respectively. The molar ratio of complexes are 1:1,the effect of the interferences was studied and reported as well.The samples were taken from west of Iraq region and gave a satisfactory results.

**Keywords:** *Porphyrin, Ferric, Manganese and Coblat Spectrophotometry.*

## 1. INTRODUCTION

The porphrin molecule is a tetradentate ligand,and has four nitrogen atoms,the amino nitrogens(-N=) and the pyrrole nitrogens (-NH-).The amino nitroge-ns are accepting protons only and acting as basic centers,while the pyrrole nitrogens are capable of either accepting or losing protons and thus can either act as basic or acidic centres[1].The most important properties of Porphyrin molecules is their ability to coordinate to metal ions,yielding stable metallopro-phyrins.This reaction can be achieved by the metal replacing the two hydrogen atoms on the pyrrole nitrogen atoms in addition coordinating to the two lone pairs on the amino nitrogen atoms. These processes of formation of the metal complexes (metallation) can be represented by two possible mechanisms:(a)Dissociation reaction by removing the protons from the pyrrole nitrogens :or(b)Displa-cment reaction in which the protons on the two pyrrole nitrogens are displaced by the metal ion to form metalloporphyrin[2].Iron protoporphyrin is the prosthetic group of a larg number of metalloporphy-rins and their role as nature's catalysis[3].Because of of their biological importance and analytical app-lications have been studied as anature products e.g. chlorophylls (magnesium Porphyrin derivatives with five isocyclic rings and one or two reduced pyrrole ringe[4],cytochromes they are used to tranport(hae-moglobin)[5],to store oxygen(myoglobin),in the hydroxylation of a wide range of substrates(cytochrom P450)[6]and vitamin B12 contain cobalt macrocycles are catalytic intermediates and hydrogen transfer catalysts are present in Porphyrin molecules[7-8],to accept electrons from the respairatory chain and reduce $O_2$ to $H_2O$ (cytochrome C oxidase)[9],in ele-ctron transport, enzymes(cytochrome C,b)and nonpr-otens such as photosystem II which contain Mn atom.Because the porphyrins are the higly sensitive chromogentic reagents for spectrophotometric determination of several metal ions based on the use of the so-called soret band at 400-500nm [10-12] . TPPS4,THPP and TBPP were applied previously as a complexing reagents of many metal ions such as Hg(ll),pb(ll),cd(ll),zn(ll)and Fe(lll) to determined trace amount of many transition metals such as Cu,Ni and other elements [11,13-20].In this work we report the spectrophotometric study on the reaction between 5,10,15,20 tetra(4-Bromophenyl)porphyrin (TBPP, see figure.1.0) and Fe(lll), Co(lll) ions in organic solvent by using the soret band and calibra-tion curve method.

## 2. EXPERIMENTAL SECTION

### 2.1 Apparatus

Spectrophotometer model 6800 Jenway with 1cm silica cells was used throughout this research work with hp type computer for spectra recording.
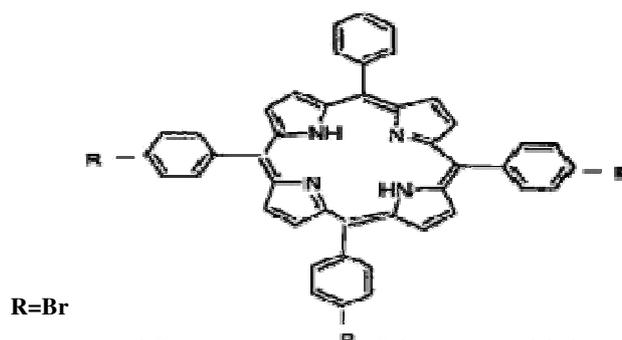


R=Br

**Figure 1 Shows the structure of Porphyrin(TBP-P).**

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## 2.2 Materials and Reagents.

Most materials used were of analytical grade and w-ere obtained from fluka.

### 2.2.1 Tetra (p-Bromophenyl) porphyrin.

TBPP was prepared by refluxing of 2.88 ml pyrrole with 7.77 gm p-Bromobenzaldehyde 1:1 mole ratio in propionic acid media for 1.5 hours[21].After cooling to the room temperature the solution was filtered and the product washed with aminimum quantity of ethanol and distilled water,a blue crystals of TBPP were obtained,yield percentage was 21.5 %.

Chemical analysis of formula($C_{44}H_{26}$ $N_4$ $Br_4$) .Calc (EXP):C:56.7 9(56.81±0.22) ,H:2.79 (2.77± 0.15) , N:6.02(5.99±0.19).

### 2.2.2 Preparation of solid FeTBPPCl Complex

The complex was prepared by refluxing( 0.25gm) of H2TBPP in 25ml DMF solvent with (1.0gm) of FeCL2.4H2O for 25 min [22-24 ]. The completeness of the reaction can be checked by measuring the UV-Vis spectrum of the reaction mixture; the five band spectrum of H2TBPP should be absent, being replac-ed by two band spectrum of the product. When the reaction is complete cooled to room temperature slo-wly and 300ml of acidic water was added (1ml 6 N HCl ),a brown precipitate was collected and dried in oven at 50-70Č for30 minutes, the product weight-ed of 0.25gm (91%). Chemical analysis of formula (C44H24N4Br4.Fe.Cl).Calc(EXP):C:51.79(51.71±0.22 )H:2.35(2.36±0.13),Fe:5.49(5.50±0.15).

### 2.2.3 Preparation of solid MnTBPPCl complex.

The complex was prepared by refluxing of( 0.25) gm TBPP with (1.0)gm of $MnSO_4$ in 25ml DMF solvent, after 4 hours of heating at 120Č, the color change to green brown and the λmax was at 466nm,after cooling the solution to the room temperature,300ml of acidic water(1ml 6N HCl) was added,black green crystals were collected by filteration and dried in oven at 50-70 c° for 30 minutes,the product weight-ed 0.214gm (78.4%). Chemical analysis of formula ($C_{44}H_{24}N_4Br_4Mn.Cl$).Calc(EXP):C:51.84(51.86±0.12 ),H:2.35 (2.36±0.14) ,N:5.49 (5.50±0.24) ,Mn:5.40 (5.39±0.09).

### 2.2.4 Preparation of solid CoTBPPCl complex.

The complex was prepared by heating a mixture of 0.25gm TBPP with 0.33gm of $CoCl_3$ in 30 ml DMF solvent on the hot plate at 250 C° with magnetic stirring for 30 minutes,the color changes from bro-wn to green-brown, after cooling the solution to the 2C° for 30 minutes,the deep-brown crystals were collected by filteration,dried in oven at 50C° for 20 minutes and weighted of 0.2gm (73.0%).Chemical analysis of formula ($C_{44}H_{24}N_4Br_4.Co.Cl$).Calc (EXP) : C: 51.63 (51.60±0.33) ,H:2.34 (2.34±0.18 ), N:5.47 (5.50 ±0.24),Co:5.7 (5.70±0.27).

## 2.3 Preparation of Standard Solutions

### 2.3.1 Standard solution of ($4.3 \times 10^{-4}$M)TBPP

The solution was prepared by dissolving 0.01gm of TBPP in 25ml DMF solvent.

### 2.3.2 Standard solution of FeTBPPCl,MnTBPPCL and CoTBPPCL complexes

These solution were prepared by dissolving 0.005gm ,0.01gm and 0.01gm from solid complexes of FeTBPPCL,MnTBPPCL,and CoTBPPCL in 25ml of DMF solvent to give concentrations of $2.452 \times 10^{-4}$M, $3.927 \times 10^{-4}$M and $3.911 \times 10^{-4}$M respectively.

### 2.3.3 Standard solution of $Fe^{+2}$,$Mn^{+2}$ and $Co^{+3}$ ions

They were prepared by dissolving 0.05 gm of $FeCl_2$. $4H_2O$, 0.05gm of $MnSO_4$ and 0.01gm of $CoCl_3$ in 25 ml DMF solvent to give concentrations of $10^{-2}$ M $Fe^{+2}$,$6.6 \times 10^{-3}$M $Mn^{+2}$and $2.0 \times 10^{-3}$M of $Co^{+3}$ respectively.

### 2.4 Composition of complexes.

Determination of composition of the forming comp-lexes were conducted using mole ratio method for Fe(lll) and Co(lll) ions .Metal Fe(lll) and Co(lll) in the concentration range $1 \times 10^{-6}$-$4 \times 10^{-5}$M were added to $1 \times 10^{-5}$M porphyrin solution , After20 minutes of reaction on the hot plate, the absorbance at wave length of 416nm and 418 nm were measured,but the method was used for Mn(lll) determination is a con-tinuous variable method(Job method), seven volume-tric flasks containing(0-10)ml of $10^{-5}$M Mn(ll)ion a-nd(10-0)ml of $10^{-5}$M TBPP were mixed together, to give the total volume of 10 ml, then they heated for 4 hours to complete the reaction, the absorbance at wave length of 466nm was measured against blank reagent.

### 2.5 Construction of Calibration Curve for Ions

Ten of 5ml volumetric flasks containing a liguos of standard FeTBPPCl, MnTBPP and CoTBPP soluteo-ns

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in the range of (0.137-1.373)µg/5ml Fe(lll) ion, (0.0107-0.1077)µg/5ml Mn(lll) and (0.011-0.46) µg/5ml Co(lll) respectively, the volume of solutions was completed to the mark by using DMF solvent, and the absorbance was measured at λmax for each ion against blank reagent.

## 2.6 Determination of Fe(lll),Mn(lll) and Co(lll) ions in phosphate crude stones

2 grams of phosphate crude stones was dissolved in 3ml of concentrated nitric acid, then heated for 10 min, with stirring until most of vapors of nitric oxid-es are not seen. Solution was diluted with 50 ml of distil water and filtered.The solution concentrated on the hot plate for 30 minutes and the solid collected by drying in oven at 100C$^o$ for (30)minutes too. 100mg from product was dissolved in 50 ml DMF solvent, 200 microliter from solution sample was added to 10 ml of TBPP (5X10$^{-6}$M), four samples were used to determine the elements. All samples were heated on the hot plate for 30 min for Fe(lll) and Co(lll) but more than 4 hours for Mn(lll) ion determination. After cooling these samples solutions to the room temperature, the absorbance was measu-red at the soret band of each elements in this study against blank reagent. The calculations were made and recorded.

## 3. RESULTS AND DISCUSSION

### 3.1 Spectrophotometric Study of Porphyrin and Metals Porphyrin

Solution of 1x10$^{-5}$M TBPP in DMF solvent is purple color and exhibit five absorption maxima,one is soret band at 416nm($ε=2.2x10^5$L.M$^{-1}$.cm$^{-1}$),512nm($ε=1.1 x10^4$ L.M$^{-1}$.cm$^{-1}$),548nm($ε=5.6x10^3$L.M$^{-1}$.cm$^{-1}$) ,590 ($ε=3.8x10^3$L.mol$^{-1}$.cm$^{-1}$)and 646 ($ε=3.5x10^3$L.M$^{-1}$.cm$^{-1}$).FeTBPPCl complex spectrum shows soret band at 416nm($ε=8.6x10^4$ L.M$^{-1}$.cm$^{-1}$) and at 566 nm ($ε=8.5x10^3$ L.M$^{-1}$.cm$^{-1}$), where MnTBPPCl complex spectra was at 466nm λmax ($ε=5.9x10^4$L.M$^{-1}$.cm$^{-1}$), 398nm($ε=3.3x10^4$L.M$^{-1}$.cm$^{-1}$), 566nm($ε=9.5x10^3$L. M$^{-1}$.cm$^{-1}$) and at 604nm ($ε= 7 .3 x10^3$L.M$^{-1}$.cm$^{-1}$).
CoTBPPCl complex spectrum shows soret band at 418nmλmax ($ε=1.3x10^5$ L.M$^{-1}$.cm$^{-1}$) and at 538 ($1.9x10^4$ L.M$^{-1}$.cm$^{-1}$). All spectra were measured in DMF solvent. Figure.2.0 shows these complexes spectra together.



**Λnm**
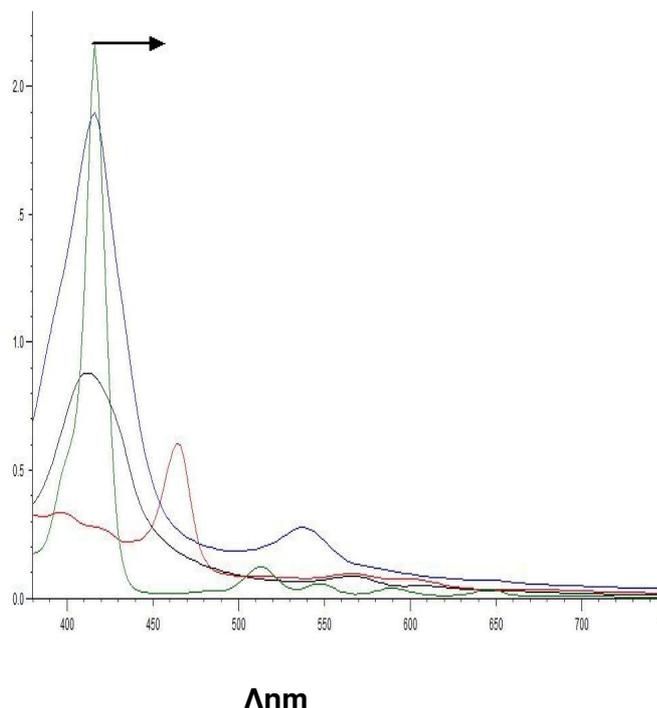**Figure 2.0 shows the spectra (1)1×10$^{-5}$M TBPP ,(2) 1.17×10$^{-5}$M CoTBPPCL, (3)1×10$^{-5}$M FeTBP-PCL, (4 ) 1×10$^{-5}$ M MnTBPPCL, in DMF solvent at 25 C$^o$.**

### 3.2 Composition of Complexes

Mole ratio method was used to calculate the composition of Fe(lll) and Co(lll) ions at λmax 416nm and 418nm respectively,the continuous variation method was used for Mn(lll) at λ 466nm to the TBPP, the ratio was found 1:1 for all complexes, see the figures.3.0 and 4.0.
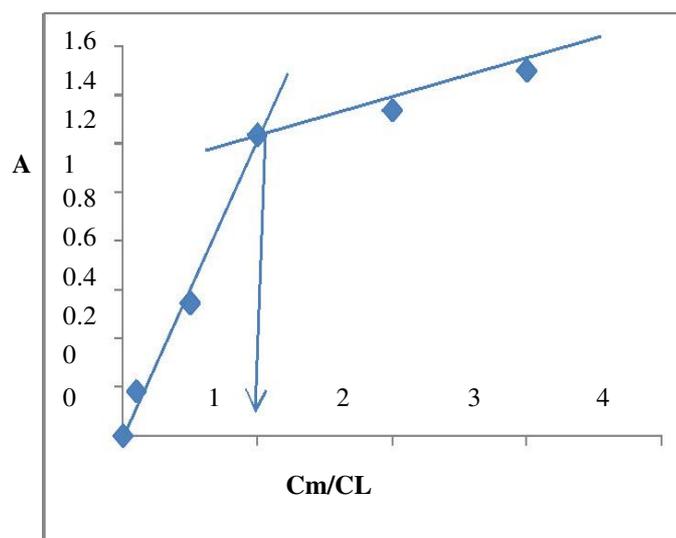


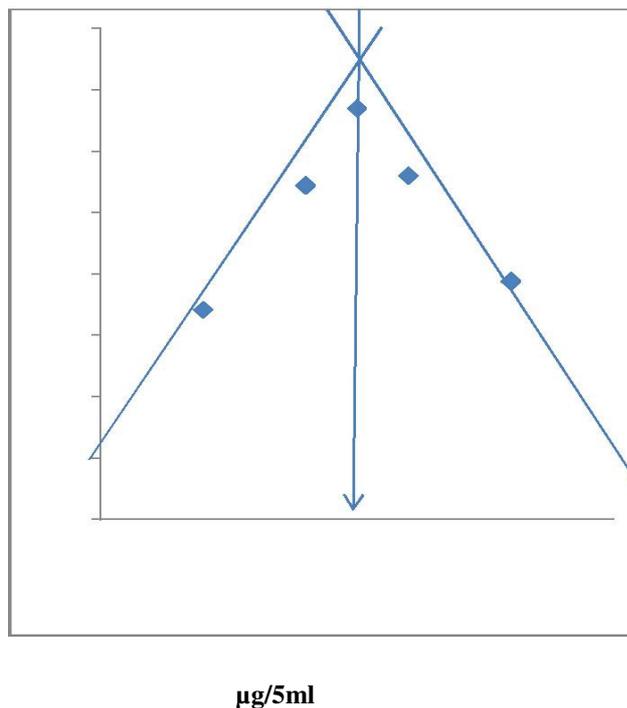**Figure 3: The mole ratio method plot for Fe (lll) ion with TBPP ligand at λ416nm**

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**µg/5ml**

**Figure 5:The calibration curve for Co(Ill)ion withTBPP ligand**

**Table 1: The Analytical and Regression Parameters**

| Parameters | Fe(lll) ion | Mn(lll) ion | Co(lIl) ion |
|---|---|---|---|
| Beer's law limits(µg/5ml) | 0.01- 1.1 | 0.01-0.1 | 0.01-0.115 |
| Molar absorptivity(L.M$^{-1}$.cm$^{-1}$) | $6.8 \times 10^4$ | $1.1 \times 10^5$ | $1.3 \times 10^5$ |
| Sandell's sensitivity (µg.cm$^{-2}$) | 0.0008 | 0.0005 | 0.0004 |
| Average recovery(%) | 100.25 | 99.71 | 99.18 |
| Correlation coefficient($R^2$) | 0.983 | 0.990 | 0.993 |
| Regression equation. y | ----- | ------ | ------- |
| Slope. a | 0.244 | 0.398 | 0.455 |
| Intercept. b | 0.028 | 0.006 | 0.0.008 |
| RSD(%) | 0.002 | 0.003 | 0.01 |

**Y$^{*}$=ax+b, Where x is the concentration of ions**

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## Table 2.The Effect of Foreign Ions on Determination of Fe(lll)and Co(lll) Ions

| Compound | µg/10ml interferences | Average recovery% | RSD% | $Fe^{+3}$µg/10ml |
|---|---|---|---|---|
| $Fe^{+3}$ + TBPP | ---- | 1oo | ---- | 24.677 |
| $Fe^{+3}$ + TBPP +$CU^{+2}$ | 1 | 98.84 | 0.0152 | 24.168 |
| $Fe^{+3}$ + TBPP +$Pb^{+2}$ | 1 | 99 | 0.0264 | 20.760 |
| $Fe^{+3}$ + TBPP +$Cd^{+2}$ | 1 | 99.9 | 0.022 | 16.716 |
| $Fe^{+3}$ + TBPP +$Ni^{+2}$ | 1 | 102 | 0.0129 | 9.240 |
| Compound | µg/10ml interferences | Average recovery% | RSD% | $Co^{+3}$ µg/10m |
| $Co^{+3}$+ TBPP | ------ | 100 | ---- | 9.72 |
| $Co^{3}$+ TBPP+$Cd^{+2}$ | 1 | 103.8 | 0.004 | 10.091 |
| $Co^{+3}$+ T BPP+$Cu^{+2}$ | 1 | 102 | 0.02 | 12.495 |
| $Co^{+3}$+ TBPP+$Ni^{+2}$ | 1 | 101 | 0.054 | 12.914 |
| $Co^{+3}$+ TBPP+$Pb^{+2}$ | 1 | 99.2 | 0.0124 | 10.898 |
| Compound | µg/10ml interferences | Average recovery% | RSD% | $Mn^{+3}$ µg/10m |
| $Mn^{+3}$ +TBPP | 1 | 100 | ------- | 20.20 |
| $Mn^{+3}$ +TBPP+$Zn^{+2}$ | 1 | 102 | 0.013 | 20.684 |
| $Mn^{+3}$ +TBPP+$Cu^{+2}$ | 1 | 103 | 0.012 | 20.806 |
| $Mn^{+3}$ +TBPP+$Cd^{+2}$ | 1 | 99.5 | 0.011 | 20.099 |
| $Mn^{+3}$ +TBPP+$pb^{+2}$ | 1 | 99.8 | 0.013 | 20.159 |

## 3.4 Analytical application of method for determination of Fe(lll),Mn(lll) and Co(lll) ions in phosphate stones.

The proposed method was applied to the determination of these ions in four samples. The results are listed in table 3, and comparative data obtained by AAS method are also presented. It was found that most of results are not far away from that recorded by proposed method when the interference of foreign ions has been taken in our calculations. The recovery percentage was found

affected in the present of heavy metals ions such as Pb,Cd and Ni,due to the interference of those ions. There is no interference of foreign ions on the recovery of Mn(lll) because the absorbance of Mn(lll) ion λmax 466nm is seprated very well from the ligand soret band and other ions in this study.

## 4. CONCLUSIONS

In this study TBPP used for determination of Fe(lll), Mn(lll) and Co(lll) ions . The proposed method is simple, accurate and cheap if the interferences should be

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previouly removed by other analytical methods.The analysis shows that the data of the molar absorbance and the range of determination from proposed method for these ions are in good agreement with those of the reported method see table 4,addition to that the color reaction does not require long time for heating or buffer except for Mn(lll)ion. The color complexes are stable up to many days, which is sufficient time for the analyst to perform the analysis.

**Table 4: Spectrophotometric Determination of Metal Ion with Porphyrin Reagent**

| Metal ion | Reagent | Condition | Absorption Spectra $\lambda_{max}$, nm $\epsilon(x10^5)$ $L.M^{-1}.cm^{-1}$ | Range of determination | Interference | Ref. |
|---|---|---|---|---|---|---|
| Cd(ll) | T$_4$BPP | pH 10 byHPLC | 436 | 0.01-120µgl$^{-1}$ | ---------- | [21] |
| Fe(lll) | TPPS$_4$ | PH 5 (NH$_2$OH,100C$^o$,10min) | 394,3.88 | 0.01-200 µgl$^{-1}$ | --------- | [13] |
| Cu(ll) | p-NO$_2$Bz-TPPS | pH 5 (90C$^o$ ,7 min) | 413 , 4.2 | 130µgl$^{-1}$ | Co(ll),Pd,Fe(lll) | [28] |
| Cd(ll) | T(1-MPy)P | pH 9.8+Pb(ll)+L-tryptophan | 448, 1.7 | 0.3-23 µgl$^{-1}$ | Zn,Hg(ll) | [ 29] |
| Pd(ll) | TPPS$_4$ | pH 4 +ascorbic acid(1ooC$^o$,7min) | 411,2.2 | --- | Cu,Hg(ll) | [ 30-33] |
| Fe(lll) | TBPP | DMF(120C$^o$25min) | 416,0.68 | 0.01-1.1 µg/5ml | Cu(ll), Pb(ll), Cd(ll) Ni(ll). | This work |
| Co(lll) | TBPP | DMF(250C$^o$,30min) | 418,1.3 | 0.01-0.115 µg/5ml | Cd(II),Cu(ll), Ni(ll),Pb(ll). | This Work |
| Mn(lll) | TBPP | DMF(120C$^O$,4hours) | 466,1.1 | 0.01-0.1 | ------------ | This work |

**T$_4$BPP=Tetra-(4-bromophenyl)-porphyrin, TPPS$_4$=meso-Tetrakis(4-sulfophenyl)Porphyrin p-**

**NO$_2$BZ-TPPS=N-4-Nitrobenzyl-tetrakis(4-sulfonatophenyl)porphyrin T(1-MPy)P=meso-**

**Tetrakis(1-methylpirydinium-4-yl)porphyrin**

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