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## Novel Electrochemical behavior of 3-(5-(3-Methyl-1-phenylpyrazolazo)-1-nitroso-2-naphthol and use it for Spectrophotometric Determination of Iron(III) in Blood samples

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### ABSTRACT

The azo reagent 3-(5-(3-methyl-1-phenyl pyrazolazo)-1-nitroso-2-naphthol was synthesized and characterized by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>CNMR spectral techniques. The electrochemical behavior of the azo reagent and its complex with Fe(III) has been studied at glassy carbon disk GCE electrode in different supporting electrolyte at concentration (1M) and scan rate (100mvs-1). Spectrophotometric determination of Iron (III) is based on the formation of a 2:1 complex with above reagent. The complex has  $\lambda_{max}$  at (454) nm and  $\epsilon_{max}$  of (1.7982\*10<sup>4</sup>)L.mol<sup>-1</sup>.cm<sup>-1</sup>. A linear correlation (0.1 – 3.0  $\mu$ g. ml<sup>-1</sup>) was found between absorbance at  $\lambda_{max}$  and concentration. The effect of diverse ions on the determination of copper (II) to investigate the selectivity of the method were also studied. The stability constant of the product was (2.869\*10<sup>8</sup>). The proposed method was successfully applied to the analysis of honey sample.

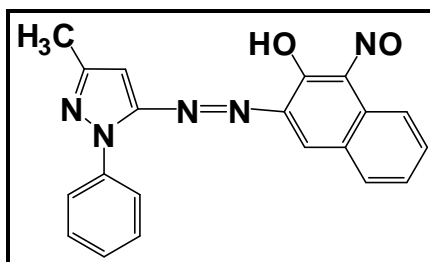
**Keywords:** Cyclic voltammetry, 3-(5-(3-methyl-1-phenyl pyrazolazo)-1-nitroso-2-naphthol, Iron(III), spectroscopy

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### INTRODUCTION

Azo compounds are among the most profoundly explored class of organic compounds both from theoretical and practical viewpoints. These are the largest group of organic dyes for their wide spread applications in many areas of dye- stuff industry, pharmacy and dosimetry due to the presence of azo(-N=N-) linkage [1,2]. Azo compounds are still a very important class of chemical compounds receiving much attention in scientific research due to their chromphoric properties and their usage in analytical chemistry and industry [3,4]. The synthesis and spectral properties of several azo dyes as well as of their transition metal complexes have been reported in the literature [5-7]. The electro chemical behavior and electrode reaction path ways of numerous azo- dyes in various supporting electrolytes were studied and discussed [8-10].

In the present work, azo- derivatives from 5- amino-3-methyl-1-phenyl pyrazol was synthesized and characterized. According to the best of our knowledge, this reagent has not been reported in the literature as being used for any cation determination. In this study, we wish to report the electrochemical behavior of this reagent and as a selective reagent in spectrophotometric determination of micro amounts of Iron (III) MPANN is a bidentate via azo group and hydroxyl group: it has the following structure:-



Structure of (MPANN)

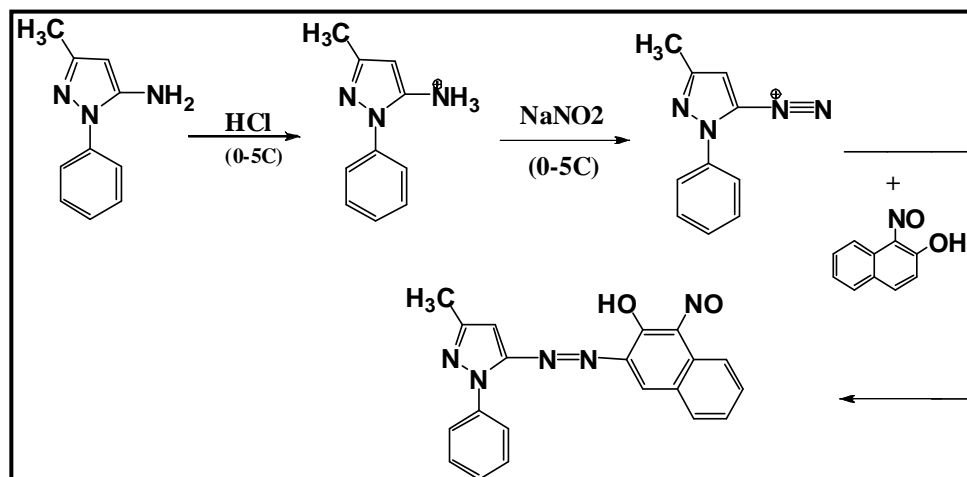
## MATERIALS AND METHODS

All chemicals used in this work were of analytical grade.

In this study the FT-IR spectra of azo compound was recorded on Shimadzu FT-IR spectrophotometer model in KBr wafer and the NMR spectra was obtained on BRUKER AV 400 Avance III 400MHz instrument using DMSO as solvent and reported relative to TMS as internal standard , CE440CHN/O/S Elemental Analyser was made by EAI while voltammetric experiment as were carried out using a computer – controlled electroanalysis system using an (EZ-State by NuVant) system. A three-electrode combination system was an Ag /AgCl reference electrode, a Pt wire auxiliary electrode and glassy Carbone electrode as working electrode, the potential range selected was in the Range(1-1.25) mV. All measurements were carried out at room temperature.

### Synthesis of pyrazol derivative

5-amino-3-methyl-1-phenyl pyrazol (0.0057 mole)1.0000g was diazotized by dissolving it in a small amount of ethanol then 5ml of HCl(4M) was added keeping the temperature at (0-5°C) and then adding NaNO<sub>2</sub> solution gradually and left solution about 15 min to cool well ,1- Nitroso -2- Naphthol (0.0057 mole)(0.999g) was dissolved in ethanol as well 10 ml of NaOH(4M) was added and leave to cool well ,then this solution was added to diazonium salt solution slowly drop by drop to maintain temperature (0-5°C). The mixture was allowed precipitate was filtered off and washed several times with (1:1) (alcohol:water) mixture then recrystallized from boiling ethanol and left to dry. Scheme.1). Dark brown powder m.p.( 183°C°), Anal(calc) for C<sub>20</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub>: C(67.15%), H(4.197%), N(19.59%). Found%:(66.03%) ,H(4.56%) ,N(19.01%).



Scheme(1): Synthesis of azo compound (MPANN)

### Reagents:

**Iron stock solution ( 100 µg.ml<sup>-1</sup>):** The solution was prepared by dissolving ( 0.0968 g) of Iron chloride hexa hydrate in ( 200 ml) of deionized water.

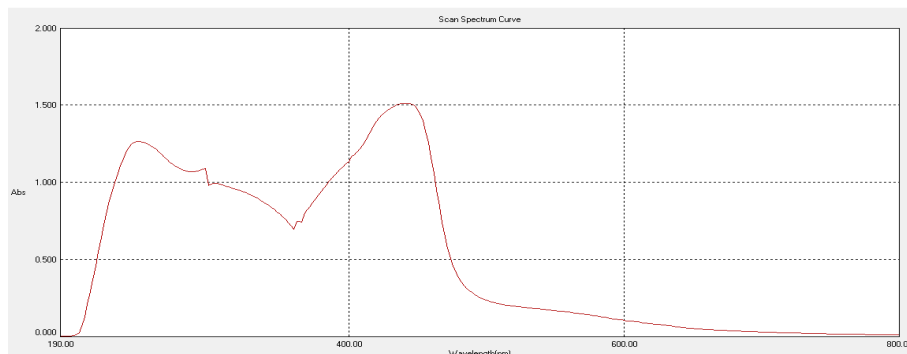
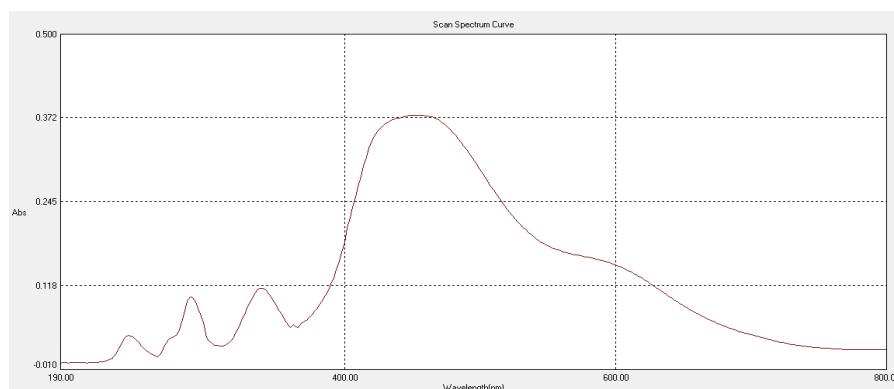
**MPANN(1x10<sup>-3</sup>M):**This solution was prepared by using ( 0.0714 g) of reagent in (200 ml) of ethanol.

**Other ions (foreign) solution** .All of ions were prepared by using a suitable amount of the compound in deionized water in a calibrated flask.

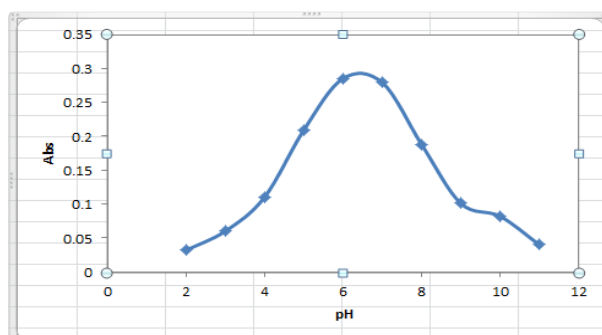
## RESULTS AND DISCUSSION

**Absorption Spectra:**

The reagent (MPANN) nm possess a maximum absorption at ( 440 nm)(Fig. 1) reacts with ( FeCl<sub>3</sub>.6H<sub>2</sub>O) at room temperature to give a (MPANN-Fe(III)) colored complex at pH 6. . The absorption spectrum shows a maximum at 588 nm, whereas the reagent blank give no absorption at this wavelength ( Figure .2)

**Fig(1).** Absorption spectrum of ( MPANN)**Fig.(2).** Absorption spectrum of ( MPANN-Fe)complex

The effect of various parameters on the absorption intensity of the formed products was studied and the reactions condition was optimized. The reaction of(MPANN) with Fe(III) was studied at different pH by using HCl or NaOH( 0.05N)in the range (2-11). It was found that the chelating complex was formed at pH 6. (Fig. 3) . It was found that absorbance rises with increasing reagent concentration and got its maximum value on using ( 2.5 ml of  $1 \times 10^{-3}$  M ) in subsequent experiment.

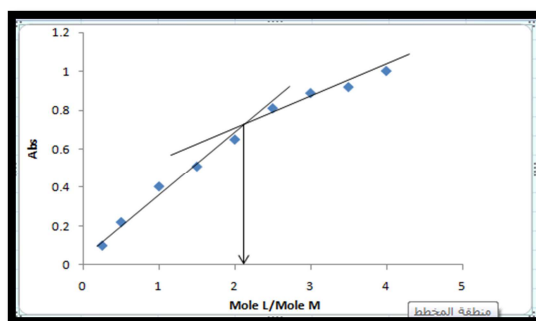
**Fig (3).** Effect of pH on the absorption intensity of (MPANN-Fe(III)) complex**Quantification:**

In order to study the range in which the colored complex adhere to Beer's law the absorbance of the complex was measured at  $\lambda_{max}$  for sequence of solutions containing increasing amounts of Fe(III) at optimum conditions. The validity of Beers law, molar absorptivity and Sandells sensitivity values were estimated and are given in Table .1, showed that the method is sensitive. The proposed method showed a good linearity for the determination of Fe(III)

with a good correlation coefficient (0.9954). The relative standard deviation %(RSD) for the analysis of six replicates of Fe(III) is equal to (0.52) showed that the method is precise and accurate, while detection limit is equal to (0.0156)  $\mu\text{g}\cdot\text{ml}^{-1}$ . The stoichiometric ratio of (MPANN) and Fe(III) was studied applying the continuous variation (Jobs) and mole ratio methods [11,12] using equimolar solutions of the new ligand and Fe(III) ( $1 \times 10^{-4}$ ). It was found that (MPANN) forms a dye coupled product with Fe(III) in the ratio 2:1 as in Fig. 4.

**Table (1) characteristics data of MPANN-Fe(III) complex**

parameter	Values
Beers law limits ( $\mu\text{g}\cdot\text{ml}^{-1}$ )	(0.1-3.0)
Molar absorptivity ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ )	$1.7982 \times 10^4$
LOD ( $\mu\text{g}/\text{ml}$ )	0.01569
R.S.D %	0.52%
Correlation coefficient	0.9954
Sandells sensitivity $\mu\text{g}\cdot\text{cm}^{-2}$	0.0031

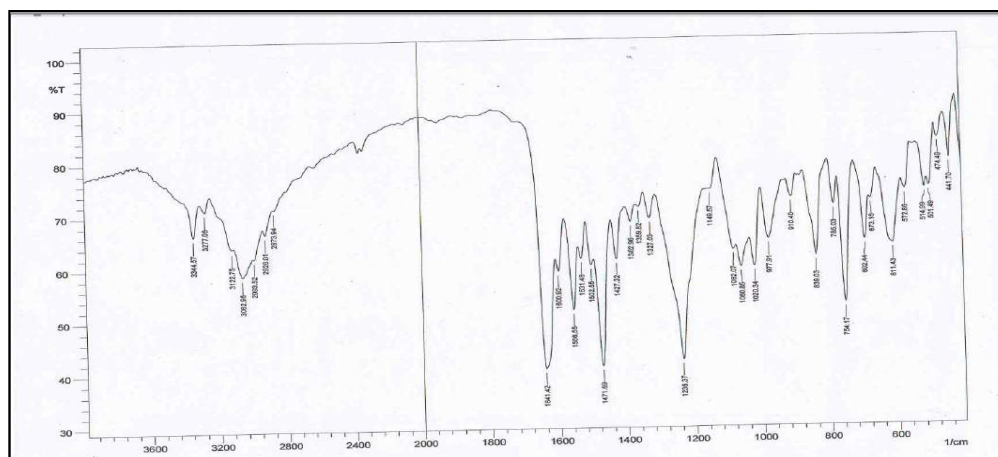


**Fig.(4). Mole Ratio Plot of The Fe-MPANN**

#### **FT IR Analysis:**

The FT-IR spectra of the free ligand have a broad band about ( $3344.5\text{-}3414$ )  $\text{cm}^{-1}$  which could be attributed to (OH) stretching vibration, the shape and intensity of band were changed that led to expect coordination was accurate in complex (Fe-MPANN), likewise the  $\nu(\text{N}=\text{N})$  stretching band in the free ligand is observed at  $1471.8 \text{ cm}^{-1}$  (m) is shifted to lower with low intensity at  $1431.18 \text{ cm}^{-1}$  (s) frequency value upon complexation suggesting chelation via the (M-N) [13].

The bands at frequency ( $1651\text{-}1593$ )  $\text{cm}^{-1}$  of (C=N) also was changed as well as the band at ( $1305\text{-}1201$ )  $\text{cm}^{-1}$  which corresponding with (C=N=N-C) and (C=N-N=C) were shifted towards lower frequency [14,15] in complex. The FT-IR spectra of copper complex also shows additional bands in ( $559.30$ )  $\text{cm}^{-1}$  (w) which is due to the formation of (M-O) and ( $481.85$ )  $\text{cm}^{-1}$  for (M-N). (Fig. 5.6)



**Fig.(5). The FT- IR Spectrum of the dye (MPANN)**

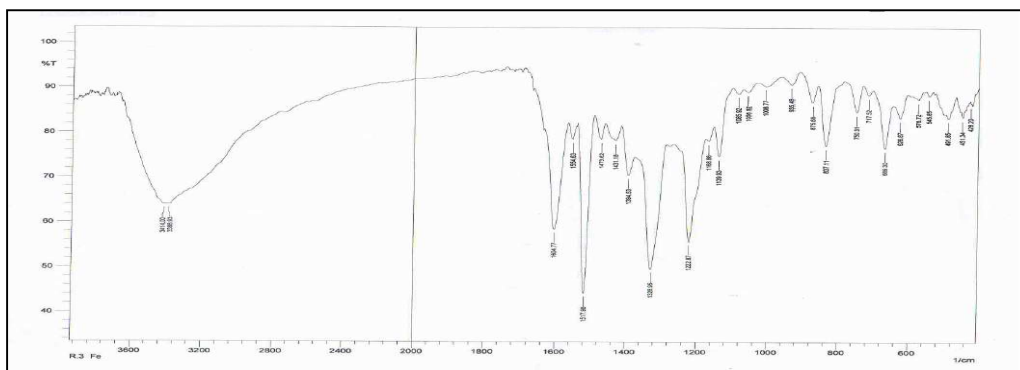


Fig.(6). The FT-IR Spectrum of (Fe-MPANN) complex

**<sup>1</sup>H-NMR of (MPANN) and Fe(III) complex :**

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of the prepared azo compound was made ligand in DMSO solution with tetramethylsilane as an internal standard indications the following signals as in Table. 2 . Fig .7,8.

Table (.2). <sup>1</sup>H-NMR data of MPANN and it complex with Iron(III)

compound	C-OHAr	Ar-H benzene of pyrazol-	Ar-H naphthalene	CH pyrazol	CH3 of pyrazol	CH3 of DMSO
MPANN	9.05	7.504-7.41	7.709-7.509	6.497	2.663	2.5
Fe-MPANN	10.2	7.452	8.820-8.289	----	3.470	2.028

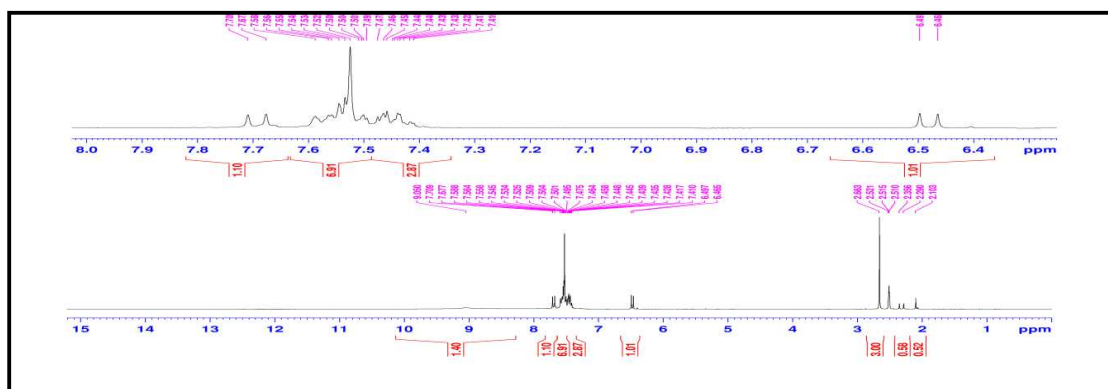


Fig (7). <sup>1</sup>H-NMR of azo compound (MPANN)

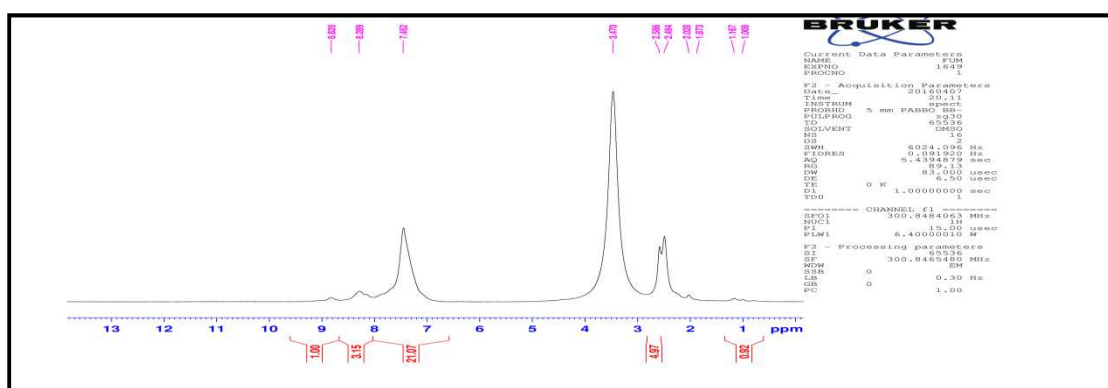
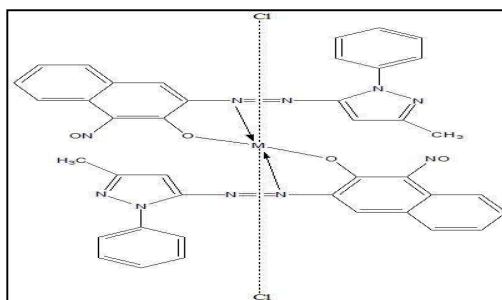


Fig .( 8) :The <sup>1</sup>H-NMR spectrum of(Fe-MPANN)complex

According to the results of the FT-IR, <sup>1</sup>H-NMR , stoichiometric and elemental analysis the structure of complex can be suggested as the following:



Structure of (MPANN-Fe) complex

### Interferences

The effect of different ions in the determination of Iron (III) was studied. Fe(II) can be determined in presence of 10 or more fold excess of cation and the interference via the various ions were removed by using suitable masking agent Table .3 .

**Table.( 3 ) :Interference of ions and removed them by masking agent**

No	Foreign ions	Conc. ppm	Error%	Masking agent	Error%
1	Co <sup>+2</sup>	10	17.19	Thiourea(1ml)	0.93
2	Cd <sup>+2</sup>	10	23.15	NaNO <sub>3</sub> (0.5 ml)	0.72
3	Sr <sup>+2</sup>	10	0.34	----	----
4	Ni <sup>+2</sup>	10	28.06	NaNO <sub>3</sub> (1ml)	0.33
5	Sn <sup>+2</sup>	10	2.7	----	----
6	Cs <sup>+2</sup>	10	1.52	----	----
7	Zn <sup>+2</sup>	10	0.34	----	----
8	Pb <sup>+2</sup>	10	0.38	----	----
9	Mn <sup>+2</sup>	10	1.02	----	----
10	Hg <sup>+2</sup>	10	0.317	----	----
11	Ag <sup>+1</sup>	10	18.02	Thiourea(1ml)	0.29
12	Cu <sup>+2</sup>	10	25.21	KCl(1ml)	0.41

### Estimation of Iron(III) in the blood samples taken from patients with diabetes and adults:

After collecting blood samples in tubes made of polyethylene saves at (-20 C°) temperature. First transferred to baker, a concentrated Nitric acid (10 ml) was added and heating quietly, when the reaction start to be activity, sample solution was removed and left to cool well .Then , (1ml)of H<sub>2</sub>SO<sub>4</sub> concentrated was added . Next, (1.5ml) of 1% KMnO<sub>4</sub> was added also and mixed well. After this (1ml) of Sodium azid ( NaN<sub>3</sub>) (2.5%) and (0.5 ml )of 70% HClO<sub>4</sub> were added with heating under 70 C° for 30 min to remove any excess of NaN<sub>3</sub>. Finally the solution was left to cool then neutralization with dilute Ammonium hydroxide (NH<sub>4</sub>OH), next the solution transferred to volumetric flask(200 ml) and diluted to the mark with deionized water. All samples were ready for UV-Visible and atomic absorption spectrometric analysis' [16] . The results are shown in Table 4, indicate that satisfactory precision and accuracy could be attained with proposed method.

**Table.( 4 ) :Fe(III) levels in bloods of human**

blood samples	A mount found by our spectrophotometric method (µg.ml <sup>-1</sup> )	A mount found by Atomic Absorption (µg.ml <sup>-1</sup> )
Normal adult (male)	0.35	0.3156
Diabetes patient	0.45	0.3911

### Electrochemical behavior of azo dye(BTHN)and redox mechanism in aqueous solution

Electrochemical properties of (MPANN) have been studied by cyclic voltammetry in various supporting electrolyte such as(KCl,KNO<sub>3</sub>,K<sub>2</sub>HPO<sub>4</sub>,NaH<sub>2</sub>PO<sub>4</sub>,Na<sub>2</sub>HPO<sub>4</sub>,NaCl,KClO<sub>3</sub>,) at concentration (1M) and scan rate (0.1vs-1). The results are summarized in Table .5,6..

The reduction mechanism of the synthesized azo dye is proposed as follows depending on literature [17-20 ] scheme. 2.



Different supporting electrolyte was be used with the reagent(MPANN) at GCE with scan rate ( $0.1\text{Vs}^{-1}$ ) for all cyclic voltammogrames Fig 9-15 .All voltammogrames are shows reduction peak of azo group (-N=N-) at potential ranged (-500mv -750mv). The choice of the better supporting electrolyte depends on the higher current for oxidation peak and clarity of peak .

For reagent (MPANN) was proposed that the best supporting electrolyte is ( $\text{Na}_2\text{HPO}_4$ ) Fig. 14 ,despite getting a high current with some supporting electrolyte but they have not chosen because precipitation as in ( $\text{K}_2\text{SO}_4$ ) Fig .12 , cyclic voltammogram shows irreversible electrochemical system in which the electron transfer rates are significantly less than the rate of mass transport and the reduction in one step. All current peak ratio shows irreversibility of electrochemical system at different electrolyte due to the  $I_{pc}/I_{pa}\neq 1$ , the deviation from number one due to the chemical reaction that arises subsequent transmission electron ,such interactions can be complex , involving dissociation and isomerization[21].

Table(.5). Current –Potential data of (MPANN) in several supporting electrolyte Solution (1M) with scan rate ( $0.1\text{Vs}^{-1}$ )

MPANN	Supporting Electrolyte	Ia <sub>1</sub> μA	Ea <sub>1</sub> mv	Ia <sub>2</sub> μA	Ea <sub>2</sub> mv	Ia <sub>3</sub> μA	Ea <sub>3</sub> mv	Ic <sub>1</sub> μA	Ec <sub>1</sub> mv	Ic <sub>2</sub> μA	Ec <sub>2</sub> mv	Ic <sub>3</sub> μA	Ec <sub>3</sub> mv
1	KCl	10.2	446	8.04	141	---	---	23.7	497	---	---	---	---
2	KNO <sub>3</sub>	9.65	548	8.25	57.8	2.94	293	28.7	645	---	---	---	---
3	K <sub>2</sub> SO <sub>4</sub>	14.5	443	10.9	114	7.27	184	41.4	627	---	---	---	---
4	NaCl	11.0	461	7.41	129	---	---	21.4	510	27.0	653	---	---
5	Na <sub>2</sub> HPO <sub>4</sub>	10.2	465	10.8	63.6	---	---	30.6	632	36.5	853	---	---
6	NaH <sub>2</sub> PO <sub>4</sub>	10.8	141	---	---	---	---	26.2	543	---	---	---	---

Enhancement in current of peak follows the following sequence

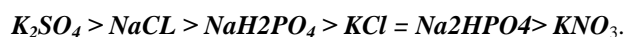
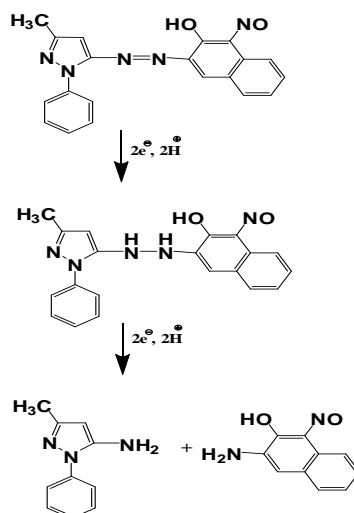


Table ( 6 ).Current –Potential data for azo compound (MPANN) at different supporting electrolyte (1M) and scan rate (  $0.1\text{Vs}^{-1}$ )

	Supporting electrolyte	Ea <sub>1</sub> mV	Ec <sub>1</sub> mV	Ia <sub>1</sub> μA	Ic <sub>1</sub> μA	ΔE <sub>1</sub> mV	E <sub>1/2</sub>	Ia <sub>1</sub> /Ic <sub>1</sub>
1	Na <sub>2</sub> HPO <sub>4</sub>	465	632	10.2	30.6	1097	-83.5	0.333
2	NaH <sub>2</sub> PO <sub>4</sub>	141	543	10.8	26.2	684	-201	0.4122
3	NaCl	461	510	11.0	21.4	972	-24.5	0.514
4	KCl	446	497	10.2	23.7	943	-25.5	0.4303
5	KNO <sub>3</sub>	548	645	9.65	28.7	1193	-48.5	0.336



Scheme.(2) Proposed mechanism of voltammetric reduction of (MPANN)

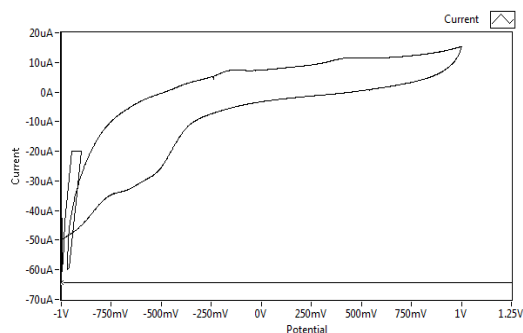


Fig.9. CV for (MPANN) in supporting electrolyte 1M of KCl

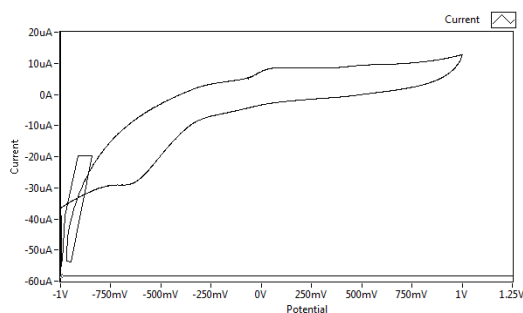


Fig.10. CV for (MPANN) in supporting electrolyte 1M of KClO<sub>3</sub>

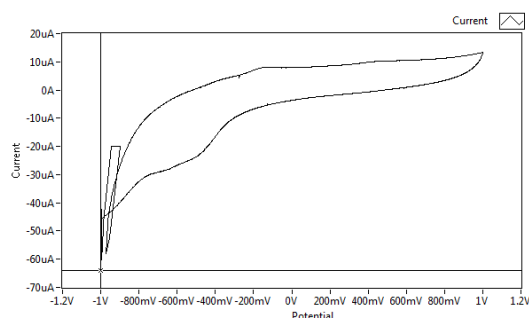


Fig.11. CV of (MPANN) in supporting electrolyte 1M of KNO<sub>3</sub>

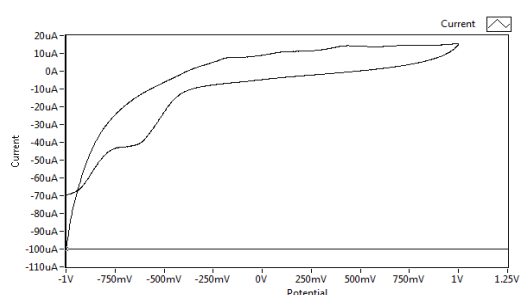


Fig.12. CV of (MPANN) in supporting electrolyte 1M of K<sub>2</sub>SO<sub>4</sub>

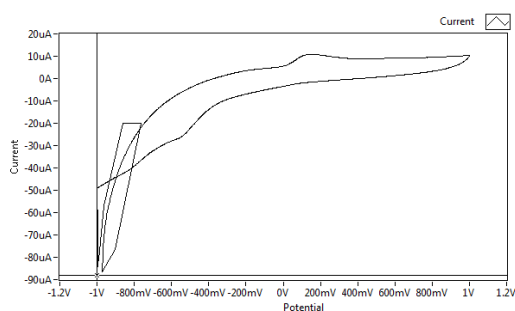


Fig.13. CV of (MPANN) in supporting electrolyte 1M of NaH<sub>2</sub>PO<sub>4</sub>

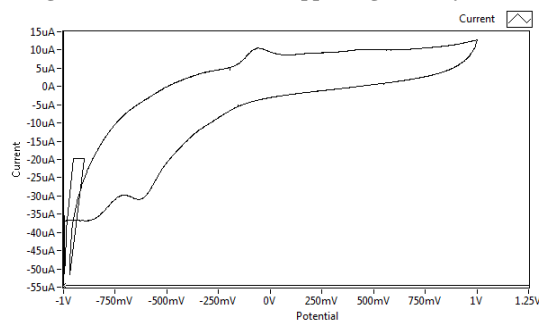


Fig.14. CV of (MPANN) in supporting electrolyte 1M Na<sub>2</sub>HPO<sub>4</sub>

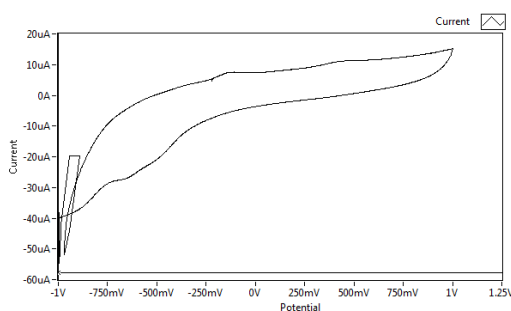


Fig.15. CV of (MPANN) in supporting electrolyte 1M of NaCl

**Redox behavior of (MPANN-Fe) complex:**

Different supporting electrolyte was used with the reagent (MPANN) at GCE with scan rate (0.1Vs<sup>-1</sup>) for all cyclic voltammograms Fig 16-21 , Table .7.

The cyclic voltammogram of Iron (III) complex shows two redox couples peaks in (Na<sub>2</sub>HPO<sub>4</sub>(1M) as in Figure ( ). The first redox couple at Epc<sub>1</sub>=(−618 mv) vs Ag/AgCl(Ipc<sub>1</sub>=17.3 μA),and Epa<sub>1</sub>=(236 mv)vs Ag/AgCl(Ipa<sub>1</sub>=15.6 μA).The second redox couple at Epc<sub>2</sub>=(866 mv) (Ipc<sub>2</sub> =21.4 μA ) and Epa<sub>2</sub> =63.6 mv) (Ipa<sub>2</sub>= 12.3 μA ) Table . 8.The first reduction peak was attributed to (Fe<sup>+3</sup> +e- ----- Fe<sup>+2</sup>), while the second reduction peak was attributed to reduction of (-N=N) azo group to a hydrazo. The position of reduction peak of this group was not changed from



those in CV for blank. When the scan is reversed, the first oxidation was attributed to oxidation of  $Fe^{+2}$  to  $Fe^{+3}$ , while the second oxidation peak was attributed to oxidation of a hydrazo group to azo group, that has not changed from those in CV for the blank.

It was observed that  $\Delta Ep_1$  values equal to (854 mv),  $\Delta Ep_2 = (802.4\text{ mv})$  Table .9 and the ratio of first anodic to cathodic peak currents ( $I_{pa}/I_{pc} \neq 1$ ) corresponds to more than one electron transfer process also the second peak . The difference in the value of ( $E_{pc}-E_{pa}$  is  $\Delta Ep$ ) which is greater than the value required for a reversible process ( 59 mv) indicating that , reduction of Iron(III) complex at silver electrode is irreversible [22,23] .

Table .( 7). Current –Potential data for(MPANN-Fe) complex at different supporting electrolyte (1M) at scan rate ( 0.1 Vs<sup>-1</sup>)

	Supporting Electrolyte	Ia <sub>1</sub> $\mu A$	Ea <sub>1</sub> mv	Ia <sub>2</sub> $\mu A$	Ea <sub>2</sub> mv	Ia <sub>3</sub> $\mu A$	Ea <sub>3</sub> mv	-Ic <sub>1</sub> $\mu A$	Ec <sub>1</sub> mv	Ic <sub>2</sub> $\mu A$	Ec <sub>2</sub> mv	Ic <sub>3</sub> $\mu A$	Ec <sub>3</sub> mv
1	KCl	28.7	1.14V	--	--	--	--	6.29	237	--	--	--	--
2	KNO3	14.3	410	11.8	279	1.54	106	8.11	63.6	11.7	99.4	22	304
3	K2SO4	19.5	1.07V	11.5	118	5.87	570	18.3	550	--	--	--	--
4	NaH2PO4	4.74	185	--	--	--	--	2.11	4.24	5.05	203	--	--
5	Na2HPO4	15.6	236	12.3	63.6	--	--	17.4	618	21.4	866	--	--
6	NaCl	31.2	837	11.2	134	--	--	--	--	--	--	--	--

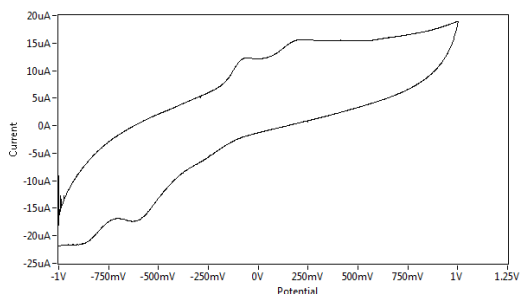


Fig. 16.CV for( MPANN-Fe) complex in(Na<sub>2</sub>HPO<sub>4</sub>) (1M)

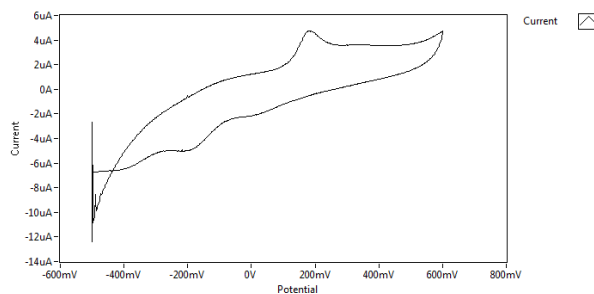


Fig.17.CV for( MPANN-Fe )complex in(NaH<sub>2</sub>PO<sub>4</sub>) (1M)

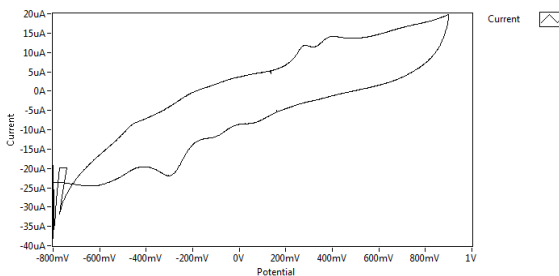


Fig.18.ICV for( MPANN-Fe) complex in(KNO<sub>3</sub>) (1M)

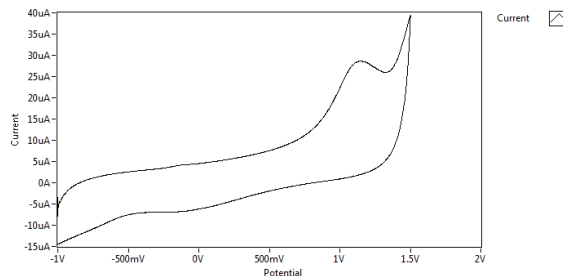


Fig.19.CV for( MPANN-Fe )complex in(KCl) (1M)

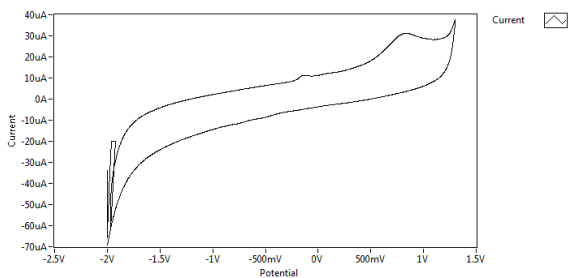


Fig.20.CV for ( MPANN-Fe )complex in(NaCl) (1M)

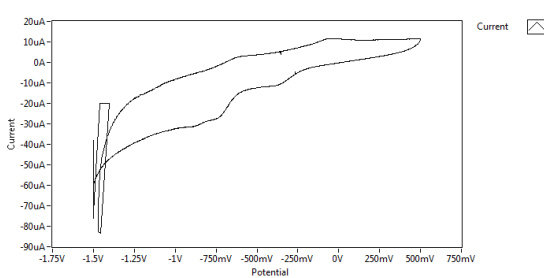


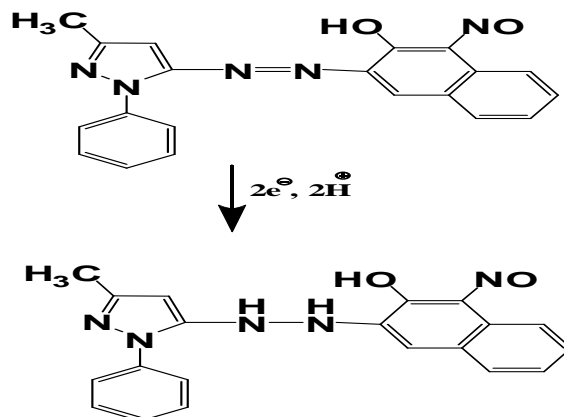
Fig. 21.CV for( MPANN-Fe )complex in(K<sub>2</sub>SO<sub>4</sub>) (1M)

Table (.8). Current –Potential data for(MPANN-Fe) at (Na<sub>2</sub>HPO<sub>4</sub>)(1M) as supporting electrolyte at scan rate ( 0.1 Vs<sup>-1</sup>)

compound	Ea <sub>1</sub> mV	Ec <sub>1</sub> mV	Ia <sub>1</sub> $\mu A$	-Ic <sub>1</sub> $\mu A$	$\Delta Ep_1$	(I <sub>pa</sub> /I <sub>pc</sub> ) <sub>1</sub>	[E <sub>1/2</sub> ] <sub>1</sub>
MPANN-Fe complex	236	618	-15.6	-17.4	854	0.896	-191
	Ea <sub>2</sub> mV	Ec <sub>2</sub> mV	Ia <sub>2</sub>	Ic <sub>2</sub>	$\Delta Ep_2$	(I <sub>pa</sub> /I <sub>pc</sub> ) <sub>2</sub>	[E <sub>1/2</sub> ] <sub>2</sub>
	-63.6	-866	12.3	-21.5	-802.4	0.572	-929.6

## CONCLUSION

This work is employing 3-(5-(3-methyl-1-phenyl pyrazolazo)-1-nitroso-2-naphthol) was successfully applied for the estimation of Iron(III) ion. Due to the sensitivity, rapidly and selectivity of the method, its application can be estimation of this ion in biological sample. The cyclic voltammetric system of (MPANN) led to the formation of same hydrazine derivative which remains at the electrode surface according to equations:



The cyclic voltammetric system of complex (MPANN-Fe) led to the formation of two reagent molecule and Iron (III) ion.

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