Spectrophotometric Determination of Fe(II)&Ni(II) as Complexes with New Derivative of Antipyrine azo Orcinol

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ABSTRACT

A spectrophotometric method was developed for the determination of Fe(II) and Ni(II). The method was based on the formation of Fe (II), Ni(II) 4-[(4-antipyl azo)]orcinol(APAO) complexes. The complexes have been characterized by spectroscopic methods such as UV-Visible ,FT-IR,molar conductivity measurements ,melting points . The maximum absorbance of complexes are at 469 and 461nm with molar absoptivity of (0.4032×10^4) and (0.107×10^5) $L.mol^{-1}.cm^{-1}$ of Fe(II) and Ni(II) respectively .Mole ratio of the complexes which is formed between Fe(II) and Ni(II) with APAO are 1:2 and 1:1 which was calculated by both the mole ratio and continuous variation methods. The absorbance of the complexes obeys Beer´s law in the concentration range of (0.2-1.5)µg.ml for Fe(II)and (0.4-2.8)µg.ml for Ni(II). The stability constant of the complexes under optimized conditions and at room temperature was $(0.14 \times 10^7 ,0.14 \times 10^4)L.mol^{-1}$ for Fe(II) and Ni(II) respectively .this procedure can be carried out in the presence of many cations and anions in the presence or absence of the masking agents. The method was successfully applied to the determination of Fe(II) ion and Ni(II) in analytical samples.

Key words: 4-($\grave{4}$- antipyriyl azo) orcinol ,Iron(II) and Ni(II) determination ,spectrophotometry.
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INTRODUCTION

Azo –dyes widely used in analytical chemistry because of their ability to form coloured complex with many metal ion in water .In recent years they have been employed in sorption spectroscopic test method more extensively then in conventional spectrophotometry[1] . Also ,hetero aryl ring azo compounds are of considerable interest because of their chemistry and potentially beneficial biological activities ,such as anti bacterial ,antiviral and anti _malarial activities [2-4] for these reasons a number of these azo compounds were synthesized and their abilities as chelating ligands [5-8]. Azo compounds are know to be involved in a number of biological reaction such as inhibition of DNA,RNA and protein synthesis ,carcinogenesis and nitrogen fixation [9] .The pyrazole derivatives and its metal complexes can be used as inkjet ,they have got fastness properties for dying papers [10] and process high dying power on fibers [11]. Various methods for the assay of nickel (II) and iron (II) have been reported. adsorptive stripping voltammetry [12-15], reverse phase high performance liquid chromatography [16,17] ,flame and electro thermal atomic absorption [18-20] ,flow injection and flow injection –inductively coupled plasma optical emission spectrometry[21,22] and simple spectro photometric methods [23-28] . The aim of the present work is to develop an easy ,rapid method for the determination of nickel (II) and iron(II) .The method is based on the reaction of -[(4-antipyl azo)]orcinol(APAO),with forms coloured complexes which forms coloured complexes with Ni(II) and Fe(II) ions.

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MATERIALS AND METHODS

Experimental .
All chemical used were of analytical grade

Apparatus
Spectrophotometric measurements were made with shimadzu UV-Visible -1700 double beam spectrometric using (1.0) cm glass calls .The pH measurements were performed with AWTW pH –meter 720 . Electric molar conductivity measurements were carried out at room temperature using an Alpha digital conductivity model -800 .Vibration spectra were recorded an Testscan Shimadzu FT.IR 8000 series .

preparation of reagent (APAO)
The reagent was prepared by coupling orcinol with diazotate 4-amino antipyrin in alkaline alcoholic solution. A diazonium solution was prepared by taking 1g 4- amino antipyrin in 15 ml of ethanol and concentrated hydrochloric acid with 5 ml of distilled water ,and adding sodium nitrite solution drop wise at 0-5 ℃. Orcinol 1.2 g was dissolved in 50 ml of ethanol and 30 ml of 0.1M were added at (0-5℃) .The mixture was left to stand over night .The precipitate was filtered off and recrystallized from ethanol scheme 1.

preparation of Iron(II) complex
The complex was prepared by stoichiometric amount from ligand in 50 ml of ethanol then added drop wise with stirring to a stoichiometric amount 1:2 for Palladium salt in (25) ml hot distilled water. The solid product thus formed off , washed with ethanol and dried .

preparation of Nickel (II)complex
The complex was prepared by stoichiometric amount from ligand in 50 ml of ethanol then added drop wise with stirring to a stoichiometric amount 1:2 for nickel salt in 25 ml hot distilled water. The solid product thus formed off , washed with ethanol and dried .

Reagents
Iron (II) stock solution (1000 $\mu g.ml^{-1}$)
Dissolve 0.0271 gm of $FeSO_4$ in 500ml of distilled water, working standard Fe(II) solution were prepared by dilution of the appropriate volume of standard Fe (II) solution (100 µg/ml) with distilled water .

Nickel (II) stock solution (200µg ml $^{-1}$)
Dissolve 0.4033 gm of $NiCl_2 .6H_2O$ in 500ml of distilled water ,working standard Ni (II) solution were prepared by dilution of the appropriate volume of standard Ni(II) solution (100 µg/ml) with distilled water .

2. 4-(4- antipyriyl azo) orcinol ($1x10^{-3}$ M)
0.0338 gm of regent (APAO) was dissolved in250ml of ethanol.

Foreign ion solutions (100 µg ml^{-1})
These solutions were prepared by dissolving an amount of the compound in distilled water completing the volume in a volumetric flask.

Recommended procedure for determination of Fe (II) and Ni(II)
In to a series of 10 ml calibrated flask, transfer increasing volume of Fe (II) and Ni(II) working solutions (100 µg ml^{-1}) to the range of the calibration curve, add 1.5 ml and 2.5 ml of $5x10^{-4}$M of (APAO) for Fe(II) and Ni(II) respectively .The pH (8.0,6.5) for Fe (II) and Ni (II) was adjusted by 0.05 M HCl and NaOH . The complexes formed were solubilized in water and diluted up to 10 ml with distilled water. The concentration range 0.2-1.5 µg/ml and 0.4-2.8 µg/ml of Fe(II) and Ni(II), respectively . Measure the absorbance at 469 nm for Fe(II) and at 461 nm for Ni(II) complexes against a reagent blank .

RESULTS AND DISCUSSION

Properties of APAO and its metal chelates APAO is a didentate with coordination of azo group nitrogen and carbonyl groups; it has following structure:

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4(4´-antipyriyl
azo)orcinol
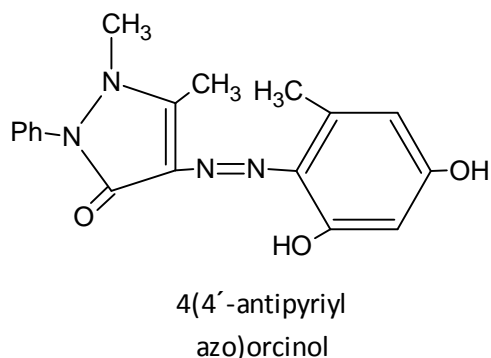
Owing to the large conjugated, the compound showed excellent chelation ability to form metal chelates. APAO and its metal chelates can be easily solubilited in an aqueous solutions .

The mechanism of reagent reaction.
The reaction sequence in procedure of reagent involves tow steps. In the firstly 4-amino antipyrine react with nitrite to form diazoniuum ion the second including the diazanium ion is coupling with orcinol to form dark yellow azo dye[29,30].scheme 1.
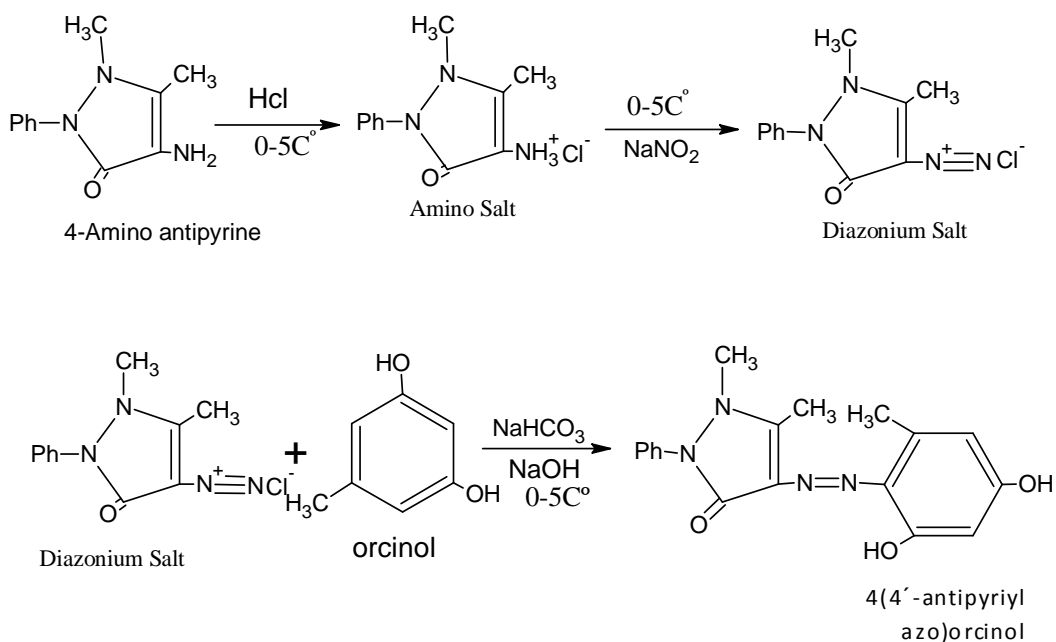
Scheme 1: The reaction of antipyrine and orcinol

The effect of various parameters on the absorbance intensity of the formed products were studied and the reaction conditions were optimized .

Absorption spectra
The results of this investigation indicated that the reactions of Fe(II) and Ni(II) with 4(4´–pyrazolon azo) orcinol yields highly soluble colored complexes which can be utilized as a suitable assay procedure for determination of Fe(II) and Ni(II). These colored complexes have a maximum a absorption at 469 nm for Fe(II) and at 461 nm for Ni(II),the blank at these wavelengths shows zero absorbance Fig 1, 2.
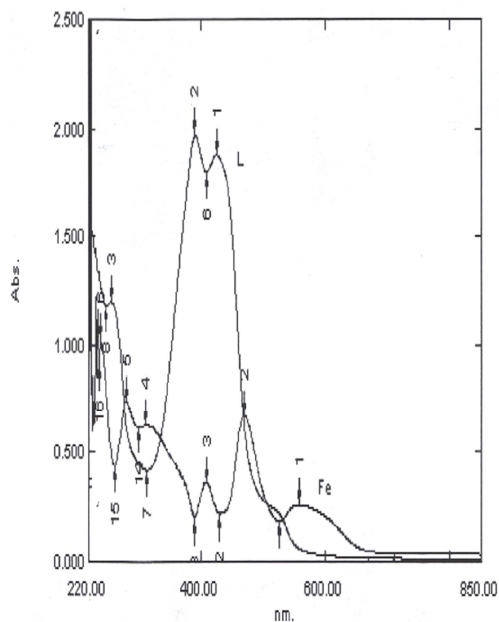
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Fig.1. Absorption spectra of (R-Fe) treated as described under procedures and measured against a reagent blank and R the reagent blank against ethanol
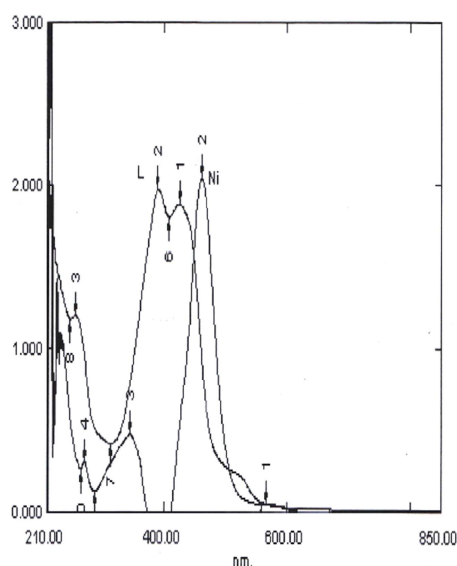

Fig.2. Absorption spectra of (R-Ni) treated as described under procedures and measured against a reagent blank and R the reagent blank against ethanol

The effect of various parameters on the absorption intensity of the formed products was studied and the reactions condition were optimized.

Effect of pH
To establish the optimum condition (stability of the product from the reaction of Iron (II) ion with the azo reagent, minimum blank value and relatively rapid reaction rate), the effect of pH (4.0-9.5) was studied . Only pH 8.0 and 6.5 was found to be optimum for Pd(II) and Ni(II) . Acid and alkaline results in low sensitivity and was not stable for Fe(II) and Ni(II) respectively. pH change on the electronic absorption spectra of the complex was studied by adding a small amount of 0.05 M HCl and 0.05 M of NaOH .The UV-Visible spectra of complexes gives the band centered at 469 nm for Pd(II) and at 461 nm for Ni(II) .The bands appearing in the range of 279-311 nm for Fe (II) and 216-345 are attributed to $\pi \rightarrow \pi^*$ transition. The other band observed in the region of 498 and nm is attributed to $n \rightarrow \pi^*$ electronic transition[31-33] for Fe(II) and Ni(II) respectively Fig.3 Table l.
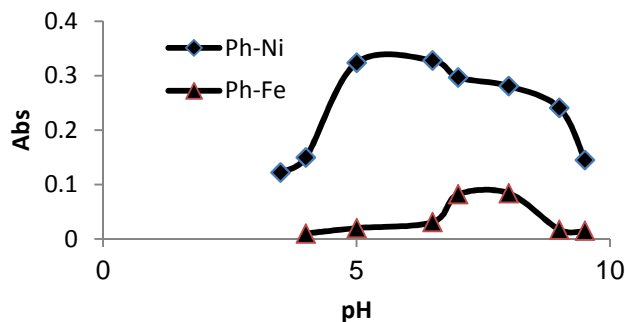
Fig .3.Effect of pH

Effect of regent concentration

various concentrations of APAO solution were added to a fixed amount of Fe(II) and Ni(II) 1.5ml and 2.5 ml of $5\times10^{4-}$ M where found enough to develop the color to its full intensity and give a minimum blank value and were considered to be optimum for the concentration range (0.2-1.5) (0.4 -2.8) µg/ml of Fe(II) and Ni(II) respectively Fig 4 .
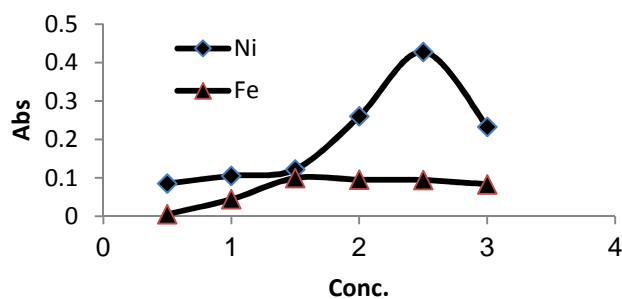

Fig .4.Effect of concentration

Effect of reaction time

The color intensity reached a maximum after the Fe(II) and Ni(II) has been reacted immediately with APAO therefore one minute development time was selected in the general procedure. The color obtained was stable for a least 24 hr Fig 5.
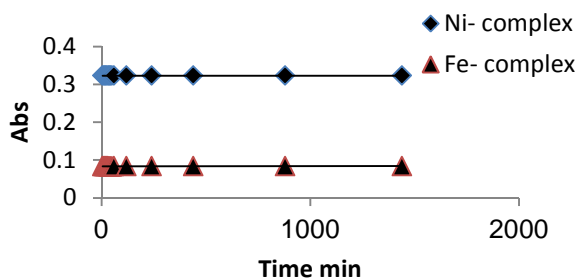

Fig .5.Effect of time

Effect of temperature

The effect of temperature on the colour intensity of the product was studied .In practice, the same absorbance was obtained when the colour was developed at room temperature (30-40°C) a loss in color intensity and stability were observed ,therefore it is recommended that the colour reaction should be carried out at room temperature for both complexes Fig.6.
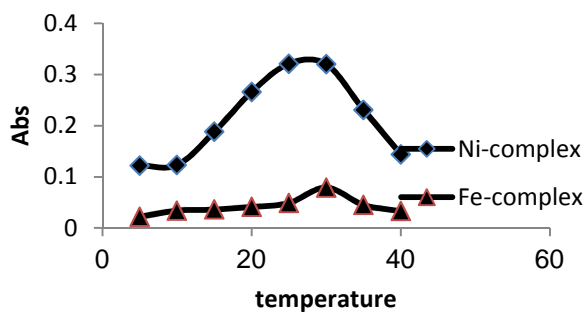
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Fig .6.Effect of temperature

Order of addition of reagents

To obtain the optimum results, the order of addition of materials should be followed as give by the procedure, otherwise a loss in stability are observed.

Table 1 :-Analytical characteristics of Pd-APAO and Ni-APBP complexes .

Characteristic	Fe (II)	Ni(II)
Absorption maxime (nm)	469 nm	461 nm
Berrs low range (μg/ml)	0.2-1.5	0.4-2.8
pH range	7-8	5-6.5
Sandell ᐧS sensitivity μg.cm^{-2}	0.05	0.015
Molar absorptivity (L.mole^{-1}.cm^{-1})	0.403 x10^4	0.107 x10^5
Stability constant (L.mol^{-1})	0.14×10^7	0.14 x10^4

Calibration graph

At optimum conations ,a linear calibration graphs for Fe (II) and Ni(II) were obtained ,that Beers low is obeyed over the concentration range of (0.2-1.5 ppm) and (0.4-2.8 ppm) with a correlation coefficient (0.9979) and (0.9894) respectively. The results of analytical performance are summarized in Table 1.

Interferences

The effect of diverse ions in the determination of these metal ions were studied. To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions. In the experiment, a certain amount of standard iron (II) or nickel (II) solution, coexisting ion solution and masking agent (or absence of masking agent) were added. The results are listed in Table 2.

Table 2 :- Effect of foreign ions

Foreign ion	Amount added μg/ml	Interferences with Fe(II)	Interferences with Ni(II)
Fe^{+3}	100	-	12.3
Zn^{+2}	100	0.12	0.23
Mn^{+2}	100	0.46	1.20
Ag^{+1}	100	-0.01	0.08
Cr^{+3}	100	-0.12	0.21
Co^{+2}	100	31.40	23.50
Pb^{+2}	100	19.32	22.13
Ni^{+2}	100	56.86	-
Cd^{+2}	100	26.86	13.60
Pd^{+2}	100	-0.07	0.53
Cu^{+2}	100	34.45	22.60
Cl^{-1}	100	-0.08	0.03
SO_4^{-2}	100	0.09	0.04
CO_3^{-2}	100	0.06	0.01
NO_3^-	100	0.31	-0.12
NO_2^-	100	0.46	-0.23

In the experiment ,a certain amount of standard Fe (II) or Ni(II) solution coexisting ion solution and masking agent (or absence of masking agent) were added .It is found that large amount of, Ag^+, $CO_3^=$, Mn^{+2}, Zn^{+2}, KCN, NaF, EDTA and ascorbic acid do not interfere the determination of Fe(II) and Ni(II) .comparing in the presence of masking agents KCN,EDTA, NaCN, NaF and ascorbic acid test cations .Its found that Cu^{++},Co^{++}, Cd^{+2},Pb^{+2}, Ni^{+2} and Fe^{3+} interfere seriously .However, their interferences are masked efficiently by addition of 1.5 ml of (0.1M) NaCN,2.0 ml of (0.1M) EDTA and 1.5 ml of (0.5 M) ascorbic acid .

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Conductivity measurements

The solubility of the complexes in dimethylformide   and ethanol permitted of the molar conductivity of 10^{-3} M solution at 25C° and , by comparison, the electrolytic nature for complexes .The low values of the molar conductance data listed in Table 3 indicate that the complexes are electrolytes.

Table.3:Conductivity values of complexes

Complex	Molar conductivity S mole^{-1} cm^2	
	DMF	Ethanol
Fe(APAO)$_2$XH$_2$O	50.3	60.6
Ni(APAO) $_2$XH$_2$O	161.5	105.8

Composition of the complexes

The FT.IR bands of the (APAO) and its iron(II) and nickel (II) complexes with their probable assignment are give in Table. 4 .The stretching band of υ(N=N) in the free ligand is observed at 1585 cm^{-1}.This band is shifted to lower with low intensity 1535 and 1521 cm^{-1} frequency value upon complexation for both Fe(II) and Ni(II) respectively .Also the FT-IR spectrum of the ligand reveled a sharp band at 1650 cm^{-1}dueto (C=O) .This band is shifted to lower with low intensity 1635and 1624 cm^{-1}frequency in the complex indication to the metal ion[34,35] .The bonding of oxygen to the metal ion provided by the occurrence of bands at 510 and 495 cm^{-1} as the result of υ(M-O)[36] . The compoisition of complexes was studied in the excess of reagent solution by the mole – ratio method. A break at a 1:2 (M:L) mole ration suggested the formation of both complexes where M=Pd(II),Ni(II) and L=APAO under the given condition .Fig 7,8.
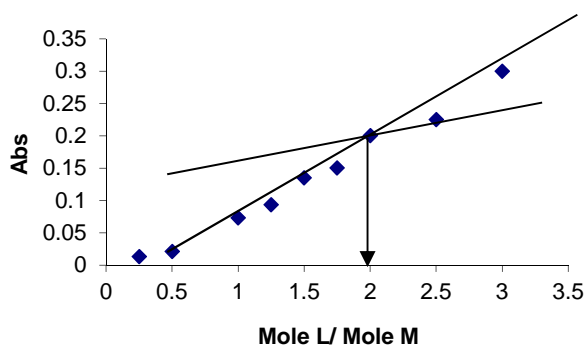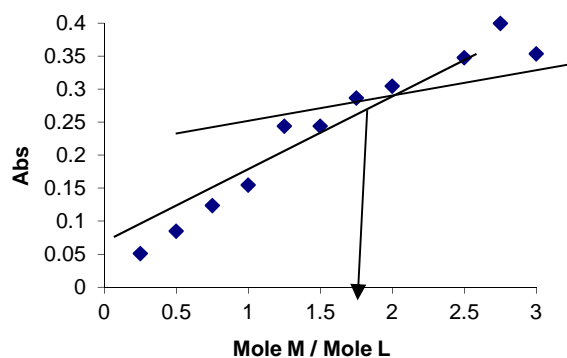

Fig .7.Mole-ratio method of Fe –Complex

Fig .8.Mole-ratio method of Ni -Complex

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Table 4:- Selected IR data of (APAO) and its complexes with Fe(II)&Ni(II)

Compound	ν (C=N)	ν(N=N)	ν (C=O)	ν (M-O)	ν (M-N) azo
H₂L	1685s	1558m	1650s	-	-
[Fe(HL)₂]XH₂O	1545s	1535m	1630s	510w	430w
[Ni(HL)₂]XH₂O	1555s	1521m	1625s	495w	435w

S: sharp, m: medium ,w: weak

On the basis of FT-IR and stoichiomtric data the structure of complex can by suggested as follows Fig.9.
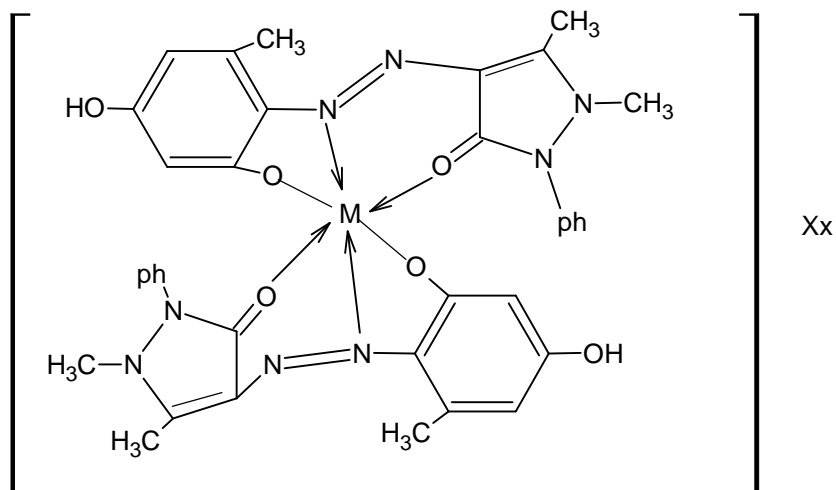
M =Fe ,Ni

x= cl ,SO₄

Fig(9) :- The proposed structural formula of complexes with (APAO)

Application
The propose method ware applied to the determination of Fe(II) and Ni(II) in synthetic mixture were analyzed by the procedures described above and results displayed in Table .5.

Table 5:- Determination of Fe(II) in synthetic mixtures and Ni(II)

Composition of mixture µg.ml⁻¹	Found by present method µg.m⁻¹	*%R.SD of the Fe(II) and Ni(II) complex
Fe⁺⁺(1ppm) ,Mn⁺⁺(10) ,Co⁺⁺(10),Cd⁺⁺(10	1.02	1.8
Ni⁺⁺(2ppm),Fe⁺⁺⁺(10),Mn⁺⁺(10),Cd⁺⁺(10)	1.97	2.3

For five determinations

CONCLUSION

In the present work, a new, simple and sensitive method with the Fe(II) and Ni(II) - APAO complexes was developed for the determination of Iron (II) and Nickel in biological, and certified samples .The analytical results were satisfactory. The proposed method should be useful for accurate, precise and rapid determination of Fe(II) and Ni(II).

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