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Rapid and Simple Spectrophotometric Determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) Ions in Natural Samples Using 2-(2-Hydroxynaphth-1-ylazo)-pyridine

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THE MEDIUM effect on the electronic absorption spectra of 2-(2-hydroxynaph-1-ylazo)-pyridine (HL) was studied. 2-(2-hydroxynaph -1-ylazo)-pyridine has been found to be a good chromogenic reagent for determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions. In aqueous buffer solution of different pH values (2-12) containing 30 % (v/v) methanol-water, HL reacts with Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions to form 1:1 and 1:2 (M:L) chelates. The formed complexes exhibiting absorption maxima at 580, 555, 577, 561 and 551 nm with apparent molar absorptivities 2.42 x 10^4, 0.58 x 10^4, 2.14 x 104, 4.54 x 10^4 and 2.09 x 10^4 (L mol^{-1} cm^{-1}) for Mn(II), Fe(III), Co(II), Ni(II) and Cu(II)-complexes, respectively. The optimum conditions (pH, time, temperature, reagent concentration, sequence of addition and solvent ratio) for chelates formation are studied. The spectrophotometeric analytical characteristics (linearity ranges, Ringbom ranges, stability constants and free energy changes) of the formed complexes are determined. Relatively large amounts of co-existing elements, including all other metals, can be tolerated. The advantages of this method are: simple and rapid, with high sensitivity and good selectivity and was applied to the determination of the mentioned metal ions in natural samples with satisfactory results. Some solid HL-complexes are prepared and studied by different analytical and spectral techniques in order to investigate the mode of bonding in the formed complexes.

Keywords: 2-(2-Hydroxynaph-1-ylazo)-pyridine, Mn(II), Fe(III), Co(II), Ni(II), Cu(II) determination.

The arylazo pyridine dyes are very important class of colorants (1). The success of azo compounds as choromogenic reagent is due to the simplicity of their synthesis by diazotization and azo coupling. Also, numerous numbers of azo dyes with different

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structures can be obtained by variation of the diazo compounds and the coupling components. These compounds generally have high molar extinction coefficient, and medium to high light and wet fastness properties. A series of azodyes was derived from pyridine as the coupling components and various diazonium salts. The absorption of these dyes was limited to the spectral region between green-yellow and orange (2, 3). The physico-chemical properties of arylazo pyridine derivatives are closely related to their tautomerism(3,4). On the other hand, N-heterocyclic azophenols are known to react with Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions forming colored complexes which can be used for the detection and estimation of these metal ions(5-10) . 2,6-Bis(1-hydroxy-2-naphthylazo)pyridine was used as a sensitive reagent for iron(11) and pyridyl-2-azo-chromotropic acid (disodium salt) is proposed as a reagent for the determination of nickel and cobalt in the presence of many ions(12). These methods which based on the UV-Vis spectrophotometry technique are widely used, due to the resulting experimental rapidity, simplicity, and wide applications. The present method is concerned with the possibility of using 2-(2-hydroxynaph-1-ylazo)-pyridine (HL) as a new chromogenic reagent for determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions in investigated samples. The spectral characteristics of the used ligand in different media are studied. The structures of the resulting complexes are investigated and their spectrophotometric analytical characteristics are determined.

Experimental

All chemicals were analytical-reagent grade and deionized water was used through the preparations. 2-(2-Hydroxynaph-1-ylazo)-pyridine was purchased from Aldrich.

Solutions and reagents

Stock solutions ($1x10^{-3}$ M) of manganese, iron, cobalt, nickel and copper ions were prepared from their acetate salts. The prepared solutions were standarized as previously recommended (13, 14). More dilute solutions were obtained by accurate dilution with appropriate amount of bidistilled water. A stock azo dye solution ($1x10^{-3}$ M) was prepared by dissolving an accurate amount of the reagent (97 % purity) under investigation in the required volume of methanol and the required lower concentrations were freshly prepared by accurate dilution. Universal buffer solutions (pH 2-12) were prepared by mixing phosphoric, acetic and boric acids. 0.04 M of each chemical solution and sufficient amount of 0.2 N NaOH is added to 100 ml of the mixture(15).

Apparatuses

All UV-Vis spectral measurements were performed out at room temperature within the wavelength range 190-700 nm using a Shimadzu UV–Vis (2450-220V) double beam recording spectrophotometer. A digital ORION pH-meter model 201 of sensitivity ± 0.02 pH unit was used in adjusting the pH of the solutions. The elemental microanalyses (C, H and N) of the solid complexes were measured in the Microanalytical Center, Tanta University using a Perkin Elmer 2400 elemental analyzer. Electron spray ionization (ESI) mass spectra were recorded using a Shimadzu LCMS-2010 eV spectrometer at the Gakushuin University (Japan). Metal contents were determined complexometrically(13,14). The thermal gravimetric analysis (TGA) was carried out in a dynamic nitrogen atmosphere (20 ml min^{-1}) with a heating rate of 10 ◦C min^{-1} using Shimadzu TG-50 thermogravimetric analyzer in the temperature range 25-800°C. The molar conductivities (in DMF) of the solid complexes were measured using a conductance bridge of the type 523 conductometer. The IR spectra of the ligand and the solid complexes were recorded as KBr discs using a JASCO FT-IR-4100 spectrometer in the range 4000–200 cm^{-1}. The room temperature X-band powder electron spin resonance spectra of the complexes were recorded using Joel spectrometer model JES-FE2XG equipped with an E101 microwave bridge. The magnetic field was calibrated with dipicrylhydrazyl. Magnetic measurements were measured by Gouy's method using magnetic susceptibility instrument (20 Kilo Gauss) at room temperature. Molar susceptibilities were corrected for diamagnetism of the component atoms applying the Pascal's constants (16).

Preparation of the samples for measurements

Known amount of the standard solution of each cation, methanolic solution contains the required amount of the ligand and 4.0 ml of buffer solution of the recommended pH value were placed in a 10 ml measuring flask and completed to the mark with deionized water. The final concentration of these solutions reached 3.30, 2.75, 7.66, 3.52 and 6.35 ppm for Mn(II), Fe(III), Co(II), Ni(II) and Cu(II), respectively. Finally, the spectra of the solutions were measured against a blank solution prepared in the same manner without the metal ions.

Determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) in water samples

25 ml of the tap water, Nile water, and agricultural waste water samples were used for the determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) in the water samples. Each water sample was mixed with 10 ml HCl (conc.), 4 ml HNO_3 (conc.) and 5 ml $HClO_4$, the mixture was boiled for 3 min, and then filtered off . The obtained filtrate was evaporated until its volume became nearly 5 ml, and then the volume was completed with de-ionized water in 10 ml measuring flask. To 1 ml of the treated water sample, 3 ml ($1x10^{-3}$ M) methanolic solution of the azo dye and 4 ml of universal buffer solution of the recommended pH value were added in 10 ml calibrated flask and then diluted up with de-ionized water. The mixture was allowed to stand for 10 min. The absorbance at the maximum wavelength (λmax) was measured against a blank solution. The concentration of each metal ion was determined from its absorbance-concentration calibration graph (Fig. 2).

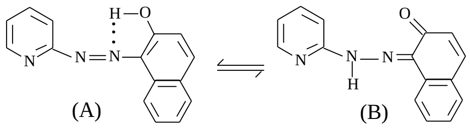
Preparation of the solid complexes

The solid chelates with stoichiometric ratio 1:1 (M:L) of the metal ions under test were obtained by mixing 0.001 mol solution of HL dissolved in 50 ml methanol with 0.001 mol of metal acetate dissolved in 30 ml bidistilled water. The mixture was then refluxed for ≈ 8 hr except for copper complex which formed at once, and allowed to cool. The formed precipitate was filtered off, washed with methanol and ether, then dried in vacuo over silica gel. The obtained solid complexes were studied using different analytical and spectral techniques in order to investigate the mode of bonding and geometry of the formed complexes.

Results and Discussion

Electronic spectra of HL in different organic solvents

UV-Vis spectra of the ligand were recorded over the range of 190-700 nm in ten organic solvents of different polarities, namely; methanol, ethanol, isopropanol, acetone, dioxane, DMF, chloroform, carbontetrachloride, toluene and benzene. The spectra display three main bands; the first band located at 225 nm and attributed to the moderate energy π—π^* transitions corresponding to $^1L_a \leftarrow {}^1A$ state in the aromatic moieties (17). The n—π^* transition within the N=N group is represented by the weak bands at ≈ 300 nm (18). These bands are nearly independent on by the type of solvent used. The longer wavelength band (above 400 nm) is due to an electronic transition involving charge transfer (CT) interaction within the whole molecule. This CT band appears as band and a shoulder at 450-465 and 408-415 nm, respectively. This may be attributed to the existence of azo-hydrazone tautomeric equilibrium originating from the OH group in *o*-position to the N=N center which can be represented as given in scheme 1(1,19). The CT band resulting from the absorption region of the lower energy site is due to the hydroxyl-azo form (A), while that at higher energy region may be attributed to the absorption by the *o*-quinone hydrazone (B) species(1,20).



Scheme 1. The azo-hydrazone tautomeric equilibrium and hydrogen bonding in HL.

The azo-hydroxy form is more stable due to its ability to form intramolecular hydrogen bonding (Scheme 1)(20). The CT band displays a general red shift with increasing the solvent polarity denoting higher stabilization of the excited state which is a good confirmation of the CT character of this band(21). This can be confirmed by determining the energy of this charge transfer band (in ethanol) from λ_{max} value using the relation (1) and comparing the obtained value with those calculated from the Briegleb relation (2)(22).

$$E_{CT} = 1241.6 / \lambda^{CT}_{\max} \qquad (1)$$

$$E_{CT} = I_p - (E_A + C) \qquad (2)$$

in which I_p: is the ionization potential of the donor part, E_A: is the electron affinity of the N=N acceptor group (-1.1 eV) and C is the columbic force between the electron transferred and the positive hole left behind (5.2 or 5.6)(22).

The obtained value for E_{CT} from equation (1) equals to ECT from equation (2) using C=5.6 and has small difference (0.37 eV) with it when C=5.2 (Table 1). The ionization potentials of HL were determined from the electronic absorption spectra applying the relation (3).

$$Ip = a + b\nu \qquad (3)$$

where a and b are constants having values (4.93 & 0.857)(23) (5.156 & 0.778)(24) or (5.11 & 0.701)(25); ν is the energy of the lowest π—π* transition. The values obtained together with the mean values are given in table 1. The value of the oscillator strength (*f*) of the CT band was also determined (Table 1) from equation (4); in which $\Delta\nu_{1/2}$ is the band width at half absorbance value and $\varepsilon_{\max}$ is the maximum molar extinction coefficient.

$$f = 4.6\mathrm{x}10^{-9}\, \varepsilon_{\max}\, \Delta\nu_{1/2} \qquad (4)$$

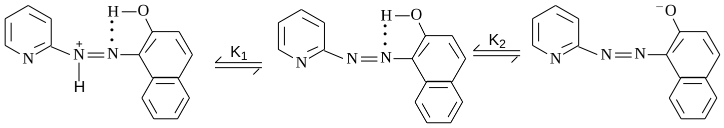
TABLE 1. Data obtained from UV/Vis spectra of HL in ethanol.

$\lambda_{\max}$ (nm)	**E_{CT} (eV) from $\lambda^{CT}_{\max}$**	**E_{CT} (eV) from Briegleb relation(22)**		**$\varepsilon_{\max}$**	***f***	**I_{P1} (eV)**	**I_{P2} (eV)**	**I_{P3} (eV)**	**Meane I_P (eV)**
465	2.67	**C = 5.6**	**C = 5.2**	2.00	0.522	7.218	7.33	6.981	7.144
		2.67	3.04						

$\varepsilon_{\max}$ is the molar extinction coefficient (L mol $^{-1}$ cm $^{-1}$ x 10^{-4}) and *f* is the oscillator strength (L mol $^{-1}$ cm $^{-2}$).

Electronic spectra of HL in buffer solutions of different pH values

The absorption spectra of HL (2 x 10^{-5} M) are studied in universal buffer solutions with different pH values containing 30 % (v/v) methanol-water mixture. The spectra displayed five bands at 225, 300, 410, 475 and 570 nm. The intensity of the first two bands has negligible changes with changing the pH. With increasing the pH from 2 to 8, the intensity of the third band decreases while that of the fourth band increases. This indicates that the equilibrium set in acid solution is between the protonated N-atom of the azo group and the deprotonated form of the molecule(18). With increasing the alkalinity of the solution (pH 8 to 12), the intensity of both the third and fourth bands decreases with a pronounced increasing in the intensity of the fifth band at 570 nm. This behavior may be attributed to the existence of two acid-base equilibria between three forms containing protonated N-atom of azo group, non-ionized and ionized OH groups (Scheme 2). This means that HL has two ionizable protons (hydrogen protonated to N-atom of the azo group and the hydrogen ion of the hydroxyl group; pK_1^H and pK_2^H). The pH-absorbance curves are utilized for the determination of the acid dissociation constant (pK_1^H) of HL using the half-height(26) and the limiting absorbance(27) methods (pK_1^H = 5.32 and pK_2^H = 10.51). The phenolic –OH group is weakly acidic, indicating a stronger hydrogen bonding (Schemes 1 and 2)(28).



Scheme 2. Acid-base equilibria in HL.

where K_1 and K_2 are the acid dissociation constants for this compound.

Analytical studies of HL complexes

Optimization

The electronic spectra of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes with HL were investigated in aqueous buffer solutions with different pH values and compared to those of the free ligand. The absorption spectra of the formed complexes are characterized by a new and intense band absorbing maximally at λ_{max}; 580, 555, 577, 561 and 551 nm for Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes, respectively which confirmed the formation of the chelate. The evaluation of the optimum condition for the determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions using HL as new chromogenic reagent included a careful investigation of all factors involved in the procedure. Measurements have shown that the absorbance of the formed complexes increases with increasing the pH of the medium (Fig. 1) due to decreased acidity of the medium and enhanced ionization of the hydroxyl group. The absorbance decreases at higher pH values due to formation of new species of the hydroxo-complex or presumably to the hydrolysis effect. The optimum pH values for maximum color development are 12, 3, 7, 6 and 4 for Mn(II), Fe(III), Co(II), Ni(II) and Cu(II)-complexes, respectively. Experiments on the effect of solvent ratio have shown that the clear colored complexes appear at a ratio 30% (v/v) methanol-water mixture. The results of the different sequences of addition to select the most suitable one for the maximum absorbance of the complexes under study show that the sequence ligand-buffer-metal ion is the best one for the formation of all complexes except for Co(II) complexes where the best sequence is ligand-metal-buffer. The absorbance of the complexes increases with increasing the reagent concentration and attained maximal and constant value when the reagent concentration becomes three times as that of the metal ion, so the amount of reagent is to be used in large excess. The effect of time showed that the color of the complexes is completely developed spontaneously and remains constant for at least 2 hr, then it suffers a slight decrease in absorbance and retains the original value by shaking. It was found that raising the temperature up to 45 °C has no effect on the absorbance of HL complexes with the metal ions under interest.

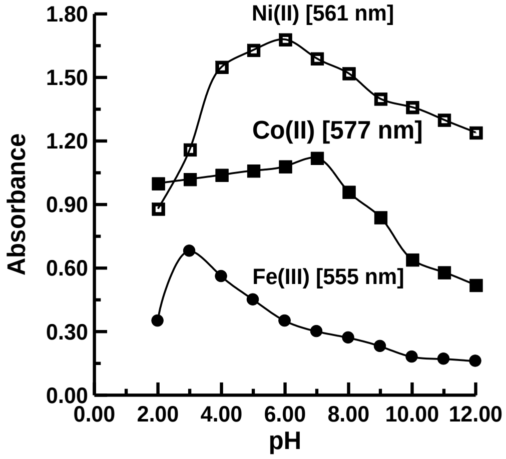


Fig. 1. Absorbance *vs* pH curves for Fe(III), Co(II) and Ni(II) complexes.

Composition and stability of the formed complexes

The stoichiometry of the formed chelates was determined by mole ratio, continuous variation, and logarithmic form of the straight line methods(29-31) which revealed the formation of 1:1 and 1:2 (M:L) complexes. The logarithmic stability constants (log β_n) and the free energy changes (ΔG^*) of the formed complexes were calculated from the data of continuous variation and mole ratio methods applying equations (5) and (6)(32).

$$\beta_n = \frac{\frac{A}{A_m}}{[1-\frac{A}{A_m}]^{n+1} C_l^n n^2} \rightarrow \qquad (5)$$

$$\Delta G^* = -RT \ln \beta_n \rightarrow \qquad (6)$$

where β_n is the stability constant of the metal chelate, A is the absorbance at ligand concentration C_L, A_m is the absorbance at full color development, n is the order of the formed complex, T is the absolute temperature and R is the gas constant. The obtained values (Table 2) for 1:2 (M:L) complexes are nearly double those of (1:1) complexes which reveal that the stability of the complexes increases with increasing the number ligand molecules attached to the central metal ion.

Calibration graphs and quantification

Regarding *Beer's* law, it was found to be obeyed satisfactory up to 3.30, 2.75, 7.66, 3.52 and 6.35 ppm for Mn(II), Fe(III), Co(II), Ni(II) and Cu(II), respectively (Fig. 2). The absorbance-concentration plots have very small standard deviations and their correlation coefficients are very high which confirm the possible application of these calibration curves for the spectrophotometric micro-determination of the metal ions under interest.

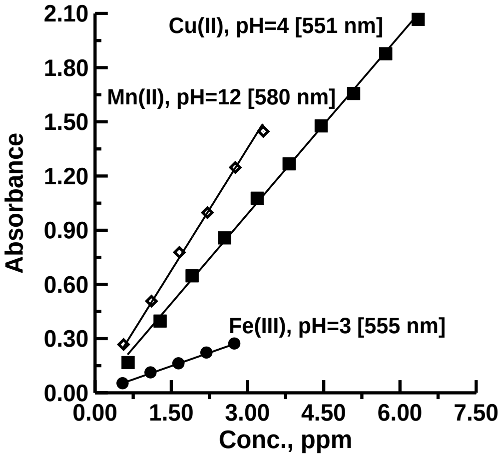


Fig. 2. Absorbance *vs* concentration plots for Mn(II), Fe(III) and Cu(II) complexes.

The optimum working ranges for the determination of each metal ion using HL were determined from Ringbom plots(33) (Table 2). The molar absorptivities for these complexes are 2.42 x 10^4, 0.58 x 10^4, 2.14 x 10^4, 4.54 x 10^4 and 2.09 x 10^4 L mol^{-1} cm^{-1} whereas the *Sandell* sensitivities(34) were found to be 0.0023, 0.0097, 0.0028, 0.0013 and 0.0030 (μg/cm^2) for Mn(II), Fe(III), Co(II), Ni(II) and Cu(II)-complexes, respectively.

TABLE 2. The optimum conditions and analytical characteristics of HL-complexes.

Metal ion	pH (λ_{max})	M/L Ratio	Log β_n	- ΔG*	ε x 10^{-4} (S.S.)	U.L. *Beer* (R.R.)	C.C. (S.D.)
Mn(II)	12.0	1:1	5.40	7.36	2.4152	3.30	0.9996
	(580)	1:2	11.50	15.67	(0.0023)	(0.55-2.20)	(0.0057)
Fe(III)	3.0	1:1	5.91	8.05	1.5923	2.75	0.9995
	(555)	1:2	11.60	15.81	(0.0097)	(1.10-2.20)	(0.0018)
Co(II)	7.0	1:1	5.23	7.36	2.1442	7.66	0.9999
	(577)	1:2	11.28	15.37	(0.0028)	(0.59-2.95)	(0.0010)
Ni(II)	6.0	1:1	5.00	6.81	4.5404	3.52	0.9999
	(561)	1:2	10.00	13.63	(0.0013)	(1.76-3.52)	(0.0002)
Cu(II)	4.0	1:1	5.96	8.13	2.0937	6.35	0.9992
	(551)	1:2	12.90	16.62	(0.0030)	(0.64-2.54)	(0.0040)

λ_{max} – a suitable wavelength in nm; log β_n – logarithm of stability constant; (ΔG*) – free energy changes (KJ mol^{-1}); ε – molar extinction coefficient (L mol^{-1} cm^{-1}); (S.S.) – Sandell sensitivity (μg/cm^2); U.L. *Beer* – upper limit in Beer's plot (μg mL^{-1}); (R.R.) – Ringbom range (μg mL^{-1}); C.C. – correlation coefficient; (S.D.) – standard deviation.

The obtained values (Table 2) reveal the stability of the complexes and the sensitivity of the proposed method. The detection limits were found to be 3.00 x 10^{-6} M whereas the limits of quantification were found to be 1.00 x 10^{-5} M, for all the metal ions under interest.

Effect of foreign ions

In order to assess the possible analytical advantages of HL as chromogenic reagent, the effect of diverse ions that often associate with Mn^{2+}, Fe^{3+}, Co^{2+} , Ni^{2+}, and Cu^{2+} ions were studied. The tolerance of the method to foreign ions was investigated with solution containing 16.50, 44.70, 17.70, 17.60, and 19.20 μg/10 ml^{-1} of Mn(II), Fe(III), Co(II), Ni(II), and Cu(II), respectively, and various amounts of foreign ions. The tolerance criterion for a given ion was taken to be the deviation of the absorbance values by more than 5% from the value expected for the metal ion alone. The obtained results (Table 3) reveal that the method can be applied for the spectrophotometric determination of trace amounts of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with out separation. The metal ions under interest have interference effects on each others in different pH values recommended for determination with various tolerance limits. From this study it is clear that, many ions have a very small interference effect except for the cations of the first transition series which interfere most strongly because they form colored complexes with the reagent used. On the other hand, the presence of CN^-, SCN^-, EDTA and CDTA causes a decrease in absorbance of spectral bands (<5%) and therefore they should not present in excess during the determination process.

TABLE 3. Tolerance limits of foreign ions in the determination of 16.50, 44.70, 17.70, 17.60, and 19.20 μg/10 ml^{-1} of Mn(III), Fe(II), Co(II), Ni(II), and Cu(II), respectively and various amounts of foreign ions.

Foreign ion	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)
$NaNO_3$	79.14	44.48	86.36	77.30	38.86
K_2SO_4	26.54	68.29	18.94	12.54	17.28
Mn^{2+}	—	14.36	19.30	19.90	37.40
Fe^{2+}	66.47	—	13.70	23.40	11.72
Co^{2+}	37.67	19.34	—	12.40	5.46
Ni^{2+}	29.89	13.43	15.26	—	24.80
Cu^{2+}	41.36	12.19	14.89	11.40	—
Zn^{2+}	27.94	16.55	18.30	15.40	16.62
Mg^{2+}	26.95	38.16	53.00	22.10	20.60
Al^{3+}	23.00	84.78	74.79	18.60	25.36
Carbonate	62.49	9.42	59.05	36.60	42.50
Phosphate	90.62	12.39	69.86	24.50	26.13
Chloride	34.68	39.70	15.58	13.40	12.31
Acetate	44.20	11.77	40.36	96.10	26.96
Iodid	13.21	24.00	197.08	45.90	12.80

Precession and accuracy

In order to determine the accuracy and precision of the proposed method, solutions containing 16.47, 21.97, 23.57, 17.61 and 19.08 µg/10 ml of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions were prepared and analyzed using HL at the recommended pH value and the suitable wavelength for each metal ion (six determinations each). The values of standard analytical error, relative error, standard deviation and coefficient of variation are very small indicating the high precision and good accuracy of the investigated method (Table 4).

TABLE 4. Accuracy and precession of the proposed method.

Parameter	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)
Taken (µg/10 ml)	16.47	21.97	23.57	17.61	19.08
Found[a] (µg/10 ml)	16.42	21.91	23.52	17.54	19.04
Standard error	0.05	0.06	0.05	0.07	0.04
Error (±%)	0.30	0.27	0.21	0.40	0.21
Standard deviation (S.D.)	0.09	0.08	0.06	0.12	0.05
Coefficient of variation (C.V.)	0.55	0.36	0.26	0.68	0.26

[a] Average of six determinations.

Application of the proposed method

To confirm the usefulness of the proposed method, it was extended for the determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions in different water samples using HL as new chromogenic reagent as described in the experimental part (Table 5). Comparison between the experimental mean values obtained by the investigated method and the values obtained by AAS was carried out by calculating F- and t-values (Table 5). It was found that for the investigated method F-values = 1.08-3.22 and t-values = 0.87-2.10 for five degree of freedom (P=0.05) and six replicates (n=6) at 95 % confidence level. The tabulated values did not exceed the theoretical F-values (5.05) and t-values (2.57)(35) which mean that all samples are not subjected to systematic error (accurate). Also, the values of standard deviation (SD) and variance coefficient (VC) are very small indicating high precision of the proposed method.

Mode of bonding in the formed complexes

In order to elucidate the structure of the formed complexes, the solid [1:1 (M:L)] complexes of HL with Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions were prepared and subjected to different analytical and spectral techniques. All the metal complexes are stable and non-hygroscopic in nature. The complexes are insoluble in common organic solvents but soluble in DMF and DMSO. The elemental analysis shows that, Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) complexes are of the type $[ML(AcO)_m(H_2O)_n].xH_2O.yCH_3OH$ wherein HL acts as a bidentate ligand.

TABLE 5. Spectrophotometric determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions in various natural water samples.

Water sample	Metal ion	Conc. of the metal ion (µg/25 ml)		F-value	t-value	S.D.	V.C.
		Using AAS	Using HL				
Tap water [A]	Mn(II)	32.10	32.45	2.10	1.88	0.248	0.773
	Fe(III)	60.21	60.64	1.55	1.34	0.304	0.505
	Co(II)	28.33	28.64	3.22	2.10	0.291	1.027
	Ni(II)	66.50	66.23	1.42	1.04	0.191	0.287
	Cu(II)	42.33	42.68	1.68	0.95	0.248	0.586
River water [B]	Mn(II)	33.45	33.66	1.96	1.46	0.148	0.442
	Fe(III)	64.00	64.28	2.54	1.13	0.207	0.322
	Co(II)	29.44	29.67	2.32	1.24	0.163	0.554
	Ni(II)	67.52	67.22	1.56	1.21	0.212	0.314
	Cu(II)	44.87	44.52	1.62	0.87	0.248	0.553
Agricultural waste water [C]	Mn(II)	34.44	34.21	1.99	1.56	0.163	0.473
	Fe(III)	62.23	62.55	1.08	0.88	0.226	0.363
	Co(II)	31.00	31.24	2.05	1.49	0.170	0.548
	Ni(II)	68.88	68.65	1.64	1.33	0.163	0.237
	Cu(II)	46.00	45.82	1.84	1.54	0.127	0.276

Theoretical F-values at 95% confidence level = 5.05.

Theoretical t-values at 95% confidence level = 2.57.

AAS: Atomic absorption spectroscopy; S.D.: Standard deviation; V. C.: Variance cofficient; [A]: tap water sample, [B]: water sample from Nile branch, [C]: agricultural waste water sample (all samples were collected from Kafr-Elshikh city, Egypt).

The electron spray ionization mass spectra of $[MnL^1(AcO)(H_2O)3].8H2O$ (1), [CoL(AcO)(H2O)3].4H2O.2CH3OH (3), [NiL(AcO)(H2O)3].4H2O.2CH3OH (4) and [CuL1(AcO)(H2O)3].4CH3OH (5) showed a molecular ion peak M^+ at m/z 560.1, 556.2, 552.2 and 555.1, respectively that are equivalent to their molecular weights which is in satisfactory agreement with the suggested molecular formulae (Table 6).

TGA curve of Fe(III)-HL complex gives excellent information about the structure of the formed complex. $[FeL(AcO)_2(H_2O)_2].2H_2O$ (**2**) was thermally decomposed in four successive decomposition steps. The first estimated mass loss of 7.45 % (calcd. 7.29 %) within the temperature range 80–100 ºC is attributed to the volatilization of two hydration water molecules. The second step occurred within the temperature range 110–220°C with an estimated mass loss 7.55 % (calcd. 7.29 %), can be accounted for the removal of two coordinated water molecules. The third decomposition step corresponds to the loss of two coordinated AcO^- anions with an estimated mass loss of 23.67% (calcd. 23.89%) within 230-400°C temperature range. The last step occurred within 410-630ºC temperature range is due to the removal of ligand molecule leaving Fe_2O_3 as metallic residue with an estimated weight 32.50 % (calcd. 32.31 %). All these data infer the analytical and physical measurements which are in agreement with proposed molecular formulae for the obtained complexes (Scheme 3). The molar conductance values (Table 6) are very low to account for any dissociation of the complexes in DMF, indicating the nonelectrolytic nature of the complexes(36).

TABLE 6. Elemental analysis and physical properties of the HL-metal complexes.

Com. No.	**Mol. Wt. (Cal. Mol. Wt.)**	**Color (Λ_m)**	**Elemental analysis**			
			Found % (Calcd.)			
			%C	**%H**	**%N**	**%M**
1	560.10	Reddish orange	36.82	6.70	7.85	10.21
	(560.41)	(21.82)	(36.44)	(6.29)	(7.50)	(9.80)
2	493.66	Dark purple	46.62	4.96	8.88	11.71
	(494.26)	(20.8)	(46.17)	(4.89)	(8.50)	(11.30)
3	556.20	Dark red	41.50	6.52	7.41	10.88
	(556.43)	(18.55)	(41.01)	(6.34)	(7.55)	(10.59)
4	555.20	Greenish brown	41.33	6.69	7.74	10.29
	(556.20)	21.32)	(41.03)	(6.34)	(7.56)	(10.55)
5	555.10	Bright brown	45.77	6.74	7.48	11.77
	(553.07)	(22.69)	(45.61)	(6.38)	(7.60)	(11.49)

[a] All the synthesized complexes decompose with out melting above 280 °C. Yield = 82%. Mol. Wt. = Molecular weight obtained from mass spectra and TGA measurements. ($\Lambda_{m)}$ = Molar conductance (Ω^{-1} cm^2 mol^{-1}).

IR spectral studies

Useful information about the structure of the ligand in the free and bonded states as well as the groups involved in complex formation can be obtained by comparing the prominent infrared spectral bands of azodye (HL) with those of the metal complexes (Table 7). The IR spectra of free ligand display bands at 3427, 1677 and 1435 cm^{-1}, assigned to ν(O-H), ν(C=O) and ν(N=N)(37,38), respectively, in addition to a band at 3047 cm^{-1} assigned to ν(N-H). Such IR data could be taken as a new evidence for the existence of this compound as a mixture of enolazo and ketohydraz tautomeric forms in the solid state owing to the presence of a hydroxyl group adjacent to N-H and CH as shown in Scheme 1. In the IR spectra of the HL complexes, the ν(N-H) disappeared, indicating that HL reacts with the metal ions in its enolazo form(39) whereas the appearance of ν(C=O) in the 1602-1620 cm^{-1} range can be attributed to the acetate group attached to the metal ion. Mn(II) and Fe(II), Co(II), Ni(II) and Cu(II), complexes exhibited the band of ν(N=N) in the region 1439-1467 cm^{-1}; showing the shift of band to higher wave numbers indicating coordination of N=N group to the metal ions, a result which is substantiated by the appearance of bands at 410-440 cm^{-1} region that is assignable to ν(M-N)(40). The spectra of all complexes show broad bands centered in the 3419-3452 cm^{-1} range, strong to medium bands in the 1201-1207 cm^{-1} and bands in the 822-842 cm^{-1} ranges are assignable to stretching, scissoring and twisting/rocking vibrational modes of coordinated water molecules, respectively(40). Also, HL complexes show non-ligand bands in the 484-511 cm^{-1} range due to ν(M-O)(40). Thus the IR spectral results provide strong evidences for the complexation of HL with metal ions in the enolazo form *via* the enolic oxygen of the o-hydroxyl group and the azo group in bidentate mode.

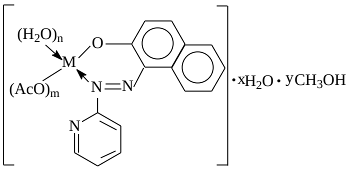
TABLE 7. Assignment of the important infrared frequencies (in cm^{-1}) of HL and its metal complexes.

No.	ν(OH) and/ or ν(H_2O)	ν CH (Ar)	ν C=O	ν C=N	ν N=N	δ OH	γ OH	ν M-O	ν M-N
HL	3427 (m)	2925 (w)	1677 (m)	1501 (s)	1435 (m)	1201 (s)	842 (s)	----	----
1	3444 (br)	2923 (w)	1620 (s)	1508 (s)	1439 (m)	1202 (s)	840 (m)	498 (w)	410 (w)
2	3452 (br)	2922 (w)	1602 (s)	1500 (s)	1450 (m)	1204 (s)	833 (s)	509 (m)	432 (w)
3	3423 (br)	2900 (w)	1605 (s)	1502 (s)	1467 (m)	1207 (s)	825 (s)	484 (w)	430 (w)
4	3419 (br)	2920 (w)	1608 (s)	1515 (s)	1440 (m)	1203 (m)	835 (m)	503 (w)	440 (w)
5	3419 (br)	2920 (w)	1604 (s)	1506 (s)	1448 (m)	1202 (s)	822 (m)	511 (w)	416 (w)

s = strong, m= medium, w= weak, br = broad.

Electronic, ESR spectra and magnetic moment measurements

The electronic spectrum of the Mn(II) complex in DMF displays absorption bands at 17391 and 19048 cm^{-1} corresponding to $^6A_{1g}\rightarrow{}^4T_{1g}$(G) and $^6A_{1g}\rightarrow{}^4E_g$(D) transitions, respectively, characteristic of octahedral geometry for d^5 system$^{(41)}$. The room temperature magnetic moment of complex 1 equals 5.91 B.M. which is indicative of the presence of five unpaired electrons. The solid state ESR spectra of complex 1 shows a broad signal with geff 1.5935 which confirms the existence of high spin Mn2+ complex has octahedral arrangement$^{(41)}$. The electronic spectrum of the Fe(III) complex 2 exhibits an absorption band at 17730 cm-1 can be assigned to 6A1g→4T1g transition in octahedral arrangement $^{(41)}$. Its magnetic moment value (5.14 B.M.) is in agreement with the high spin Fe(III) ion. Co(II) complex 3 shows absorption bands at 16393 and 17331 cm-1 due to 4A1g(F)→4T2g(F) and 4A1g(F)→4T1g(P) transitions in high spin octahedral Co(II) complex$^{(42)}$. Co(II) complex 3 exhibits magnetic moment value of 4.76 which is within the octahedral range of 4.3-5.2 BM$^{(43)}$. Complex 3 exhibits ESR broad signals with g-value (2.1755) characteristic of high spin octahedral Co(II) complex$^{(42)}$. Ni(II) complex 4 exhibits two bands at 17575 and 19120 cm-1, which are attributed to the 3A2g →3T1g(F) and 3A2g →3T1g(P) transitions indicating octahedral geometry around Ni(II) ion$^{(44)}$. Ni(II) complex showed the magnetic moment value of 3.24 which is within the range of 2.8-3.5 BM suggesting consistency with their octahedral environment$^{(43)}$. The electronic spectra of Cu(II) complex 5 displays a broad band at 14476 cm^{-1} is assignable to $^2T_{2g} \rightarrow {}^2E_g$ transition. The Cu(II) complex shows magnetic moment 1.75 BM, is slightly higher than the spin-only value 1.73 BM expected for one unpaired electron, which offers possibility of an octahedral geometry(45). On the basis of electronic spectra distorted octahedral geometry around Cu(II) ion is suggested(46) which is confirmed from the shape of ESR signals and g_{eff} value (1.6448 B.M.) of complex 5.



Scheme 3. Representative structure of HL complexes. Where m=1, n=3, x=8, y=0 for Mn(II)-complex (**1**); m=2, n=2, x=2, y=0 for Fe(III)-complex (**2**); m=1, n=3, x=4, y=2 for Co(II) and Ni(II)-complexes (3 and 4), while m=1, n=3, x=0, y=4 for Cu(II)-complex (5).

Conclusions

In conclusion, this study has demonstrated the feasibility of the use of 2-(2-hydroxynaph-1-ylazo)-pyridine (HL) as a new and good chromogenic reagent for determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions. The spectrophotometric and analytical characteristics of HL and its complexes with the mentioned metal ions are studied and discussed in relation to their molecular structures. With more study, further development and careful optimization, all factors affecting complex formation are studied. The proposed method has been applied successfully in determination of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions in tap water, Nile water and agricultural waste water samples with high precession and good accuracy. Based on the obtained results, the bonding of HL to metal ions in the obtained complexes can be determined (Scheme 3).

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التقدير الطيفي البسيط والسريع لأيونات المنجنيز والحديد والكوبلت والنيكل والنحاس في العينات الحقيقية باستخدام 2-(2-هيدروكسي نافث-1-يل ازو)-بيردين

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تم دراسة تأثير الوسط علي طيف الأمتصاص الأليكتروني ل2-(2-هيدروكسي نافث-1-يل ازو)-بيردين. حيث وجد أنه كاشف لوني جيد لتقدير أيونات المنجنيز والحديد والكوبلت والنيكل والنحاس. في الأوساط المائية متغيرة الرقم الهيدروجيني المحتوية علي 30٪ ميثانول يتفاعل مع أيونات المنجنيز والحديد والكوبلت والنيكل والنحاس ليكون متراكبات حلقية بنسب 1:1 و 2:1 (فلز:مرتبط). والمتراكبات المتكونه يكون لها قمم أمتصاص ضوئي عند طول موجي 580 و555 و577 و561 و551 نانو متر وبمعامل امتصاص $2.42 x 10^{4}$ و$0.58 x 10^{4}$ و$2.14 x 10^{4}$ و$4.54 x 10^{4}$ و$2.09 x 10^{4}$ لتر لكل مول لكل سنتيميتر لمتراكبات المنجنيز والحديد والكوبلت والنيكل والنحاس علي الترتيب. وتم دراسة الظروف القياسية (الرقم الهيدروجيني والزمن ودرجة الحرارة وتركيز الكاشف وترتيب الأضافة ونسبة المذيب) لتكون المتراكبات. كما تم تحديد الخواص الطيفية التحليلية (النطاقات الخطية و مدي رينجبوم وثوابت الاستقرار والتغير في طاقة التكوين) للمتراكبات المتكونة وتقدير التداخل من عدد كبير من الأيونات. وقد وجد ان هذه الطريقة هي طريقة بسيطة وسريعة ولها حساسية عالية وانتقائية جيدة حيث أمكن تطبيقها علي عينات حقيقية بنتائج مرضية. كما تم تحضير عدد من المتراكبات الصلبة ودراستها بالطرق الطيفية والتحليلية المختلفة وتحديد نوع الأرتباط في المتراكبات المتكونة.