

Spectrophotometric Determination of Iron in Different Samples Using some Azo Dyes Derivatives of 3-Amino-1,2,4-triazole

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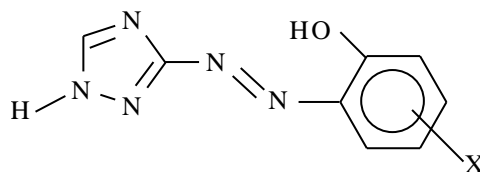
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Summary: The synthesis and analytical application of six azo dyes derived from coupling of 3-amino-1,2,4-triazole diazonium salt with some substituted phenols (Scheme 1) are described. These reagents react with Fe(II) in universal buffer solution to produce 1:1 and 1:2 (M:L) coloured complexes. The effect of pH, time, temperature, reagent concentration, sequence of addition and solvent ratio as well as diverse ions on the spectrophotometric determination of Fe(II) was investigated. Under optimal conditions, Beer's law is obeyed over Fe(II) concentration depending on the ligand used. L^1 , L^3 , and L^6 were found to be the most favorable reagents, which form intense red, green and brown complexes having absorption peaks at 530, 670 and 690 nm respectively. The method has been applied to the spectrophotometric determination of iron in soil, various natural waters and multivitamin samples with satisfactory accuracy.

Introduction

Due to the great importance of iron⁽¹⁻³⁾, a number of methods has been developed⁽³⁻¹⁰⁾ for its determination as ferric ion based on extraction of iron as a complex into an organic phase, followed by spectrophotometric measurement. These methods were not satisfactory due to coextraction and strong interference of many other metal ions.

In the present work, a new sensitive method for direct spectrophotometric determination of iron as ferrous ion without need to oxidation or extraction has been established. The method is based on the formation of stable colored Fe(II)-complexes with some azo dyes derived from 3-amino-1,2,4-triazole and substituted phenols (Scheme 1). A number of parameters have been evaluated. The developed method is employed for the determination of iron in different real samples with satisfactory results.



Scheme 1. Structure of the free ligands (L^1 - L^6).

X = m-OH (L^1), p-Br (L^2), p-COCH₃ (L^3),
p-COOC₂H₅ (L^4), p-CHO (L^5) and p-CH₃ (L^6)

Experimental

All chemicals used in the present investigation were of high purity from Aldrich, BDH or Porlabo. Bidistilled, deionized water was used throughout.

Solutions and reagents

Iron (II) stock solution (1×10^{-3} M) was prepared by dissolving the appropriate amount of FeCl₂ in bidistilled water and was standardized with EDTA⁽¹¹⁾. Working solutions were prepared by suitable dilutions with deionized water.

The azo dyes (L^1 - L^6) were prepared according to the recommended method⁽¹²⁾, recrystallized from ethanol and their structures were confirmed by elemental analysis and IR spectra.

The azo dyes (L^1 - L^6) stock solutions (1×10^{-3} M) were prepared by dissolving the accurately weighted amount of the dye in the required volume of methanol.

The solutions used for investigation of the effect of diverse ions were prepared from sulfate or nitrate of the tested cations and sodium or potassium salts of the tested anions.

The universal buffer solutions of varying pH values were prepared as described by Britton⁽¹³⁾.

Recommended procedures

Determination of Fe(II) in standard sample

To 0.5 ml (1×10^{-3} M) of iron (II), 4 ml (1×10^{-3} M) methanolic solution of the azo dye and 5 ml of universal buffer solution of the recommended pH value

were added in 10 ml calibrated flask and then diluted up to the mark with deionized water. The mixture was allowed to stand for 10 min. The absorbance at the maximum wavelength (λ_{\max}) was measured against a blank solution prepared in the same manner. The six calibration graphs were prepared by using the same procedure⁽¹⁴⁾ (eleven concentration points) and were linear passing through the origin.

Determination of total iron in soil sample

About 500 mg of a soil sample were dissolved in 50 ml HCl (1:1) and 15 ml of HNO₃ (1:2) by heating and stirring on a hot plate. The solution was cooled and filtered. The filtrate was evaporated and the residue was dissolved in 30 ml HCl (1:1) and diluted to 250 ml with deionized water. Fe(III) was reduced to Fe(II) by bubbling a fine spray of SO₂ [obtained from the reaction of HCl (1:1) with sodium sulfite] through the solution for at least 50 min, then the total content of iron was determined as described for standard sample.

Determination of total iron in various natural waters

100 ml of the Nile, tap and underground water samples were used for the determination of the total iron in the water samples. The iron content was reduced to Fe(II) ion by bubbling SO₂, then the iron content was analyzed according to the developed procedure.

Determination of Fe(II and III) in pharmaceutical multivitamins

In a 25 ml crucible, a definite weight of the pharmaceutical sample containing iron (II and III) was treated with few drops of nitric acid and digested at 500 °C. The residue was dissolved in 3-5 ml HCl and heated in a water bath for 2 min. Then it was diluted with 5-10 ml of doubly distilled water and filtered; if necessary, the crucible and the filter paper were washed three times with 5 ml portions of doubly distilled water. The iron content of the obtained solution was then determined after reduction of Fe(III) to Fe(II) according to the procedure used for the standard sample⁽¹⁴⁾.

Preparation of Fe(II)-L¹ solid complexes

A stirred solution of 0.001 or 0.002 mol of L¹ dissolved in 50 ml methanol was mixed with 0.001 mol of Fe(II) chloride dissolved in 30 ml of bidistilled water. The mixtures were stirred and refluxed for 6 h. The solid Fe(II)-complexes were separated and filtered off, then washed with dry methanol and dried in *vacuo*.

The solid complexes obtained were subjected to elemental and thermal analyses, conductance, IR, electronic spectra and magnetic susceptibility measurements in order to characterise their mode of bonding and geometry. Apparatus and working procedures were the same as those previously described⁽¹⁵⁾.

Results and discussion

Effect of pH and selection of suitable wavelength

Investigation of the effect of pH of solution on the absorption spectra of Fe(II)-complexes with ligands (L¹-L⁶) showed that the absorbance of the complexes depends on the pH of the solution. The optimum pH values for color development are listed in Table 1. Addition of 4.0-6.0 ml of universal buffer gave maximal and constant absorbance of the complexes, so addition of 5.0 ml of buffer solution was considered as appropriate.

As shown in Fig. 1, the absorption spectra of Fe(II)-complexes with ligands (L¹-L⁶) have three maxima, two of which overlap with the maxima of the ligands at shorter wavelengths below 500 nm. The third maximum appeared above 500 nm at which the ligands have no absorption peaks. The longer wavelength peak is attributed to increased delocalization of the π -electrons of the ligand on complexation which decrease the energy gap between the excited and ground states⁽¹⁶⁾. So these longer wavelength peaks have been used in all subsequent measurements of the absorbance.

The Fe(III)-complexes with L¹, L², L⁴ and L⁵ have strong absorption peaks at the same position of absorption peaks of Fe(II)-complexes with the same ligands (Fig. 1). So the Fe(II) sample must be freed from Fe(III) during measuring using these

ligands, whereas Fe(III)-complexes with L³ and L⁶ have too small absorption peaks within the absorption region of Fe(II)-complexes with the same ligands.

Table 1. Electronic spectral data of Fe(II)-complexes with ligands (L¹-L⁶).

Ligand	pH	λ_{\max} (nm)	Molecular stoichiometry			$\log \beta_n$	$-\Delta G^*$
			C.V.M.	M.R.M.	L.S.L.M.		
L ¹	10	530	1:1	1:1	1:1	4.29	24.88
			1:2	1:2	1:2	8.01	46.46
L ²	8	680	1:1	1:1	---	3.57	20.71
			1:2	1:2	1:2	7.07	41.98
L ³	8	670	1:1	1:1	1:1	3.96	22.97
			1:2	1:2	1:2	7.41	42.98
L ⁴	9	675	1:1	1:1	---	3.46	20.07
			1:2	1:2	1:2	7.01	40.66
L ⁵	10	585	1:1	1:1	---	3.75	21.75
			1:2	1:2	1:2	6.51	38.21
L ⁶	10	690	1:1	1:1	1:1	4.05	23.49
			1:2	1:2	1:2	8.51	49.36

Ligand	Beer's law up to ($\mu\text{g ml}^{-1}$)	ϵ $\text{l mol}^{-1}\text{cm}^{-1}$	S.S. $\mu\text{g cm}^{-1}$	C.C.	S.D.	R.R. ($\mu\text{g ml}^{-1}$)
L ¹	3.07	3.45×10^4	0.0016	0.9999	0.0004	0.28-1.68
L ²	48.87	0.20×10^4	0.0283	0.9996	0.0002	2.09-48.78
L ³	7.68	1.39×10^4	0.0040	0.9999	0.0002	0.70-4.89
L ⁴	76.79	0.14×10^4	0.0040	0.9998	0.0001	2.09-76.78
L ⁵	55.85	0.18×10^4	0.0318	0.9991	0.0003	3.49-55.85
L ⁶	9.08	1.24×10^4	0.0045	0.9999	0.0007	0.70-6.29

C.V.M.: Continuous variation method. M.R.M.: Molar ratio method.

L.S.L.M.: Logarithmic form of the straight line method.

$\log \beta_n$: Log stability constant. ΔG^* : Free energy changes (kcal mol^{-1}).

ϵ : Molar absorptivity ($\text{l mol}^{-1}\text{cm}^{-1}$). C.C.: Correlation coefficient.

S.S.: Sandell's sensitivity ($\mu\text{g/cm}^2$). S.D.: Standard deviation.

R.R.: Ringbom range.

This indicates that Fe(III) ion has very small interference with the absorbance of Fe(II)-complexes with L³ and L⁶. The maximum absorption peaks which appeared at longer wavelengths due to complexation of Fe(II) with ligands (L¹-L⁶) are listed in Table 1.

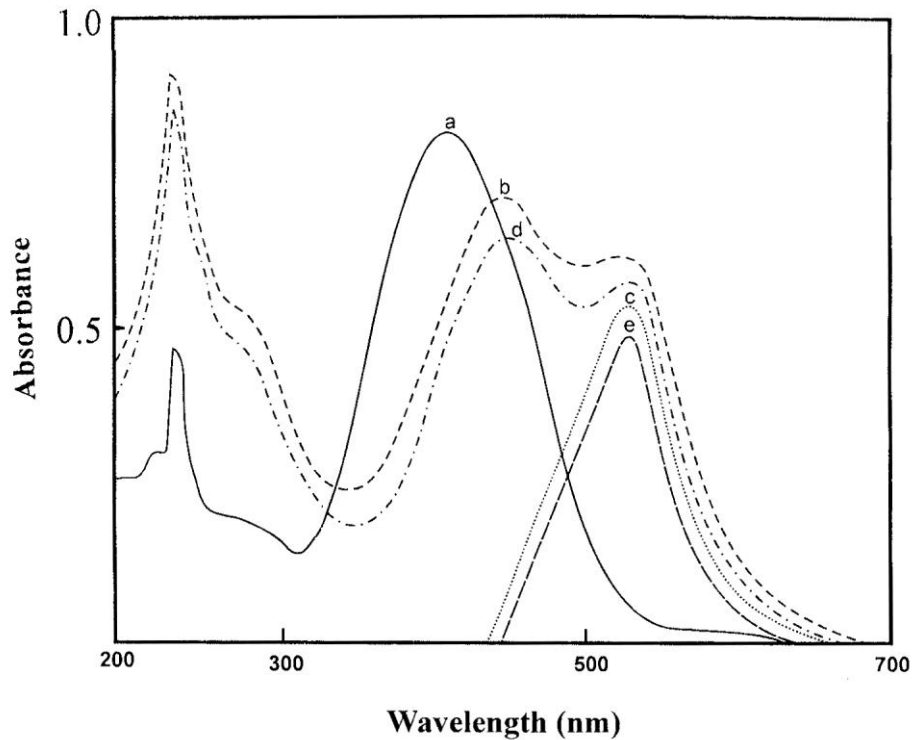


Fig. 1. The electronic absorption spectra of L^1 and its Fe(II and III) complexes in buffer solution of pH = 10.

- a- Ligand against methanol and buffer as a reference.
- b- Fe(II)-complex against methanol and buffer as a reference.
- c- Fe(II)-complex against ligand, methanol and buffer as a reference.
- d- Fe(III)-complex against methanol and buffer as a reference.
- e- Fe(III)-complex against ligand, methanol and buffer as a reference.

Effect of reagent concentration

The effect of reagent concentration on the intensity of the colour development for the complexes was investigated by varying the reagent concentration while other variables were held constant. For 27.92 $\mu\text{g}/10$ ml of Fe(II), a constant and maximal absorbance was obtained when the reagent (L^1 - L^6) concentration exceeded 1.5×10^{-4} M. So the reagent should be used in large excess during the determination of Fe(II) ion.

Effect of time, temperature, sequence of addition and solvent ratio

Preliminary studies of the influence of various experimental factors on the formation of Fe(II)-complexes revealed the following points:

- (a) The minimum standing time after shaking for complete color development of Fe(II)-complex with ligands (L^1-L^6) was found to be 5 min at room temperature and remained constant for at least 48 h. This was achieved by measuring the absorbance of some samples at different time intervals⁽³⁾.
- (b) Absorbance measurements at different temperatures indicated that raising the temperature from 25 up to 70 °C has no influence on the absorbance of Fe(II)-complexes under study.
- (c) The sequence of addition (ligand-metal ion-buffer) is the best one for the colour development of Fe(II)-complexes with all reagents and the colors of the complexes attained a maximum value at a ratio of 40% (v/v) methanol.

Stoichiometry, stability constants and free energy changes

The continuous variation, mole ratio and logarithmic form of the straight line methods⁽¹⁷⁻²⁰⁾ are used to investigate the stoichiometric composition of Fe(II)-complexes with ligands (L^1-L^6) and revealed the formation of 1:1 and 1:2 [Fe(II):L] complexes (Table 1). The results of continuous variation and molar ratio methods are used to calculate the conditional stability constants (β_n) of the formed complexes (Table 1) using equations (1)^(17, 19, 21, 22):

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

in which A is the absorbance at ligand concentration C_L , A_m is the maximum absorbance, n is the stoichiometry of the formed complex.

The free energy change (ΔG^*) was calculated from the equation (2):

$$\Delta G^* = -RT \ln \beta_n \rightarrow (2)$$

in which T is the absolute temperature and R is the gas constant.

The calculated β_n values denoted that 1:2 [Fe(II):L] complexes have values almost double those of the 1:1 complexes for the same ligand molecule which means that the stability of the complexes increases with increasing the number of ligand molecules attached to the central metal ion. Also, the obtained results proved

that the ligands containing electron donating groups (m-OH, p-COCH₃ and p-CH₃) form more stable complexes compared to those containing electron withdrawing groups (p-Br and p-CHO). This indicates that the stability of the formed complexes is strongly affected by the substituent present on the phenolic ring.

Calibration graphs and statistical treatments of results

After optimization of the conditions for the spectrophotometric determination of Fe(II) with ligands (L¹–L⁶), obedience to Beer's law was tested. On plotting the absorbance as a function of Fe(II) concentration linear relationships (Fig. 2) were obtained up to 3.07, 6.98, 7.68, 7.68, 6.98 and 9.08 μg ml⁻¹. The molar absorptivities are 3.45 x 10⁴, 0.20 x 10⁴, 1.39 x 10⁴, 0.14 x 10⁴, 0.18 x 10⁴ and 1.24 x 10⁴ L mol⁻¹ cm⁻¹. The Sandell's sensitivities⁽²³⁾ were 0.0004, 0.0002, 0.0002, 0.0001, 0.0003 and 0.0007 μg ml⁻¹ at 530, 680, 670, 675, 585 and 690 nm with high correlation coefficients using L¹–L⁶ respectively. The statistical parameters for calibration graphs are summarized in Table 1.

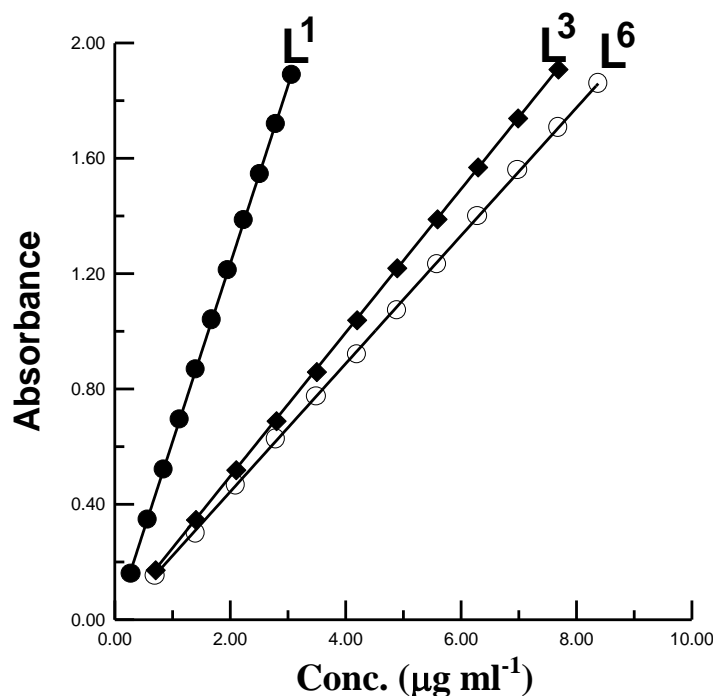


Fig. 2. Absorbance – concentration plots of Fe(II)-L¹ [$\lambda=530$ nm], Fe(II)-L³ [$\lambda=670$ nm] and Fe(II)-L⁶ [$\lambda=690$ nm] systems.

The high values of correlation coefficients and small values of standard deviations indicate the good linearity of all calibration graphs and the confirmatory of Beer's law to absorbance measurements. The optimum ranges for the determination of Fe(II) using L¹–L⁶ as chromogenic reagents were determined from Ringbom plots (Table 1). The obtained results indicated that L¹, L³ and L⁶ are very sensitive chromogenic reagents and can be used for the spectrophotometric microdetermination of Fe(II) as revealed by their relatively high ϵ values.

Effect of foreign ions

The effect of the presence of diverse ions in the direct determination of iron (II) using L¹, L³ and L⁶ was studied under the optimum conditions. Cations and anions in varied concentrations were added to the sample and the results of measurements were compared with the blank sample. The tolerance of the method to foreign ions was investigated with solutions containing 27.92 μg of Fe(II) per 10 ml 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 expected value⁽¹⁴⁾, the data are collected in Table 2. From the obtained results we conclude that most anions and cations have small interference effect except for cations of the first transition metal series which have strong interference effect especially when L¹ is used as the chromogenic reagent. The interference has an obvious decrease when L³ and L⁶ are used. In general the selectivity of the investigated reagents increases in the following order $L^1 < L^6 < L^3$.

Applications of the proposed method

Eleven successive measurements were carried out on a standard solution containing 2.79 $\mu\text{g ml}^{-1}$ of Fe(II) using ligands L¹, L³ and L⁶ as chromogenic reagents in order to test the accuracy and precision of the proposed method. The calculated standard deviations are 0.0020, 0.0030 and 0.0050 for reagents L¹, L³ and L⁶, respectively.

Table 2. Tolerance limits of foreign ions in the determination of 27.92 μg of Fe(II) per 10 ml and various amounts of foreign ions.

Foreign ion	L ¹		L ³		L ⁶	
	Tolerance limit (μg)	Ion / Fe(II)	Tolerance limit (μg)	Ion / Fe(II)	Tolerance limit (μg)	Ion / Fe(II)
K ₂ SO ₄	15172.4	543.4	10002.3	358.3	5421.1	194.2
NaNO ₃	3644.9	130.6	7246.4	259.5	3741.2	134.0
NaNO ₂	19722.2	706.4	1668.6	59.8	2125.2	76.1
Fe ³⁺	4.6	0.2	160.6	5.8	92.9	3.3
Mn ²⁺	5.7	0.2	187.4	6.7	62.7	2.3
Co ²⁺	10.9	0.4	182.7	6.5	38.6	1.4
Ni ²⁺	4.5	0.2	83.4	3.0	53.1	1.9
Cu ²⁺	4.5	0.2	309.6	11.1	177.9	6.4
Zn ²⁺	4.7	0.2	311.6	11.3	180.8	6.5
Cd ²⁺	220.2	7.9	280.3	10.0	256.8	9.2
Hg ²⁺	245.3	8.8	380.0	13.6	283.5	10.2
Pb ²⁺	513.5	18.4	1536.0	55.0	1227.3	44.0
Ca ²⁺	400.8	14.4	1366.7	49.0	1234.5	41.2
Sr ²⁺	320.7	11.5	332.9	11.9	325.7	11.7
Ba ²⁺	365.9	13.1	389.7	14.0	376.4	13.5
Mg ²⁺	194.9	7.0	414.4	14.8	415.9	14.9
Al ³⁺	204.8	7.3	135.3	4.9	131.9	4.7
Cr ³⁺	1651.4	59.2	591.0	21.2	276.1	9.9
Ce ³⁺	238.9	5224.5	8.6	187.1	1078.8	38.6
In ³⁺	965.3	34.6	4350.6	155.8	2537.6	90.9
Bi ³⁺	1120.9	40.2	1326.4	47.5	1230.3	44.1
Ga ³⁺	920.4	33.0	1080.2	38.7	986.6	35.3
Ag ⁺	325.9	11.7	346.7	12.4	334.6	12.0
Au ⁺	360.6	12.9	410.9	14.7	394.4	14.1
Cl ⁻	1320.0	47.3	1431.8	51.3	1222.9	43.8
Br ⁻	1292.8	46.3	592.3	21.2	523.6	18.8
I ⁻	1301.8	46.6	1761.0	63.1	456.6	16.4
CO ₃ ²⁻	3998.9	143.2	3860.4	138.3	1318.6	47.2
HCO ₃ ⁻	1413.7	50.6	6118.0	219.1	1399.8	50.1
S ₂ O ₃ ²⁻	2342.4	83.9	2728.0	97.7	2029.2	72.7
S ₂ O ₈ ²⁻	491.5	17.6	30.4	1.1	1739.3	62.3
SO ₃ ²⁻	1673.8	60.0	717.9	25.7	1368.9	49.0
S ²⁻	148.3	5.3	266.2	9.5	172.0	6.2
PO ₄ ³⁻	2627.8	94.1	2159.7	77.4	1125.4	40.3

Table 3. Spectrophotometric determination of iron content in soil, water and multivitamin samples.

Soil (mg gm ⁻¹), Water (mg l ⁻¹) and Multivitamin (mg/T) samples	Iron content (mg gm ⁻¹)												
	AAS	L ¹				L ³				L ⁶			
	Conc.	Conc.	F- value	t- value	RS D	Conc.	F- value	t- value	RSD	Conc.	F- value	t- value	RS D
Siol 1 ^A	15.82	15.85	0.87	2.20	0.02	15.79	0.97	2.14	0.02	15.84	1.27	1.21	0.01
Siol 1 ^B	17.96	18.01	2.05	2.45	0.04	17.98	1.00	1.21	0.01	17.92	1.35	2.45	0.03
Nile water ^C	53.24	53.28	1.13	2.56	0.03	53.26	1.13	1.22	0.04	53.22	2.56	0.94	0.07
Tap water ^D	51.66	51.64	0.55	1.35	0.01	51.68	1.10	1.17	0.01	51.63	1.11	1.75	0.02
Underground water ^E	62.23	62.25	0.58	1.09	0.01	62.26	1.05	1.43	0.02	62.21	1.63	0.85	0.01
Hemoton ^F	115.04	115.08	0.41	2.03	0.03	115.09	0.53	2.43	0.04	114.99	0.72	2.30	0.04
Theragran ^J	21.92	21.96	0.60	1.70	0.03	21.94	0.29	0.95	0.01	21.89	0.67	1.25	0.02
Materna ^H	19.72	19.75	0.64	1.37	0.02	19.71	0.39	0.50	0.01	19.73	1.41	0.47	0.01

Number of replicates is 6.

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

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

AAS: Atomic absorption spectroscopy; RSD: Relative standard deviation; A: Soil sample from Tanta, Elghrbia, Egypt; B: Soil sample from Qutor, Elghrbia, Egypt; C: Water sample from Nile branch, Tanta, Elghrbia, Egypt; D: Water sample from a tap, Tanta, Elghrbia, Egypt; E: Water sample from Tanta, Elghrbia, Egypt; F: Capsules manufactured by Glaxo Wellcome Egypt S.A.E., El Salam City, Cairo, A. R. E.; J: Tablets produced by Bristol-Myers Squibb Egypt A Bristol-Myers Squibb Company New York Cairo; H: Tablets produced by Global Napi pharmaceuticals-Egypt from Wyeth – Egypt under licence from Wyeth-Ayerst Inc., Canada.

To confirm the usefulness of the proposed method, it was extended for the determination of the iron content in soil, water and multivitamin samples using ligands L¹, L³ and L⁶ as chromogenic reagents (Table 3).

Comparison between the experimental mean values for each sample (A-H) obtained by the investigated method and the values obtained by AAS was carried out by calculating F- and t-values. From Table 3, it is found that for the investigated method F-values = 0.29-2.56 and t-values = 0.47-2.56 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)⁽²⁴⁾ which means that all samples are not subject to systematic error (accurate). Also, the values of relative standard deviations (RSD) are very small indicating high precision of the investigated method.

Structural elucidation of the solid Fe(II)-chelates

The prepared solid 1:1 and 1:2 (M:L) Fe(II)-complexes with L¹ were investigated as described in the experimental part in order to characterise the molecular structure of the formed chelates. The found and calculated values of elemental microanalysis are in satisfactory agreement with each others supporting the suggested molecular formulae (Table 4).

Table 4. Data of elemental and thermal analyses of Fe(II)-complexes (1) and (2).

No.	Molecular formula (Empirical formula)	Elemental analysis				Thermal analysis	
		Found (calcd.) (%)				Found (calcd.) (%)	
		C	H	N	Fe(II)	Loss of H ₂ O	FeO Residual
(1)	[FeL ¹ Cl(H ₂ O) ₃]	27.3	3.7	20.5	5.821	15.1	20.9
	(C ₈ H ₁₂ FeN ₅ O ₅)	(27.5)	(3.5)	(20.0)	(16.0)	(15.5)	(20.6)
(2)	[Fe(L ¹) ₂ (H ₂ O) ₂]	38.8	3.6	28.4	11.4	6.8	14.8
	(C ₁₆ H ₁₆ FeN ₁₀ O ₆)	(38.4)	(3.2)	(28.0)	(11.2)	(7.2)	(14.4)

The low molar conductance (Δ_m) values (4.2 and 3.7) of Fe(II)-complexes (1) and (2) reflects the non-ionic character of the complexes and showed that the chloride ion is coordinated to Fe(II) in case of complex (1)^(25, 26). This character was confirmed by AgNO₃ test.

The bulk magnetic susceptibilities (μ_{eff}) values are 5.2 and 5.1 B. M. for complexes (1) and (2) at room temperature (300 K). These values are indicative of four unpaired electrons per Fe(II) ion (high spin complexes).

The bonding of the ligands to Fe(II) ion was investigated by comparing the IR spectra of complexes (1) and (2) with that of the free ligand L¹ where the following points could be concluded:

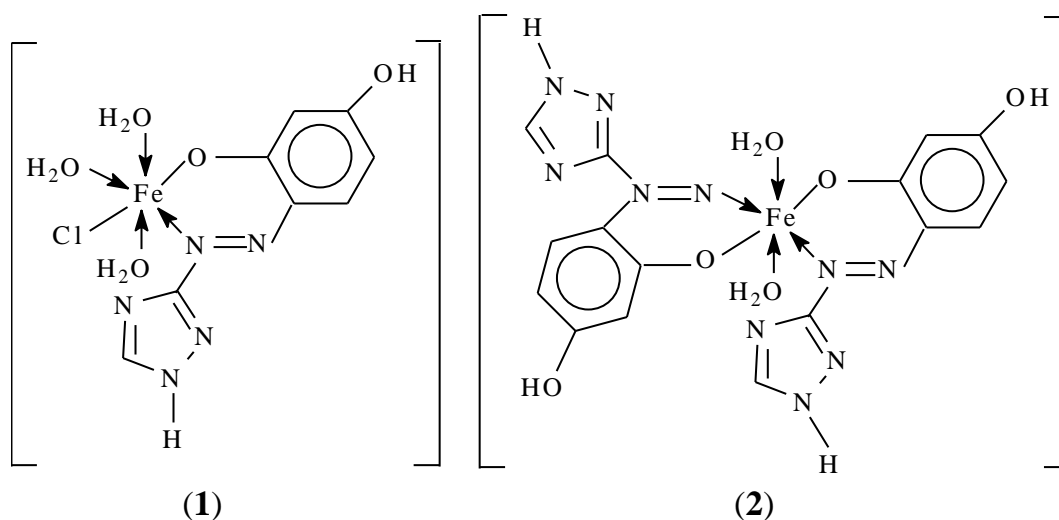
- (i) The IR spectra of complexes (1) and (2) exhibit broad bands at 3415 and 3405 cm⁻¹, respectively that may be attributed to $\nu(\text{OH})$ of the associated water molecules. The presence of coordinated water molecules in the complexes makes it difficult to consider the behavior of the $\nu(\text{OH})$ band of the phenolic groups.
- (ii) The $\nu(\text{N}=\text{N})$ band of the free ligand at 1395 cm⁻¹ is shifted to lower frequency and appeared at 1389 and 1390 cm⁻¹ in the spectra of complexes (1) and (2). This indicates the participation of N=N group in coordination.
- (iii) Also, the deformation vibration band of OH at 1320 cm⁻¹ for the ligand disappeared in the spectra of Fe(II)-complexes whereas the C-OH band at 1080 cm⁻¹ for the free ligand is shifted to lower frequencies and appeared at 1060 cm⁻¹ in case of complex (1) and 1071 cm⁻¹ in case of complex (2) due to participation of OH group in coordination by displacement of the proton by Fe(II) ion .
- (iv) The coordination of L¹ to Fe(II) through the azo nitrogen $\nu(\text{M}-\text{N})$ and phenolic oxygen $\nu(\text{M}-\text{O})$ is confirmed by the appearance of two new bands at 598 and 484 cm⁻¹ in the spectra of complex (1) and at 588 and 489 cm⁻¹ in the spectra of complex (2)^(27, 28).

The electronic absorption spectra of complexes (1) and (2) were studied in DMF solution and as nujol mull; the λ_{max} values are 231 (233), 280 (285), 420

(422) and 534 (535) nm for complex (1) and 234 (236), 285 (286), 425 (427) and 530 (532) nm and for complex (2). The shifts of the intra ligand bands together with the change of colour indicate complex formation. The ligand bands can be assigned to a $\pi-\pi^*$ transition within the aromatic ring system, a $\pi-\pi^*$ transition within N=N group and an intramolecular charge transfer transition (CT band) within the ligand molecule. These bands display large shifts when compared with those of the free ligand L¹. The longer wavelength band at 530-535 nm corresponding to the $^5T_{2g}-^5E_g$ (D) transition of the Fe(II) in an octahedral environment⁽²⁹⁾.

The TGA curves of the complexes (1) and (2) displayed thermal stability up to 130 and 135 °C which is a good evidence that they are free from hydration water molecules⁽³⁰⁾, in good agreement with the suggested molecular formulae listed in Table 4. The TGA curves of complexes (1) and (2) display the first thermal decomposition steps at 130-145 and 135-148 °C due to the liberation of coordinated water molecules. The second decomposition step at 237-278 and 217-239 °C can be assigned to partial degradation of the organic parts of the complexes. The third decomposition step at 332-380 and 335-387 °C corresponds to the complete thermal decomposition of the organic rest leading to FeO as final product (Table 4).

Based on the above results, the bonding of L¹ to Fe(II) in complexes (1) and (2) can be represented as follows (Scheme 2):



Scheme 2. Representative structures of Fe(II)-complexes (1) and (2).

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