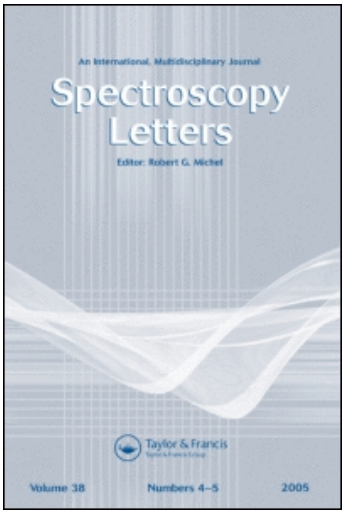

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Spectrophotometric Studies of the Reaction of Zinc(II) with Some Azo-Triazol Compounds and Its Application to the Spectrophotometric Determination of Microamounts of Zinc(II)

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Abstract: A new, simple, and sensitive quantitative spectrophotometric method for the rapid determination of zinc(II) using six azo compounds based on 3-amino-1,2,4-triazole, namely {3-(2,4-dihydroxy-1-phenylazo)-1,2,4-triazole) (I), 3-(2-hydroxy-5-methyl-1-phenylazo)-1,2,4-triazole) (II), 3-(2-hydroxy-5-acetyl-1-phenylazo)-1,2,4-triazole) (III), 3-(2-hydroxy-5-ethylcarboxylate-1-phenylazo)-1,2,4-triazole) (IV), 3-(2-hydroxy-5-formyl-1-phenylazo)-1,2,4-triazole) (V), and 3-(2-hydroxy-5-bromo-1-phenylazo)-1,2,4-triazole) (VI), has been developed for use in aqueous media containing 40% (v/v) methanol. Linear calibration graphs are obtained up to 2.6, 5.9, 5.2, 5.2, 8.2 and 9.0 $\mu g\,mL^{-1}$ using ligands I, II, III, IV, V, and VI, respectively. Absorption maxima, molar absorptivities, and Sandell's sensitivities of 1:2 (M:L) complexes were found to be 490, 530, 505, 520, 550, and 510 nm, 4.86×10^4, 2.10×10^4, 1.26×10^4, 0.10×10^4, 0.19×10^4, and $0.29 \times 10^4\,L\,mol^{-1}\,cm^{-1}$, and 0.0014, 0.0031, 0.0052, 0.0662, 0.0348, and 0.0225 $\mu g\,cm^{-1}$ for ligands I, II, III, IV, V, and VI, respectively. Using the masking agents, the color reactions are free from interference by more than 30 ions investigated. The method has been applied to the spectrophotometric determination of trace amounts of zinc in pharmaceutical formulations and human hair samples. A study of some zinc solid complexes showed that

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chelation takes place through one nitrogen atom of the azo group and proton displacement from the hydroxyl group.

Keywords: Azo-triazole, spectrophotometric determination, zinc(II)

INTRODUCTION

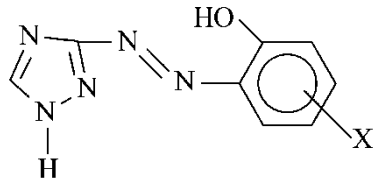
Numerous organic azo compounds are known to be sensitive and selective chromogenic reagents for the spectrophotometric determination of different metal ions,[1–6] but few of them give high sensitivity and simple operation in case of zinc.[7,8]

In the current work, a series of monoazodyes derived from 3-amino-1,2,4-triazole moiety (Scheme 1) were synthesized in our laboratory according to the recommended method.[9] These azo compounds give a sensitive color reaction with zinc(II) in presence of universal buffer solution of different pH values containing 40% (v/v) methanol due to instantaneous formation of 1:2 (M:L) zinc complexes. The best conditions for the formation of zinc–ligands (I–VI) complexes as well as the effect of foreign ions were studied in detail. The molecular stoichiometry, the stability constants, and the free energy changes of the complexes were determined spectrophotometrically. Recommended procedure for the spectrophotometric determination of trace amounts of zinc(II) in pharmaceutical formulations and human hair samples using ligands (I and II) had been introduced. The solid zinc chelates with ligands I and VI were prepared and characterized to confirm the formation of zinc-azo complexes in solution and investigate the structure of the formed complexes.

EXPERIMENTAL

Instruments

Electronic absorption spectra were recorded using a Shimadzu UV-Vis 240 spectrophotometer. The blank used was the buffer solution only or the



X = m-OH (I), p-CH_3 (II), p-$COCH_3$ (III),
p-COC_2H_5 (IV), p-CHO (V) and p-Br (VI)

Scheme 1. Structure of the azodyes under study.

buffer solution containing the same concentration of the ligand as in the test solution. A digital ORION pH meter model 201 of sensitivity ± 0.02 pH unit was used in checking the pH value of universal buffer solution. Carbon, hydrogen, and nitrogen contents of the solid complexes under investigation were determined at the microanalytical unit, Tanta University (Tanta, Egypt). IR spectra of the solid complexes were recorded over the $4000-200\,cm^{-1}$ range using a Perkin Elmer 1430 spectrophotometer as KBr disks. Conductivity measurements were measured at 25°C using a conductance bridge of the type 523 conductometer. The thermogravimetric analysis (TGA) was performed using the TG 50-thermogravimetric analyzer (Shimadzu) in the range 25°C up to 800°C with 10°C/min heating rate using nitrogen as an atmosphere.

Chemicals

All chemicals used were of analytical reagent grade. Redistilled water, pure methanol, or pure ethanol was used for the preparation of solutions.

Chromogenic Reagent (I, II, III, IV, V, and VI) Stock Solutions

The chromogenic reagents (I–VI) were synthesized as described previously.[9] This was achieved by diazotization of 3-amino-1,2,4-triazole by dissolving it in hydrochloric acid, cooling it to 0–5°C, and adding an equivalent amount of ice-cooled sodium nitrite solution with vigorous stirring. The cooled diazonium salt solution was then coupled with different substituted phenols. The azo compounds were recrystallized from ethanol, and their purity was confirmed by elemental analysis as well as melting point constancy.

A stock solution of $2 \times 10^{-3}\,mol\,L^{-1}$ was prepared by dissolving an accurately weighed amount of the purified reagent in the requisite volume of methanol.

Standard Zinc Solution

A $5 \times 10^{-3}\,mol\,L^{-1}$ stock solution of zinc acetate was prepared by dissolving the required amount of the Analar reagent in redistilled water. The zinc solution was standardized complexometrically with EDTA.[10]

Solutions of diverse ions used for interference studies were prepared from Analar products of nitrates or sulfates of the tested metal ions and potassium or sodium salts of the anions to be tested.

The universal buffer solutions of pH values 2–12 were prepared as given previously.[11]

Recommended Procedures

Procedure for Studying the Color Reactions of Zinc

Take a test solution containing definite amounts of zinc and reagent solutions in a 10 mL calibrated flask, add 5 mL of universal buffer, dilute to the mark while keeping the methanol ratio 40% (v/v), and mix well. Measure the absorption spectrum within the range 300–700 nm in a 1.0-cm cell against a buffer or reagent blank.

Procedure for the Determination of Zinc in Standard Sample

To 0.3 mL (1×10^{-3} M) of zinc solution, 4 mL of 1×10^{-3} M reagent and 5 mL of universal buffer solution of pH 10.0 or 9.0 for reagents I or II, respectively, were added. The volume was completed to the mark with doubly distilled water in a 10-mL measuring flask. The solutions were thoroughly mixed and the mixture allowed to stand for 5 min. The absorbance at 490 and 530 nm was measured against a reference blank solution prepared in the same manner for reagents I and II, respectively. The calibration graphs were prepared by using the same procedure (10 concentration points) and were linear passing through the origin.

Procedure for the Determination of Zinc in Pharmaceutical Formulations

In a 25-mL crucible, a definite weight of the pharmaceutical sample powder was treated with a few drops of nitric acid then digested at 500°C. The residue was dissolved in 3–5 mL concentrated HCl and heated in a water bath for 2 min. Then it was diluted with 5–10 mL of doubly distilled water and filtered when necessary, and the crucible and the filter paper were washed three times with 5 mL portions of doubly distilled water. The solution was transferred into a 100-mL calibrated flask, diluted to volume with distilled water, and mixed well. Then, 0.1 mL of the solution was transferred into a 10-mL calibrated flask, then treated with 1–2 drops of 2 M sodium hydroxide, 0.2 mL of 10% sodium potassium tartarate, and 0.1 mL of 5% thoiurea. The amount of zinc(II) was then determined following the above-recommended procedure.

Procedure for the Determination of Zinc in Human Hair Samples

The hair sample was placed in a 100-mL beaker, treated with a sufficient 1% detergent solution to cover it, and soaked for 30 min at 60°C. The detergent solution was poured and the hair washed with distilled water until the foam completely disappears. Then, acetone was added and soaked for 2 hr. The acetone was poured out and the hair washed three times with distilled water

then dried for 90 min at 120°C and stored in a desiccator. Then, 0.2 g of treated human hair was placed in a 100-mL beaker, 5.0 mL of concentrated nitric acid was added then heated at low temperature to decompose the sample and evaporated to almost 1.5 mL (the color of the solution is bright orange-yellow). After cooling, 1 mL 30% hydrogen peroxide were added and heated continuously until the solution becomes colorless. The solution was then transferred into a 10-mL calibrated flask, diluted to the mark with distilled water, and mixed well. Then, 1.0 mL of this solution was pipetted into a 10-mL calibrated flask, and 2–4 drops of 2 M sodium hydroxide and 0.2 mL of 10% sodium potassium tartarate were added. The zinc content of this solution was then determined as mentioned above.

Preparation of the Zinc Solid Chelates with Ligands I and VI

The solid chelates of zinc with ligands I and VI were obtained by mixing ethanolic solutions of azo compounds with a hot ethanolic solution of the zinc acetate with stoichiometric ratios 1:1 and 1:2 (M:L). The mixture was then refluxed on a water bath for ≈2 hr and allowed to cool whereby the solid complexes separated. The collected solids were washed with ethanol and then dried in vacuum over silica gel.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of ligands (I–VI) and their zinc chelates were investigated in buffer solutions of different pH values. The absorption spectra of the complexes formed in solution exhibited one broad band, the maxima of which are listed in Table 1. The absorption maxima of the complexes shifted to longer wavelengths compared with those of the free ligands (Fig. 1). This shift of λ_{max} may be attributed to increased delocalization of the electrons on complexation leading to a decrease in the energy gap between the excited and ground states.[12]

Conditions for Complex Formation

Investigation of the effect of pH of solution on the development of the colored complexes showed that the absorbance of the complexes depends on the pH of solution. The pH-absorbance curves give only one maximum, referring to the best pH value for the formation of Zn(II) complexes with ligands (I–VI). The optimum pH values are listed in Table 1. Addition of 4.0–6.0 mL of universal buffer gave maximal and constant absorbance of the complexes. Hence, an addition of 5.0 mL of buffer solution was considered as appropriate. The

Table 1. Electronic spectral data of Zn(II) complexes with ligands (I–VI)

Ligand	pH	λ_{max} (nm)	Molecular stoichiometry C.V.M.	M.R.M.	L.S.L.M.	log β_n	$-\Delta G^*$
I	10	490	1:1	1:1	1:1	3.75	5.15
			1:2	1:2	1:2	7.93	10.88
II	9	530	1:1	1:1	—	4.04	5.54
			1:2	1:2	1:2	8.65	11.87
III	10	505	1:1	1:1	—	3.37	4.62
			1:2	1:2	1:2	7.23	9.93
IV	10	520	1:1	1:1	—	3.64	5.00
			1:2	1:2	1:2	7.52	10.32
V	8	550	1:1	1:1	1:1	3.36	4.61
			1:2	1:2	1:2	7.28	9.99
VI	10	510	1:1	1:1	1:1	3.60	4.94
			1:2	1:2	1:2	7.18	9.86

C.V.M., continuos variation method; M.R.M., molar ratio method; L.S.L.M., logarithmic form of the straight line method; log β_n, log stability constant; ΔG^*, free energy changes (Kcal mol^{-1}).

sequence of addition (ligand–metal ion–buffer) is the best one for the formation of the zinc complexes with all reagents used. The effect of organic solvent ratio showed that the colors of complexes attained a maximum value at ratio of 40% methanol. The colors of all complexes are formed instantaneously and are stable for more than 24 hr. Temperature exhibits no obvious influence on color development. Under the condition employed, the absorbance of the complexes increases with increasing the reagent concentration and attained maximal and constant absorbance when the reagent concentration became three times that of the zinc concentration in the sample solution, so the reagent is to be used in large excess during the determination of zinc(II) ion.

Stoichiometry of the Complexes

The stoichiometric composition of the complexes was determined by the continuous variation, molar ratio, and logarithmic forms of the straight line methods,[13–15] which revealed the formation of 1:1 and 1:2 (M:L) complexes. The conditional stability constants and the free energy changes (ΔG^*) of the formation of Zn(II) complexes with ligands (I–VI) were calculated using the results of continuous variation and molar ratio methods using the following equations:[16]

$$\beta_n = \frac{A/A_m}{[1-(A/A_m)]^{n+1} C_L^n n^2} \quad (1)$$

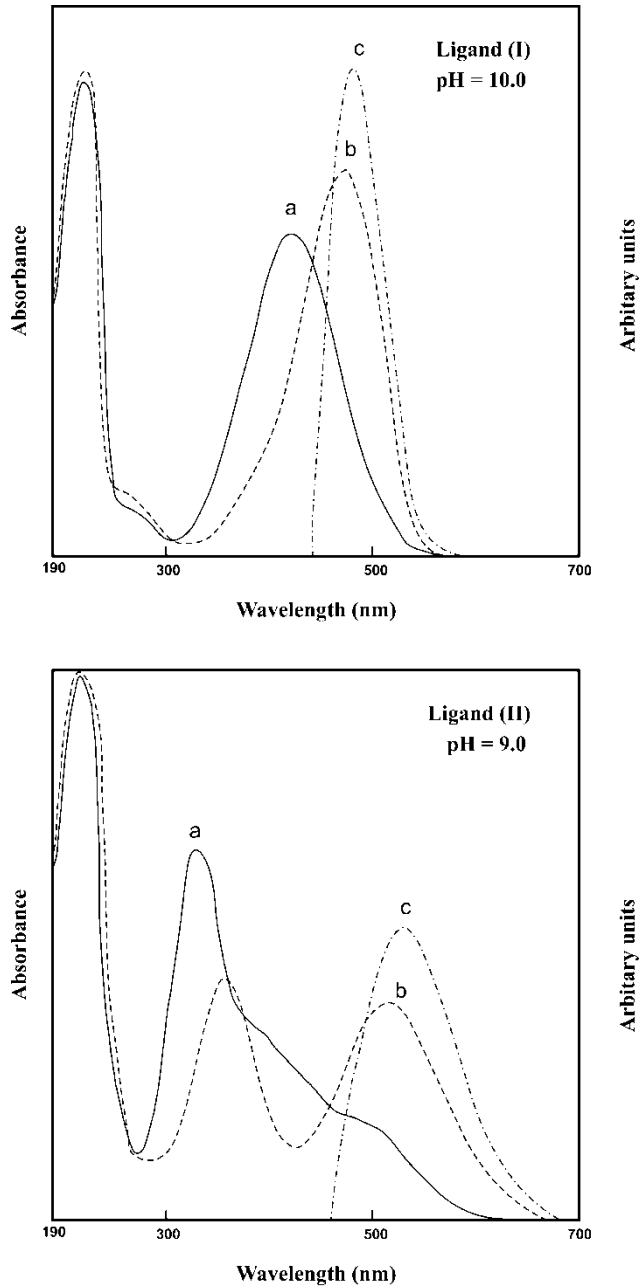


Figure 1. The electronic absorption spectra of ligands I and II and their Zn(II) complexes at the recommended pH values. *a*, Ligand against methanol and buffer as a reference. *b*, Zn(II) complex against methanol and buffer as a reference. *c*, Zn(II) complex against ligand, methanol, and buffer as a reference.

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, and n is the order of the complex formed;

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

where β_n is the stability constant of the metal chelates, T is the absolute temperature and R is the gas constant.

The values obtained (Table 1) for the 1:2 species are larger than those of the 1:1 (M:L) complexes. The stability constants are higher in case of ligands containing electron donating groups (*m*-OH and *p*-CH_3) than those with electron withdrawing groups (*p*-CHO and *p*-Br); this may be attributed to increased electron density around the coordination center in case of electron donating groups and its decrease in case of electron accepting ones, which reflects the substituent effect on the stability of the formed complexes.

Adherence to Beer's Law, Sensitivity, and Results of Statistical Analysis

Under the optimum conditions cited above, linear calibration graphs for Zn–ligands (I–VI) complexes were obtained for the concentration ranges 0.0–2.62, 0.0–5.88, 0.0–5.23, 0.0–5.23, 0.0–8.17, and 0.0–8.99 $\mu g\,mL^{-1}$ with molar absorptivities 4.86×10^4, 2.10×10^4, 1.26×10^4, 0.10×10^4, 0.19×10^4, and $0.29 \times 10^4\,L\,mol^{-1}\,cm^{-1}$ and Sandell's sensitivities[17] (0.0014, 0.0031, 0.0052, 0–0.0662, 0.0348, and 0.0225 $\mu g mL^{-1}$) at 490, 530, 505, 520, 550, and 510 nm using ligands I, II, III, IV, V, and VI, respectively.

Ringbom plots gave the optimum working ranges for the determination of zinc(II) ion by using the reagents under investigation (Table 2). These results confirm the possible application of ligands I and II as very sensitive chromogenic reagents for the spectrophotometric microdetermination of

Table 2. Spectral data of Zn(II) complexes with ligands (I–VI)

Ligand	Beer's law up to (ppm)	ε ($L\,mol^{-1}\,cm^{-1}$)	S.S. ($\mu g\,cm^{-1}$)	C.C.	S.D.	R.R. (ppm)
I	2.62	4.86×10^4	0.0014	0.99996	0.0013	0.00–1.57
II	5.88	2.10×10^4	0.0031	0.99999	0.0006	0.00–3.27
III	5.23	1.26×10^4	0.0052	0.99975	0.0016	1.31–5.23
IV	5.23	0.10×10^4	0.0662	0.99995	0.0001	1.96–3.92
V	8.17	0.19×10^4	0.0348	0.99647	0.0017	2.45–6.54
VI	8.99	0.29×10^4	0.0225	0.99964	0.0003	3.27–8.17

ε, molar extinction coefficient ($L\,mol^{-1}\,cm^{-1}$); C.C., correlation coefficient; S.S., Sandell's sensitivity ($\mu g/cm^2$); S.D., standard deviation; R.R., Ringbom range.

Zn(II) ($\varepsilon = 4.86 \times 10^4$ and $2.1 \times 10^4\,L\,mol^{-1}\,cm^{-1}$), and ligand (IV) is the least preferable reagent ($\varepsilon = 0.10 \times 10^4\,L\,mol^{-1}\,cm^{-1}$) for this method.

In order to test the accuracy and precision of the method, eight successive measurements were carried out with a standard solution containing $1.9617\,\mu g\,mL^{-1}$ of Zn(II) using ligands I and II as chromogenic reagents. The standard deviations were found to be 0.0020 and 0.0048 for reagents I and II, respectively.

Effect of Diverse Ions

To assess the usefulness of the proposed method, the effect of diverse ions that often associate with Zn(II) were studied using reagents I or II [the best chromogenic reagents selected from the above studies] under the optimum conditions as described in the procedure given. The tolerance of the method to foreign ions was investigated with solution containing $1.9617\,\mu g\,mL^{-1}$ of zinc(II) ion 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 Zn(II) alone. As shown in Table 3, most of the interfering ions can be masked, and the sensitivity of the method can be improved. Therefore, the method can be applied for the spectrophotometric determination of trace amounts of zinc without separation.

Application to Pharmaceutical Formulations and Human Hair Samples

The suggested method has been applied to the determination of zinc(II) in pharmaceutical formulations and human hair samples using ligands I or II as chromogenic reagents.

The results obtained for zinc(II) content of pharmaceutical formulations (Table 4) was in good agreement with the certified values except for Minervit analysis due to the high concentrations of Fe^{2+} and Ca^{2+} present in Minervit. The high concentrations of the two metal ions would lead to appreciable formation of some sort of complexes with the ligand used, which would absorb in the region of Zn(II)–ligand complex.

Also, the results obtained for several samples of human hair (Table 4) agreed well with those obtained by atomic absorption spectrophotometry.

Structure Elucidation

The chemical composition of the solid chelates was determined by elemental analysis (Table 5). The metal content was determined according to the

Table 3. Tolerance limits of foreign ions in the determination of 1.9617 μg mL^{-1} of Zn(II) per 10 mL and various amounts of foreign ions

	Using ligand I		Using ligand II		
Foreign ion	Tolerance limit (μg)	Ion/Zn(II)	Tolerance limit (μg)	Ion/Zn(II)	Comment
$NaNO_3$	1529.88	77.99	910.72	46.42	
K_2SO_4	1473.54	75.12	848.87	43.12	
Ag^{+}	100.12	5.10	98.84	5.04	
Au^{+}	112.16	5.72	102.86	5.24	
Ca^{+2}	320.62	16.34	227.29	11.59	
Sr^{+2}	330.68	16.85	310.88	15.85	
Ba^{+2}	310.48	15.82	304.66	15.52	
Mg^{+2}	198.86	10.14	174.43	8.89	
Cd^{+2}	68.24	3.48	64.88	3.31	
Hg^{+2}	80.24	4.09	629.46	3.21	DDTC
Pb^{+2}	199.45	10.17	268.86	13.71	DDTC
Mn^{+2}	155.75	1.83	63.39	4.38	
Fe^{+2}	57.46	2.93	85.93	4.38	SPT
Co^{+2}	42.46	2.16	41.40	2.11	DDTC
Ni^{+2}	38.41	1.96	44.13	2.25	DDTC
Cu^{+2}	63.55	3.24	38.13	4.76	Thiourea
Al^{+3}	198.81	10.10	121.00	6.17	NaF
Cr^{+3}	204.55	10.43	97.64	4.98	
Ce^{+3}	45.85	2.34	43.97	2.21	
In^{+3}	60.92	3.51	36.55	4.61	
Bi^{+3}	330.86	16.86	315.48	16.08	
Ga^{+3}	220.64	11.25	212.66	10.84	
Carbonate	195.48	9.97	76.35	3.82	
Bicarbonate	150.93	7.69	90.82	4.63	
Chloride	197.88	10.0	119.35	6.08	
Bromide	442.44	22.56	266.05	13.56	
Iodide	379.14	19.33	227.83	11.61	
Nitrite	662.44	33.77	410.16	20.45	
Thiosulfate	474.34	24.18	284.99	14.53	
Persulfate	1016.48	51.82	614.07	31.30	
Sulfite	778.36	39.68	453.68	23.13	
Phosphate	760.00	38.74	426.00	21.72	
Benzoate	414.87	21.15	248.97	12.69	
Sulfide	52.36	2.67	175.26	8.93	
Thiourea		0.1 mL (5%)			No interference
Sodium fluoride		0.4 mL (10%)			No interference
Sodium diethyl thiocarbamate (DDTC)		0.1 mL (3%)			No interference
Sodium potassium tartarate (SPT)		0.2 mL (10%)			No interference

DDTC, sodium diethyl thiocarbamate; SPT, sodium potassium tartarate.

Table 4. Spectrophotometric determination of zinc in pharmaceutical formulations and human hair samples using reagents I and II

	Zinc content				
		Using ligand I		Using ligand II	
Pharm. formulation	Certified value (ppm)	Conc. (ppm)	R.S.D.	Conc. (ppm)	R.S.D.
Minervit[a]	14.9912	15.7676	0.5490	15.2888	0.2104
Feroglobin[b]	12.0000	11.9872	0.0091	12.2995	0.2118
Osteocare[c]	5.0000	5.0047	0.0033	5.1066	0.0033
Hair samples	AAS	Conc. (ppm)	R.S.D.	Conc. (ppm)	R.S.D.
The hair sample of a child	0.425	0.4224	0.0021	0.4204	0.0033
The hair sample of a youth	0.385	0.3928	0.0057	0.3674	0.0279
The hair sample of an old man	0.245	0.2744	0.0205	0.2491	0.0816

R.S.D., relative standard deviation; AAS, atomic absorption spectroscopy.
[a]Egyptian Int. Pharmaceutical Industries Co., Tenth of Ramadan City, A. R. E.
[b,c]El Pharaonia Pharmaceutical for Manayer Egypt Medical Co., Cairo A. R. E., under licensees of Vitabiotics Ltd., England.

recommended methods of analysis.[18] The calculated and found values of the elemental microanalysis and metal content are in satisfactory agreement with each other with high accuracy, supporting the suggested molecular formulae listed in Table 5. The molar conductance (Δ_m) values for the complexes under study in DMF are in the range $0.22-0.42\,\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ (Table 5) indicating their non-ionic nature[19] (i.e, the anions, where present, are present inside the coordination sphere).

The electronic spectra of the zinc(II) chelates with ligands I and VI (Table 6) showed mainly the intramolecular charge transfer (CT) band of the ligand molecule with large shift when compared with the free ligands within the range 26,316–27,027 and 25,974–28,571 cm^{-1} using Nujol mull and DMF, respectively. The weak new bands appearing in the spectra of Zn(II) complexes (not present in the spectra of ligands) within the ranges 19,608–20,161 and 19,608–20,618 cm^{-1} would be assigned to the metal–ligand interaction. The small changes of ν (cm^{-1}) values of the CT band on going from Nujol mull to DMF show that the metal ion environment does not differ in the solid state from that in solution, hence the metal–ligand band is slightly influenced on going from the solid state to solution.

Table 5. Molecular formula, elemental analysis and metal content of Zn(II) complexes with ligands I and VI

Complex	Mol. form.	% C Cal. (Fou.)	% H Cal. (Fou.)	% N Cal. (Fou.)	% M Cal. (Fou.)
I_1	$C_{10}H_{21}N_5O_{10}Zn$	28.14 (28.68)	4.92 (5.02)	16.42 (16.73)	15.33 (15.63)
I_2	$C_{16}H_{20}N_{10}O_8Zn$	34.31 (35.20)	3.57 (2.73)	25.02 (25.67)	11.86 (11.99)
VI_1	$C_{10}H_{12}N_5O_5ZnBr$	28.01 (28.08)	2.80 (2.81)	16.34 (16.38)	15.27 (15.30)
VI_2	$C_{16}H_{14}N_5O_4ZnBr$	30.02 (30.23)	2.19 (2.20)	21.89 (22.04)	10.23 (10.29)

On examining the infrared spectra of the zinc(II) complexes in comparison to those of the corresponding free ligands I and VI (Table 7), the following can be pointed out:

1. The absorption bands for the free ligands occurring at 1395 and 1405 cm^{-1} due to ν(N=N) for ligands I and II, respectively, are shifted to lower or higher frequency in zinc(II) complexes, indicating the participation of nitrogen atom from the azo group to complex formation, which is supported by the appearance of a new band in the region 536–582 cm^{-1} due to ν(M–N).[5]
2. The IR spectra of zinc(II) complexes show broad bands at 3424–3446 cm^{-1}, which can be assigned to ν(OH) of the water molecules associated with the complexes. The presence of lattice water molecules in the complexes makes it difficult to consider the behavior of the ν(OH) band of the phenolic group.
3. The infrared spectra of the zinc(II) chelates under investigation show new bands at 651–662 cm^{-1}, which is characteristic of M–O bond[20] resulting from the interaction between hydroxylic oxygen atom with

Table 6. UV-Vis spectral data and molar conductance measurements of zinc complexes with ligands I and VI

	DMF		Nujol mull		
Complex	Band (A)	Band (B)	Band (A)	Band (B)	Δ_m
I_1	28,571	20,000	26,596	20,161	0.42
I_2	25,974	20,618	26,666	20,000	0.29
VI_1	27,548	20,408	27,027	20,000	0.22
VI_2	28,169	19,608	26,316	19,608	0.15

Δ_m, the molar conductance in DMF (ohm^{-1} cm^2 mol^{-1}).

Table 7. IR spectral data of ligands I and VI and their zinc complexes

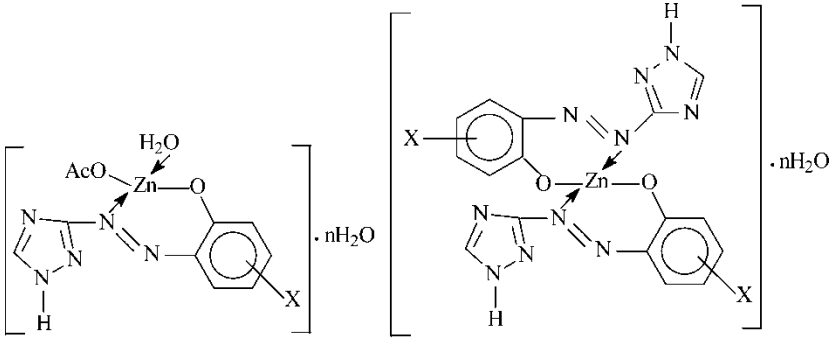
Compound	ν(OH)	ν(N=N)	δ(OH)	δ(M–O)	δ(M–N)
I	3399	1395	1320	—	—
I_1	3424	1398	1293	651	536
I_2	3425	1399	1257	658	582
VI	3402	1405	1260	—	—
VI_1	3424	1401	1283	662	581
VI_2	3446	1398	1282	658	582

central metal ion, denoting that the azo dyes are bonded to the metal through a covalent bond with the oxygen atom of the OH group.

4. The infrared spectra of zinc(II) complexes (I_1) and (VI_1) displayed new bands at 1589 and 1595 cm^{-1}, which can be assigned to the stretching of the C=O bond of the acetate groups.

Accordingly, the metal ions will be chelated covalently with the oxygen of the phenolic OH group and coordinately with a nitrogen of the azo group. This indicates that the azo dyes under investigation behave as monobasic bidentate ligands toward Zn(II) ion.

The TGA curves show a weight loss occurs at 95.0–112°C, which is interpreted as the loss of hydration water molecules. The partial decomposition of the organic part of the complexes occurs along the second decomposition step within the temperature range 400–430°C. At the final stage (600–800°C), the metal oxide was formed after decomposition of the whole organic molecule. The final product would be ZnO, the amount of which is in agreement with Zn(II) content of the complexes.



Scheme 2. Representative structures of the prepared Zn(II) complexes.

Based on the knowledge gained from the studies of the solid complexes, the structure of the 1:1 and 1:2 (M:L) Zn(II) complexes would be formulated as in Scheme 2.

CONCLUSIONS

The article describes a new spectrophotometric method for the determination of zinc(II) with 3-(2,4-dihydroxy-1-phenylazo)-1,2,4-triazole) (I) and 3-(2-hydroxy-5-methyl-1-phenylazo)-1,2,4-triazole) (II). In comparison with other reagents, this method has the following aspects: high sensitivity ($\varepsilon = 4.86 \times 10^4$ and $2.10 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ for ligands I and II, respectively), reaction rapidity, condition mildness, good reproducibility, and relatively little interference. Other reagents give less sensitivity ($\varepsilon = 1.34 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$)[8] or need addition of emulsifiers in order to increase the method sensitivity.[7] When applied to determinate Zn(II) ion in pharmaceutical formulations and human hair samples, the method gave very close results to the certified values and the results obtained from atomic absorption spectroscopy.

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