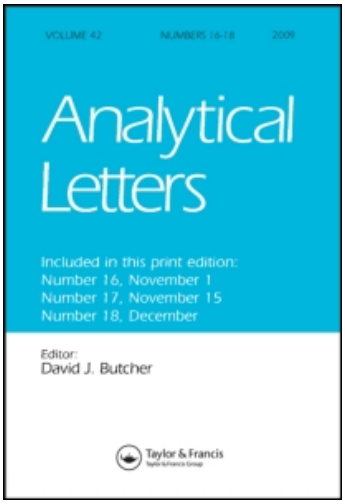

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Spectrophotometric Determination of Zinc in Pharmaceutical Samples with Some Salicylic Azo Compounds

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SPECTROPHOTOMETRIC DETERMINATION OF ZINC IN PHARMACEUTICAL SAMPLES WITH SOME SALICYLIC AZO COMPOUNDS

Key Words : The salicylic azo compounds, determination of zinc in pharmaceutical preparations.

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ABSTRACT

A sensitive spectrophotometric method for zinc has been established by reacting zinc with three salicylic acid azo dyes 2-hydroxy (Ia), 2-carboxy (Ib) and 4-(2-arsonophenylazo) salicylic acid (Ic) in universal buffer solution of pH 8.4, 7.1 and 6.0, respectively. The molar absorptivities are 1.16, 1.39 and 1.36 X 10^4 l/mol.cm at 515, 450 and 525 nm using reagents Ia, Ib and Ic respectively. The formed complexes have the molar ratios of zinc to ligands 1 : 1 and 2 : 1. Beer's law is obeyed upto 7.19 ppm of zinc whereas the optimum concentration range as evaluated by Ringbom's method is 0.5-7.00 ppm. Sandell sensitivities of the method are evaluated. The method has been used to determine zinc in various pharmaceutical products.

INTRODUCTION

Zinc in trace amounts is essential for enzymatic reactions in animal nutrition. Its deficiency causes serious hazards, but overdosage results in poisonous effects. From this physiological point of view, the determination of zinc in pharmaceutical compounds is important. Numerous reagents have been used for the spectrophotometric determination of zinc [1-7]

The proposed method is relatively simple, rapid, and does not require extraction or temperature control. The method

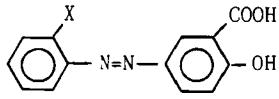
finds a wide range of applications in the analysis of commercial drug samples containing zinc.

EXPERIMENTAL

Reagents

Analytical grade chemicals were used throughout. The stock solution of zinc was prepared by dissolving 2.875 g of $ZnSO_4$-$7H_2O$ in 100 ml of bidistilled water. The solutions of lower concentrationswere prepared by suitable dilution.

Solutions of ligands (10^{-3}m) Ia, Ib and Ic were prepared by dissolving accurate weight of the solid, prepared and purified according to the previous method [8,9] in ethanol.



X = OH (Ia) COOH (Ib) and ASO $(OH)_2$ (Ic)

Universal buffer solutions of pH values 2.04-12.56 were prepared as recommended previously [10].

Apparatus

An Orion Research Model 601 A/Digital Ionalyzer, pH-meter with a combined saturated calomel-glass electrode was used for pH measurements. A Perkin Elmer Λ 3B recording spectrophotometer, equiped with 10 mm matched silica cells was used. All experiments and measurements were carried out at ambient temperature.

Procedure

Transfer a suitable aliquot (upto 5 ml) of a sample solution containing 6.5-180 μg of zinc into a 25-ml measuring flask. Add with mixing 15 ml of buffer solution of suitable pH value for different ligands and 5 ml of ligand (Ia, Ib or Ic) solution. Shake the mixture well for 2 min, dilute to the mark with bidistilled water and measure the

absorbance at the recommended wavelength against a reagent blank similarly prepared.

RESULTS AND DISCUSSION

The ligands are characterized by an intense broad band in the wavelength range 270-420 nm [Fig. (1)]. On the addition of Zn ions these bands are shifted to longer wavelengths as a result of complex formation. The following is a study of the optimum condition for the spectrophotometric determination of zinc ions using the reagents under investigation Ia-c.

Effect of time and temperature

It was found that the full colour development of the complex is obtained after shaking for 2 min and remains constant for 15 hr., after which the solutions suffer a decrease in absorbance. It was also found that raising the temperature up to 60°C has no effect on the absorbance of Zn-complexes, whereas boiling destroys the colour of formed complexes.

Effect of pH

The Britton universal buffers [10] were the most suitable media for developing the orange-red complexes of Zn^{2+}. Measurements have shown that the pH at which the maximum complex formation occurs depend on the ligand used [Fig. (1)]. The absorption spectra of the ligands and their Zn-complexes at the recommended pH values indicate that the visible absorption bands of the free ligands are bathochromically shifted in the presence of Zn^{2+} ions to 515, 450 and 525 nm using reagents Ia, Ib and Ic respectively [Fig. (2)].

Effect of reagents concentration

The effect of reagents concentration has been studied by measuring the absorbance at 515, 450 and 525 nm using pH's 8.4, 7.09 and 6.01 for Ia, Ib and Ic respectively, of

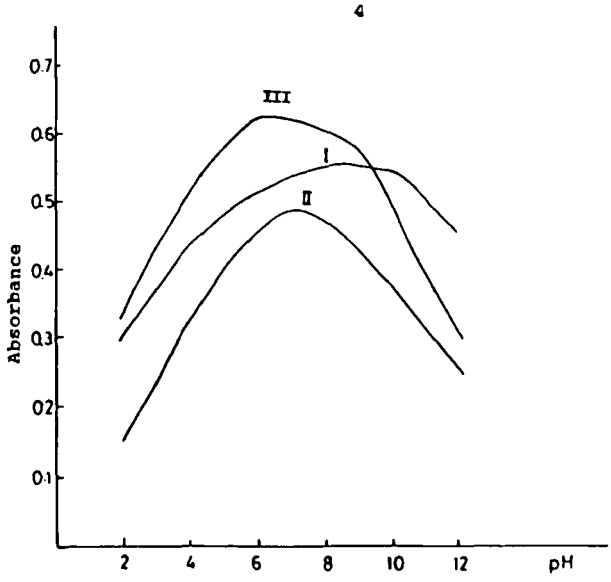


Fig. (1): Effect of pH values on the absorbance of the complexes formed between 2 X 10^{-4}M (Ia, Ib and Ic) with 3.9 ppm of Zn^{3+} ions at pH = 7.0 and 6.01 at λmax = 515, 450 and 525 nm respectively.

solutions containing 3.9 ppm of Zn^{2+} ions. A 2 X 10^{-4}M of the reagent is adequate for the full development of orange-red colour. Addition of excess reagent has no adverse effect on the absorbance.

The stoichiometry of the complexes:

Investigation of the molecular ratio of Zn^{2+} complexes with Ia, Ib and Ic in the light of the spectrophotometric results obtained from the molar ratio and continuous variation methods revealed the formation of 1 : 1 and 2 : 1 (M : L) complexes. The stability constants of these complexes are calculated from the data of molar ratio and continuous variation methods applying the Harvey and

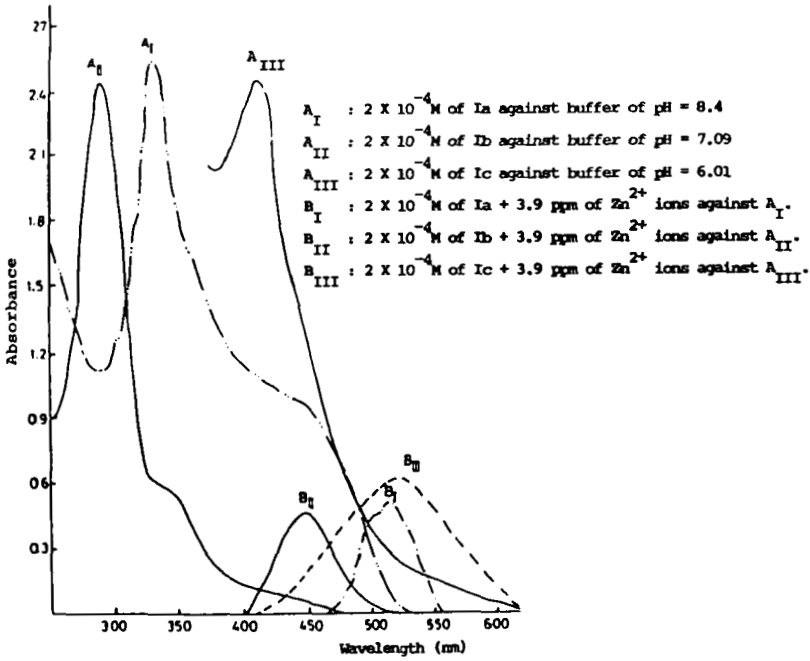


Fig. (2): Absorption spectra of ligands Ia, Ib and Ic and their complexes with Zn^{2+} ions.

Manning euqation[11]. The values of the log of K_f amount to 8.2, 8.5 and 7.4 for 1 : 1 complexes, whereas for 2 : 1 complexes the log of K_f are 5.9, 6.3 and 4.8 for Ia, Ib and Ic respectively.

Spectrophotometric characteristics:

In presence of excess ligands only 1 : 1 complex is formed and thus used for analytical purposes. Beer's law is obeyed for the range 0.26-6.54, 0.26-5.88 and 0.26-7.19 ppm for complexes of Ia, Ib and Ic respectively. The molar absorptivity of the 1 : 1 Zn complexes were 1.16, 1.39 and 1.36 X 10^4 liters/mol. cm, whereas the Sandell sensitivity were 8.6, 7.1 and 7.3 ng/cm^2 at 515, 450 and 525 nm for Ia, Ib and Ic - Zn^{2+} complexes respectively.

Table(1): Effect of foreign ions on spectrophotometric determination of 3.9 ppm of zinc.

Tolerance limit ppm	Foreign Ions
500	Ba^{2+}, Sr^{2+}, Ca^{2+}, Bi^{3+}, Al^{3+}, Fe^{3+}, As^{3+}, Sb^{3+}, V^{5+}, Cr^{3+}, Mo^{6+}, U^{6+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-}, tartrate, oxalate, borate, perchlorate, acetate.
300	Mn^{2+}, Mg^{2+}, Pb^{2+}, Pd^{2+}, Au^{3+}, Zr^{4+}, Th^{4+}, Pt^{2+}, benzoate, citrate, thiourea.
120	Ag^{+}, In^{3+}, La^{3+}, Sc^{3+}, Y^{3+}, Sm^{3+}, Gd^{3+}, Eu^{3+}, W^{6+}, Pr^{3+}, thiosulphate, carbonate, bicarbonate, urea.
40	Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, Ascorbic acid.

Effect of foreign Ions

Interference studies showed that a large number of cations and anions do not interfere (yielding less than 2% error in analytical recovery). The effect of foreign ions and their tolerance limits in the determination of zinc applying the described method are reported in Table (1).

Analysis of Pharmaceutical Samples

Stresstabs* 600 and Vitazinc (capsules):

A capsule was dissolved in aqua regia and the solution was evaporated to dryness, to the residue add 2 ml of concentrated sulphuric acid and the solution was evaporated to dryness, again the process was repeated, then dissolved in 100 ml of bidistilled water. An aliquot was taken for estimation of zinc per capsule by the recommended procedure [Table (2)].

Table (2): Analysis of pharmaceutical samples.

Sample	Composition		Amount of zinc certified	Amount found by ligands Ia	Ib	Ic
Stresstabs® 600 (I) (capsules of zinc sulphate with vitamin C, E, B_1, B_2, B_4, B_{12})	Zinc sulphate	23.9 mg;	9.67 mg (per capsule)	9.68 (per capsule)	9.65 (per capsule)	9.70 (per capsule)
	Thiamine monohydrate	20 mg;				
	Riboflavin	10 mg;				
	Nicotinamide	100 mg;				
	Pyridoxine Hydrochloride	10 mg;				
	Cyanocobalamine	25 mg;				
	Calcium pantothenate	25 mg;				
	Cupric oxide	3 mg;				
Vitazinc (capsules) (II)	Zinc gluconate	175 mg;	25.0 mg (per capsule)	25.0 mg (per capsule)	24.8 (per capsule)	24.9 (per capsule)
	Vitamin A	50000 Iu;				
	Vitamin E	100 mg;				
Hamoderme (powder for skin irritations) (III)	Each 100 gm contains:		243 mg (per 1 gm)	244 mg (per 1 gm)	245 (per 1 gm)	240 (per 1 gm)
	Zinc sulphate	0.5 g ;				
	Copper sulphate	1.0 g ;				
	Camphor	2.0 g ;				
	Zinc oxide	30.0 g ;				
	Talc purified	66.5 g .				
Prozoline zinc (IV) (solution)	Each 100 ml contains:		10.1 mg (per 10 ml)	10.1 mg (per 10 ml)	10.1 mg (per 10 ml)	10.1 mg (per 10 ml)
	Zinc sulphate	250 mg;				
	Naphazoline HCl	50 mg;				
	Maleate	50 mg;				
	Cetrimide	2 mg;				

(I) Manufactured by Medical Union Pharma.Company, Abusultan, A.R.E.

(II) Manufactured by Egyptian International Pharma. Ind. Company.

(III) Manufactured by The Nile Company for Pharma & Chem. Ind. Cairo, A.R.E.

(IV) Manufactured by Kahira Pharma & Chem. Ind. Company Cairo, A.R.E.

Hamoderme (talc powder):

The sample (25 mg) was treated with 3 ml of concentrated sulphuric acid, the solution was diluted, washed with water and filtered to remove the white residue. The filtrate and washings were completed to 50 ml and analysed for zinc as previously discribed. The calculated amount of zinc per one gram was recorded in [Table (2)].

Prozoline zinc (solution):

A 10-ml portion of the solution was evaporated to dryness and the soluble salts were dissolved in 2 ml of concentrated sulphuric acid. The solution was filtered to remove the insoluble residue and washed 3 times with bidistilled water. The filtrate was made up to 25 ml in a measuring flask. An aliquot was analysed for zinc per 10 ml as described and the results were recorded in Table (2).

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