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Spectrophotometric determination of zinc ions with the use β -correction method

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ABSTRACT

The β -correction method for the spectrophotometric determination of zinc based on colour reaction with PAR is proposed. The use of this modification improved the precision and accuracy of the method. Using the β -correction method zinc was determined in range 0.5-10ppm with limit of detection 0.07ppm. The RSD% of determination was 0.35% at 5ppm level.

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KEYWORDS

Dual-wavelength spectrophotometric procedure;
 β -correction method;
PAR complexes;
Zinc determination;
Pharmaceuticals.

INTRODUCTION

UV-Vis spectrophotometry is one of the most common instrumental technique used in analytical laboratories. Its popularity is caused by many valuable properties such as precision and accuracy of measurements, fast and easy operation and analytical friendly procedures. The main disadvantage of spectrophotometric determination is its low selectivity. Spectrophotometric assay of analyte in complex mixture usually required some additional operation as a separation from matrix, masking reactions or at least a use of mathematical corrections. The last mentioned group of removing interferences belongs to non-invasive techniques which operate on recorded spectra. One of them is a β -correction method invented first time by Gao et. al^[1]. The β -correction technique belongs to the methods of background correction, which derive from dual-wavelength spectrophotometric procedure^[1]. It is used for elimination of interference caused by an excess of the coloured ligand and to determine the real absor-

bance of the chelate formed. The application of the β -correction enabled to obtain the better sensitivity, precision and accuracy than the usual procedure. This approach was used for determination of beryllium in waste water^[1]. The same author used the β -correction method for the spectrophotometric determination of calcium^[2]. Wróbel et. al.^[3] applied the β -correction technique for the determination of magnesium in human serum. This approach was applied successfully for the investigation of properties of the noble metals complexes^[4]. The β -correction was used for improving selectivity and sensitivity of spectrophotometric determination of zirconium ion^[5]. Recently the combination of β -correction with PLS method was proposed for simultaneous determination of zinc and lead in the form methylthymol blue complexes^[6].

In the presented work, the mentioned method was applied for the determination of zinc in the form of complexes with PAR as chelating agent. Zinc is the common element, which plays important role in living organisms, therefore it always occurs in multivitamins or multimineral pharmaceuticals. The US

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Pharmacopoeia^[7] recommends for its determination AAS-technique or extractive-spectrophotometric methods. The most popular procedure applied for standard determination of zinc(II) ion is the extractive-spectrophotometric method based on generation of dithizone complexes^[8].

The aim of the presented work is to develop the simple, sensitive and accurate method for zinc (II) ion determination using PAR as the complexing and chromogenic agent. PAR ((4-2(-pyridylazo)-resorcinol) is the colour, water soluble reagent which belongs to the azo-dyes commonly used for analysis of d-electron metal ions^[8]. The spectrophotometric methods based on complexation reaction with these reagents are characterised by high sensitivity but low selectivity^[8]. Additional disadvantage is an interference caused by an excess of used colour reagent. The β -correction procedure proposed in presented paper is a very efficient approach which allows to avoid or minimise the effect connected with the presence of unreacted colour reagent.

MATERIALS AND METHOD

Reagents

PAR (4-2(-pyridylazo)-resorcinol, monosodium salt, stock solution: the aqueous (0.025%) stock solution of PAR was prepared from the pure product (SIGMA) by dissolving an appropriate weight in 1 l of double distilled deionised water.

Standard zinc(II) solution, (1000ppm) was prepared by dissolving an appropriate weight of $ZnCl_2$ in redistilled deionised water. The working solutions were prepared just before use by an appropriate dissolving in redistilled deionised water.

Borate buffer pH 9.11 prepared by mixing 90 ml of 0.05 M solution of $Na_2B_4O_7$ and 10ml 0.5 M H_3BO_4 solution.

Apparatus

A Hewlett-Packard HP-8452A diode array spectrophotometer coupled to the User Data version software was used for the acquisition and storage of spectral data. The 1.0cm quartz cuvette was used for the spectral analysis.

Procedures

Calibration curve

An appropriate aliquot of zinc, the equivalent to 0.5-10ppm was placed into a 10ml calibration flask, then 2ml of boric buffer (pH 9.11) and 2ml of PAR (concentration 0.025%) were added. Next the mixture was fulfilled to the mark with deionised redistilled water. The absorbance (A' and A) at $\lambda=414$ and 494nm, respectively was recorded in a 1cm cell against mixture of reagents without metal ions as a blank. Calculate βA from equation (2) and use this value for quantification of zinc contents.

Sample preparation

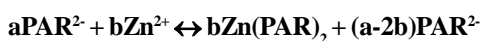
Multivitamin tablets multi tabs

Not less than 10 tablets, each included 10mg of zinc, 1mg of manganese, 15mg of iron and additionally cooper (1mg), selenium (20mg), chromium (20 μ g), iodide (70mg) and organic matrix: vitamins A, B, C, D, E, starch, microcrystalline cellulose and some auxiliary appetising substances were weighed and finely powdered. An accurately weighed portion, equivalent to about 10 mg of zinc, was transferred into a 1000ml calibrated flask and diluted to volume with deionised water. The powder was completely disintegrated by a mechanical shaker, and solution was filtered. 1ml of such prepared tablet's solution was transferred into a 10-ml calibration flask, 1ml of 10ppm solution of sodium phosphate (V) and 1ml of 40ppm solution of sodium citrate were added. Next absorbances were recorded according to procedure described in the calibration section.

RESULTS AND DISCUSSION

The theoretical base

The reaction of Zn(II) with colour reagent (PAR) can be presented as follow:



where a and b are the initial amounts of ligand and metal ion, and (a-2b) is an excess of ligand in the solution in the equilibrium state. The absorption spectra of both PAR and the Zn-PAR complex are shown in figure. As can be seen from figure the real absorbance of complex is lower then that of the reaction solution. In order

to measure the true value of complex absorbance, the b-coefficient is determined. It is expressed by the following equation:

$$b = A_0/A'_0 = A_{494}/A_{414} \quad (1)$$

where A_0 and A'_0 absorbance of PAR measured at $\lambda_1=494$ and $\lambda_2=414$ against water as reference.

The real absorbance of chelate is computed from the following equation:

$$Ab = A - bA'$$

Where A-absorbance of complex at 494 nm measured against the reagent blank;

A'-absorbance of complex at 414 nm against reagent blank.

The figure shows that if λ_1 and λ_2 are selected as minimum and maximum of absorbance spectrum of complex, the sensitivity of determination is the best. The values of Ab can be used for the quantification of zinc contents using the relationship between Ab and concentration of its standard solutions. The absorption maximum and minimum of Zn-PAR are measured at 414 and 494nm, respectively. The value of b coefficient calculated from the spectrum 1 is equal 0.2899.

Chemical variables

The run of reaction PAR-Zn(II) ion depends on reagent concentration, pH of reaction medium and kind of used buffer. In order to find the optimum conditions, the influences of the reaction variables on absorbance of reaction solution were studied. The experiments were carried out using the recommended procedure. Because PAR creates in alkaline solution diverse negative ion,

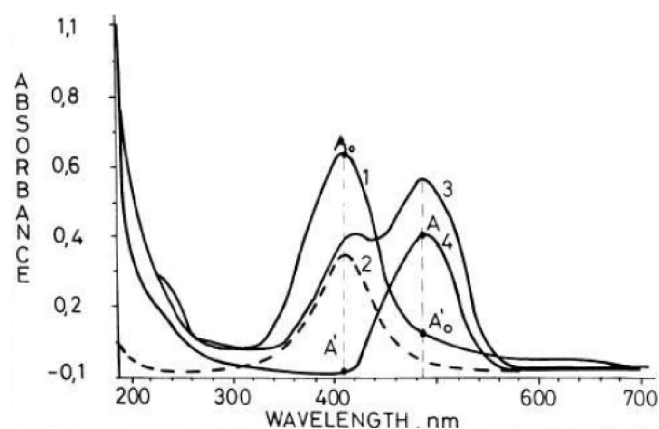


Figure 1 : The spectra of PAR (0.025%) vs. water -curve 1, the excess of reagent (Theoretical curve 2), complex PAR-Zn vs. water ($C_{Zn} = 5 \mu\text{g/ml}$) -curve 3, complex PAR- Zn vs. reagent blank ($C_{Zn} = 5 \mu\text{g/ml}$) -curve 4.

initially the influence of reaction medium pH was studied. For this purpose the ammonia, boric and phosphoric buffers were examined. The absorbance of investigated complex was found to be stable and maximal in boric buffer at pH 9.11. The chosen optimal volume of used buffer was 2 ml in 10–ml total volume. The effect of PAR concentration was also investigated. For this purpose were provided experiments with constant concentration of studied ion (1ppm), pH of reaction medium equal 9.11 and with variable concentration of the complexation reagent. The analytical signal increases with the increase in the reagent concentration up to the concentration of PAR equals 0.005%, above, that it slightly decreases. So the concentration of PAR at 0.005% was applied for further experiments.

Under the experimental conditions described above, the calibration graph for investigated ion was constructed. TABLE 1 gives the equation obtained and other figures of merit, such as limit of detection (S_L)^[9], correlation coefficient and range of linearity. In order to estimate the precision (RSD) of the method, replicate samples ($n=5$) containing $1 \mu\text{g/ml}$ of zinc were measured individually.

Effect of foreign ions

The effect of foreign ions and compounds which

TABLE 1 : Analytical characteristic of elaborated method

Quantification range / $\mu\text{g/ml}$	0.5-10
Equation of calibration curve	$y = (6.62 \times 10^{-2} \pm 1.75 \times 10^{-4})x + 2.41 \times 10^{-2} \pm 9.08 \times 10^{-4}$
Correlation coefficient	0.9999
RSD (%), $n=5$ (at $5 \mu\text{g/ml}$ level)	0.35
Limit of detection/ $\mu\text{g/ml}$ (taken as $s_L = a + 3s_{y/x}$) ^[9]	0.07
Limit of quantification/ $\mu\text{g/ml}$ (taken as $s_L = a + 10s_{y/x}$) ^[9]	0.25

TABLE 2 : The results of zinc (II) determination in multivitamin preparation by b-correction method

Zn(II) content	Found by described method ($n=5$ replications)/mg	Found by dithizone method ^[8] ($n=5$ replications)/mg
	10.01	10.35
Declared value/mg	10	10
Relative error (versus declared value)	+ 0.1	+ 3.5
RSD/%	0.29	6.43
Confidence interval $\pm t_{0.95s}$	± 0.025	± 0.063

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can be found in multivitamin formulation on results of the determination with b-correction was studied. Synthetic solutions containing $1\mu\text{g/ml}$ of the investigated ion and various amounts of foreign substances were measured. The tolerance limit was taken as the concentration of the foreign ion caused an error below 5% in the results of the determination of the studied ion concentration. The obtained results showed that the most common ions presented usually in multivitamin formulations do not influence on the results of the determination of zinc. The most serious interference is caused by ions, which create stable complexes with PAR as e.g. Cu^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} . In order to reduce the interference of diverse ions the 1ml of $40\mu\text{g/ml}$ solution of sodium citrate and 1ml of $10\mu\text{g/ml}$ solution of sodium phosphate (V) were added to reaction solution. The none of following ions affected direct determination: Na^+ , K^+ , Ca^{2+} , Mg^{2+} , I^- , Cl^- , SO_4^{2-} . The other trace components of pharmaceutical like selenium or chromium ions due to their minute amount in preparation do not interfere with zinc assay. The organic compounds of the investigated pharmaceuticals also do not influence the determination.

Analysis of real samples

The content of zinc was determined in the tablets of the multivitamin preparation *Multi* tab in order to complete validation of elaborated method. For this purpose five individual samples were determined. The same samples were determined by classical single wavelength dithizone method^[8]. The results presented in TABLE 2 show that using the b-correction method the more precise and accurate results were obtained. The error of determination does not exceed $\pm 0.1\%$.

CONCLUSIONS

The b-correction method has been applied successfully to the determination of zinc in the form of colour complexes in presence of complicated matrix. The method is simple and fast and allows to obtain the better results then classical single-wavelength method.

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