Simultaneous determination of Zinc(II) and Cobalt(II) by First order derivative Spectrophotometry in Triton X-100 Micellar Media

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Abstract

A derivative spectrophotometric method was developed for simultaneous determination of Zn(II) and Co(II) in an aqueous solutions without the use of chemical separation process. The method was based upon the formation of the pink colored complexes of metal and alizarin red S (ARS). The optimal conditions for the complexation of metal species in 10-ml solution were found at the pH of 7.0 and 1.0 mL of 0.01% (w/v) ARS in Triton X-100 micellar media. The visible absorption peaks of Zn(II)-ARS and Co(II)-ARS were found overlapping at λ_{max} of 535 nm and 548 nm, respectively. The first derivative spectra was acquired by calculating the rate of change in absorbance with the wavelength as a function of wavelength. The molar absorptivity and sandell's sensitivity for zinc(II) and cobalt(II) complexes are $1.143 \times 10^4, 1.358 \times 10^4 L.mol^{-1}.cm^{-1}$ and 0.003, 0.007 $\mu g/cm^2$ respectively. The developed derivative procedure, using the zero crossing technique, has been successfully applied for the simultaneous analysis of Zn (II) and Co(II) in spiked water samples

Keywords: Zinc, cobalt, alizarin red S., simultaneous, derivative spectrophotometry, triton X-100.

Introduction

Spectrophotometric methods are widely used for quantitative analysis of metals. Metal species react with ligands or complexing agents to form colored-complexes. However, most of the ligands are not selective. The spectra of those generated complexes often closely overlap, rendering serious spectral interference. Chemical separation processes have been successfully employed for removing the interfering matrices. Nevertheless, the chemicals used in the processes may introduce additional interfering species.

Alizarin red S (ARS) is a complexing agent commonly used for determination of several metals[1-5] zinc and cobalt, both react with ARS and give rise to chemical interference when present together. Chemical separation and chemometric methods have been in use for resolving the problems. These methods, have disadvantages, *e.g.* chemical waste, harmful process, expensive, *etc.*

Several techniques such as ion chromatography[6], liquid-liquid extraction with atomic absorption spectrometry[7], atomic fluorescence spectrometry[8], X-ray fluorescence spectrometry[9,10] graphite furnace atomic absorption spectrometry[11], inductively coupled plasma atomic emission spectrometry[12] and chemometrics method[13] have been applied for the simultaneous determination of zinc and cobalt ions in different samples. Among the most widely used analytical methods are those based on UV-visible spectrophotometry techniques[14], due to both experimental rapidity and simplicity and the wide application.

Derivative spectrophotometry (DS) is defined as a spectral measurement technique in which the shape of the spectrum is modified via derivative calculation[15,16]. The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands, that means it is resolving two overlapping spectra and eliminating matrix interferences in the assay of two component mixtures using zero-crossing technique. Here we report the simultaneous first order derivative spectrophotometric determination of Zn(III) and Co(II) using Alizarin red S in Triton X-100 micellar media.

Material and Methods

Equipment: A Shimadzu-1800 UV-Vis scanning spectrophotometer equipped with 1.0-cm path length quartz cell used for all absorbance studies and amplitude measurements in derivative spectrophotometery. Digital century pH-meter CP 901 with a combined glass electrode was used for pH measurements

Reagents: All chemicals used were of analytical reagent grade unless otherwise stated. Double distilled water was used throughout. A stock solution (0.01 M) of Zn (II) and Co (II) were prepared in a standard flask. Further dilutions were made as and when required.

An aqueous solution of (0.01% w/v) Alizarin red S was prepared in double distilled water. Solutions of different surfactants such as Tw-20 (1.0%v/v), Tw-80 (1.0% v/v), SLS (1.0%w/v), CPB (1.0%w/v), CTAB (1.0% w/v) and TX-100 (1.0% v/v), were prepared in hot double distilled water. The pH of the working solution was adjusted at 7.0 using 0.5M ammonium hydroxide and 0.5M ammonium chloride buffers.

Recommended procedure: (a) Determination of zinc(II) and cobalt(II) (zero order method): An aliquot of the solution

containing zinc(II) or cobalt(II) in the analytical concentration range (Zn(II) = .320 - 4.55μg/mL; Co(II) = 0.293-4.124 µg/mL), 2 mL of buffer solution (pH = 7.0), 2.0 mL of Triton X-100 (1%) and 0.5-0.5 mL of (0.01%) alizarin red S solution for both Zn(II) and Co(II) were mixed in a 10 mL standard flask and the reaction mixture was diluted to mark with doubly distilled water. The absorbance was measure at 535 nm and 548 nm for zinc (II) and cobalt(II) respectively. The measured absorbance was used to compute amount of metal ion from the respective calibration plot.

Determination of nickel(II) and copper(II) (first order derivative method): For the above solution the first order derivative spectra was recorded in a wavelength range 400 to 650 nm. The first order derivative peak height (h) was measured by peak-zero method. The peak height at 480 nm and 500 nm are proportional to the concentration of Zn(II) and Co(II) respectively. Therefore, peak height method was employed for the construction of calibration plots.

Simultaneous determination by derivative spectrophotometry: For simultaneous determination of Zn(II) and Co(II), a solution containing both Zn(II) and Co(II) in the optimum concentration range (Zn(II) = 0.320 - 4.55μg/mL; Co(II) = 0.293-4.124 µg/mL) was used in the above procedure. The derivative amplitude measured at 548 nm and 535 nm were proportional to the concentration of Zn(II) and Co(II) respectively. Calibration curves are prepared between amplitude and amount of metal ion at their respective wavelength. The amount of metal ion [Zn(II) or Co(II)] was calculated from calibration graphs.

Results and Discussion

Absorption spectra: The complexes of Zn(II)-ARS and Co(II)-ARS were found to form almost instantly after mixing the reagents shown in figure 1. Both complexes appear to be the same pink color. Maximum absorption of Zn(II)-ARS and Co(II)-ARS were found at λ_{max} of 535.0 nm and 548.0 nm, respectively in TX-100 micellar media. The close overlap of the two absorption peaks renders serious spectral interference between the two complexes. However when they present together can be simultaneously determined using derivative spectrophotometry.

Optimization of various parameters: Effect of pH on complex formation: The optimal pH for complexation of metal-ARS was investigated by varying the pH of the system from pH 4-9.5. The effect of pH on the formation of Zn-ARS and Co-ARS is shown in figure 2. Maximum absorption of Zn-ARS and Co-ARS was found over the pH range of 6.0-7.0. Hence, the two complexes are practically formed over the same pH range. The pH of 7.0 was selected for subsequent complexation of both complexes and was maintained by adding 2.0 ml of 0.5 M ammonium chloride/ 0.5M ammonium hydroxide buffer solution.

Effect of nature of surfactant: Different solutions containing fixed amount of individual metal ion and reagent at optimum pH value of 7.0 were prepared. The complexes were dissolved in solution of different surfactants and the spectra were recorded.

Zn(II) and Co(II) - ARS complex showed maximum absorbance with TX-100. So, for simultaneous determination of Zn(II) and Co(II) 2.0.ml of 1.0 % TX-100 was selected as the working micellar medium for further studies. Effect of different surfactants on the absorbance of metal complexes is shown in figure 3.

Amount of complexing agent: The effect of different amounts of reagent for the fixed metal concentration was studied The solution was adjusted at optimum pH value of 7.0 and solubilized in TX 100. The maximum absorbance was observed when 0.5 mL and 0.5 mL of 0.01% ARS was used for individual calibration of Zn(II) and Co(II) as shown in figure 4. It was expected that increasing ARS concentration causes an increase in absorbance because increase in ARS concentration caused an increase in Zn(II) and Co(II) complexes concentration. At higher concentrations of ARS, the concentration of complex did not change significantly but the concentration of uncomplexed ARS increased significantly. Therefore, much probably decrease in absorbance at higher concentrations of ARS. To ensure the complete complexation for simultaneous determination of Zn(II) and Co(II) by derivative spectrophotometry method, 1.0 mL of 0.01% ARS was used for further studies.

Derivative spectrophotometric determination of Zn(II) and Co(II): Derivative spectrophotometry is a useful technique because it decreases the interference i.e. ,increase the tolerance limit value of foreign ions and may be advantageously used for the determination of metal ion having overlapping spectra. The conceptual simplicity, relatively quick and easy realization, increased selectivity in the analysis of minor components is the main reasons why the interest in derivative spectra is constantly growing for practical applications. The recommended derivative procedure was employed for the determination of zinc(II) and cobalt(II).

In the zero-crossing derivative method it is necessary that zero-crossing wavelengths do not change with varying concentrations of the related species. To evaluate the condition, changes in the zero-crossing wavelengths for zinc and cobalt were tested in the presence of different concentrations of another species.

Two sets of mixtures were studied: one with increasing amounts of Zn(II) from 0.320 - 4.55μg/mL at constant concentration of Co(II) and a second with increasing amounts of Co(II) from 0.293- 4.124 µg/mL at constant concentration of Zn(II). The analytical determination of Zn(II) was performed by measuring the first derivative amplitudes at 535 nm and that of Co(II) was performed at 548 nm . At 535 nm Zn(II) complex has a zero crossing point, which is independent of the metal ion concentration and at this wavelength Co(II) has an appreciable amplitude. According to the results given in figures 5 and 6, no shift in the zero-crossing wavelengths was observed.

On comparing Zn(II) and Co(II) first order derivative spectra ,it can be observed that Co(II) has zero or very negligible amplitude at 548 nm, while at 548 nm the amplitude of Zn(II) is appreciable and proportional to the concentration of metal ion. Calibration plots were constructed at 535 nm and 548 nm by plotting the derivative

amplitudes against the corresponding amounts of Co(II) and Zn(II) respectively.

The plots thus obtained are linear obeying the relationship:
Zn(II)A_{548}=0.014C+0.001
Co(II)A_{535}=0.016C+0.001

It was noticed from the linear plots that the derivative amplitude was proportional to the concentration of the metal ions in the range of 0.320- 4.55 µg/mL of Zn(II) and in the range of 0.293-4.124 µg/mL of Co(II).

Calibration graphs and statistical analysis of results: Various statistical parameters were calculated for Zn(II) and Co(II) with zero derivative. The analytical parameters corresponding to zero order and for the simultaneous determination by derivative spectrophotometry are shown in table 1 and 2. The regression equation obtained from calibration curves were calculated for first order derivative spectra are also given in table 2. The values of correlation coefficient and intercept on the axes indicate the good linearity of calibration graphs and correspondence to Beer's law for derivative measurements.

Table-1
Statistical analysis for the determination of Zn (II) and Co(II) by zero order spectrophotometry

Parameters	Results	
	Zn(II)	**Co(II)**
λ_{max}(nm)	535	548
Beer's law range (µg/mL)	0.291 - 4.676	0.279 - 2.233
Molar absorptivity (Lmol^{-1} cm^{-1})	1.143×10^4	1.358×10^4
Sandell's scale sensitivity (µgcm^{-2})	0.003	0.007
Regression Equation	Y = 0.015C + 0.001	Y = 0.012C + .008
Correlation coefficient	0.9993	0.9996

Table-2
Statistical analysis for the determination of Zn(II) and Co(II) in mixtures in presence of Triton X-100 by derivative spectrophotometry

Analyte	λ_{max} (nm)	Regression Equation	r^2	Linear range (µg/ml)	LOD (µg/ml)	LOQ (µg/ml)	RSD (%)
Zn(II)	535	A_{548}=0.014C+0.001	0.9999	0.320-4.55	0.018	0.06	0.290
Co(II)	548	A_{535}=0.016C+ 0.001	0.9998	0.293- 4.124	0.002	0.008	0.242

Table-3
Simultaneous determination of Zn (III) and Co(II) in spiked water samples

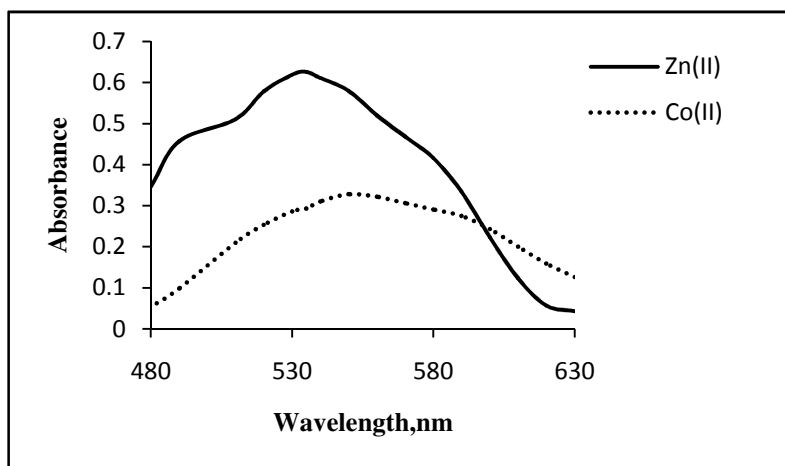| Water sample	Added(µg/ml)		Found(µg/ml)		Recovery (%)	
	Zn(II)	**Co(II)**	**Zn(II)**	**Co(II)**	**Zn(II)**	**Co(II)**
River water	0.350	0.670	0.348	0.672	99.42	100.29
Tap water	0.455	0.600	0.458	0.602	100.6	100.3
Lab water	0.520	0.360	0.523	0.362	100.5	100.5

Figure-1
Absorption spectra of Zn (II) and Co(II) with 1.0 mL ARS (0.01%) solution and 2.0 mL Triton X-100 (1%) at pH 7.0
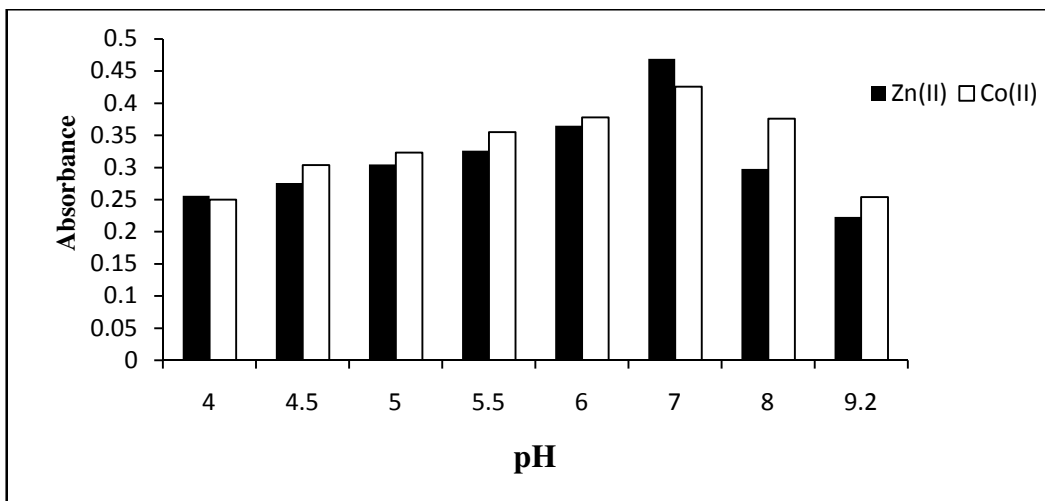
Figure-2
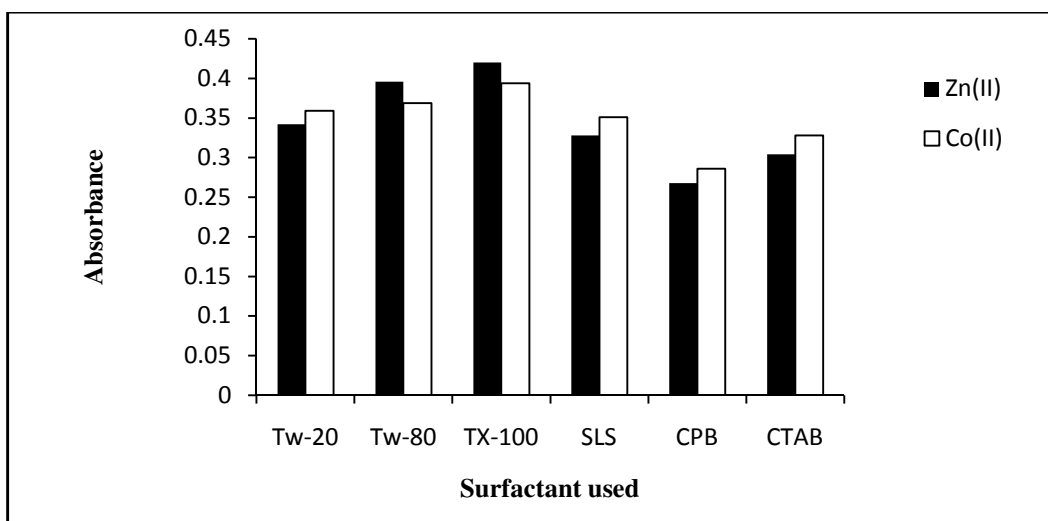**Effect of pH on formation of Zn(II)-ARS and Co(II)-ARS complexes**

Figure-3
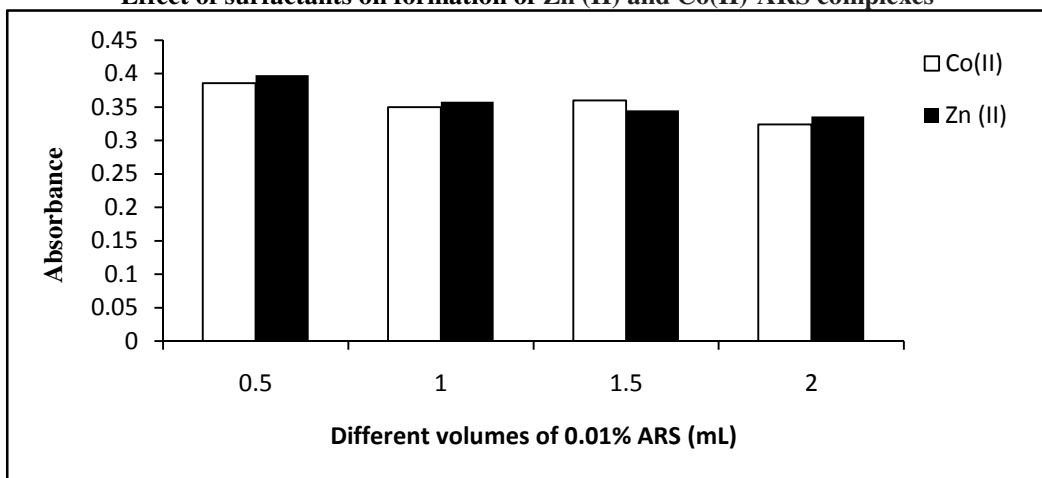**Effect of surfactants on formation of Zn (II) and Co(II)-ARS complexes**

Figure-4
Effect of reagent concentration on the change in the absorbance of Zn (II) and Co (II)-ARS complexes
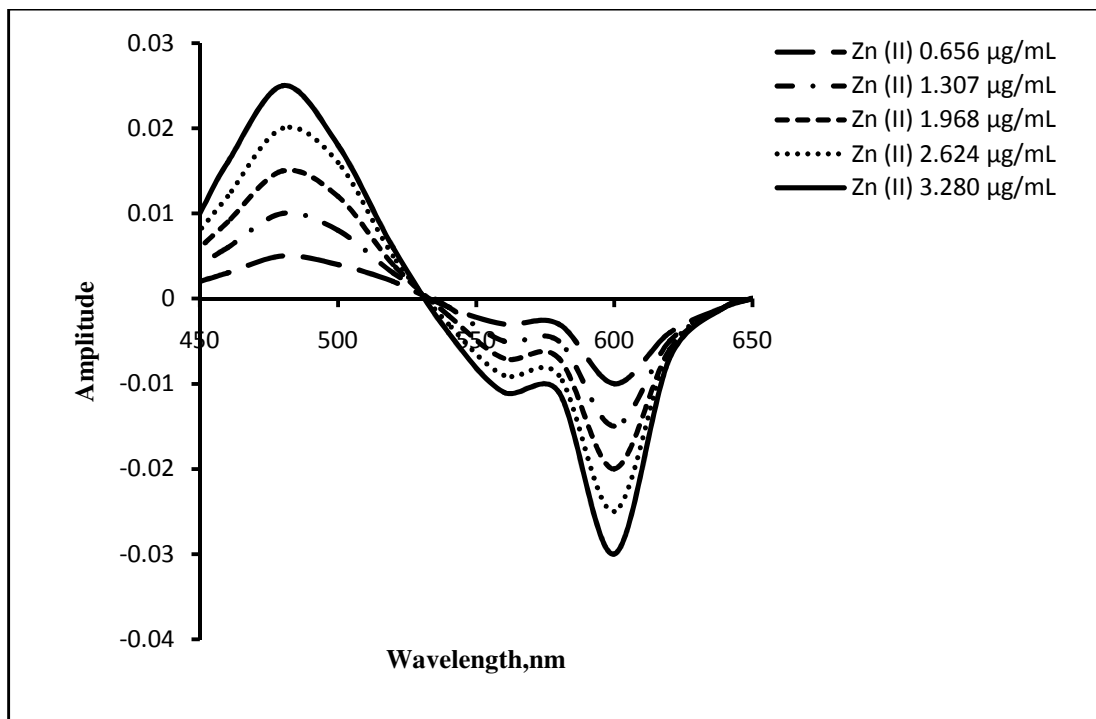
Figure-5
Typical first order derivative spectra of Zn(II)-ARS complex Vs Reagent as blank,
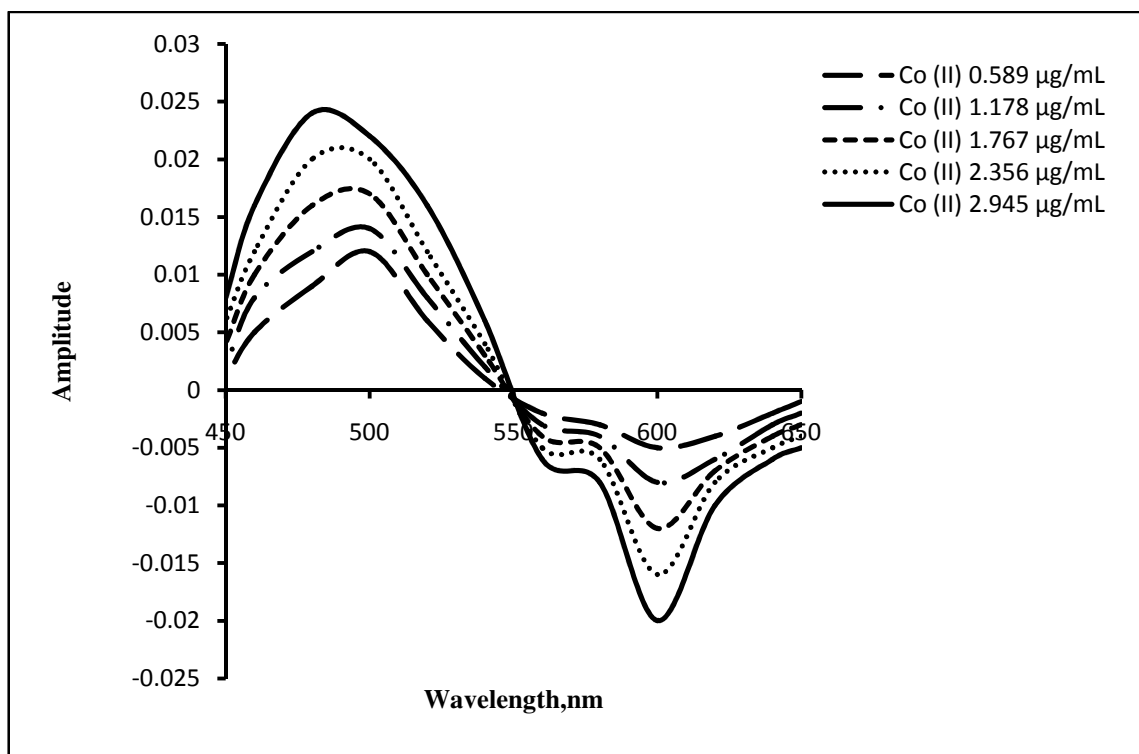**[Conditions: Co (II) = 1.0 μg/mL, ARS(0.01%) = 1.0 mL, pH = 7.0 , Triton X-100 (1%) = 2.0 mL]**

Figure-6
Typical first order derivative spectra of Co(II)-ARS complex Vs Reagent as blank
[Conditions: Zn (II) = 0.750 μg/mL, ARS(0.01%) = 1.0 mL, pH = 7.0 , Triton X-100 (1%) = 2.0 mL]

Effect of foreign ions: The effect of various diverse ions on the absorbance of a solution containing 1.0 μg/mL each of Zn(II) and Co(II) was studied. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample greater than 5%. Among the anions examined F^-, I^-, Br^-, Cl^-, CO_3^{2-}, SO_3^{2-}, SO_4^{2-}, NO_3^-, IO_3^-, NO_2^-, $S_2O_3^{2-}$, CH_3COO^- did not interfere at concentrations 1000 times higher than those of the analytes but EDTA, oxalate ions interfered strongly. Among the cations Hg^{2+}, Cd^{2+} and Cu^{2+} were masked with 1.0 mL of 5% sodium fluoride solution. Bi^{2+} was masked with 2.0 mL of 1 M sodium citrate solution.

Applications: Drinking water resources must contain levels of zinc and cobalt below their critical values. Evaluation of the method for the analysis of high amounts of the 2 metals in drinking water and river water matrices should be performed. For analysis of the water samples, standard zinc and cobalt solutions was spiked into a 10.0 mL flask together with 2.0 mL of the tap and natural water samples. Then the zinc and cobalt contents were analyzed by simultaneous first derivative spectrophotometric procedure (table 3).

Conclusion

The proposed method offers significant advantages over conventional methods because of its speed and ease of operation. This method works without the need of preconcentration or extraction steps. Thus, the inherent errors involved in these time-consuming steps using toxic and carcinogenic organic solvents are avoided, and determination in aqueous phase using micellar system makes the procedure eco-friendly. The proposed derivative spectrophotometric method has appreciable sensitivity with a low detection limit. Moreover, low cost of the instrument, easy handling, lack of requirement for consumable and almost no maintenance have made spectrophotometry still a popular technique.

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