

***H*-Point Standard Addition Method for Simultaneous Determination of Zinc and Nickel in Micellar Media**

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Abstract: The *H*-point standard addition method (HPSAM) has been applied for simultaneous determination of Zn(II) and Ni(II) at trace levels, using Alizarin Red S (ARS) as chromogenic reagent. Both Ni(II) and Zn(II) form red colored complex with Alizarin red S at pH 7.0 which are soluble in triton x-100. Zn(II) and Ni(II) have been determined simultaneously in the concentration range of 0.320-4.55 µg/mL and 0.293-4.676 µg/mL respectively with satisfactory accuracy and precision. The results of applying *H*-point standard addition method show that Zn(II) and Ni(II) ions can be determined simultaneously with concentration ratio of 15:1 and 1:16 of Zn(II) to Ni(II). This method is based on the difference in the absorbance of Zn(II) and Ni(II) - ARS complexes at pH 7.0 using different wavelength pairs.

Keywords: HPSAM, Zinc, Nickel, Simultaneous determination and triton x-100

Introduction

Zinc and nickel appear together in many real samples. Zinc compounds have biocidal activity because they precipitate and denature the bacterial proteins. For this reason it has been used in dermatology as an antiseptic and disinfectant agent in ophthalmic and mouthwash solutions and mineral-vitamin preparations. Nickel is the metal component of the enzyme urease and as such is considered to be essential to plants and some domestic animals. Nickel can cause allergic reactions and that certain nickel compounds may be carcinogenic

Several techniques such as x-ray fluorescence¹, atomic fluorescence spectrometry², polarography³, chromatography⁴, atomic absorption spectrometry⁵ *etc.* have been used for the simultaneous determination of these ions in different samples. Among the most widely used analytical methods are those based on the UV-Vis spectrophotometric techniques⁶⁻¹³ due to the resulting experimental rapidity, simplicity and the wide application. However, the simultaneous determination of these ions by the use of the traditional spectrophotometric techniques is difficult because, generally, the absorption spectra overlap in a bright region and the superimposed curves are not suitable for quantitative evaluation.

In 1988, Bosch - Reig and Campins - Falco¹⁴ delineated the fundamentals of *H*-point standard addition method (HPSAM), with which two species with mostly or even totally overlapping spectra can be determined. HPSAM is applied to work at two selected wavelengths where analytical signal due to one of the species (interferent) is constant and for another one (analyte) to be different as much as possible. By plotting the analytical signals versus added analytical concentration, two straight lines are obtained that have a common point H with coordinates (C_H , A_H); C_H is the unknown analyte concentration and the A_H is the analytical signal due to the interferent species. The HPSAM has been used, eliminating blank bias error due to the use of an absorbent blank¹⁵⁻¹⁶. HPSAM has also been applied to liquid chromatography¹⁷, analysis kinetic data analysis¹⁸⁻²¹ with an additional variant time and in metal speciation²²⁻²⁴.

Micelles possess a high potential for multicomponent analysis, which can be used as special reaction media because they alter the rate, equilibrium position, products and stereochemistry of many reactions. However, micelles also change the effective microenvironment around dissolved solutes and their physicochemical properties, such as absorptivity, equilibrium constant and spectral profile. Surfactants can interact with dye and/or the metal-dye complex as an individual molecule or aggregates. The addition of surfactant-active substances improves the selectivity and sensitivity of the metal determinations.

In the present work a very simple, sensitive, selective and low cost HPSAM for simultaneous determination of zinc and nickel using alizarin red S in triton x-100 micellar media is described. The method has been successfully applied for simultaneous determination of nickel and zinc in synthetic samples and spiked real water samples.

Experimental

A Shimadzu -1800 UV-Vis scanning spectrophotometer was used to record the absorbance spectra with 1.0-cm path length quartz cell. 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 standard Ni(II) and Zn(II) solution were prepared in a standard flask. Working standard solutions were obtained by appropriate dilution of the stock solution. An aqueous solution of (0.01% w/v) Alizarin red S was prepared in double distilled water. A (1.0% v/v) triton x-100 solution was prepared in hot distilled water. The pH of the working solution was adjusted at 7.0 using 0.5 M ammonium hydroxide and 0.5 M ammonium chloride buffers.

Procedure

Appropriate volumes of Zn(II) and Ni(II) standard solutions (Beer's law was obeyed in the concentration range 0.320-4.55 $\mu\text{g/mL}$ of Zinc and 0.293-4.676 $\mu\text{g/mL}$ of nickel), 2.0 mL of 1.0% triton x-100, 2.0 mL of buffer solution (pH 7.0), 1.0 mL of 0.01% alizarin red S solution were added into a 10.0 mL standard flask and volume was made up to the mark with double distilled water. A portion of the solution was transferred into a quartz cell and variations of absorbance were recorded for each sample.

Binary - HPSAM

For the determination of Zn(II) and Ni(II) ions using HPSAM, the synthetic solution containing Zn(II) and Ni(II) ions at different concentration ratios were prepared with 1.0 mL of ARS solution, 2.0 mL of buffer solution (pH 7.0) and 2.0 mL of triton x-100 1.0% in 10-mL volumetric flasks. Absorbance of solution was measured at 564 nm and 504 nm (when standard solution of Ni(II) was added) or 592 and 510 nm (when standard solution of Zn(II) was added) against a reagent blank and graphs of absorbance vs. concentration were plotted. C_H and A_H were obtained from the point of intersection of the two derived straight lines.

Results and Discussion

Absorption spectra

The absorption spectra for Zn(II) and Ni(II) complexes with ARS against blank solution are shown in Figure 1. As Figure 1 shows, the spectra of the complexes overlap with each other, and therefore each compound interferes in the spectrophotometric determination of the other. But simultaneous determination of Zn(II) and Ni(II) is possible by using HPSAM.

Optimization of various parameters

To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimised. These parameters were optimised by setting all parameters to be constant and optimizing one each time.

Effect of pH

The effect of pH on the spectra of a constant concentration of each complex was investigated in the range of 3.5-9.5. The results from Figure 2 showed that the pH of 7.0 gives the highest sensitivity for determination of Zn(II) and Ni(II) respectively. For both cations pH 7.0 was selected as the suitable one for simultaneous analysis of Zn(II) and Ni(II).

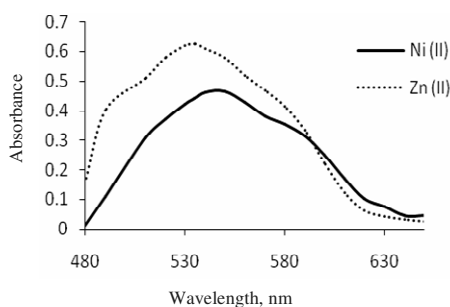


Figure 1. Absorption spectra of Zn(II) and Ni(II) with 1.0 mL ARS (0.01%) solution and 2.0 mL triton x-100 (1%) at pH 7.0

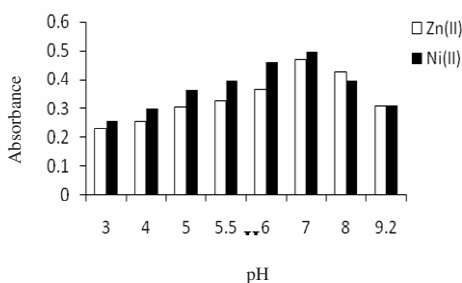


Figure 2. Effect of pH on the change in the absorbance of Zn(II) and Ni(II)-ARS complexes

Effect of nature of the surfactant

Various surfactants such as triton x-100, Tween-20, Tween-80, cetylpyridiniumbromide (CPB), cetyltrimethylammonium bromide (CTAB) and sodium lauryl sulphate (SLS) were tried as solubilizing agents. Both for Zn(II) -ARS and Ni(II) -ARS complex absorbance was maximum with triton x-100 as shown in Figure 3. So, for simultaneous determination of Zn(II) and Ni(II), 2.0 mL of 1.0% triton x-100 was selected as the working micellizing agent for further studies.

Effect of Alizarin red S (ARS) concentration

Effect of different amounts of ARS on the absorbance of Zn(II)–ARS and Ni(II) –ARS complexes was studied. The maximum absorbance in both the cases was observed when 0.5 mL and 0.5 mL of 0.01% ARS was used for individual calibration of Zn(II) and Ni(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 Ni(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 Ni(II), 1.0 mL of 0.01% ARS was selected as the optimum .

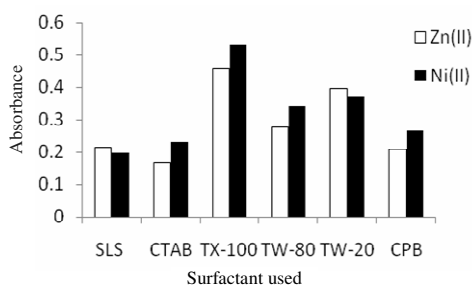


Figure 3. Effect of surfactants on complex formation of Zn(II) and Ni(II)-ARS

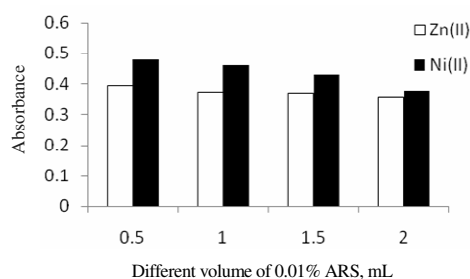


Figure 4. Effect of reagent concentration on the change in the absorbance of Zn(II) and Ni(II)-ARS complexes

Applying H-point standard addition method (HPSAM)

Either Zn(II) or Ni(II) can be selected as analyte when applying binary-HPSAM. When Zn(II) was selected as an analyte, many pairs of wavelengths showing the same absorbance for Ni(II) -ARS complex were possible. In the selection of one pair of wavelengths for obtaining good accuracy, the absorbance differences at the two selected wavelengths for Zn(II)-ARS complex must be as large as possible. Based on the absorption spectra of Zn(II) or Ni(II) complexes, one of the best pair of wavelengths was 592.0 nm and 510.0 nm when standard solution of Zn(II) were added *i.e.* Zn(II) was selected as analyte. Similarly, best pair of wavelengths for applying binary –HPSAM was 564.0 and 504.0 when Ni(II) was selected as an analyte. C_H and A_H were obtained from the point of intersection of the two derived straight lines in the *H*-point graphs of absorbance versus analyte concentration where $-C_H$ was the concentration of analyte and A_H the analytical signal due to interferent species.

Several experiments for evaluating HPSAM on the determination of Zn(II) and Ni (II) in a series of samples containing fixed amounts of Zn(II) with different amounts of Ni(II) (Figure 5) or fixed amounts of Ni(II) with different amounts of Zn(II) (Figure 6) were carried out by adding Zn(II) standard solutions. The applicability of HPSAM was also tested for determination of Ni(II) and Zn(II) in a series of samples containing fixed amounts of Ni(II) together with different amounts of Zn(II) (Figure 7) or fixed amounts of Zn(II) together with different amounts of Ni(II) (Figure 8) were carried out by adding Pb(II) standard solutions. The results show that Zn(II) and Ni(II) contents in the samples could be determined accurately.

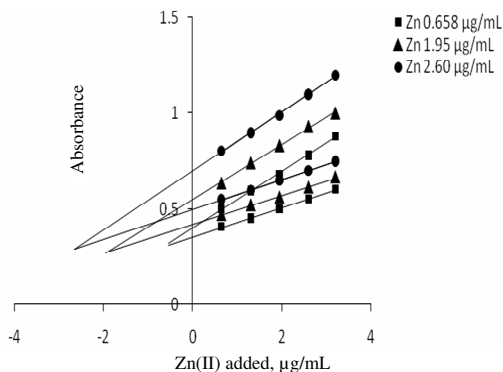


Figure 5. Plot of *H*-point standard addition method for simultaneous determination of fixed amounts of Ni(II) and different amounts of Zn(II). [Condition: pH 7.0, 2.0 mL of 1.0% triton x-100, 2.0 mL of 0.01% alizarin red S and 0.586 µg/mL Ni(II) and different concentration of Zn(II), when different amounts of standard Zn(II) solutions are added]

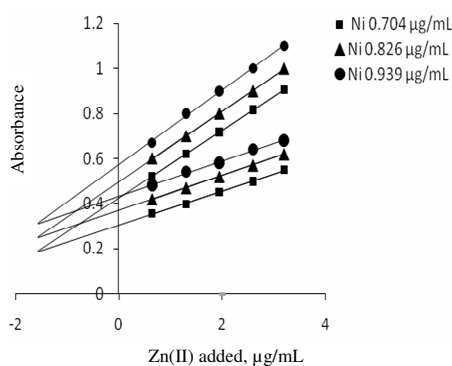


Figure 6. Plot of *H*-point standard addition method for simultaneous determination of fixed amounts of Ni(II) and different amounts of Ni(II). [Condition: pH 7.0, 2.0 mL of 1.0 %triton x-100, 2.0 mL of 0.01% Alizarin red S and 1.25 µg/mL Zn(II) and different concentration of Ni(II), when different amounts of standard Zn(II) solutions are added]

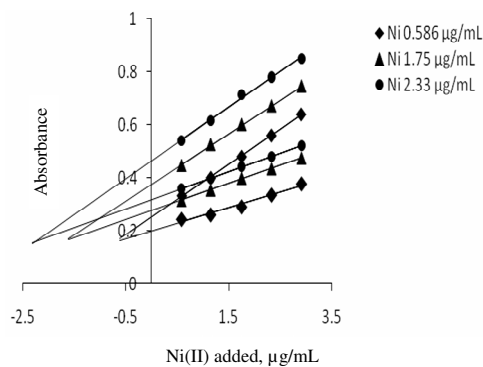


Figure 7. Plot of *H*-point standard addition method for simultaneous determination of fixed amounts of Zn(II) and different amounts of Ni(II). [Condition: pH 7.0, 2.0 mL of 1.0% triton x-100, 2.0 mL of 0.01% alizarin red S and 0.656 µg/mL Zn(II) and different concentration of Ni(II), when different amounts of standard Ni(II) solutions are added]

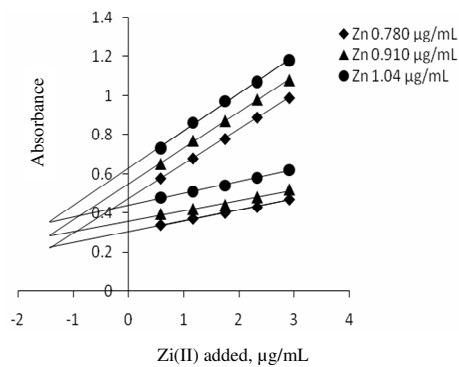


Figure 8. Plot of *H*-point standard addition method for simultaneous determination of fixed amounts of Ni(II) and different amounts of Zn(II). [Condition: pH 7.0, 2.0 mL of 1.0% Triton x-100, 2.0 mL of 0.01% alizarin red S and 1.30 µg/mL Ni(II) and different concentration of Zn(II), when different amounts of standard Ni(II) solutions are added]

Reproducibility of the HPSAM

Under optimum conditions described above, simultaneous determination of Zn(II) and Ni(II) were made using HPSAM. To investigate the reproducibility of the method, four replicate

measurements of the Zn(II) and Ni(II) were performed (Table 1). The concentrations of both species were obtained from C_H values. The relative standard deviation (R.S.D.) for determination of Zn(II) and Ni(II) were obtained as 0.764 and 0.1493%, respectively.

Table 1. Results of several experiments for the analysis of Zn(II) and Ni(II) mixtures in different concentration by HPSAM

A-C Equation	r^2	Present, $\mu\text{g/mL}$		Found, $\mu\text{g/mL}$		(%Recovery)	
		Ni	Zn	Ni	Zn	Ni	Zn
$A_{564}=0.213C_i+0.774$	0.9985	0.586	1.43	0.561	1.42	95.73	99.30
$A_{504}=0.034C_i+0.669$	0.9994						
$A_{564}=0.369 C_i+0.523$	0.9998	1.170	1.43	1.172	1.39	100.17	97.20
$A_{504}=0.225 C_i+0.354$	0.9996						
$A_{564}=0.413C_i+ 0.526$	0.9999	0.708	1.569	0.704	1.559	99.43	99.36
$A_{504}=0.230C_i+0.397$	0.9988						
$A_{564}=0.395C_i+0.558$	0.9989	0.826	1.569	0.839	1.561	101.57	99.49
$A_{504}=0.221C_i+0.412$	0.9986						
$A_{592}=0.195C_i+0.251$	0.9985	1.29	0.650	1.31	0.653	100.46	101.55
$A_{510}=0.097C_i+0.187$	0.9996						
$A_{592}=0.189C_i+0.267$	0.9989	1.29	1.307	1.27	1.304	98.44	99.77
$A_{510}=0.107 C_i+0.160$	0.9998						
$A_{592}=0.117C_i+0.240$	0.9999	1.40	1.430	1.43	1.470	102.14	102.79
$A_{510}=0.073 C_i+0.175$	0.9998						
$A_{592}=0.091 C_i+0.318$	0.9985	1.40	1.560	1.38	1.580	101.28	98.57
$A_{510}=0.043 C_i+0.242$	0.9984						

Precision and accuracy of the HPSAM

In order to obtain accuracy of the method several synthetic mixtures with different concentration ratios of Zn(II) and Ni(II) were analyzed using the proposed HPSAM. The results are given in (Table 2). As can be seen in (Tables 1 and 2), the precision and accuracy of the method are both satisfactory.

Table 2. Results of four replicate experiments for the analysis of Zn(II) and Ni(II) mixtures

A-C Equation	Present, $\mu\text{g/mL}$		Found, $\mu\text{g/mL}$	
	Ni	Zn	Ni	Zn
$A_{564}=0.197C_i+0.250$	0.650	0.950	0.653	0.948
$A_{504}=0.099C_i+0.186$				
$A_{564}=0.191C_i+0.252$	0.650	0.950	0.645	0.949
$A_{504}=0.095C_i+0.190$				
$A_{564}=0.195C_i+0.248$	0.650	0.950	0.642	0.951
$A_{504}=0.097C_i+0.185$				
$A_{564}=0.194C_i+0.246$	0.650	0.950	0.645	0.948
$A_{504}=0.098C_i+0.184$				
Mean			0.645	0.949
RSD, %			0.764	0.149
LOD			0.014	0.004
LOQ			0.049	0.014

Interference analysis

The effect of various diverse ions on the absorbance of a solution containing 1.0 µg/mL each of Zn(II) and Ni(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⁻, CO₃²⁻, SO₃²⁻, SO₄²⁻, NO₃⁻, IO₃⁻, NO₂⁻, S₂O₃²⁻ and CH₃COO⁻ did not interfere at concentrations 1000 times higher than those of the analytes but ethylenediamine tetraacetate ion, oxalate ions interfered strongly. Among the cations Hg²⁺, Cd²⁺ and Cu²⁺ were masked with 1.0 mL of 5% sodium fluoride solution. Bi²⁺ was masked with 2.0 mL of 1 M sodium citrate solution.

Application

HPSAM was applied to the determination of Ni(II) and Zn(II) in several real matrix samples. For this purpose, diverse spiked water samples were analysed. The results of analysis are shown in Table 3. The good agreement between these results and known values indicates the successful applicability of the proposed method for simultaneous determination of Ni(II) and Zn(II).

Table 3. Determination of Ni(II) and Zn(II) mixtures in different water samples by Binary-HPSAM

Water sample	Spiked, µg/mL		Found, µg/mL	
	Zn(II)	Ni(II)	Zn(II)	Ni(II)
Yamuna River water*	0.455	0.670	0.449	0.676
Ganga River Water**	0.355	0.655	0.357	0.656
Industrial waste water***	0.65	1.00	0.70	1.05
	0.350	0.380	0.352	0.376

* Collected from Yamuna Nagar. ** Collected from Haridwar, *** Collected from NAHAR industries Ltd.; Bhanut

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 spectrophotometric method has a low detection limit which enhances its sensitivity. Moreover, low cost of the instrument, easy handling and almost no maintenance have made spectrophotometry still a popular technique.

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