SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF Ni(II) AND Zn(II) IN WASTE WATER BY H-POINT ADDITION STANDARD METHOD USING 5-BROMOSALICYLALDEHYDE THIOSEMICARBAZONE

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Optimized and validated spectrophotometric method is proposed for the determination of nickel and zinc simultaneously. 5-bromosalicylaldehyde thiosemicarbazone (5-BSAT) reacts with nickel(II) and zinc(II) to form [Ni(II)-(5-BSAT)$_2$] and [Zn(II)-5-BSAT] complexes, respectively. The maximum absorbance of these complexes was found at 378 nm and 381 nm, respectively. For [Ni(II)-(5-BSAT)$_2$], Beer's law is obeyed over the concentration range of 2.0×10^{-6} M $-$ 6.0×10^{-5} M with molar absorptivity, ε of 0.92×10^4 L.mol^{-1}.cm^{-1}. [Zn(II)-5-BSAT] complex obeys Beer's law in 2.0×10^{-6} M $-$ 6.0×10^{-5} M range with molar absorptivity, ε of 1.08×10^4 L.mol^{-1}.cm^{-1}. A simultaneous spectrophotometric H-point standard addition method (HPSAM) is proposed for the determination of these metals. The proposed method is successfully employed in the analysis of waste water sample for the determination of nickel and zinc content.

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Introduction

In the literature, due to a strong environmental and biological impact, trace metal ions determination has received particular attention in the last years. UV-Vis spectrophotometry, atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), X-ray fluorescence spectrometry, inductively coupled plasma - mass spectrometry (ICP-MS), voltammetry, high performance liquid chromatography (HPLC) and ion selective electrode (ISE) have been used for the determination of metal ions in different samples. Among these methods, spectrophotometry is a simple, sensitive and effective method for analysis.

In 1988, H-point standard addition method (HPSAM) was reported based on the principle of dual wavelength spectrophotometry and the standard addition method. The greatest advantage of HPSAM is that it can remove errors resulting from the presence of an interference and reagent blank. In order to apply HPSAM to resolve mixtures, the interferent(s) species should be known.[1-3] Due to advantages, HPSAM has applied incresingly in the field of simultaneous determination of binary mixtures.

Schiff base ligands have played an integral and important role in coordination chemistry since the late 19th century and containing strong donor sites like phenoxo oxygen atoms as well as imine nitrogen atoms and find extensive applications in different fields for their special coordination ability with transition metal ions.

Schiff bases have been developed as chelating ligands/catalysts for oxy-genation and oxidation reactions of organic compounds, redox systems in biological processes, aldol reactions, degradation of dyes through decomposition of hydrogen peroxide and other reagents, epoxidation and many other applications.[4-12]

Nickel and zinc are metals that appear together in many real samples. Few reports have been published on the simultaneous determination of these ions in different samples. This paper describes simultaneous spectrophotometric determination of Ni^{2+} and Zn^{2+} based on their complexes with potential active Schiff base ligand, 5-bromosalicylaldehyde thiosemicarbazone (5-BSAT)), with the aid of chemometric approaches, (HPSAM).

Experimental

Chemicals

Stock solutions of nickel(II) and zinc(II) (0.01 M) were prepared from a suitable mass of respective compounds in double distilled water and made up to the mark in a 100-ml volumetric flask. Working solutions of these ions were prepared by diluting the stock solution to an appropriate volume. Buffer solutions were prepared from a suitable amount of acetic acid and sodium acetate. All solutions were prepared with doubly distilled water. Solutions of various diverse ions of suitable concentrations were prepared by using A.R grade chemicals. A 0.01 M reagent solution was prepared by dissolving 0.0685g of 5-BSAT in 25 ml dimethylformamide (DMF).

Working solutions were prepared by diluting the stock solution to an appropriate volume. Working solution of reagent was prepared by diluting the stock in DMF solution to an appropriate volume.

Apparatus

UV-visible spectra were measured with a Perkin – Elmer Lambda 25 spectrophotometer equipped with a 10 mm path length quartz cell. The pH value of the solutions was measured with a Mettler Toledo digital pH meter.

Results and Discussion

Spectra and composition of complexes

Fig. 1 shows the absorption spectra for Ni-5-BSAT and Zn-5-BSAT complexes at pH 6.8 in wavelength range 365–500 nm. The maximum wavelengths of two complexes are 378 nm and 381 nm, respectively. As shown in Fig. 1, the absorption spectra of the complexes overlapped and cannot be well resolved by the traditional procedures using simple calibrations. Therefore, the metal ions interfere in the spectrophotometric determination of each other. To solve this problem, we used H point standard addition method (HPSAM). The HPSAM's principle for binary mixtures is easy to understand and is presented in many sciencetific article. [1-3]

Wavelength Selection

To select the appropriate wavelength pair for HPSAM, the following principles were applied. At the selected wavelengths the analyte signal must be linear to its concentration, and the interfering signal must remain unchanged when changing the analyte concentration. The analytical signal obtained from a mixture containing the analyte and the interfering ion should be equal to the sum of the individual signals of the two components. In addition, the difference in the slopes of the two straight lines measured at the two selected wavelengths (λ_1 and λ_2) must be as large as possible in order to obtain good accuracy and sensitivity. In this case there were several pairs of wavelengths. As shown in Figure 1, the best wavelength pair was 370 and 399 nm (λ_1 and λ_2) and therefore these wavelengths were chosen. Standard solutions of Ni^{2+} and Zn^{2+} were initially tested to validate the applicability of the chosen wavelengths.

The composition of complexes was determined by molar ratio method. Two plots for two complexes confirmed a 1:2 composition for Ni^{2+} complex and a 1:1 for Zn^{2+} complex.
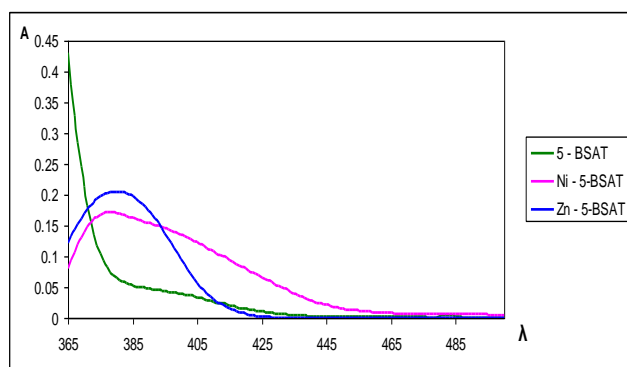

Figure 1. Absorption spectra of 5-BSAT reagent, Ni-5-BSAT and Zn-5-BSAT complexes at pH 6.8

Influence of experimental factors

The overall processes are influenced by pH of the solution, concentration of Schiff base and time of the reactions which affect the absorbance of the colored products. So, the various experimental parameters affecting the development of the colored complexes were carefully studied and optimized.

Effect of pH

The complex formation reactions of metal ions with 5-BSAT depend on pH. In order to find the optimum pH, the effect of pH in the range 5–8 on the complex formation reactions of a constant concentration of each cation with 5-BSAT was investigated (Figure 2). From the results, it was observed that the complexes exhibit maximum absorbance in the pH range 6.5–7.0. Hence, further studies were carried out at pH 6.8.
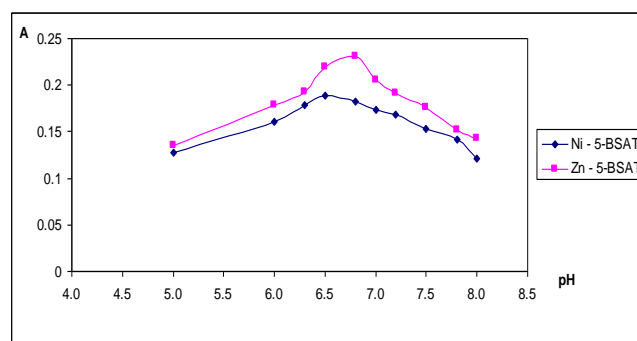

Figure 2. Effect of pH to the formation of two complexes

Effect of reagent concentration

The effect of 5-BSAT concentration over the range 2.0×10^{-5} to 1.6×10^{-4} mol L^{-1} on the determination of 2.0×10^{-5} M each of Ni^{2+} and Zn^{2+} ions at pH 6.8 buffer solution was studied to obtain the maximum color formation. As Figure 3 shows, it is apparent that lower concentrations of 5-BSAT lead to lower complex formations. Therefore from the absorbance values, it was observed that, 1.6×10^{-4} mol.L^{-1} 5-BSAT, eightfold excess over maximum concentration of metals, was sufficient to get maximum complex formation.
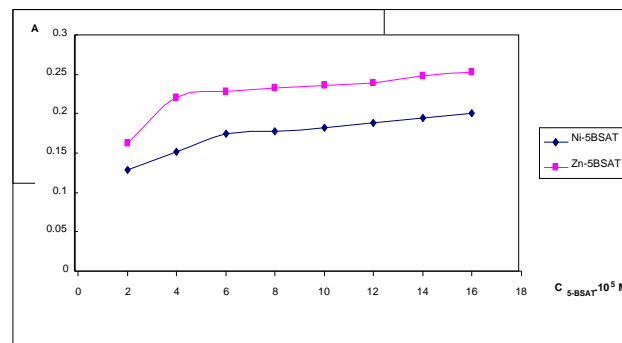

Figure 3. Effect of reagent concentration to complexation

Time effect

To measure completeness of complex formation reaction, the absorbance values of metal-5-BSAT complexes were monitored at different intervals of time. For both Ni^{2+} and Zn^{2+} ions, complex formation was completed after 5 min and stable for 20 min. Therefore, absorption measurements were performed at the range 5 - 20 min after mixing of reagents.

Individual calibration graphs

A set of sample solutions with different metal ion concentrations were prepared and measurements were carried out under the optimum conditions. The calibration curves of two analytes measured at different ranges were linear in the ranges $2.0 \times 10^{-6} – 6.0 \times 10^{-5}$ mol.L^{-1}, for Ni^{2+} and Zn^{2+}. The molar absorptivitys, ε of two complexes were 0.92×10^4 and 1.08×10^4 L.mol^{-1}.cm^{-1}, respecttively.

Study of interferences

The effects of foreign species on the simultaneous determination of Ni^{2+} and Zn^{2+} were investigated by measuring the absorbance of the solutions containing 2.0×10^{-5} mol L^{-1} of each metal ion in the presence of various amounts of other ions. The tolerance limit was taken as the amount of added ion causing less than 5% relative error in the determination of Ni^{2+} and Zn^{2+}.

Table 1 summarizes the maximum tolerances of the investigated cations and anions. The results show that Cu^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Cd^{2+} ions interfere strongly in the complexation of Zn^{2+} and Ni^{2+} with 5-BSAT.

Table 1. Interference concentration of Fe^{3+}, Cd^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+} ions to the mixture of Ni(II) – 5-BSAT 2.10^{-5}M and Zn(II) – 5-BSAT 2.10^{-5} M

Ion	$C•10^6$ (M)	Ion	$C•10^6$ (M)
Fe^{3+}	4	Co^{2+}	8
Cd^{2+}	12	Pb^{2+}	40
Cu^{2+}	4	Ca^{2+}	very large
Mg^{2+}	100	Mn^{2+}	40
Al^{3+}	32	Cr^{3+}	4

Analytical application

Analysis of synthetic samples

Application of the proposed methods to the analysis of prepared mixtures (Table 2) showed satisfactory results for the simultaneous determination of Ni^{2+} and Zn^{2+}.

Analysis of real samples

To demonstrate the applicability of the optimized methods to real samples, it was applied to the simultaneous determination of Ni^{2+} and Zn^{2+} in waste water. The concentrations of Ni^{2+} and Zn^{2+} were determined by HPSAM at a wavelength pair of 370 and 399 nm. Concentrations of Ni^{2+} and Zn^{2+} in the samples were also determined by atomic absorption spectrometry (AAS). The results are given in Tables from 3 to 6. The amounts of

metal ions obtained by the proposed methods were in good agreement with those obtained by AAS (SMEWW 3500-2005). Moreover, the calculated results proved that the proposed method was suitable for the simultaneous determination of Ni^{2+} and Zn^{2+} in complex mixtures.

Table 2. Results of several experiments for the analysis of Zn^{2+} and Ni^{2+}mixture in different concentration ratios by HPSAM at wavelength pair $\lambda_1 = 370$ nm, $\lambda_2 = 399$ nm where **C** is the concentration.

Mixture		$C_{added}•10^6$ (M)	$C_{found}•10^6$ (M)
H_1	Zn^{2+}	5.00	4.97 ± 0.24
	Ni^{2+}	5.00	4.98 ± 0.24
H_2	Zn^{2+}	5.00	5.05 ± 0.15
	Ni^{2+}	10.00	9.97 ± 0.06
H_3	Zn^{2+}	10.00	9.99 ± 0.21
	Ni^{2+}	5.00	5.03 ± 0.13
H_4	Zn^{2+}	10.00	10.05 ± 0.09
	Ni^{2+}	10.00	9.93 ± 0.09

Table 3. Analytical results of Ni^{2+} and Zn^{2+} mixture in ceramic waste water of by HPSAM

No	Equation A – C*	R	C_1	C_2
1	A=0.0159C+0.1363	0.9990		
	A=0.0072C+0.0987	0.9991		
2	A=0.0162C+0.1366	0.9993	6.96	4.48
	A=0.0072C+0.0963	0.9992		
3	A=0.0160C+0.1359	0.9990	7.40	4.24
	A=0.0073C+0.0990	0.9988		
Average concentration (mol L-1)			7.26 ± 0.64	4.35 ± 0.30
Average concentration (mg L^{-1})			2.30 ± 0.19	1.42 ± 0.09

*Equations of of the standard addition calibration lines at λ_1=370 nm, λ_2=399 nm, respectively; C is the added Zn^{2+}concentration, C_1=Zn^{2+} concentration $x10^{-6}$; C_2-Ni^{2+} concentration x 10^{-6}.

Table 4: Comparison between experimental contents of Ni^{2+} and Zn^{2+} in ceramic waste water of by HPSAM and AAS method

	Ions	Results by HPSAM,mg L^{-1}	Results by ASS method (mg L^{-1})	Reco-very,%
1	Ni^{2+}	2.13	2.21	96.38
2	Zn^{2+}	1.42	1.48	95.95

Table 5. Analytical results of Ni^{2+} and Zn^{2+} mixture in plated waste water of by HPSAM

No	Equation A – C	R	C_1	C_2
1	A=0.0161C+0.1350	0.9994	8.33	3.63
	A=0.0073C+0.1031	0.9990		
2	A=0.0159C+0.1362	0.9992	8.24	3.80
	A=0.0074C+0.1039	0.9991		
3	A=0.0157C+0.1387	0.9992	8.47	3.85
	A=0.0071C+0.1054	0.9988		
Average concentration (mol/l)			8.35 ± 0.29	3.76 ± 0.29
Average concentration (mg/l)			2.45 ± 0.09	1.23 ± 0.10

Table 6. Comparison between experimental contents of Ni^{2+} and Zn^{2+} in plated waste water of by HPSAM and AAS method

No	Ions	Results by HPSAM, mgL^{-1}	Results by ASS method, mgL^{-1}	Recovery (%)
1	Ni^{2+}	2.45	2.55	96.08
2	Zn^{2+}	1.23	1.30	94.62

Conclusion

   Spectrophotometric measurements using a new Schiff base (5-BSAT), as an analytical reagent, and chemometric modeling showed that the HPSAM are simple and efficient methods for simultaneous determination of mixtures of Ni^{2+} and Zn^{2+} in waste water. High analytical potential of the HPSAM created satisfactory results. The methods offer good procedures for the analyzing of complex mixtures, using simple spectrophotometer, which is available in most laboratories and without any separation steps.

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