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RESEARCH ARTICLE

H-Point Standard Addition Method for Simultaneous Spectrophotometric Determination of Cobalt and Nickel Using 3-Hydroxy-3-phenyl-1-(4-trifluoro-methylphenyl)triazene

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Abstract: Simultaneous spectrophotometric determination of cobalt and nickel by *H*-point standard addition method (HPSAM) is described. The method was based on different colour reactions of 3-hydroxy-3-phenyl-1-(4-trifluoromethyl phenyl)triazene (HPTPT) with cobalt and nickel in aqueous medium at pH 7.5-9.0 in the presence of surfactant triton x-100 at two wavelength 410 and 445 nm. Experimental conditions such as colour development, reagent concentration, pH of the medium were optimized. The developed method has also been successfully applied to spectrophotometric determination of Co^{2+} and Ni^{2+} in synthetic samples with RSD of 0.55 and 0.10%, respectively.

Keywords: Hydroxytriazenes, Simultaneous Spectrophotometry, Cobalt, Nickel

Introduction

Hydroxytriazenes are one of the most common chelating agents widely used as reagent is spectrophotometric determination of transition metals[1-4]. It is well known that cobalt is always found in nature in association with nickel[5]. They are essential trace elements in human diet[6]. Several methods for simultaneous determination of Co^{2+} and Ni^{2+} have been reported including HPLC[7], atomic absorption spectroscopy (AAS)[8], electrothermal atomic absorption spectroscopy (ETAAS)[9], flame atomic absorption spectroscopy (FAAS)[10], x-ray fluorescence (XRF)[11] and differential pulse polarography (DDP)[12] *etc*. Most widely used technique is spectrophotometric determination due to its simplicity and broad application. A few spectrophotomteric methods have been developed for simultaneous spectrophotometric determination cobalt and nickel using colour developing reagents[13,14]. In view of its significant application the present work reports a sensitive HPSAM method for simultaneous determination of cobalt and nickel using hydroxytriazenes.

Experimental

HPTPT was synthesized by the standard method as reported[15-18]. In this method nitrobenzene (50 mmol) was reduced with Zn dust (10 g) in the presence of NH_4Cl (2.76 g) at 50-60 °C to obtain the phenyl hydroxylamine. The diazotized product was obtained by adding sodium nitrite (3 g) in small portions to 4-aminobenzotriflouride (50 mmol) dissolved in a mixture of HCl (8 mL) and water (10 mL) at 0-5 °C with constant magnetic stirring. The diazonium salts was coupled with the phenyl hydroxylamine at 0-5 °C under constant stirring with occasional addition of sodium acetate solution to maintain the pH close to 5. After coupling, the resulting product was purified by recrystallization from absolute alcohol. The compound was identified by recording M.P, IR, NMR and MASS spectra.

Apparatus

UV-Visible absorbance spectra of Co-HT and Ni-HT were recorded on an Elico SL-210 double beam scanning spectrophotometer using a 1.0 cm path length quartz cell. A Digital Pen pH-meter having glass electrode was used for pH measurements.

Reagents

Standard Co^{2+} and Ni^{2+} solutions (M/100) were prepared by dissolving an appropriate amount of hydrated Co^{+2} and Ni^{2+} nitrate salt in a volumetric flask. The solutions were standardized by complexometric titration method. An alcoholic solution of the HPTPT (M/100) was prepared fresh as and when required. The pH of the working solution was adjusted using Tris buffer.

Procedure

Individual calibration

In a 10 mL volumetric flask, 5.0 mL of hydroxytriazene (M/1000) solution, 2 mL of triton x-100 (10%), 1 mL of tris buffer solution (1%) and an appropriate amount of sample solution containing Co^{+2} and Ni^{+2} were added. The concentration range of Co^{+2} and Ni^{+2} was taken between $1x10^{-6}$ - $50x10^{-6}$ for each complex. The absorbance were measured at 426 nm against a reagent blank for both Co^{2+} and Ni^{2+}.

H-point standard addition method

Mixtures of synthetic solutions having different concentration of cobalt and nickel were prepared from standard solutions. For simultaneous determination of Co^{2+} and Ni^{2+}, 0.4 mL of synthetic mixture, 5 mL of $1x10^{-3}$ M hydroxytriazenes, 2 mL of triton x-100 (10%) and 2 mL of tris buffer (1%) were added in a 10 mL volumetric flask and standard additions of Co^{2+}, $1x10^{-5}$ to $5x10^{-5}$ were made. The solution was diluted to 10 mL with water and allowed to stand for 10 min at room temperature (25 °C). A portion of the solution was then transferred into a 1 cm quartz cell to measure the absorbance against a reagent blank at the appropriate wavelengths. Using HPSAM, the simultaneous determination of Co^{2+} and Ni^{2+} was performed by measuring the absorbance at 410 and 445 nm with the standard addition of Co^{2+} solution and graphed to ascertain the concentration of Co^{2+} in mixture. Two straight lines for concentration and absorption were plotted and the values for the absorption and concentration at the intersection of these two lines termed CH and AH, respectively, were obtained by extrapolation.

Result and Discussion

Characterization of 3-hydroxy-3-phenyl-1-(4-trifluoromethylphenyl)triazene (HPTPT)

The presence of following characteristic absorption bands in infra red and ^1H NMR and Mass spectrum confirms the purity of HPTPT. The HPTPT reacts with cobalt and nickel to form light brown and light green colored complexes respectively. Yellow-light-powder solid M.P. 83 °C Solubility = Ethanol, FTIR (KBr) cm^{-1}: 3425(ν^{O-H}), 3198 (ν^{N-H}) 1431 ($\nu^{N=N}$) 1325 ($\nu^{N\rightarrow O}$) 1224 (ν^{C-N}) 1177 (ν^{N-N}) 1482 (ν_b^{N-H}) 1067 (ν_b^{O-H}) 1591(ν^{N-O}), 1349 (ν^{C-N}). ^{1}H NMR (DMSO-D6) δ: 12.35 (s, 1, O-H), 7.57-8.13 (m, 9, Ar-H), Anal. Found for CHN: C; 55.02, H; 2.97, N; 14.36%. Calcd: C; 55.46, H; 3.55, N; 14.93%, Mass *m/z*; 281.

UV-VIS spectra of Co^{+2}-HPTPT and Ni^{+2}-HPTPT complexes

HPTPT forms colored complexes with Co^{2+} and Ni^{2+}. The complexation reaction of Co^{2+} with the ligand HPTPT was found to be faster than that of Ni^{2+} in the same conditions. Figure 1 shows the absorption spectra for the individual colored Co^{+2}-HPTPT and Ni^{+2}-HPTPT complexes overlap with each other, which interferes with the spectrophotometric determination of the ions. Therefore simultaneous determination of Co^{2+} and Ni^{2+} is possible using binary HPSAM.

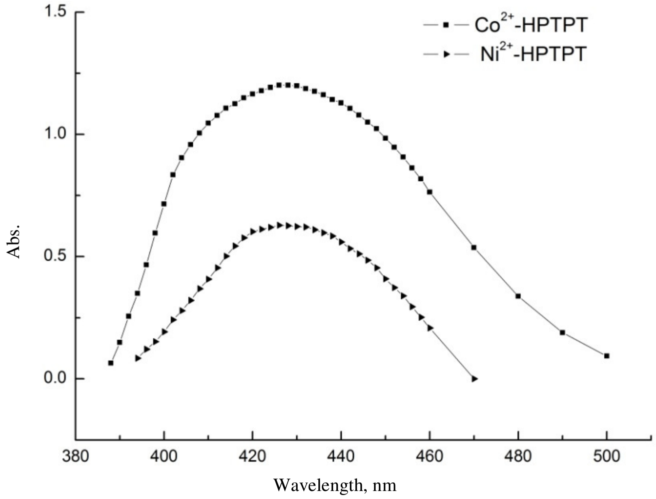

Figure 1. Absorption spectra of Co^{2+}-HPTPT complex (C_{Co} $5x10^{-5}$, C_{HPTPT} $5x10^{-4}$) and Ni^{2+}-HPTPT complex (C_{Ni} $5x10^{-5}$, C_{HPTPT} $5x10^{-4}$)

Effect of pH

The effect of pH of medium on the absorbance of Co^{+2}-HPTPT and Ni^{+2}-HPTPT complexes was studied in the pH range of 4.5 to 10 using tris buffer solution. The absorbance for both Co^{+2}-HPTPT and Ni^{+2}-HPTPT complexes increases up to 9.2 after which absorbance decreases. Therefore a pH range of 8-9.2 was selected for further study.

Effect of reagent concentration

The effect of the HPTPT concentration on the absorbance of Co^{2+}-HPTPT and Ni^{2+}-HPTPT complexes were investigated in the range of $5x10^{-4}$ to $20x10^{-4}$ of HPTPT at 426 nm. The results given in Figure 2 show that the absorbance increases with increasing [HPTPT] up to $20x10^{-4}$ M, remaining constant thereafter. Thus, HPTPT was used at a concentration of $5x10^{-4}$ M.

Effect of surfactant

To investigate effect of surfactant on absorption spectra of cobalt and nickel complexes, individual calibration of Co^{2+} and Ni^{2+} were studied in the presence or absence of triton x-100. The molar absorptivity for Co-HPTPT and Ni-HPTPT complexes at their λ_{max} were 29710 and 9882 L mol^{-1} cm^{-1} respectively. In the absence of any surfactant these results were 19121 and 9705 L mol^{-1} cm^{-1} for Co^{2+} and Ni^{2+} respectively. These results are summarized in Table 1 and 2. The results reveal that the use of nonionic surfactant enhances the stability and solubility of complexes in aqueous media.

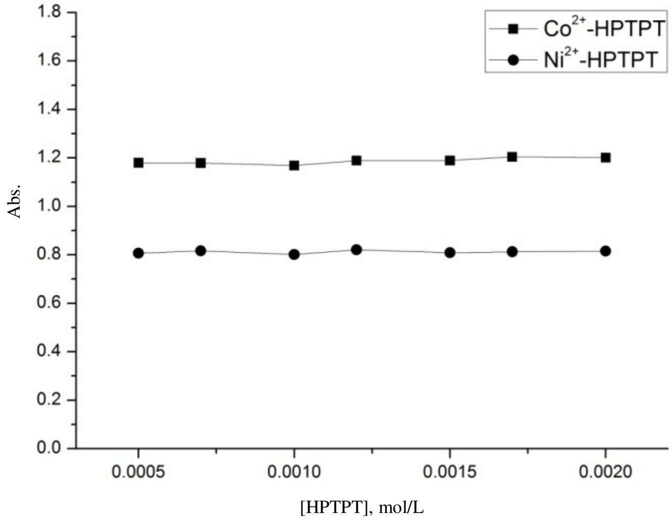

Figure 2. Effect of HPTPT conc^n on absorption spectra of Co^{2+}-HPTPT and Ni^{2+}-HPTPT complex

Table 1. Effect of surfactant on absorbencies of cobalt and nickel complexes

S.No.	Concentration of metal	Absorbance			
	[Co/Ni]	without surfactant		with surfactant	
		A_{Co}^{426}	A_{Ni}^{426}	A_{Co}^{426}	A_{Ni}^{426}
1	6×10^{-6}	0.32645	0.19236	0.65821	0.38951
2	1×10^{-5}	0.41373	0.23947	0.81112	0.44377
3	2×10^{-5}	0.6133	0.34063	1.15611	0.56255
4	3×10^{-6}	0.7961	0.43778	1.44381	0.66045
5	4×10^{-6}	0.9956	0.53169	1.7235	0.75008
6	5×10^{-6}	1.1669	0.6205	1.96445	0.82287

Table 2. Statistical analysis of Co^{2+} and Ni^{2+}

Parameters	Co^{2+} at 426 nm		Ni^{2+} at 426 nm	
	Without triton x-100	With triton x- 100	Without triton x-100	With triton x- 100
Molar absorptivity (L mol^{-1} cm^{-1})	19121.5	29710.94	9705.54	9882.51
R^2	0.9991	0.9939	0.9986	0.989
Linear range (mol L^{-1})	6x10^{-6} to 5x10^{-5}	6x10^{-6} to 5x10^{-5}	6x10^{-6} to 5x10^{-5}	6x10^{-6} to 5x10^{-5}

H-point standard addition method

In the proposed system, Co^{2+} and Ni^{2+} ions are the analyte and interfering ions, respectively. Figure 3 shows typical HPSAM plot for simultaneous determination of Co^{2+} and Ni^{2+} at the selected wavelengths of λ_1 = 410 and λ_2 =445 nm, the Co^{2+}-HPTPT complex signal increases linearly with concentration of Co^{+2}, whereas signal for Ni-HPTPT complex does not change with the increase in analyte concentration. The concentration of Co^{2+} ion is determined by HPSAM using two wavelengths, whereas the concentration of Ni^{2+} was determined by employing the ordinate value obtained from H point to calibration line as shown in Figure 4.

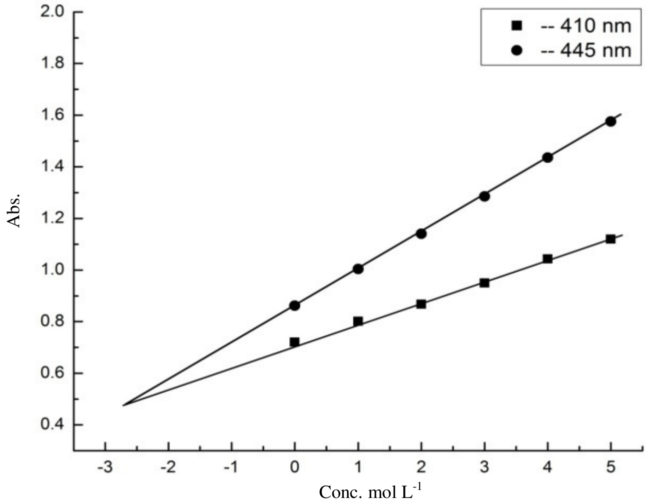

Figure 3. HPSAM plot for simultaneous determination of cobalt and nickel under optimized condition with a C_{Co} 2.66x10^{-5} and C_{Ni} 1.33x10^{-5}

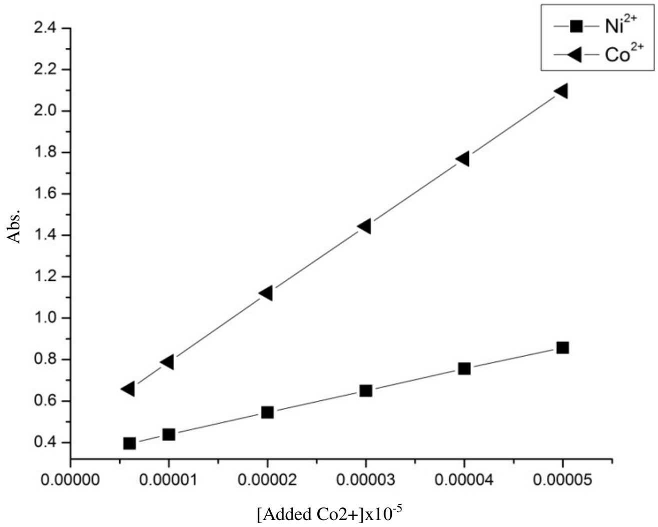

Figure 4. Calibration curve of Co-HPTPT (◀) at 526 nm & Ni-HPTPT (■) complex at 426 nm, C_{HPTPT} 5x10^{-4} M, pH 8 in triton x-100 (10%v/v)

Reproducibility of the method

Simultaneous spectrophotometric determination of cobalt and nickel under optimum conditions were performed. To investigate the reproducibility of H point standard addition method, five replicate experiments of binary samples of Co^{2+} and Ni^{2+} were done. The relative standard deviations (R.S.D) were 0.55% and 010% for 3.2x10^{-5} M of Co^{2+} and 0.8x10^{-5} M of Ni^{2+} respectively are presented in Table 3.

Table 3. Results of Five replicate simultaneous determination of Cobalt and Nickel

Taken	mol L^{-1}	Found,	mol L^{-1}
Co^{2+}	Ni^{2+}	Co^{2+}	Ni^{2+}
3.2x10^{-5}	0.8x10^{-5}	3.18x1 0^{-5}	0.8x10^{-5}
3.2x10^{-5}	0.8x10^{-5}	3.16x10^{-5}	0.79x10^{-5}
3.2x10^{-5}	0.8x10^{-5}	3.18x10^{-5}	0.79x10^{-5}
3.2x10^{-5}	0.8x10^{-5}	3.21x10^{-5}	0.81x10^{-5}
3.2x10^{-5}	0.8x10^{-5}	3.18x10^{-5}	0.80x10^{-5}
Mean		3.182x10^{-5}	0.798x10^{-5}
S.D.		1.78x10^{-7}	8.36x10^{-8}
R.S.D.		0.55%	0.10%

Analysis of cobalt-nickel mixtures

Three synthetic mixtures having different concentration ratios of Co^{2+} and Ni^{2+}were analyzed to test the accuracy of H point standard addition method for the simultaneous determination of both ions. The results are given in Table 4.

Table 4. Simultaneous determination of Co and Ni by HPSAM (Triple determination, n=3)

Taken		Found		% Recovery	
Co^{2+}	Ni^{2+}	Co^{2+}	Ni^{2+}	Co^{2+}	Ni^{2+}
2.66x10^{-5}	1.33x10^{-5}	2.653x10^{-5}+0.011	1.32x10^{-5} + 0.005	99.62	99.25
3.0x10^{-5}	1.00x10^{-5}	2.98x10^{-5}+0.017	0.99x10^{-5} + 0.011	99.33	99.00
3.20x10^{-5}	0.8x10^{-5}	3.2x10^{-5}+0.011	0.79x10^{-5}+ 0.005	99.06	98.75

Effect of foreign ions on simultaneous determination of Co^{2+} and Ni^{2+}

Interference of several cations and anions in the simultaneous determination of cobalt and nickel was studied at 100, 50 and 10 ppm level. Following diverse ions Na^+, K^+, NH_4^+, Br^-, CH_3COO^-, NO_3^- and CO_3^{-2} are tolerable up to 100 ppm level, Ba^{2+}, F^-, Cl^-, I^- and SO_4^{-2} are tolerable up to 50 ppm and Sn^{2+}, Al^{3+} and PO_4^{3-} are also tolerable up to 10 ppm level and some ion Zn^{2+}, Hg^{2+}, Ca^{2+}, Pb^{2+} and SCN^- are highly interfering ions are intolerable at all levels studied.

In case of the past reagents reported for spectrophotometric determination of cobalt, molar absorptivity values have been in the range of 1000-24000 L mol cm^{-1} for hydroxytriazenes and other reagent have slightly better value than hydroxytriazenes. The present reagent has molar absorptivity values 29710 L mol cm^{-1} for cobalt and 9882 L mol cm^{-1} for nickel in aqueous medium and is one of the most sensitive reagent among hydroxytriazenes reported. Further this is first report on the use of hydroxytriazene for simultaneous spectrophotometric determination of cobalt and nickel.

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