

NOTE

Spectrophotometric Determination of Nickel(II) with 2,4-Dihydroxy-5-Bromopropiophenone Thiosemicarbazone

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2,4-Dihydroxy-5-bromopropiophenone thiosemicarbazone (DHBPT) was synthesized and used as a spectrophotometric reagent for nickel. Ni(II) forms yellow coloured complex between pH range 7.0 to 10.0 and shows maximum absorption at 375 nm. Molar absorptivity for Ni(II)-DHBPT is 2.586×10^3 L/mole cm. Ni(II)-DHBPT has 1 : 2 (M : L) stoichiometry. Beer's law is obeyed up to 16.49 ppm for Ni(II). The reagent has been found to give satisfactory results for the analysis of nickel in german-silver alloy. Formation of the complex has been supported from the IR spectral data.

Key Words: Spectrophotometric determination, Nickel(II), 2,4-Dihydroxy-5-bromopropiophenone thiosemicarbazone.

Many organic compounds like phenylhydrazones¹, oximes², semicarbazones³, thiosemicarbazones^{4,5} have been used for spectrophotometric determination of nickel(II). Here, we report the new reagent 2,4-dihydroxy-5-bromopropiophenone thiosemicarbazone (DHBPT) for the spectrophotometric determination of Ni(II).

Spectrophotometric measurements were made on a Shimadzu UV-160 recording spectrophotometer. All pH measurements were done on Systronics digital pH-meter (model 335) and buffer solutions of required pH were obtained using disodium hydrogen phosphate-potassium dihydrogen phosphate. Borax-hydrochloric acid and ammonia-ammonium chloride of suitable concentrations. The IR spectra were recorded on Perkin-Elmer spectrophotometer (model RX-1) in KBr pellets.

Synthesis of 2,4-dihydroxy-5-bromopropiophenone thiosemicarbazone (DHBPT)

Respropiophenone was prepared according to the method of Brewster and Heris⁶. 2,4-Dihydroxy-5-bromopropiophenone (DHBP) was prepared by bromination of respropiophenone using bromine in glacial acetic acid at 20–25°C; the pale yellow compound was crystallized from ethanol (m.p. 157°C). DHBPT was prepared using DHBP, thiosemicarbazide in ethanol and HCl. The mixture was refluxed on a water-bath at 80–85°C for 4 h. Excess of ethanol was distilled off and yellow solid thiosemicarbazone was obtained. It was crystallized from ethanol (m.p. $107 \pm 1^\circ\text{C}$).

Preparation of Solutions: All the chemicals used in the work were of analytical grade purity. Stock solution of ligand (DHBPT) (0.02 M) was prepared by dissolving thiosemicarbazone in ethanol. Stock solution of Ni(II) (0.05 M) was prepared by dissolving nickel sulphate in double distilled water with little free acid and standardized titrimetrically⁷.

Preparation of Ni(II)-DHBPT Complex: A series of buffer solutions with pH values ranging from 7.0 to 10.0 were prepared using $\text{Na}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$, Borax-HCl and $\text{NH}_3\text{-NH}_4\text{Cl}$. 1.0 mL of 0.005 M Ni(II) solution and 5.0 mL of 0.02 M ethanolic solution of DHBPT were taken in 50 mL beaker. The pH of the solution was adjusted within the range where maximum colour develops. This solution was diluted to 25 mL with aqueous ethanol so as to keep 50% concentration of alcohol in final solution. The spectra of the above solutions were recorded from 350 nm to 800 nm. The absorbance constantly increases towards shorter wavelength. A shoulder was obtained at 375 nm and hence all measurements were done at this wavelength.

In case of Ni(II) maximum complex formation occurs at 9.0; hence in all further studies, this pH value was used. Obedience of Beer's law was studied for Ni(II) at 375 nm. Results of Job's method of continuous variation and mole ratio method indicated 1 : 2 (M : L) ratio for Ni(II) complex.

Interference: Interference due to associated ions was examined in the determination of 16.49 ppm of Ni(II) at pH 9.0 using the reagent DHBPT. Many anions like fluoride, chloride, bromide, nitrate, sulphate do not interfere in the determination of nickel at pH 9.0, even when they are present in 50-fold excess. Thiourea (22), thiosulphate (20), oxalate (5) can be tolerated. A 24-fold excess of Zn(II), Sr(II), Ca(II), Mg(II), Cd(II), Al(III), Na(I), Ba(II) and K(I) do not interfere. There is no interference from Fe(II), Mo(VI) at this pH.

Stoichiometry of Complex: Metal to ligand ratio in complex was determined spectrophotometrically using Job's method of continuous variation and mole ratio method. It was found to be 1 : 2. The data of these were utilized to calculate stability constant of complex.

Determination of Nickel in German-Silver Alloy: The standard sample of german-silver alloy (0.3745 g) was dissolved in nitric acid (1 : 1) by heating slowly. The excess nitric acid was removed by evaporation. The solution was diluted with distilled water to 250 mL in a volumetric flask. 10 mL of this solution was diluted to 100 mL in a volumetric flask. A suitable aliquot of solution was taken to determine Ni(II) spectrophotometrically using DHBPT at 375 nm, following the above procedure. Cu(II) was masked with Na-K tartarate. The experiment was repeated three times.

IR Spectra of Ligand and Complexes: The complexes were obtained in solid state by refluxing stoichiometric amount of ligand and metal solution for 2 h and then removing the solvent. The spectra were recorded in KBr pellets.

The IR spectra of the DHBPT shows $\nu(\text{C}=\text{S})$ band at 1310 cm^{-1} , $\nu(\text{C}=\text{N})$ band at 1595 cm^{-1} . In case of Ni(II)-DHBPT complex, $\nu(\text{C}=\text{S})$ band shows slightly downward shift at 1270 cm^{-1} , while $\nu(\text{C}=\text{N})$ band shows slightly upward shift at 1623 cm^{-1} . Band due to O—H stretching observed at 3300 cm^{-1} in ligand disappeared in spectra of complex. This indicates that metal is covalently bonded with oxygen and coordinate bonded with nitrogen.

TABLE-1
SPECTRAL DATA FOR Ni(II)-2,4-DIHYDROXY-
5-BROMOPROPIOPHENONE THIOSEMICARBAZONE COMPLEX

Characteristic	Ni(II)-DHBPT
λ_{\max} (nm)	375
Optimum pH	7.0-10.0
Colour	Yellow
Beer's law obeyance maximum concentration (ppm)	16.49
Stoichiometry (M : L)	1 : 2
Molar absorptivity $\times 10^4$ (L/mol cm)	0.2586
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	0.0227
Stability constant of complex (K_s)	2.0794×10^4
ΔG° at 25°C (kcal/mole)	-14.39

TABLE-2
DETERMINATION OF NICKEL IN GERMAN-SILVER ALLOY

Sample	Metal determined	Amount of Nickel (%) (Expected) Found	Error (%)
German-silver alloy	Nickel	(25.04) 24.57	-1.68

*Average of three determinations.

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