

2-hydroxy-4-n-butoxy-5-bromopropiophenone thiosemicarbazone as an extraction spectrophotometric reagent for Nickel (II)

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Abstract: Thiosemicarbazone compounds are established as selective and sensitive analytical reagents for the detection and determination of transition metals. In the present work, 2-hydroxy-4-n-butoxy-5-bromopropiophenone thiosemicarbazone (HBBrPT) is described as an extractive spectrophotometric reagent for nickel. The method is based on formation of Ni (II)-HBBrPT complex, which is extractable in benzene from the aqueous solution by shaking for 1-2 min. HBBrPT have been developed as new chromogenic reagent for the rapid spectrophotometric determination of micro quantities of nickel. The solid complex have been isolated and characterized on the basis of elemental analysis, and UV, IR, NMR and Mass spectra. The absorbance measured at 440 nm and the molar absorptivity is $3638 \text{ L.mol}^{-1}.\text{cm}^{-1}$. The complex system confirms the Beers law up to $14.67 \mu\text{g/ml}$. Optimum concentration range was found to be $4.40\text{--}10.27 \mu\text{g/ml}$ of Ni (II) whereas the sandell's sensitivity was found $0.01613 \mu\text{g cm}^{-2}$. The experimental conditions for the complete colour development and the interference from various ions are investigated.

HBBrPT is found to be a selective and strong chelating agent for nickel. The results deduced from Jobs method of continuous variation, the mole ratio and the slope ratio method showed that metal: ligand ratio in the complex to be 1:2. The stability constant of the complex found to be 6.41×10^8 . The free energy change for the complex formation reaction is found to be $-12.291 \text{ K cal/mole}$ at 30°C . The complex is fairly stable for about 24 h. and up to 45°C .

The newly developed method is used for the determination of nickel in its complexes and synthetic mixtures as well as industrial effluents and alloy samples. From the statistical evaluation of data, it was generalized that the method is quite precise and accurate for the spectrophotometric determination of nickel.

The statistical data evaluation showed that the method is quite precise and accurate for the spectrophotometric determination of nickel. Various commercial samples and synthetic mixtures containing Ni (II) were analyzed according to the recommended procedure and the results were compared to those obtained by standard method. It was observed that the proposed method is satisfactory in all the cases.

Keywords: 2-hydroxy-4-n-butoxy-5-bromopropiophenone thiosemicarbazone, spectral study, Spectrophotometric determination, for iron.

Introduction and experimental

Several organic compounds with phenolic photogenic group and a suitably placed electron donating atom like nitrogen, oxygen or Sulphur are found to interact with metal ions giving precipitate or

colouration due to complex formation. Various thiosemicarbazones^{1-4, 13}, have been used for the spectrophotometric determination of nickel and other transition metal ions. In the present work, we report the use of 2-hydroxy-4-n-butoxy-5-bromo propio

phenone thiosemicarbazone (HBBrPT) as a spectro photometric reagent for nickel (II).

The 0.1 M stock solution of Ni (II) has been prepared by dissolving requisite quantity of nickel sulphate (AR) in distilled water. The amount of Ni (II) in this solution was determined volumetrically using EDTA⁵.

Preparation of 2-hydroxy-4-n-butoxy-5-bromo propiophenone thiosemicarbazone:

Resacetophenone was prepared from resorcinol, prop ionic acid and anhydrous zinc chloride according to the method of Robinson and Shah⁶. 2-hydroxy-4-n-butoxypropiophenone (HBP) was prepared by using respropiophenone, n-butyl bromide and anhydrous potassium carbonate in acetone^{7,8}. Its 2-hydroxy-4-n-butoxy-5-bromopropiophenone was prepared by bromination of HBP. Its thiosemicarbazone was prepared by refluxing its alcoholic solution with thiosemicarbazide for about 4 hour⁹. It was crystallized from ethanol. pale yellow crystals were obtained [M.P. 108-109° C]. The molecular weight determination was carried out by Rast's camphor method. The reagent HBBrPT is easily soluble in ethanol, methanol, chloroform, carbon tetrachloride, benzene etc. The elemental analysis of the compound was found in table-1

Preparation of Ni (II)-HBBrPT complex:

A series of buffer solutions with pH values ranging from 6.0 to 10.0 were prepared using sodium acetate, HCl, ammonia and ammonium chloride. To 2.0 ml of 0.005 M Ni (II) solution, 28.0 ml buffer solution and 10.0 ml. of HBBrPT in benzene for about 1 min. The appearance of yellow colour indicated complex formation. The separated organic layer and absorbance was measured at 440 nm against reagent blank. The complexes was found fairly stable for about a week and 50° C.

The newly prepared compound was characterized by elemental analysis as well as spectral analysis, e.g., UV, IR, NMR and Mass method.

Results and Discussion

Spectrophotometric measurements were made on Systolic UV-VIS spectrophotometer (118). All the pH measurements were made on Systolic pH meter (324). The NMR and Mass spectra of the reagent were recorded on Model No.8400, FTIR, SHIMADZU, JAPAN NMR spectrophotometer and Jiol SX-102(FAB) Mass spectrophotometer.

The pH of the solution has a pronounced effect on the reaction between Ni (II) and HBBrPT and the stability of the complex. Absorbance also changes with wavelength. Both the parameters were, therefore, controlled to give maximum absorbance. The absorbance measurements of Ni (II)-HBBrPT complex shows that the absorbance colored solution of the complex increases continuously towards the shorter wavelength. The absorbance shows shoulder at 440 nm. Wavelength of 440 nm is selected for the present work. To determine the optimum pH for complex formation 2.0 ml. 0.005 M Ni (II) solution was taken pH adjusted by addition of buffer and a soluble complex was obtained by adding HBBrPT in benzene as stated above.

The Ni (II)-HBBrPT complex obeys Beer's law up to 14.67 µg/ml of Ni (II) ion. The molar absorptivity calculated from the beer's law plot is found to be 3638 lit mol⁻¹cm⁻¹ at 440 nm.

The method of Vosburgh and cooper's¹⁰ showed that only one complex is formed. To determine the stoichiometry of complex you and Jones mole ratio method¹¹ in graph-1 and Job's method¹² in graph-2 of continuous variation were used. These two methods show a 1:2 (metal: ligand) ratio in the complex. The values of stability constants calculated from the mole ratio methods as well as Job's method are given in Table-2 from the table average value of stability constant may be taken as 6.41X 10⁸.

Important IR bands^{14, 15} for the ligand and complex along with their tentative assignments are presented in table-3.

IR spectra of the ligand and complex were recorded on a KBr pellet using Shimadzu – Japan model No. 8400 FTIR.

Conclusions

Ni (II) forms a 1:2 stable yellow colored complex with 2-hydroxy-4-n-butoxy-5-bromo propiophenone thiosemicarbazone. This complex is used for the determination of nickel in microgram quantities. The stability constant of the complex is 6.41 X10⁸. The molar absorptivity and Sandell's sensitivity are 3638 mol⁻¹ cm⁻¹ and 0.01613 µg cm⁻² respectively. The method has been applied for the analysis of nickel in synthesized mixtures and also in alloys.

Table-1: The elemental analysis

Elements	Calculated	found
Carbon	44.08 %	44.15 %
Hydrogen	05.35 %	05.20 %
Nitrogen	11.22 %	11.07 %
Bromine	21.30 %	21.90 %
Sulphur	08.51 %	08.63 %

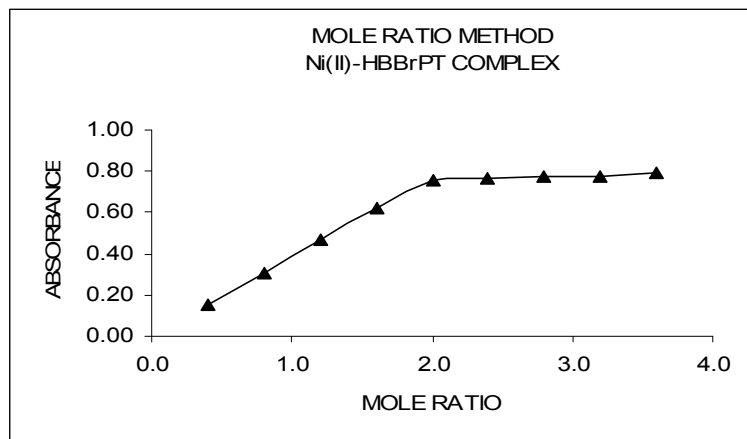
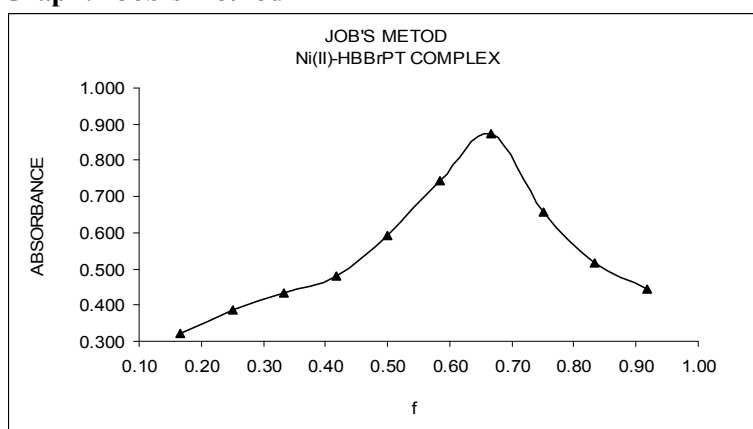
Table-2: Stability of Ni (II) HBBrPT at 32° C

Method Employed	Em	Es	α	C	K
Job's	0.911	0.875	0.03952	0.00250	6.23.E+08
Mole Ratio	0.911	0.755	0.17124	0.00025	6.60.E+08
				Average = 6.41.E+08	

Table: 3 Infrared spectral bands (cm^{-1}) of HBBrPT and Ni (HBBrPT)₂

Band	HBBrPT	Ni-(HBBrPT) ₂
V (O-H)	3600 s	-
V (-NH ₂) str	3220 s	3334 s
δ (-NH ₂) bend	1631 s	1604 vs
C-O-C	1294 s	1259 s
C=S str	858 s	835 s
V (C-N)	1460 m	1458 m
V (M-O)	-	730 m
v (M-N)	-	475 m

vs = very strong, s = strong, m = medium

Graph:1 Mole ratio method**Graph:2 Job's method****Acknowledgement**

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