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Nickel as an extractive spectrophotometric reagent of *p*-chlorobenzaldehyde - 4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone

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ABSTRACT

p-chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone [p-CBCST] is spectrophotometric reagent for nickel (II) in DMF. The metal ion reacts with *p*-Chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone [p-CBCST] forming a dark green colored complex in the pH range 4.5-5.0. The complex shows maximum absorption at 315 nm. The molar absorptivity found to be $6.090 \times 10^3 \text{ lit. mol.}^{-1} \text{ cm.}^{-1}$. The solid complexes have been isolated and characterized using elemental analysis, UV, IR, NMR spectra. p-CBCST is found to be a selective and strong chelating agent for nickel. The results deduced from Job's 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 5.551×10^{10} .

Keywords: *p*- chlorobenzaldehyde, thiosemicarbazone, p-CBCST

INTRODUCTION

Thiosemicarbazone compounds give antifungal and antibacterial activity with different transition metal ions and known as analytical reagents [1-5,22,23]. Thiosemicarbazones are also found to have biological activity [6]. Further the metal complexes formed with this reagent are of great medicinal value in the treatment of diseases like influenza [7], protozoa [8], small pox [9] and certain kinds of tumor [10]. These reagents are known for their antitubercular activity [11]. Metal chelates of these compounds inhibit tumor growth and increase the activity of some drugs [12]. In the treatment of cancer the active species is the metal chelate of thiosemicarbazone [13]. Metal chelates of these reagents are used as pesticides [14] and fungicides [15] in agriculture.

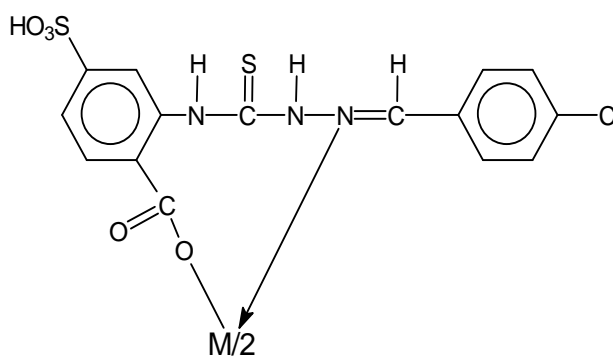
In the present work, we report the use of *p*-chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3thiosemicarbazone [16] (p-CBCST) as a spectrophotometric reagent for nickel (II).

MATERIALS AND METHODS

All the reagents used were of AR grade and were used without further purification. Salts were obtained from BDH. the reagent *p*-chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone (p-CBCST) [M.P. 196°C-198°C] was prepared by condensation of *p*-chlorobenzaldehyde with 4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazide by using the reported procedures[24].

2.17 gm (0.01 mole) 5-sulphoanthranilic acid, 30 ml ethanol and 20 ml ammonium hydroxide were mixed and cooled below 20°C. 8 ml carbon disulphide was then added with continuous stirring for 15 minutes. It was then allowed to stand for 1 hr. then 4 ml of $\text{ClCH}_2\text{COONa}$ and 14 ml of 50 % hydrazine hydrate were added and the bulk was reduced to half by heating. It was then allowed to stand overnight. The product was crystallized from DMF and water, yield 75 %, M.P. 169°C.

Its thiosemicarbazone was prepared by condensation of 4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazide (0.01 mole) and 4-chlorobenzaldehyde (0.01 mole) in ethanol (50 ml), mixed and refluxed in water-bath for 2 hr [17], the reaction mixture was allowed to stand overnight at room temperature. The product was crystallized from DMF-water, light yellow color crystals were obtained [M.P. 196°C-198°C]. The molecular weight determination was carried out by Rast's method. The reagent p-CBCST is insoluble in common organic solvent but soluble in DMF, DMSO, and NMP. The structure of Ni- p-CBCST is presented below.



Where M = Ni

The 0.1 mole stock solution of Ni (II) prepared by dissolving requisite quantity of nickel chloride in distilled water. The amount of Ni (II) in this solution was determined volumetrically using EDTA. Table 1 describes elemental analysis of the compound.

Table 1. Elemental Analysis of Compound Ni(II) p-CBCST

Element	Calculated (%)	Found (%)
Carbon	40.73	40.70
Hydrogen	2.48	2.44
Nitrogen	9.5	9.47
Chlorine	8.03	7.98
Sulphur	14.48	14.41

RESULT AND DISCUSSION

p-chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone with nickel gave dark green color in basic pH. The absorbance of dark green colored species at a wavelength corresponding to maximum absorbance i.e. 315 nm remains constant at least to 60 min. pH studies showed that the absorbance was maximum in a solution of pH 5.0. The studies relating to the effect of Ni (II) showed linear relationship between metal ion concentration and absorbance in the range 23.76 - 32.67 ppm. Table 2 describes spectrophotometric data of Ni (II) p-CBCST.

Table 2. Spectrophotometric data of Ni (II) - p-CBCST

Characteristics	Results
Molar absorptivity ($\text{L mole}^{-1}\text{cm}^{-1}$)	6.090×10^3
Stability constant(k)	5.551×10^{10}

To determine the stoichiometry of complex Job's method [18] was employed the results are plotted in figure 1 while the results obtained by mole ratio method [19] are plotted in figure 2.

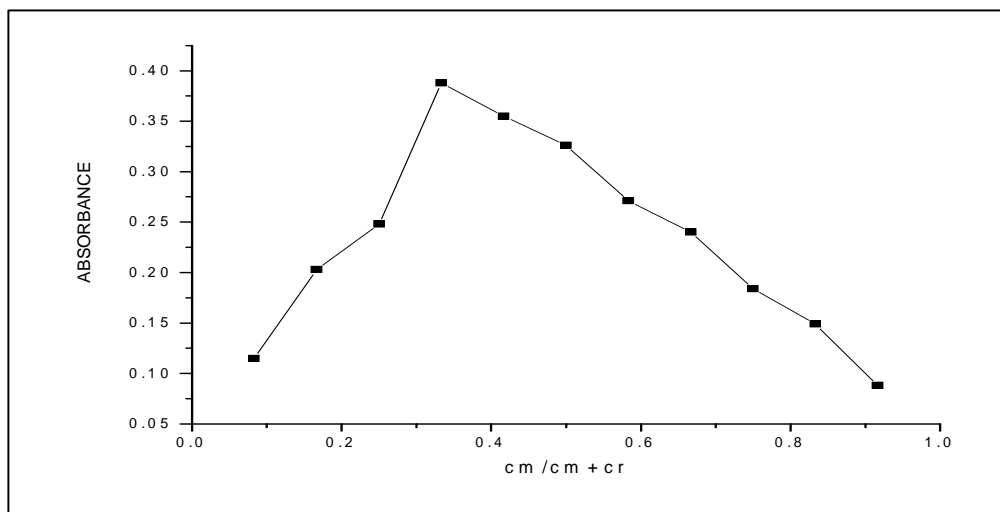


Figure 1. Job's Method

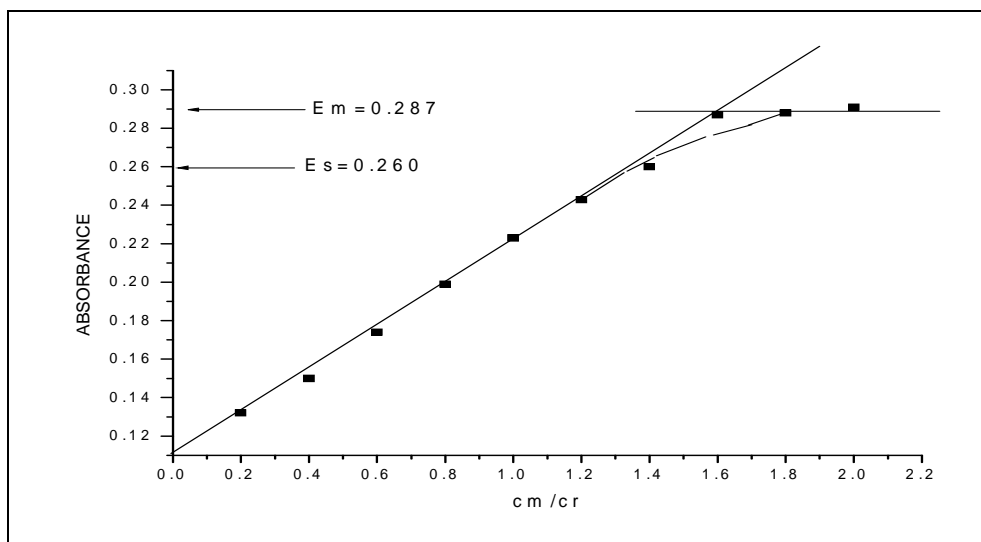


Figure 2. Mole ratio Method

Ni (II) formed a stable green colored 1:2 (metal:ligand) complex with *p*-chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone. The stability constant of the complex was found to be 5.551×10^{10} as described in Table 3.

Table 3. Stability of Ni (II) *p*-CBCST at 30° C

Method Employed	Em	Es	α	$K_s = (1 - \alpha)/4c^2\alpha^3$
Mole ratio method	0.287	0.260	0.0940	5.551×10^{10}

The synthesized compound was characterized by elemental analysis and spectral analysis viz. UV, IR, NMR method. Shimadzu 160A UV-visible spectrophotometer (Japan) equipped with 1 cm quartz cell, was used to make absorbance measurements. A pH meter EUTECH Li-127 was used for pH measurements. IR spectra of the ligand and complex were recorded using KBr pellets on Shimadzu – Japan 8400 FTIR. IR bands [20, 21] for the ligand and complex are presented in Table 4.

NMR spectra were recorded on “Varian 400” using DMSO. Table 5 describes results for Ni (II) *p*-CBCST having ratio of Metal: Ligand, 1:2.

Analytical applications

0.250 gm german silver alloy sample was dissolved in 1:1 nitric acid by heating on a water bath nearly to dryness. Resulting solution was diluted to 250 ml with deionised water. 10 ml of this solution was further diluted to 100 ml in a measuring flask.

An aliquot of alloy solution (1.0 ml) was pipette out in a 50 ml beaker, pH was adjusted to 5.0. To this solution 2.0 ml 0.001 M DMF solution of reagent was added and diluted to 10 ml with DMF.

Absorbance was measured at 329 nm.

1. Weight of german silver alloy = 0.250 gm.
2. Absorbance of the solution = 0.161 nm (Figure 3), it corresponds to 0.0220 mg of nickel in 1 ml sample solution.
3. Nickel found in german silver alloy = 22.0 % (Average of three determinations)
4. Nickel reported in german silver alloy = 21.8 %
5. Percent Relative error = 0.92%

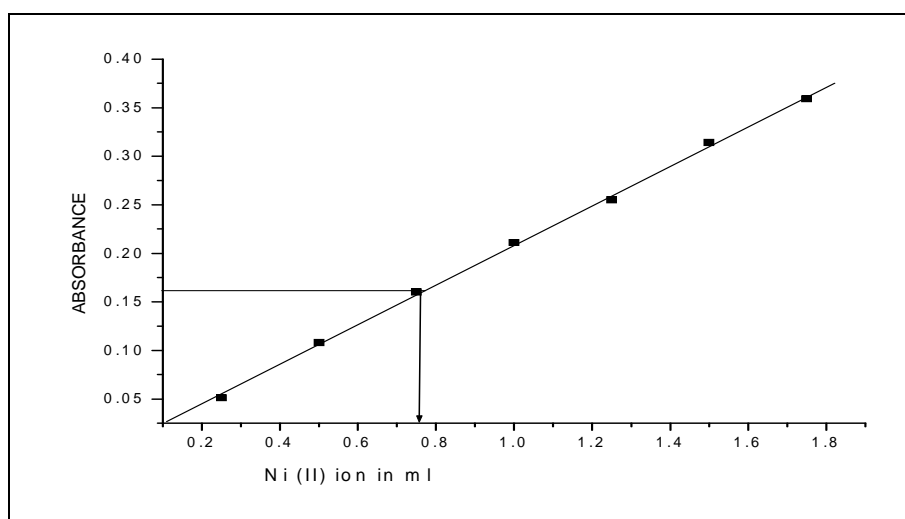


Figure 3. Ni (II) ion in ml \times 0.02936

Table 4. IR spectra of p-CBCST and Ni (II) p-CBCST

Vibration mode	Frequency in cm^{-1}	
	p-CBCST	Ni (II) p-CBCST
C=N	1578	1486
C=S	1089	1089
N-N	1275(861)	1275(861)
C=O	1622	1620

Table 5. NMR ^1H spectra data of p-CBCST

Signal no.	Signal position (ppm)	Relative no. of ^1H	Multiplicity	Inference
1	2.35	3H	singlet	-H
2	9.45	1H	singlet	-NH
3	9.97	1H	singlet	-OH or -NH
4	7.4-7.8	7H	multiplet	Ar-H

Thermogravimetric analysis

TG curve of Ni (II) complex it indicates partial decomposition of p-CBCST shows that there is no weight loss upto 200°C indicating the absence of lattice as well as co-ordinated water molecules in complexes. A gradual increase in temperature above 200°C has been accompanied by loss in weight upto 300°C. it indicates partial decomposition of ligand moiety (% wt. loss obs./cal.17.00/16.67). The remaining part of the ligand breaks at 350-400 ° C.A horizontal curves has been observed after 600°C. The total weight loss upto 550°C is nearly 82 % and equals to two

moles of ligand indicating 1:2 composition of the complex [25]. This constant weight region corresponds to metal oxides.

Antibacterial activity

The antibacterial activity of the synthesized ligand and complexes was evaluated on Gram-positive bacteria and Gram-negative bacteria: *Staphylococcus aureus*, *Escherichia coli*, *Bacillus Pumiles* and *Pseudomonas aeruginosa*. Table 6 shows the results obtained expressed by the diameter of the inhibition zone of the growth bacteria by the tested compounds.

Table 6. Antibacterial activity of p-CBCST ligands and its metal chelates.

Sample	Antibacterial activity (20 mm)			
	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Bacillus subtilis</i>	<i>Pseudomonas aeruginosa</i>
p-CBCST	14	12	13	11
Ni (II) p-CBCST	14	12	11	11

The Ni (II) complex present a slight intense effect only for *Staphylococcus aureusa* as compared to *Escherichia coli*, *Bacillus Pumiles* and *Pseudomonas aeruginosa*.

CONCLUSION

Ni (II) forms a 1:2 stable green colored complex with p-chlorobenzaldehyde-4-(2'-carboxy-5'-sulphophenyl)-3-thiosemicarbazone. This complex is used for the determination of nickel in microgram quantities. The stability constant of the complex is 5.551×10^{10} . The molar absorptivity is 6.090×10^3 lit mole⁻¹cm⁻¹. The method has been applied for the analysis of nickel in synthesized mixtures and also in alloys.

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REFERENCES

- [1] Analytical applications of thiosemicarbazones and semicarbazones: A review. Singh, R.B.; Garg, B.S.; Singh, R.P. *Talanta* .; **1978** vol. 25 issue 11-12; 619-632 DOI: 10.1016/0039-9140(78)80163-5. ISSN: 0039-9140
- [2] Reddy, K. G.; Reddy, K. H.; Reddy, D.V., *Indian J. Chem.*; **1986**, 25-A, 982
- [3] Stankoviansky S, Carsky J and Beno A, *Chim Zvesti.*; **1979**, 23, 589.
- [4] Patel, B.H.; Shah, J. R.; Patel, R.P., *J. Ind. Chem. Soc.*; **1976**, 53, 9
- [5] Vogel, A. I., *A Text Book of Quantitative Inorganic Analysis.*; **1971**, 3rd Ed. London: Longman
- [6] Seena E. B., Bessy Raj, B. N.; Prathapachandra Kurup, M. R.; Suresh. I. E.; *J. Chem. Crystallogr.*, **2006**, 36, 189
- [7] Orlova, N. N.; Sevova, A. K.; Selidovkin, D. A.; Bogdanova, G. N.; *Russ. Pharm. Toxic.*, **1986**, 348
- [8] Butler, K.; *US pat.*, **1968**, 3, 382, 266, 7
- [9] Bauer, D. J.; Vincent, L. S.; Kempe, C. H.; Downe, A. W. *Lancet.*, **1963**, vol.282, Issue No.7306, 494-496.
- [10] Patering, H. C.; Buskirk, H. H.; Underwod, G. E., **1964**, *Cancer Res.* **24**, 367-372.
- [11] Zapafonetis, C. I.; Kalas, J. P., *Proc. Soc. Expt. Boil. Med.*, **1960**, 105, 560-563., doi:10.3181/00379727-105-26176
- [12] Dwyer, F. P.; Maythew, F.; Roe E M F and Shulman, A., *Bril. J. Cancer.*, **1965**, 19, 195-199., doi:10.1038/bjc.1965.24
- [13] Gim, J. A.; Pantering, H. G.; *Cancer Res.*, **1967**, 27, 1278-1285.
- [14] Johnson, C. W.; Joyner, J. W.; Perry, R. P.; *Antibiotics Chemotherapy.*, **1952** 2, 636
- [15] Chandra, B. S.; Tyagi.; *M. J. Indian Chem. Soc.*, **2008**, 85, 42-47.
- [16] Patel, N. C.; Patel, I.J.; *J. Inst chemists (India).*, **1996**, Vol. 68, Part 5.
- [17] Patel, N. C.; *M. Phil. Dissertation.*, **1994**,
- [18] Job, P.; *Ann. Chem.* **1938**, 115, 332
- [19] Yoe, J. H.; Jones, A. L.; *Ind. Eng. Chem. Anal. Ed.*, **1944**, 16(2), 111-115 DOI: 10.1021/i560126a015
- [20] Campbell, K. J. M.; Grzeskowiask, R. J.; *J. Chem. Soc. A*, **1967**, 396-401 DOI: 10.1039/J19670000396,

- [21] Dyer, J. R.; *Application of Absorption Spectroscopy to Organic compounds*, Prentice Hall of India Private Ltd., New Delhi., **1994**
- [22] Ezhilarasi et al.; *Int. J. Res. Chem. Environ.* **2012.**, Vol.2 issue 4.,130-148.
- [23] Giorgio Pelosi; *the Open Crystallography Journal*, **2010**, 3, 16-28
- [24] N. C. Desai, B. R. Parekh and K. A. Thaker.; *J. Indian chem. soc.* **1989**, 66,344
- [25] M.G.Ram Reddy.; *J. Indian chem. soc.*, **1999**,76,498-499