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A Study on Synthesis of Novel Chromogenic Organic Reagent 3,4-dihydroxy-5-methoxy benzaldehyde thiosemicarbazone and Specrtrophotometric Determination of Nickel (II) in Presences of Triton X-100.

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ABSTRACT

The present research work 3,4-dihdroxy 5-methoxybenzaldehyde thiosemicarbazone (DHMBTSC) is proposed as a novel chromogenic organic reagent for the estimation of Nickel (II) by specterophotometry. The novel chromogenic reagent 3,4-dihdroxy 5-methoxybenzaldehyde thiosemicarbazone (DHMBTSC) form light yellow coloured complexe with Nickel(II). The colour complexe shows maximum absorption at λ_{max} 385 nm. The beer's law validity range is 0.1760 to 1.467 (µg/ml) and optimum concentration range is 0.3521 to 1.232 (µg/ml).The molar absorptivity and sandells sensitivity of the complex was found to be $2.1x10^4$ $L.mol^{-1}.cm^{-1}$ and 0.00278 $\mu g/cm^2$ respectively.The Nickel (II) forms M:L(I:I) colour complexe with DHMBTSC and stability constant of the complex was found to be. 3.08×10^6. The first order derivative amplitude was measured at 425 nm. This proposed developed method is selective, rapid and applied for the estimation of Nickel (II) in trace leveles in edible oils samples.

Keywords: chromogenic organic reagent, derivative spectrophotometry, Nickel (II) and edible oils samples.

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INTRODUCTION

Nickel is a silvery-white metal. Nickel is a essential micro nutrition element for both animals and plants. The main source comes from the hydrogenation of oils, iron factories, from the combustion of coal, diesel and residual oils, tobacco smoke, chemicals and catalysts. However, Nickel is toxic and the primary route for Nickel toxicity is mainly due to its exposure through inhalation and contaminated food and water. The soluble nickel complexes are more toxic than insoluble complexes. Nickel in human body causes dermatitis, pneumonia, lung and nose cancer. Considering the toxic effects of nickel, it has become necessary to determine the nickel content in soil and industrial effluent samples.

Number of complexe of chromogenic organic reagents were reported for the spectrophotometric estimation of the Nickel(II). In the present research work we report the new chromogenic analytical reagent for the estimation of Nickel (II) at trace levels. Today several analytical techniques and novel methods were extensively used such as AAS, ICP-AES, X-Ray flourenscence spectroscopy, voltametry, polorography, specteophotometry and other techniques. specterphotometric methods are preferred because they are cost of instrument is low, high sensitivity, accuracy results are obtained in short time [1-23].

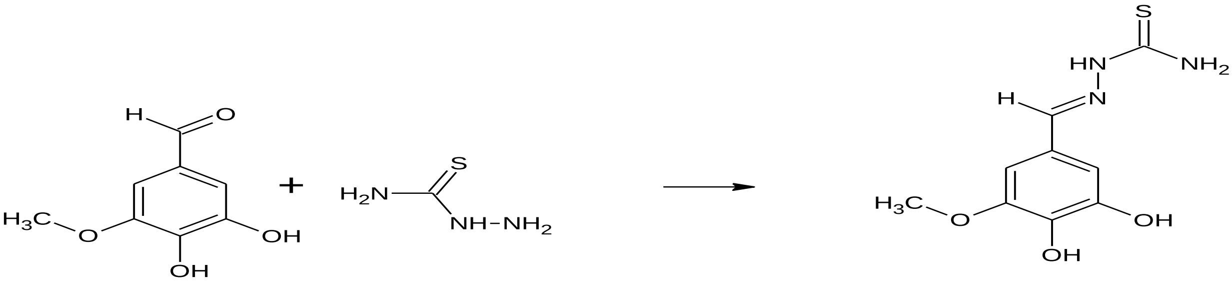
EXPERIMENTAL

Spectrophotometric measurements were made in a shimadzu 160 a micro computer based UV–Visible spectrophotometer equipped with 1.0 cm quartz cells, an ELICO LI- 120 digital pH meter. All reagents used were of analytical reagent (AR) grade unless otherwise stated. All solutions were prepared with distilled water.

REAGENT

Synthesis of 3,4-dihydroxy 5-methoxy banzaldehyde thiosemicarbazone

3,4-dihydroxy-5-methoxybenzaldehyde (0.42035g, 0.01 mole) dissolved in hotmethanol, hot methanolic solution of thiosemicarbazide (0.2275 g, 0.01 mole) were taken in a 250ml ml round bottom flask. The contents in flask were refluxed for 30 minutes using a water condenser. On cooling the reaction mixture, light yellow coloured product was separated out. It was collected by filtration and washed several times with hot water and cold methanol. This compound was recrystallised and dried in vacuom



Characterization of 3,4-dihydroxy -5-methoxy banzaldehyde thiosemicarbazone was characterized with the help of Infrared, ^{1}H-NMR and Mass spectral data.

Analytical properties of DHMBTSC

In the present work, the colour reactions of some important metal ions were examined in presence of various bufer solutions medium The analytical characteristics of the metal complexes are incorporated in table :1 The colour solution samples were prepared in 10 ml standard volumetric flasks by adding 3 ml of buffer (pH 1.0-11), 0.5 ml of metal ion ($1x10^{-3}$M) and 0.5 ml of ($1x10^{-2}$ M) DHMBTSC solutions. The colour solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-800 nm range against reagent blank.

Table 1: Analytical properties of DHMBTSC complexes in solution

Metal ion	λ max (nm)	pH	Colour of the complex	Nature of the complex
Cobalt(II)	389	4.0	Yellowish brown	1:1
Nickel(II)	385	8.5	Light yellow	1:1

RECOMMENDED PROCEDURE

Estimation of Nickel (II) (zero order)

An aliquot of the colour mixer solution containing 0.1760 to 1.4673 µg/ml of Nikel (II), 3 ml of buffer solution pH 8.0 to 9.0 and 0.5 ml of (1×10^{-2}M) novel DHMBTSC reagent were taken in a ten ml standard volumetric flask and the colour solution was diluted up to the mark with distilled water. The intensive absorbance of the solution was recorded at 385 nm in a 1.0 cm cell again corresponding reagent blank prepared in the same way but without Nickel (II) metal solution. The absorption spectra of DHMBTSC and its Ni (II) complex under the optimum conditions are shown in fig no:1. The Ni (II)-DHMBTSC complex shows the maximum absorbance at 385 nm, where as the reagent blank does not absorb appreciably.

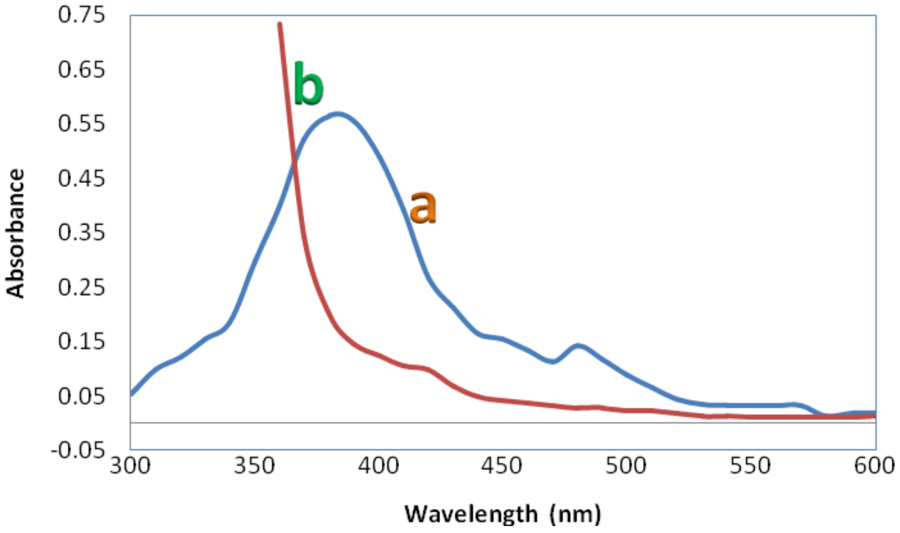


Figure 1: **Absorption spectra**

(a). [Ni (II)-DHMBTSC] complex vs reagent blank
(b). DHMBTSC vs buffer blank.

RESULTS AND DISCUSSION

In the present work 3,4-dihdroxy-5-methoxybenzaldehyde thiosemicarbazone(DHMBTSC) analytical reagent is a blend of a carbonyl compound and a thiosemicarbazide. The reagent solution is stable for more than six hours. in presence of buffer medium. The ligand presumably associated with the metal ions to give a neutral water soluble complex.

Estimation of Nickel (II) using DHMBTSC

The metal ion Nickel (II) reacts with DHMBTSC in basic buffer medium to give light yellow coloured water-soluble complex. The colour reaction between Ni (II) and DHMBTSC are instantaneous even at room temperature in presences of the pH range 8.0 to 9.0 and Triton X-100 (5%) surfacteant solution The absorbance of the light yellow coloured species remains stable for more than four hours. The maximum colour intensity is examined at pH 8.5. A 10-fold molar excess of analytical reagent is used for bright colour development. The order of addition of buffer solution, metal ion and reagent has no adverse effect on the absorbance. The intensive colour complex formation reaction between Nickel (II) and DHMBTSC has been examined in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important analytical parametrs of Nickel (II) and DHMBTSC are incorporated in table-2.

Table 2: Physico-Chemical and analytical characteristics of [Ni(II) – DHMBTSC] complex.

Characteristics	Results
Colour	Light Yellow
λ_{max} (nm)	385
pH range (optimum)	8.0-9.0
Mole of reagent required per mole of metal ion for full colour development	10- folds
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	2.1×10^4
Sandell's sensitivity ($\mu g.cm^{-2}$)	0.00278
Beer's law validity range (µg/ml)	0.176 to 1.467
Optimum concentration range (µg/ml)	0.352 to 1.232
Composition of complex (M:L) obtained in Job's and mole ratio method	1: 1
Stability constant of the complex	3.08×10^6
Relative standard deviation (%)(RSD)	0.001
Regression coefficient	0.998

The zero order beer's law verification graph suggest that this colour solution complex was sensitive and selective for estimation of Nickel (II) ion, as shown in fig no 2 ; The first order derivative spectra was shown in fig no-3. This shows that the derivative amplitudes measured at 425 nm and first order were found to be proportional to the amount of Nickel (II) respectively.

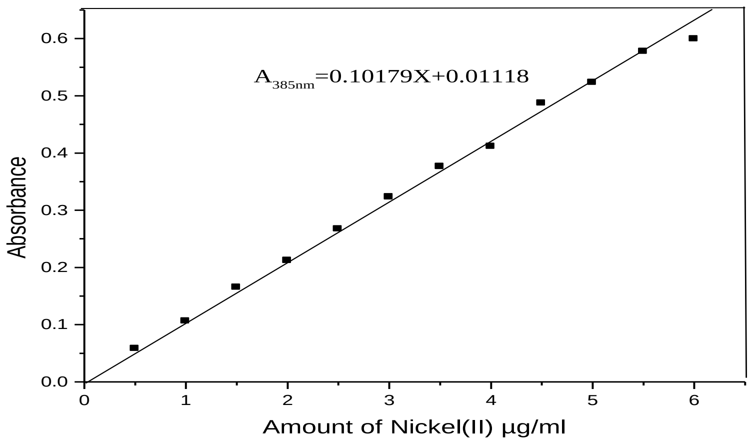


Figure 2: zero order beers law graph of [Ni(II)-DHMBTSC] Vs reagent

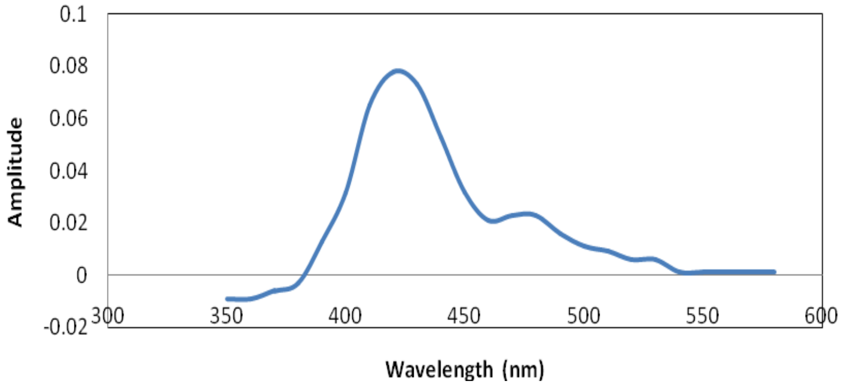


Figure 3: **First derivative spectra of [Ni(II)-DHMBTSC] Vs reagent**

Effect of Foreign Ions

Derivative spectrophotometry is a very advanced technique in the sense that it is reduced the interference, i.e, increases the tolerance limit value of foreign ions of metal ions having overlapping spectra. The proposed method have been employed for the spectrophotometric determination of Nickel (II).The effect of different diverse ions in the determination of Nickel (II) was examined to find out the tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion necessary to cause an in accuracy of ± 2 % in the absorbance or amplitude. The outcome results are incorporated in table-3.

Table 3: Tolerance limit of foreign ions in the determination of 0.2934 µg/ml of Nickel (II).

Ion added	Tolerance limit (µg/ml)	Ion added	Tolerance limit(µg/ml)
Iodide	1490	La(III)	156
Urea	443	Ba(II)	149
Thiocynate	494	Ag(I)	48
Bromide	793	Co(II)	54
Thiourea	521	Zn(II)	76
Nitrate	446	W(VI)	18
Tetraborate	1450	Zr(IV)	13
Acetate	465	Ce(IV)	43
Phosphate	821	Cu(II) [a]	2.32
Chloride	393	Hg(II) [b]	2.37
Fluoride	346	Mo(VI)	3.67
Na(I)	423	Fe(III)	2.93

'a' Masked with 765 µg/ml of phosphate;
'b' Masked with 321 µg/ml of ascorbic acid

Applications

Estimation of Nickel (II) in edible oils sample

A 50g of the oil or seed sample was heated in a 500-ml conical flask with 40 ml of concentrated HNO_3 on steam bath and shaken vigorously until fine emulsion was formed. The heating was continued with the gradual addition of 40 ml of 6% H_2O_2. The aqueous phase was transferred into a beaker. The extraction was repeated twice with further addition of 20 ml of concentrated nitric acid and 20 ml of 6% hydrogen peroxide. The combined extracts were evaporated to dryness. The residue was dissolved in minimum amount of dilute HCl and transferred into a 50-ml volumetric flask. The contents in the flask were diluted up to the mark with distilled water. The results are presented in table-4.

Table 4: Estimation of Ni(II) in edible oils samples

Oil sample	AAS Method	Amount of Nickel (II) Found	Error (%)
Sun flower oil	0.66	0.65	-1.51
Ground nut oil	0.42	0.41	-2.38

* Average value of five determination.

CONCLUSION

This research work suggest that the 3,4 - dihydroxy-5-methoxy benzaldehydethiosemicarbzone (DHMBTSC) has been proven as a sensitive and selective chromogenic organic reagent for the determination of Nickel (II) . Molar absorptivity of the colour complexe was $2.1x\ 10^4$ $L.mole^{-1}$. cm^{-1}. The present derivative method was sensitive when campared with zero order method. The proposed method is especially selective with respect to metals, wich commonly seriously interfere with the estimation of Nickel (II) as earlier methods reported. The proposed method can be successfully applied to the estimation of Nickel (II) in edible oils samples.The present method was favorably compared which eariler reported spectrophotometric[1-23] methods .

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