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Environmental risks of anthropogenic metals and their spectrophotometric determination using 4-hydroxybenzaldehydethiosemicarbazone

[1]K. P. Satheesh and [2]V. Suryanarayanarao

[1]Department of Chemistry, Gates Institute of Technology, Gootyanantapuram(v), Peddavaduguru(M), Gooty, Anantpuram Dist, [A.P.]
[2]Srikrishnadevaraya University, Anantapuram (A.P)

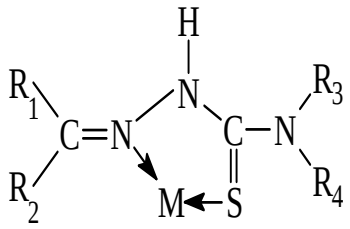
ABSTRACT

Since the second part of 20th century, there has been growing concern over the diverse effects of heavy metals on humans and aquatic ecosystems. A significant part of the anthropogenic emissions of heavy metals ends up in wastewater. Major industrial sources include surface treatment processes with elements such as Cadmium, Lead, Manganese, Copper, Zinc, Chromium Mercury, Arsenic, Iron and Nickel are discharged in wastes. Heavy metals can be hazardous even at very low concentrations, when they get in to water supplies and aqueous environments the health of plants, animals as well as humans will be impaired. As such they are stable elements and they cannot be metabolized by the body and bioaccumilative by nature. Toxic metals are commonly found in waste water and removing them efficiently poses a unique challenge. The author has developed an organic reagent"4-HydroxyBenzaldehydethiosemicarbazone"and studied the complexation reaction between various metal ions and 4-HBTS spectrophotometrically. The data pertaining to these studies reveals that heavy metals like Nickel Ni (II), copper Cu (II), and Bismuth Bi (III) shows favorable conditions for complex formation under weak acidic condition (P^H- 5-6).The author calculated the range of determination of metal in each system. The results showed that these metal ions can be determined quantitatively in µg quantities using the standard procedures. The suitability of this method for the determination of nickel is in the range 0.2348-2.348 µg/mL, for copper the range is 0.127-1.27 µg/mL and Bismuth can be estimated in the range of 0.835-8.35µg/ml in metallic sample solutions. Thus the above mentioned method has been extended for the determination of heavy metals present in wastewater sample.

Key words: anthropogenic, wastewater, heavy metals, aqueous environment, 4-HBTS, Complexation, Spectrophotometry, pH.

INTRODUCTION

Thiosemicarbazones contain nitrogen as well as sulphur. Thiosemicarbazones are good analytical reagents [1-5]. Thiosemicarbazones contain azomethine nitrogen atom and thioamide group. These reagents act as good chelating agents and form complexes with various metal ions by bonding through thioketo sulphur and hydrazino- nitrogen atom.



A good number of thiosemicarbazone ligands have been derived by simply condensing aliphatic, aromatic or heterocyclic aldehydes or ketones with thiosemicarbazide.

Nickel is versatile metal in biological chemistry. It has been reported that normal human blood plasma contains 0.012-0.085 ppm of Ni(II). Nickel is abundant in lithosphere and biosphere. Nickel is widely used in electroplating, the manufacture of Ni-Cd batteries, rods for arc welding, pigments of paints, ceramic surgical and dental prostheses, computer components, magnetic tapes and nickel catalysts. Nickel enters in to the water from dissolution of industrial process and waste disposal . Nickel was thought to be essential for plants and some domestic animals but not considered to be a metal of biological importance until 1975, when zerner discovered that urease was a nickel enzyme Nickel is moderately toxic metal, and still at low concentrations produces a general toxic effect on the human organism causing nasopharynx and lung diseases ,malignant tumors and dermatological diseases Nickel containing sewage water is harm full after ingress in to water. Several thiosemicarbazones have have been employed as chromogenic reagents for the spectrophotometric determination of nickel [6-11].

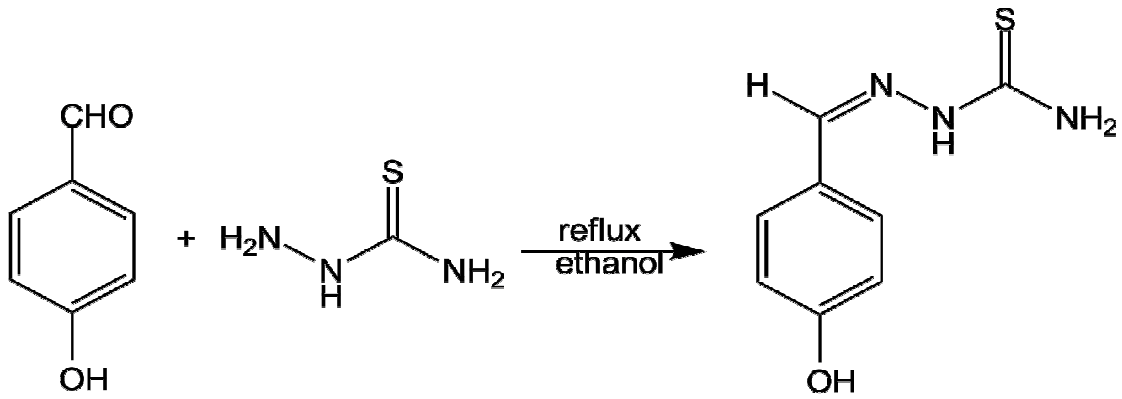
Copper is an important element in industry and biological chemistry. The human adult requirement is 2 mg per day, and adult human body contains 100-150 mg of copper. The greatest concentration occurs in liver and bones.Blood contains a number of copper proteins and copper is known to be necessary for the synthesis of hemoglobin, although there is no copper in it. Copper is essential for mammal, they become hazardous when present in excess. An excessive accumulation of copper in liver, kidney and brain, leads to liver and kidney failure and various neurological abnormalities. In plants copper reduces chlorophyll content. Several thiosemicarbazones have have been employed as chromogenic reagents for the spectrophotometric determination of copper [12-16].

Bismuth and its compounds came to be known in the fourteenth century. However the metal at first could not be distinguished from lead and tin. Its properties were first described towards the middle of the eighteenth century. It occurs in freestate as well as in the combined form. The important sources of bismuth are bismuth glance Bi_2S_2, bismuth telluride Bi_3Te_3 and bismuth oxide (Bi_2O_3).Bismuth is found in Earth's crust up to 0.0002%. it is least toxic among the heavy metals. Bismuth is used in the form of sub carbonates and subgalletes for the treatment of diarrhea, dysentery and ulcers. Bismuth is also used in the manufacture of low melting alloys which finds application in the fusible elements in automatic sprinklers, special solders, safety plugs in compressed gas cylinders and automatic shutoffs for gas and electric water heating systems Methods are also reported [17-20] for the spectrophotometric determination of bismuth. In this present article simple, selective and sensitive spectrophotometric method was developed for the determination of nickel in water, industrial waste water and in different alloys using 4-hydroxybenzaldehedethiosemicarbazone. .

MATERIALS AND METHODS

Experimental part:
The absorbance and pH measurements were made on a Shimadzu UV-Visible spectrophotometer (model UV-160A) fitted with 1.0cm quartz cells and Elico digital pH meter (modelLI20) respectively.

Preparation and characterization of 4-hydroxy benzaldehyde thiosemicarbazone:
The reagent was prepared by simple condensation of 1 mole of 4-hydroxy-benzaldehyde(1.22gm) with 1-mole (0.92gm) of thiosemicarbazide in a clean 250ml round bottomed flask 4-hydroxybenzaldeyde was dissolved in 100ml of methanol and thiosemicarbazide was dissolved in hot water. The solutions were mixed and refluxed for two hours. On cooling brown colored product was formed which was collected by filtration. It was recrystalized using methanol and dried in vacuum.



4-hydroxy benzaldehyde **Thiosemicarbazide** **4-HBTS**

The yield was 80% by weight. and the M.P. is 207-209^{0}C. The structure of the compound was established using IR spectra and NMR spectra,

Characterization:
The IR spectrum of the compound was recorded using Perkin-Elmer 137 IR spectrometer in KBr. The peaks observed at 3458cm^{-1} and 3342^{-1} may be assighned to symmetric and assymetric (–N-H) steching frequency of primary amino group. The peak observed at 3028cm^{-1} may be assighned to Ar-H stretching frequency of aromatic proton, and that observed at 1595cm^{-1} to C=N stretching frequency of azomethine. The peak observed at 3218-3092 for –OH group. A strong peak observed at 1056cm^{-1} may be assigned to C=S stretching frequency. The peaks observed in the range of 1530-1360cm^{-1}frequency were charecteristic aromatic ring stretching frequency.

The ^{1}H-NMR spectrum of the compound was recorded with DRX300 NMR spectrometer in DMF solvent. The peak observed at δ value 10.74(H) was charecterstic of phenolic –OH group. The peak found at δ value 7.86(4H) may be due to aromatic protons, the peak observed at δ value 6.8 (2H) may be due to –NH_2 protons attached to thionylgroup (C=S) and the peak observed at δ value 9.0 is due to aldehydic proton. The peak at δ value 11.5 may be due to –NH proton (azomethine).

Preparation of the solutions:
Cu(II) solution
Stock solution of copper sulphate (1 x 10^{-2} M) was prepared from 0.6242 g $CuSO_4$ (AR, BDH) with doubly distilled water and made upto 250 ml. The stock solution was standardised. The stock solution was suitably diluted to get the required concentration.

Ni(II) solution
0.5942 g of nickel sulphate (AR, BDH) was dissolved in doubly distilled water containing few drops of concentrated H_2SO_4 and made upto 250 ml. The stock solution was standardized gravimetrically using dimethyl glyoxime. The stock solution was suitably diluted to get the required concentration

Bi(III) solution
1.2126 g of bismuth nitrate (AR, BDH) was dissolved in doubly distilled water in a 250 ml volumetric flask to get 1 x 10^{-2} M solution and standardised. The stock solution was suitably diluted to get the required concentration.

Stock solution of the reagent
0.195 g of recrystalised sample of the reagent 4-hydroxybenzaldehyde thiosemicarbazone was dissolved in DMF in a 100 ml volumetric flask to obtain the stock solution (0.1 M), and it was suitably diluted to get the required concentration. Fresh reagent solutions were prepared as and when required.

Buffer solutions

The buffer solutions are prepared by mixing 1M hydrochloric acid and 1M Sodium acetate (pH 1.0-3.0) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0). Exact pH of the solution was measured using a pH meter.

RESULTS AND DISCUSSION

Ni (II)-4-HBTS Complex:

Ni(II) reacts with 4-HBTS in weak acidic pH to give a green coloured water soluble species. The colour reaction between Ni (II) and 4-HBTS is instantaneous even at room temperature. The absorption spectra of 4–HBTS with water blank and its nickel (II)complex under the optimum conditions are as shown in the **(Fig-1).**The nickel (II)- 4-HBTS complex shows the maximum absobance at 400nm , where the reagent blank does not absorb appreciably. The maximum absorbance λ_{max} of the green coloured species (complex) was observed at 400 nm which remains constant for 24 hours. Studies on the effect of pH on the absorbance revealed that the maximum colour was formed in a solution of pH 6. A ten fold excess of the reagent is adequate for complete colour development. Addition of excess of reagent has no adverse effect on absorbance.

Figure 1 Absorption spectra of Ni(II)-4-HBTS

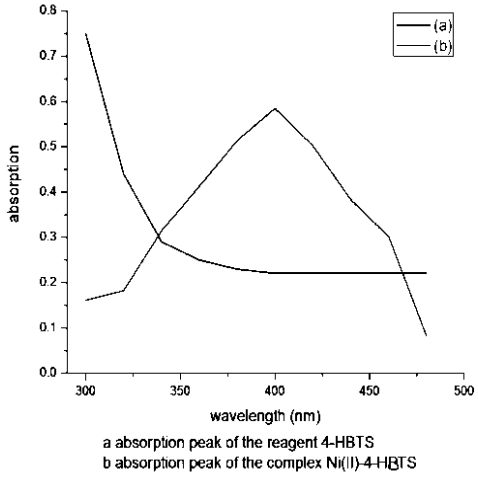


Figure 2 Beer,s Law verification

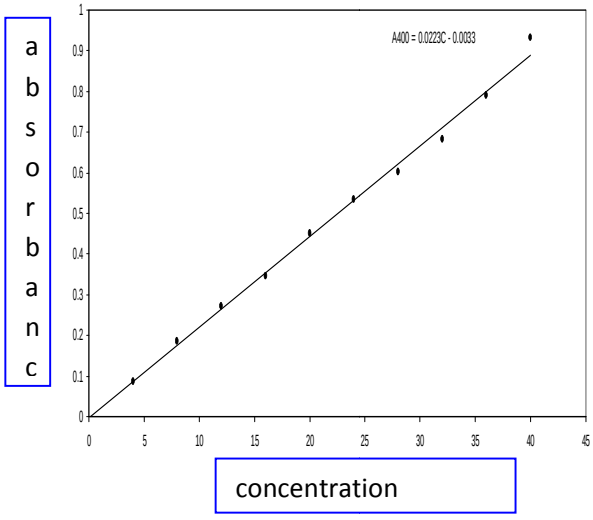
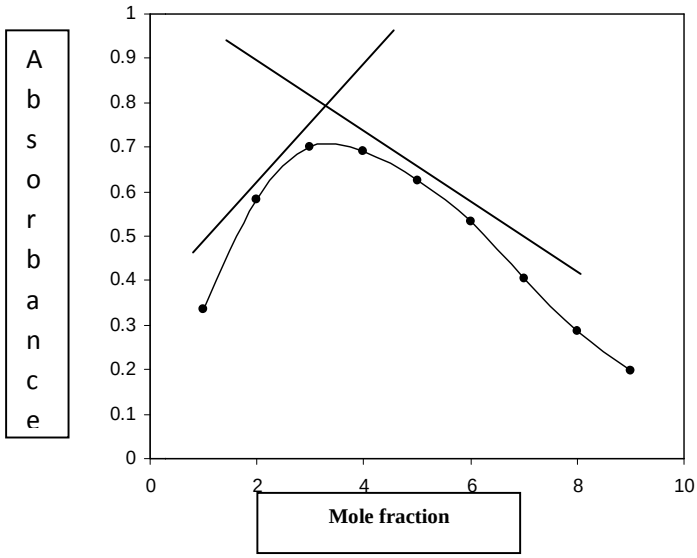


Figure -3 .Jobs method for the determination composition of the complex



The studies relating to the effect of Ni (II) revealed that a linear relationship exists between metal ion concentration and the absorbance (**Fig-2)** in the range 0.117-1.172µg/mL. The molar absorptivity and sandell's sensitivity are $2.13x10^4$L.mol $^{-1}$cm^{-1} and $2.76x10^{-3}$µg / cm^2 respectively. The effect of the reagent on absorbance is also studied, no linear relationship is found between the reagent and the absorbance. As the metal ion Ni (II) forms a coloured complex with reagent, an attempt is made to determine the composition and the stability of the complex. Job's method and mole ratio method are conducted to make these determinations. It is noticed that Ni(II) forms a stable green coloured 1:2 [M:L] **(Fig-3)** complex with 4-hydroxy benzaldehyde thiosemicarbazone. The stability complex was found to be $2.76x10^{11}$.

The metals Copper and Bismuth also form stable complexes in weak acidic medium at different λmax values. The Physico-chemical and analytical characteristics of these complexes are tabulated in table1.

Table-1: **Physico-chemical and analytical characteristics of Complexes of Ni (II), Cu (II) and Bi (II) with 4-HBTS**

Charecterstic	Nickel	Copper	Bismuth
λ_{max} (nm)	400	410	360
p ^{H} range (optimum)	5.0-6.0	4.0-6.5	4.0-6.0
Moles of the reagent required per mole of metal ion for complete colour development	10 folds	10 folds	10 folds
Molar absoptivity (Lmole $^{-1}$cm $^{-1}$)	$2.13x10^4$L.mol $^{-1}$cm^{-1}	$2.85x10^4$ L.mol $^{-1}$cm^{-1}	1.26X10 4L.mol $^{-1}$cm^{-1}
Sandell's sensitivity(µg/cm^2)	$2.76x10^{-3}$	$2.23x10^{-3}$	$1.64x10^{-3}$
Standard deviation in the determination of 1.27µg/ml of Cu(II) for ten determinations.	0.00152	0.000324	0.003447
RSD	0.13%	0.025%	0.082%
Regression equation	A_{4OO} = 0.0223C - 0.0033	A_{410} = 0.0295 C + 0.0458.	A_{360} =0.0132C+0.1189
Beer's law validity range(µg/ml)	0.117-1.172	0.06354-1.272	0.835-8.35
Composition of the complex (M:L) obtained in job's and mole ratio method.	1:2	1:2	1:2
Stability constant	2.76×10^{11}	$5.93x10^{10}$	$2.4x10^{11}$

Applications of the proposed method:

To confirm the usefulness of the proposed method, it was applied to the determination of nickel in ground water and in industrial waste water samples. For this purpose the water samples were collected from different parts of industrial estate. The water samples [1liter] were collected in clean 2 liter beakers and slowly evaporated to 25mL; then 5ml of H_2O_2 was added and evaporated to dryness. It was then dissolved in 20mL of water and filtered to remove insoluble substance. The filtarate was collected in 100mL volumetric flask quantitatively and diluted to the mark with distilled water. Two untreated waste water samples collected from different parts of industrial estate have been analyzed after treating the water sample using the procedure described above. Reliability of the method was checked by the spiking experiments and comparing the results with the data obtained by GF- AAS as shown in the table- 2, the results obtained with the proposed method agree well with data obtained by furnace atomic absorption analysis and the recovery of the spiked sample is good, suggesting that the procedure is reliable for sample examination.

Table-2: Determination of nickel in ground water and in industrial waste water samples

Sample	Added µg/mL	found µg/mL	Recovery %	GF-AAS[a] µg/mL
Ground water	15.0	ND[b] 14.7±0.3	98.7	5.3±0.2
Industrial Waste wter (1)	15.0	76.2±0.8 90.6±1.3	96	75.6±1.8
Industrial waste water(2)	15.0	68.3±1.2 82.5±1.4	94	67.8±1.2

[a] mean and standard deviation of three determinations, [b]ND – not determined.

CONCLUSION

In this study it was shown that Thiosemicarbazones could be used as a ligand for the Spectrophotometric determination of trace metal ions. The methods described in this paper are applicable for the rapid, precise and reliable determination of trace amounts of Copper, Nickel and Bismuth in water and in industrial waste water. Reliability of the method can be checked by the spiking experiments and comparing the results with the data

obtained by GF- AAS .The main benefits of the procedure are the enhanced sensitivity of the spectrophotometric method, low cost, fairly easy operation and speed of analysis.

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