

Spectrophotometric determination of copper(II) and palladium(II) using 3-hydroxybenzaldehyde thiosemicarbazone

S. Vidyasagar Babu and K. Hussain Reddy*

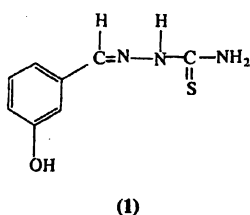
Department of Chemistry, Sri Krishnadevaraya University, Anantapur-515 003, Andhra Pradesh, India

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Abstract : The analytical properties of 3-hydroxybenzaldehyde thiosemicarbazones (HBT) are described for the first time. The reagent gives yellowish green coloured complexes with copper(II), palladium(II) in sodium acetate-acetic acid buffer medium of pH 5.5 and 2.5 respectively. The molar absorptivities of copper and palladium complexes respectively are 8.75×10^3 , and $1.25 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. These colour reactions have been investigated for the spectrophotometric determination of copper(II) and palladium(II) in aqueous medium.

Keywords : Spectrophotometric determination, thiosemicarbazone, copper(II), palladium(II).

Ortho-hydroxy substituted thiosemicarbazone have been frequently used for the spectrophotometric determination of metal ions but meta substituted thiosemicarbazones are not¹. Therefore it is considered worthwhile to investigate the analytical properties of thiosemicarbazones derived from 3-hydroxybenzaldehyde. In continuation of our previous works² herein we report the synthesis, characterization and analytical properties of 3-hydroxybenzaldehyde thiosemicarbazone (HBT) along with spectrophotometric determination of copper(II) and palladium(II) using HBT. The present method is applied for the determination of copper in synthetic alloys.



Results and discussion

The reagent 3-hydroxybenzaldehyde thiosemicarbazone (1) is easily prepared under reflux conditions. A 0.001 M solution of HBT is stable for 24 h.

In basic medium (above pH 6), the ligand presumably exists in enolic form and coordinates the divalent metal ion as mono anion. The reagent gives intense colour reaction only with copper and palladium and show maximum absorbance at 351 and 353 nm respectively. The

reagent (HBT) is considered as potential reagent for selective spectrophotometric determination of copper(II) and palladium(II).

Determination of copper(II) and palladium(II) :

Copper(II) and palladium(II) reacts with HBT in acidic pHs to give pale yellow coloured complex. The colour reaction is instantaneous even at room temperature. The order of addition of reagent, metal ion, buffer has no effect on the absorbance of the complexes provided DMF is added prior to the addition of reagent solution. The absorbance of the yellow coloured complex remains constant for 5 h. A 5-fold molar excess of the reagent is adequate for full colour development. Addition of excess reagent has no adverse effect on the absorbance of the complexes.

The system obeys Beer's law in the concentration range 0.51–4.1, 0.42–4.2 $\mu\text{g ml}^{-1}$ of copper and palladium respectively. The optimum range for the determination of copper(II) and palladium(II) from Ringbom's plot is found to be 0.25–0.85, 0.29–0.69 $\mu\text{g ml}^{-1}$. The molar absorptivity and Sandell's sensitivity of the methods for Cu and Pd are found to be 8.75×10^3 , $1.25 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.073, 0.085 $\mu\text{g cm}^{-2}$ respectively. The specific absorptivity of the system is 0.138, 0.117 $\text{ml g}^{-1} \text{ cm}^{-1}$ Cu and Pd respectively. The relative standard deviation for ten replicate analyses Cu and Pd are 0.23 and 0.25% respectively.

Job's and molar ratio methods gave the composition of the Cu and Pd complexes as 1 : 2, 1 : 1 (M : L) respectively. The stability constants of Cu and Pd com-

plexes calculated by Job's method are found to be 7.8×10^5 , 6.0×10^4 respectively.

Interferences :

The effect of some of the ions which often accompany copper and palladium has been studied by adding different amounts of anions and cations to 0.76, 2.54 (ppm) $\mu\text{g ml}^{-1}$ of copper and palladium in solution. The colour is developed as described in the recommended procedure. An error of $\pm 2\%$ in the absorbance reading is considered tolerable. The results are given in Table 1. Larger amounts of iron(III) does not interfere in the presence of fluoride, masking reagent.

Determination of copper in NTPC alloy sample :

The amount of copper present in synthetic samples whose composition corresponding to NTPC and aluminium alloys was determined by using the present method. The results are given in Table 2.

Experimental

The reagent (HBT) was prepared by simple condensation of 1 mol of 3-hydroxybenzaldehyde and 1 mol of thiosemicarbazide. In a 250-ml Erlenmeyer flask, a hot

methanolic solution of 3-hydroxybenzaldehyde (0.012 mol, 1.5 g of substance dissolved in 15 ml of methanol) and thiosemicarbazide (0.012 mol; 1.12 g of substance dissolved in 20 ml of hot distilled water and 5 ml of hydrochloric acid) were mixed and heated under reflux for 3 h. Shiny milk white crystals were separated out on cooling the reaction mixture. The crystals were collected by filtration and washed with hot water and with 1 : 1 cold methanol. The compound was recrystallised from benzene and dried *in vacuo*. Yield 65%, m.p. (d) 155–156 °C.

The compound was characterized by IR, ^1H NMR and mass spectral data. Infrared spectrum of HBT shows bands at 3442 (m), [3278 (m) and 3235 (m)], 1609 (s), 1260 (b) and 1156 (m) cm^{-1} respectively, corresponding to $\nu(\text{OH})$, $\nu(\text{NH})$ (asymmetric and symmetric), $\nu(\text{C}=\text{N})$, $\nu(\text{C}-\text{O})$ and $\nu(\text{C}=\text{S})$ stretching vibrations respectively. ^1H NMR spectrum of HBT ($\text{CDCl}_3 + \text{DMSO}-d_6$) showed signals at 7.7 (2H, s), 7.9 (1H, s), 11.4 (1H, s), 6.8–7.4 (complex 4H) and 9.1 (1H, s) due to NH_2 , NH, CH (azomethine), CH (aromatic), OH (hydroxy) respectively. Mass spectrum of HBT showed molecular ion peak at

Table 1. Tolerance limit of foreign ions in the determination of 0.76 and 2.54 $\mu\text{g ml}^{-1}$ of copper and palladium respectively

| Ion added | Tolerance limit ($\mu\text{g ml}^{-1}$) | | Ion added | Tolerance limit ($\mu\text{g ml}^{-1}$) | |
|-------------------------|---|-----------|--------------------------|---|---------------------|
| | Copper | Palladium | | Copper | Palladium |
| Iodate | 507 | 507 | Zn^{II} | 26 | 26 |
| Tartarate | 592 | 592 | Mn^{II} | 21 | 22 |
| Bromide | 319 | 319 | Ni^{II} | 23 | 23 |
| Sulphate | 384 | 384 | Fe^{III} | 11(25) ^a | 11(15) ^a |
| Nitrate | 248 | 124 | Co^{II} | 11 | 16 |
| Fluoride | 71 | 37 | Pd^{II} | 58 | – |
| Chloride | 141 | 141 | Sn^{II} | 5 | 0.2 |
| Carbonate | 240 | 240 | Cd^{II} | 9 | 18 |
| Acetate | 188 | 188 | Cr^{VI} | 1 | 0.5 |
| Cyanate | 104 | 104 | Cu^{II} | – | 0.7 |
| Oxalate | 0.2 | 35 | V^{V} | 2 | 2 |
| Thiocyanate | 0.2 | 38 | U^{VI} | 4 | 10 |
| Thiourea | 0.8 | 8 | Hg^{II} | 0.4 | 1 |
| Mo^{VI} | 96 | 65 | Ce^{IV} | 3 | 5 |
| Fe^{II} | 30 | 25 | Zr^{IV} | 18 | 25 |
| Ag^{I} | 10 | 5 | Al^{III} | 10 | 0.1 |
| Th^{IV} | 45 | 42 | W^{VI} | 73 | 73 |
| | | | Ba^{II} | 55 | 75 |
| | | | Ca^{II} | 16 | 16 |

* Masked with 180 $\mu\text{g ml}^{-1}$ of fluoride.

Table 2. Determination of copper in synthetic alloys

| Alloy | Amount of copper ($\mu\text{g/ml}$) | |
|-----------------------------|---------------------------------------|--------------------|
| | Taken | Found ^a |
| NTPC alloy ^b | 0.457 | 0.438 |
| | 0.915 | 0.864 |
| | 1.829 | 1.712 |
| Aluminum alloy ^c | 1.003 | 0.998 |
| | 2.006 | 1.990 |
| | 3.009 | 3.105 |

^aAverage of 3 determinations.^bComposition of NTPC alloy : Ni, 10; Cr, 15; Fe, 6.5; Cu, 4.5; Mn, 2%.^cComposition of aluminum alloy : Ni, 1.93; Cu, 4.10; Fe, 0.4; Mn, 0.2; Mg, 1.6 and rest Al.

m/z 195 corresponding to its molecular weight. Other peaks are 178 (M-OH^+), 119 [$\text{M-(NH}_2)_2\text{CS}$], 93 (formation of $\text{C}_6\text{H}_5\text{OH}^+$).

The reagent solution (0.01 M) was prepared by dissolving 100 mg of the compound in 50 ml of dimethylformide and it is stable for one day.

Hydrochloric acid (1 M)-sodium acetate (1 M) pH (0.5–3.5); 0.2 M NaOAc-0.2 M AcOH (pH 4–6) and 2 M NH_4Cl -2 M NH_4OH buffer solution were used in the present study. The standard copper(II), palladium(II) solutions ($1 \times 10^{-2} M$) were prepared by using analytical reagent grade $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and PdCl_2 respectively. The stock solutions of copper(II) and palladium(II) were standardized using titrimetric and gravimetric methods respectively³.

Schimadzu 160A UV-visible spectrophotometric equipped with 1.0 cm quartz cells and an Elico model LI-120 pH meter were used in present study.

The reactions of some important metal ions were tested at different pH values. The samples were prepared in 25-ml volumetric flask by mixing 10 ml of buffer, 1 ml of metal ion and 1 ml 0.01 M HBT solution. The reaction mixture was diluted to mark with distilled water. The absorbance was measured in 250–600 nm range against the reagent blank.

An aliquot of metal ion in the Beer's law validity range (0.51–4.1 $\mu\text{g/ml}$ Cu, 0.42–4.2 $\mu\text{g/ml}$ Pd), 10 ml of buffer solution (pH 5.5 for Cu, pH 2.5 for Pd) and 1 ml of $1 \times 10^{-2} M$ HBT solution were taken in 25-ml standard flask and diluted to the mark with distilled water. The absorbance of the coloured solution was measured at corresponding wavelength (351 nm for Cu, 353 nm for Pd) against reagent blank. Calibration graphs were prepared. The measured absorbance values were used to compute the amount of copper and palladium present in the unknown solution.

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