2-Hydroxy-5-methylbenzophenone oxime(HMBO) as an Analytical Reagent for Gravimetric Determination of Cu (II)

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Abstract: 2-hydroxy-5-methylbenzophenone oxime (HMBO) was developed as a new analytical reagent for the gravimetric determination of divalent copper ion. In pH rang of 3.0 to 6.0, the reagent gives a buff colored precipitate with Cu(II). Job's method and mole ratio method revealed that the stoichiometry of the complex is 1:2 (metal: ligand). Beer's law is obeyed up to 61.25 ppm of Cu(II). Molar absorptivity and Sandell's sensitivity at 400 nm were found to be $6.32 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.359 \mu\text{g/cm}^2$ respectively. The stability constant of Cu(II)-HMBO complex is found to be 2.43×10^9 . Gibb's free energy change for complex formation reaction was found to be -12.88 Kcal/mol. The reagent can be used for the analysis of brass and alloy.

Keywords: Oxime, Analytical reagent, 2-hydroxy-5-methyl benzophenone oxime, HMBO.

Introduction

In the current scenario of analytical chemistry, many reagents are widely available. They include o-hydroxy ketoximes¹⁻³, phenyl hydrazones, thiosemicarbazone^{4,6}, chalcone oximes⁷ etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. In this work, we report the use of 2-hydroxy-5-methylbenzophenone oxime (HMBO) as a gravimetric reagent for Cu(II). Spectrophotometric methods have been used to confirm the stoichiometry of complex and to determine the stability constants of the complex. The reagent is used to determine copper in brass and alloy.

Experimental

Instruments

Schimadzu UV- visible spectrophotometer (160-A) was used for all absorbance and pH of solutions were measured on Elico-pH meter (LI-10T) and buffer solution of required pH were obtained using (sodium acetate-acetic acid) and (hydrochloric acid-sodium acetate) buffers of suitable concentration.

Synthesis of 2-Hydroxy-5-methylbenzophenone oxime(HMBO)

p-Cresyl benzoate was prepared from p-cresol, water and benzoyl chloride in presence of NaOH. 2-hydroxy-5-methylbenzophenone was prepared from p-cresyl benzoate using Fries reaction in presence of anhydrous AlCl_3 . 2-Hydroxy-5-methylbenzophenone oxime was prepared from the ketone by sodium acetate method. It was crystallized from ethanol; colourless needles (m.p. $110 \pm 2^\circ\text{C}$) were obtained. The reagent is soluble in solvents like ethanol, carbon tetrachloride, acetone, DMF etc.

The elemental analysis of the reagent was found to be:

Elements	Calculated	Found
Carbon	77.66	77.56
Hydrogen	5.77	5.80
Nitrogen	12.44	12.42

Stock solution

A 0.05 M stock solution of Cu(II) was prepared by dissolving requisite amount of anhydrous $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in double distilled water, little free acid were added in it and was used after standardization with EDTA. Solutions of required concentrations were prepared by diluting above stock solution. Solution of the reagent HMBO (0.05 M) was prepared by dissolving oxime in 70 % aqueous ethanol.

Gravimetric procedure

A 0.05 M solution of the reagent in 70 % aqueous ethanol was used. Copper sulphate solution (0.05 M, 10.0 mL) taken in a clean beaker was diluted to about 100.0 mL with distilled water and pH of the solution was adjusted to 3.0-6.0 with suitable buffer. The solution was warmed at 60°C and small excess of reagent solution was added (0.05 M, 22.0 mL). A buff precipitate obtained was digested on water bath for 1 hour at 60°C . The precipitate was filtered through a previously weighed sintered glass crucible (G_4). The precipitate was washed with hot water followed by 70 % aqueous ethanol to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weigh at $110-115^\circ\text{C}$ in hot air oven, cooled and weighed.

Gravimetric determination of Cu(II)

To establish the applicability of the reagent for gravimetric estimation of Cu(II), the metal ion was determined in the pH range 3.0-6.0. The maximum error being $\pm 1\%$. Estimations were done at pH 5.0 using different aliquots of Cu(II). In all cases the error in Cu(II) content did not exceed $\pm 0.84\%$ (Table -1).

Table - 1. Result of gravimetric estimation of copper (II) at pH 5.0; Cu(II)-HMBO

Cu(II) taken mg	Cu(II) complex g	Cu(II) found mg	Error	
			mg	%
15.89	0.1289	15.88	-0.01	+0.06
31.77	0.2601	32.04	+0.27	+0.84
47.66	0.3874	47.72	+0.06	+0.13
63.56	0.5180	63.81	+0.25	+0.39

Interference

To study the effect of foreign ions on gravimetric determination of Cu(II), 8-10 mg of various cations were added to solution containing 31.77 mg Cu(II) at pH 5.0 and gravimetric estimations were done. It was observed that Mg(II), Ca(II), Mn(II), Ni(II), Sr(II), Zn(II), Ba(II), Cd(II) and Al(III) do not interfere at this pH but Pd(II), Co(II) and Fe(III) interfere seriously. Many common anions like chlorides, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

Spectrophotometric study of Cu(II)-HMBO complex

For taking the absorbance spectra 5.0 mg chelate was dissolved in 25.0 mL chloroform and the absorbance was measured in the range of 350 – 800 nm. It was observed that absorbance of the solution increased continuously towards the shorter wavelength. The absorbance spectrum showed a shoulder at 400 nm and hence all measurement was carried out at 400 nm.

The Cu(II)-HMBO complex is insoluble in methanol and ethanol. It is soluble in solvent like chloroform, MIBK, 1:4 dioxane etc. Hence the complex was extracted in chloroform. For spectrophotometric studies varying amount of Cu(II) solution was taken and pH was adjusted to 5.0 with (sodium acetate + acetic acid) buffer and HMBO solution was extracted with three 5.0 mL portion of chloroform and the volume of chloroform extract was made up to 25.0 mL the absorbance of chloroform extract was measured against reagent blank.

Validity of Beer's law

The Cu(II)-HMBO complex in chloroform obeys law up to 61.25 ppm of Cu(II). Beyond this concentration the absorbance plot showed deviation from linearity (Figure 1). Standard graph thus obtained may be used for the determination of copper in an unknown solution using HMBO. Molar absorptivity calculated from Beer's law plot was found to be $6.32 \times 10^2 \text{ lit.mol}^{-1}\text{cm}^{-1}$ for Cu(II)-HMBO complex at 400 nm and Sandell's sensitivity was calculated and found to be $0.359 \mu\text{g/cm}^2$ of Cu(II) at 400 nm.

Figure 1.*Stoichiometry of complex*

The stoichiometry of Cu(II)-HMBO complex was determined by (1) Job's method of continuous variation⁸, and (2) Yoe and Jone's mole ratio method⁹ (Figure 2-3). Both the methods gave the metal: ligand ratio of the complex 1:2. This is in agreement with the stoichiometry found from gravimetry. From this data the structure of complex can be written as follows:

Stability constants of the complex

The stability constants of the complex were calculated using the formula:

$$K_s = [1-\alpha] / [4\alpha^3 C^2]$$

$$\text{Where, } \alpha = (E_m - E_s) / (E_m)$$

E_m = maximum absorbance obtained at the intersect of the two lines.

E_s = absorbance at the stoichiometric ratio of the metal to reagent in complex

The average stability constant found from two methods is 2.43×10^9 from K_s value.

Gibb's free energy change for complex formation reaction was calculated and its value was found -12.88 K.cal/mole at 27 °C.

Figure -2. Job's method for Cu(II)-HMBO complex
Plots of Job's method of continuous variation for determination of M:L ratio
0.005 M Cu(II), 0.005 M HMBO;
pH = 5.0; $\lambda = 400$ nm.

Figure -3. Mole-ratio method for Cu(II)-HMBO complex
Plots of Yoe and Jone's method for determination of M:L ratio
0.005 M Cu(II), 0.005 M HMBO; pH = 5.0; $\lambda = 400$ nm.

Determination of Copper in Brass

Exactly sample of brass (0.5589 g) was dissolved in 50 % HNO_3 by heating for 30 minutes. The excess of nitric acid was boiled off and the solution was diluted to 100.0 mL with distilled water. The aliquot 10.0 mL was taken and Cu(II) was determined gravimetrically at pH 5.0 as described earlier. Zn(II) and other trace metal did not interfere at this pH. The experiment was repeated three times. Cu %, found: 71.01; reported: 70.50.

Gravimetric estimation of Cu(II) in german-silver using HMBO

Exactly weighed quantity of german-silver (0.9338 g) was transferred to a 250.0 ml beaker. 50.0 mL 1:1 nitric acid was put in it. The solution was heated to dissolve the alloy. Excess nitric acid was boiled off and the solution was diluted to 100.0 ml with distilled water.

10.0 mL aliquot was taken and Cu(II) was determined a pH 5.0 as described earlier. Ni(II) and other trace metal did not interfere at this pH. The experiment was repeated three times. Cu %, found: 56.44; reported: 56.00.

Conclusion

2-Hydroxy-5-methylbenzophenone oxime (HMBO) is suitable reagent for spectrophotometric determination of Cu(II). Many anions and cations were not found to interfere.

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