2'-Hydroxy-4'-Methoxychalcone Oxime [HMCO] as A Gravimetric and Spectrophotometric Reagent for The Determination of Cu(II)

INTRODUCTION:
In the current scenario, large number of organic reagents have been employed for the detection and quantitative determination of metal ions. They include o-hydroxy ketoximes1-5, phenyl hydrazones, thiosemicarbazones, chalcone oximes6-9 etc. These are generally used for spectrophotometric and gravimetric determination of transition metal ions. Here, we report the use of 2'-Hydroxy-4'-methoxychalcone oxime [HMCO] as an analytical reagent for Cu(II).

EXPERIMENTAL:

Instruments:
Spectrophotometric measurements were done on a “Milton Roy” (Spectronic 20D+) Spectrophotometer and “Abbot make UV-1100, UV-Visible Spectrophotometer”. The IR spectra were recorded on “Perkin-Elmer” FTIR Spectrophotometer (RX-1) in KBr pallet. The NMR spectra were recorded on “Bruker Avance II 400 NMR Spectrometer. All pH measurements were done on Equip-Tronic pH meter (Model No.EQ 614).

Stock solution:
Stock solution of CuSO4.5H2O (0.05 M) was prepared by dissolving 3.121 gm of CuSO4.5H2O (A.R.) in minimum quantity of water and diluted to 250 ml with doubly distilled water. Concentrated sulphuric acid was added in little amount to prevent the hydrolysis of the salt. It was used after standardization10 with EDTA.

Synthesis of Reagent [HMCO]:
Resacetophenone was prepared from resorcinol, glacial acetic acid and anhydrous zinc chloride according to the method of R. Robinson and R. C. Shah11. Resacetophenone was treated with methyl iodide and anhydrous potassium carbonate in acetone on a water bath at 65-70°C for six hours. On acidification with dilute HCl, 2-hydroxy-4-methoxy acetophenone was obtained. The 2-hydroxy-4-methoxy acetophenone was converted to chalcone by its condensation with benzaldehyde in presence of aqueous KOH for 24 hours at room temperature. The 2'-hydroxy-4'-methoxychalcone was converted to its oxime using hydroxylamine hydrochloride and sodium acetate. On crystallization from alcohol pure oxime in the form of light yellow crystals with m.p.85°C was obtained.

GRAVIMETRIC DETERMINATION OF CU(II):
Copper sulphate solution (0.05 M, 10 ml) was taken in a clean beaker and diluted to about 100 ml with distilled water. A little excess of reagent solution was added (0.05 M, 22 ml). The pH of the solution was adjusted between 3.0 to 6.0 using suitable acid buffer. A brown precipitate obtained were digested on water-bath for 60 minutes at 60°C. The precipitate were filtered through a previously weighed sintered glass crucible (G4) and washed with warm water followed by 70% aqueous ethanol to remove excess of the reagent. The chelate was dried to constant weight at 110°C in hot air oven, cooled and weighed as Cu(C16H15O3N). Duplicate experiments were performed in each case. The results are given in Table 1. The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots, keeping the optimum pH value to evaluate its applicability. The error in any case did not exceed 1.0%.

INTERFERENCE FROM OTHER IONS:
To study the effect of foreign ions on gravimetric determination of Cu(II), 8-10 mg of various cations were added to a solution containing 31.77 mg Cu(II) at pH 5.0 and gravimetric estimations were done. It was observed that Sr(II), Ca(II), Ni(II), Mn(II) and Mg(II) do not interfere at this pH but Fe(III) and Pb(II) interfered seriously. Interference of Fe(III) can be removed by masking it with H3PO4. Many common anions like nitrate, nitrite, sulphate, chloride, bromide, iodide were not found to interfere.

TABLE - 1

| pH  | Cu(II) complex in g | Cu(II) found in mg | Error in mg | % |
|-----|---------------------|--------------------|-------------|---|
| 3.0 | 0.3000              | 31.65              | -0.12       | -0.37 |
| 3.0 | 0.2999              | 31.64              | -0.13       | -0.40 |
| 3.5 | 0.3002              | 31.67              | -0.10       | -0.31 |
| 3.5 | 0.3004              | 31.69              | -0.08       | -0.25 |
| 4.0 | 0.3005              | 31.70              | -0.07       | -0.18 |
| 4.0 | 0.3007              | 31.72              | -0.05       | -0.15 |
| 4.5 | 0.3010              | 31.75              | -0.02       | -0.06 |
| 4.5 | 0.3012              | 31.76              | -0.01       | -0.03 |
| 5.0 | 0.3014              | 31.79              | +0.02       | +0.06 |
| 5.0 | 0.3015              | 31.80              | +0.03       | +0.12 |
| 5.5 | 0.3020              | 31.86              | +0.09       | +0.28 |
| 5.5 | 0.3018              | 31.83              | +0.06       | +0.18 |
| 6.0 | 0.3025              | 31.91              | +0.14       | +0.44 |
| 6.0 | 0.3022              | 31.88              | +0.11       | +0.34 |

Conversion factor = 0.1055
SPECTROPHOTOMETRIC STUDY OF Cu(II)-HMCO CHELATE: 
5 mg of chelate was extracted in 25 ml of chloroform and the absorption spectra was recorded in the range of 300 to 800 nm. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wavelength. A weak band is observed at 400 nm and hence all measurements were carried out at 400 nm.

VERIFICATION OF BEER’S LAW AND OPTIMUM CONCENTRATION RANGE: 
To 5 ml of solution (0.01 M) of the reagent HMCO, varying amount of the Cu(II) solution (0.005 M) was added and the pH was adjusted to 5.0, using [CH3COOH + CH3COONa] buffer. The resultant complex extracted in chloroform using three 5.0 ml portions of chloroform and final volume of chloroform extract was adjusted to 25.0 ml. The absorbances of these solutions were measured at 400 nm against chloroform as blank. Absorbance values were plotted against metal concentration expressed in ppm. A straight line passing through the origin, indicating obeyance of Beer’s law is obtained up to 38.12 ppm of Cu(II). The molar absorptivity of the Cu(II)-HMCO complex was found to be 6.716 x 10^4 l/mol.cm and the Sandell’s sensitivity is found to be 0.0946 µg/cm² at 400 nm.

STOICHIOMETRY: 
Job’s method of continuous variation and Yoe and Jones mole ratio method were used to determine the stoichiometry of the Cu(II)-HMCO complex. From both the methods, it was found to be 1:2 (M:L) ratio. This is in agreement with the stoichiometry found from gravimetry. The average stability constant found from both methods is 4.065 x 10^16. The Gibb’s free energy change for complex formation reaction at 30°C was found to be -11.81 K.cal/mole.

IR SPECTRA: 
Examination of the IR spectra of the chelates show that the band due to intramolecular hydrogen bonded OH stretching of 2-hydroxy group disappears in the Cu(II)-HMCO complex. From both the methods, it was found to be 1:2 (M:L) ratio. This is in agreement with the stoichiometry found from gravimetry. The average stability constant found from both methods is 4.065 x 10^16. The Gibb’s free energy change for complex formation reaction at 30°C was found to be -11.81 K.cal/mole.

RESULTS: 
1. Weight of Cu(II)-HMCO complex = 0.3842 gm
2. Copper found in 10 ml diluted solution (Average of three determinations) = 0.04058 gm
3. Copper found in brass alloy sample = 0.4058 gm
4. Percentage of copper found in brass alloy sample = 73.47%
5. Percentage of copper reported in brass alloy sample = 73.40 %
6. Percentage error = -0.095 %

THERMOGRAMMETRIC ANALYSIS (TGA) STUDY OF Cu(II)-HMCO COMPLEX: 
From the result of TGA, it is seen that the complex is stable upto temperature 150°C and so it can be dried safely without decomposition at 100-150°C. The loss in weight in the temperature range 150°C to 800°C is due to the removal of organic ligand molecule. The observed loss agrees well with the loss expected as per the given formula. This confirms the metal:ligand ratio [1:2] which is also established from the results of gravimetric analysis, elemental analysis and spectrophotometric methods. Activation energy Ea was calculated using Broido method.

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REFERENCES: 
1. A.B.Bhatt and K.K.Dessai, J.Inst.Chemists (India), (1989), 61, 5 | 2. D. Vijayakumar, R.C.Hussain and N. Appala Raju, J. Indian Chem. Soc., 67, (1990), 786. | 3. S. K. Shingadia and K. K. Dessai, (2007), E-Journal of Chemistry, 4(1), 97-102. | 4. Miss Krishna Purohit and K. K. Dessai (2005), E-Journal of Chemistry, 2(2), 161-164. | 5. J.J.Dessai, P.G.Dessai and A.G.Mehta (1999), Asian J. Chem., 11(2), 519. | 6. Sayaji Rao M., Prasad N. B. L. and Hussain Reddy K. (2004), Indian Journal of Chemistry, Sec-A: Inorganic, Physical, Theoretical & Analytical, 45(5), 1659-1662. | 7. Ambily P. Nair and Christine J. J., Biophysical and Environmental Chemistry, 2009, 4(5), 303-307. | 8. Ambily P. Nair and Christine J. J., Biophysical and Environmental Chemistry, 2013, 5(3), 100-106. | 9. Nilesh G. Limbachiya and K. K. Dessai (2013), International Journal of ChemTech Research, 5(1), 2347-2350. | 10. Nilesh G. Limbachiya and K. K. Dessai (2013), International Journal of ChemTech Research, 5(5), 2347-2350. | 11. Nilesh G. Limbachiya and K. K. Dessai (2013), International Journal of ChemTech Research, 5(5), 2347-2350. | 12. Nilesh G. Limbachiya and K. K. Dessai (2013), International Journal of ChemTech Research, 5(5), 2347-2350. | 13. Nilesh G. Limbachiya and K. K. Dessai (2013), International Journal of ChemTech Research, 5(5), 2347-2350. | 14. Nilesh G. Limbachiya and K. K. Dessai (2013), International Journal of ChemTech Research, 5(5), 2347-2350. | 15. Nilesh G. Limbachiya and K. K. Dessai (2014), International Journal of ChemTech Research, 6(1), 786-789. | 16. Vogel A. I., “A Text-Book of Quantitative Inorganic Analysis”, Longmans Green and Co., 1961. | 17. R. Robinson and R. C. Shah (1934), J. Chem. Soc., 1994. | 18. Job P. Ann. Chem., 1928, 9, 113. | 19. Yoe and Jones A. L., Ind. Eng. Chem. and Edin., 1944, 16, 111. | 20. Broido A. (1969), J. Polym. Sci., Part A-2, 7, 1761.