



2, 4-Dihydroxy-5-Bromo Hexaphenone Oxime (DHBHPO) as a Gravimetric and Spectrophotometric Reagent: Studies on Mo (VI) Complex

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ABSTRACT

Spectrophotometric study of Mo (VI) complex with DHBHPO at pH 2.5 in chloroform was performed at room temperature, at 420 nm. Beer's law was obeyed up to 46.05 ppm of Mo (VI). Molar absorptivity and Sandell's sensitivity were found to be $4.69 \times 10^2 \text{ lit. mol}^{-1} \text{ cm}^{-1}$ and $0.2046 \mu\text{g/cm}^2$ respectively. Composition of the chelate was determined using Job's method of continuous variation and Yoe and Jones mole ratio method and was found to be 1:1 (M:L). The stability constant and Gibb's free energy change for complex formation reaction were also calculated and found to be 5.115×10^5 and $-7.836 \text{ k.cal /mole}$ respectively. Gravimetric estimation of Mo (VI) metal ion was done with reagent DHBHPO within the pH range 1.0 to 5.0. Maximum complex formation occurs at pH 2.5. From TGA, the energy of activation was calculated using Broido method and found to be 9.01 and 39.26 k.cal /mole for 1st and 2nd step of decompositions. The reagent was characterized using analytical techniques like UV-visible, NMR and elemental analysis. Mo (VI) metal complex was characterized by UV-visible, IR spectra and TG analysis. The reagent was used successfully for the determination of Molybdenum from ferro-molybdenum alloy.

Keywords: Spectrophotometric, Gravimetric, Hexaphenone oxime, DHBHPO, Gibb's free energy change, Energy of activation.

INTRODUCTION

Organic reagents have been used largely for formation of coordination compounds with metal ions. Many organic reagents like o-hydroxy oximes [1-12], oximes [13-16], thiosemicarbazones [17, 18], chalcone oxime [19], anilides of aromatic aldehydes and ketones are generally used for this purpose. DHBHPO have been synthesized by us, for the rapid spectrophotometric and gravimetric determination of Mo(VI).

MATERIALS AND METHODS

Synthesis of 2, 4-Dihydroxy-5- Bromo Hexaphenone oxime (DHBHPO): 2, 4-Dihydroxy-Hexaphenone (DHHP) was prepared from resorcinol, n-Hexanoic acid and anhydrous zinc chloride according to the method of H. Nogemi [20]. 2, 4-dihydroxy-Hexaphenone was dissolved in glacial acetic acid to carry out

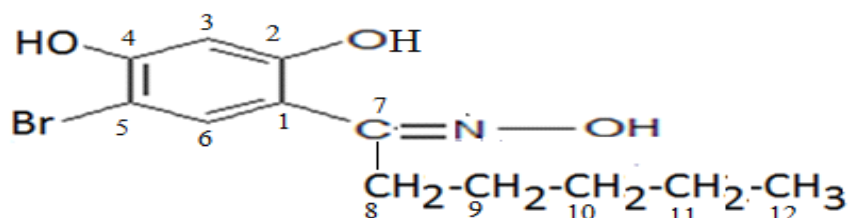
bromination. Oxime was obtained from bromo derivative after reacting it with hydroxyl amine hydrochloride and sodium acetate. The oxime was recrystallized from absolute alcohol.

Mo (VI)-metal solution: A standard solution of Molybdenum (VI) (0.05M) was prepared by dissolving an accurately weighed amount of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (A.R) (3.0243 g for 250mL) in deionized water.

All other diverse ion salt solutions were prepared in deionized water using respective salts (A.R).

RESULTS AND DISCUSSION

Characterization of Reagent: The reagent under present study is characterized by following different analytical techniques.



Structure of 2, 4-Dihydroxy-5-Bromo Hexaphenone Oxime (DHBHPO)

Elemental analysis: DHBHPO was analyzed on Perkin-Elmer 2400 elemental analyzer. The percentage elements, found are in accordance with its molecular formula. The results are given in the following Table 1.

Table 1: Elemental Analysis of the reagent

Reagent	% Found (Calculated)		
	Carbon	Hydrogen	Nitrogen
DHBHPO	47.73 % (47.68%)	5.25 % (5.30%)	4.52 % (4.63%)

TG Studies: Thermo gravimetric analysis was carried out using Universal V₃-OG TA Instrument.

UV-Visible spectral studies: Shimadzu UV-1601 UV-Visible Spectrophotometer was used for UV-Visible spectrum study in ethanol.

FT-IR Spectral studies: The IR spectrum of the reagent and the complexes were recorded on Shimadzu FTIR Spectrophotometer. Table 2, shows absorption bands observed for complex and reagent in KBr pallet.

Table 2: FT-IR spectral studies of reagent DHBHPO and it's Molybdenum chelate

Reagent	v(O-H) Phenolic	v(O-H) Oximino	v(C-H) of Alkyl group	v(C=C) aromatic	v(N-O)	v(C=N)
DHBHPO	3475cm ⁻¹	3363cm ⁻¹	2854-2956cm ⁻¹	1591cm ⁻¹	1465cm ⁻¹	1492cm ⁻¹
Mo(VI)- DHBHPO	--	3350cm ⁻¹	2829-2985cm ⁻¹	1618cm ⁻¹	1406cm ⁻¹	1440cm ⁻¹

¹H and ¹³C NMR spectral studies of 2, 4-Dihydroxy-5- Bromo Hexaphenone Oxime DHBHPO: The ¹H NMR and ¹³C NMR study for DHBHPO was carried out using CDCl₃ as solvent and TMS as reference. Assignment of signals to different protons and carbons are given in Table 3 and 4.

Table 3: $^1\text{H-NMR}$

Reagent	Alkyl group	Phenolic(-OH)	Oximino(-OH)	Aromatic Proton
DHBHPO	1.6475-0.800 ppm (multiplate)	12.9469 ppm (singlet)	6.0504 ppm (singlet)	7.9667-7.1911 ppm (multiplate)

Table 4: $^{13}\text{C-NMR}$

Assignment	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Chemical shift(δ) in ppm	112.83	150.96	98.60	155.61	99.71	129.65	161.80	31.80	26.37	24.67	22.36	13.94

Gravimetric Determination of Mo (VI): Gravimetric determination of Mo (VI) ion was studied with DHBHPO at different pH (From 1.0 to 5.0). Sodium acetate-hydrochloric acid buffer used to adjust required pH. To the warm solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.05 M, 10mL), standard solution of DHBHPO was added in excess (0.05M, 22mL). Total volume in beaker was kept around 50 mL. Complex formed was insoluble, which was digested on water bath for 1h. The precipitate was filtered and washed with warm water followed by 50% aqueous ethanol, which removes excess of reagent, precipitated on dilution. The chelate was dried in hot air oven (at 110-115 °C) till constant weight achieved. Optimum pH value for precipitation was fixed and experiment was repeated at optimum pH value, with different aliquots of metal ion solution. Findings are shown in table 5 and 6.

Table 5: Gravimetric Determination of Mo (VI) using DHBHPO
Mo (VI) taken = 47.97 mg, Drying Temperature = 110-115°C.

pH	Mo (VI) complex gm	Mo (VI) found mg	Error	
			in mg	%
1.0	0.2016	48.7265	0.7560	1.575
1.0	0.2018	48.7748	0.8048	1.6777
1.5	0.2008	48.5331	0.5631	1.1738
1.5	0.2007	48.5089	0.5389	1.1234
2.0	0.2002	48.3881	0.4181	0.871
2.0	0.2000	48.3398	0.3698	0.771
2.5	0.1978	47.8080	0.1620	-0.3585
2.5	0.1977	47.7838	0.1862	-0.3881
3.0	0.1968	47.5663	0.4037	-0.8415
3.0	0.1965	47.4938	0.4762	-0.9927
3.5	0.1952	47.1796	0.7904	-1.647
3.5	0.1950	47.1313	0.8387	-1.748
4.0	0.1945	47.0104	0.9595	-2.000
4.0	0.1940	46.8896	-1.080	-2.252
4.5	0.1927	46.5753	-1.3946	-2.9072
4.5	0.1922	46.4545	-1.5154	-3.1591
5.0	0.1901	45.9469	-2.0230	-4.2170
5.0	0.1895	45.8019	-2.1680	-4.5190

Conversion factor: 1 g complex = 241.699 mg of Mo (VI)

Table 6: Gravimetric Determination Of Mo (VI) In Different Aliquots
pH: 2.5 Drying Temperature = 110-115°C

Mo (VI) taken mg	Mo (VI) complex gm	Mo (VI) found mg	Error	
			mg	%
23.99	0.09886	23.8946	0.09536	-0.3975
23.99	0.09883	23.8880	0.1020	-0.4251
47.97	0.1978	47.8080	-0.1620	-0.3585
47.97	0.1977	47.7840	-0.1862	-0.3871
71.96	0.2967	71.7124	-0.2347	-0.3261
71.96	0.2969	71.7607	-0.2380	-0.3308

Effect of Diverse Ions: Interference due to foreign ions in gravimetric determination of molybdenum (VI) was studied. Excess amount of various cations were added to a known volume of molybdenum solution (45.00 ppm of Mo (VI)) at pH-2.5 and analysis was carried out as mentioned above.

It was observed that a 100-fold excess of Na (I), K (I), Ca (II), Sr (II), Mg (II), Zn (II), Cd (II), Ni (II) and Al (III) did not interfere. Thiourea (25), thiosulphate (20), oxalate (5) and borate (5) do not interfere. Fe (III), Ti (IV), and Cu (II) interfered even when present in traces. The interference of iron (III) can be avoided by adding sodium fluoride, as a masking agent.

Spectrophotometric Study of Mo (VI) DHBHPO: A shoulder band was observed at 420 nm in chloroform for the complex and hence this wavelength was fixed for all determinations. The graph is shown in Fig 1.

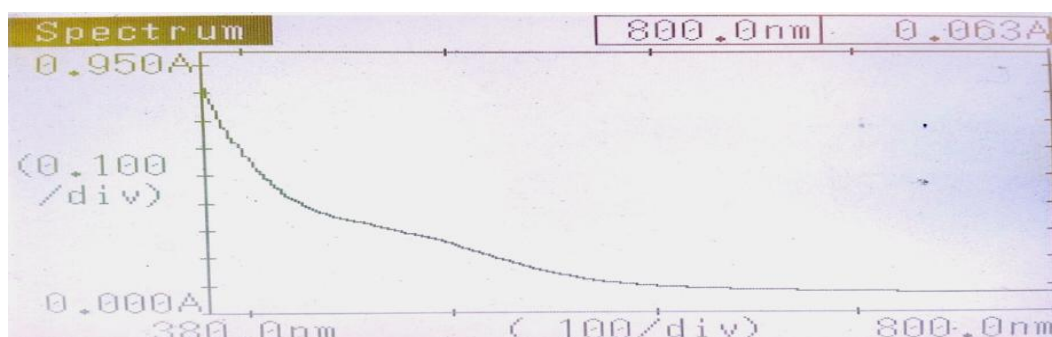


Fig 1. Absorption spectra of Mo(VI)-DHBHPO

Verification of Beer's Law: 4.0 mL of 0.01M ligand solution was added to varying aliquots of the metal ion solution (0.002 M). 2.5pH was maintained using acetic acid-hydrochloric acid buffer. Chloroform extract of the insoluble complex was diluted to 25 mL to measure its absorbance at 420 nm using the ligand as blank. Absorbances were plotted against concentration of Mo (VI). It was found that Beer's law was obeyed up to 46.05 ppm of Mo (VI). Molar absorptivity and Sandell's sensitivity [21] were found to be $4.69 \times 10^2 \text{ lit. mol}^{-1} \cdot \text{cm}^{-1}$ and $0.2046 \mu\text{g/cm}^2$ respectively (Fig. 2).

Job's method [22] and Mole ratio method [23] were used to determine the stoichiometry of the complex. It was found to be 1:1[M: L]. Stability constant was calculated using the following formula:

$$K_s = (1-\alpha) / \alpha^2 C \quad \text{where, } \alpha = (E_m - E_s) / E_m$$

E_m and E_s = Maximum absorbance and Absorbance at the stoichiometric molar ratio (M: L).

C = complex concentration

Mean stability constant derived from above methods was 5.115×10^5 and Gibb's free energy change for complex formation reaction was found to be $-7.836 \text{ k.cal.mol}^{-1}$ at 27°C.

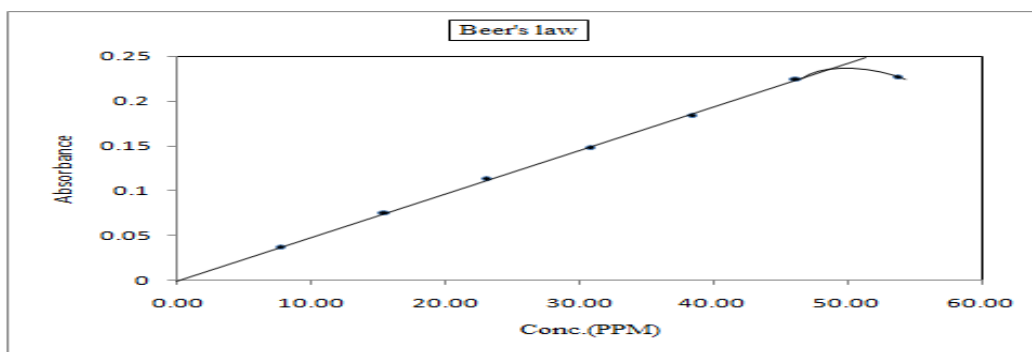


Fig 2. Beer's law plot

Thermo gravimetric analysis: A definite quantity of chelate was taken in an alumina crucible and was kept in a furnace. The temperature of the furnace was raised from 50°C to 960°C in a programmed manner at the heating rate of 10°C min⁻¹.

From thermo gravimetric analysis of the Mo (VI) chelate, it is found that there is no mass loss up to 180°C, which indicates that the chelate can be dried safely without decomposition at 140°C. Loss in mass above 180°C to 950°C is due to decomposition of chelate and loss of ligand molecules. Mass of final residue corresponds to the formula (C₁₂H₁₅O₃NBr) Mo. The observed loss and mass obtained is as per formula of chelate in which M: L ratio is 1:1. Activation Energy E_a was calculated using Broido method [24] and was found to be 9.01 and 39.26 k.cal mole⁻¹ for 1st and 2nd decomposition step respectively (Fig 3,4).

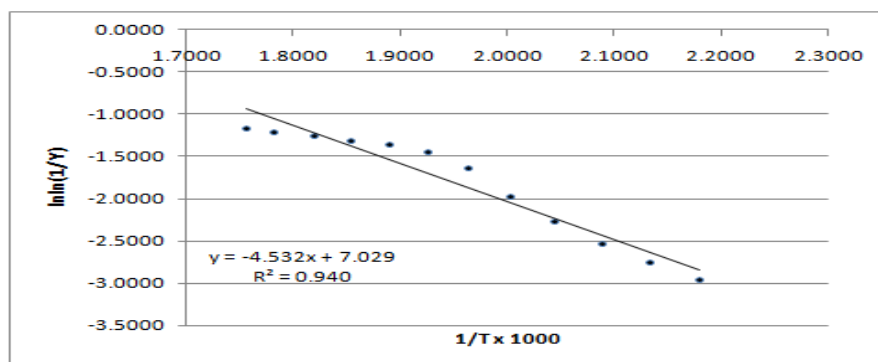


Fig 3. Broido Method: Mo (VI)-[DHBHPO] complex (Step-I)

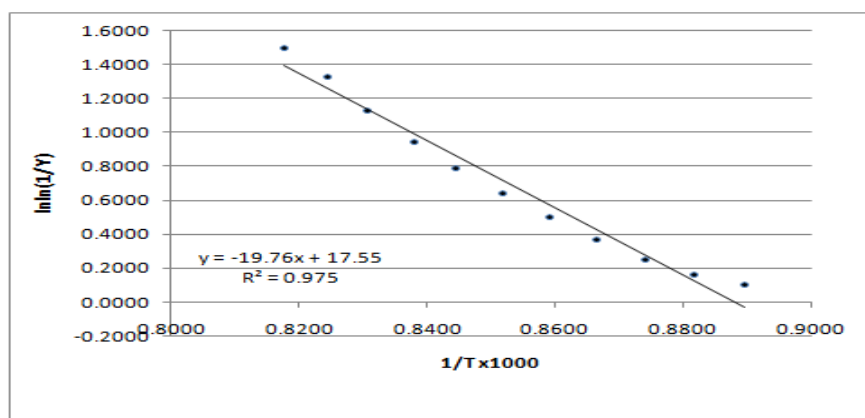


Fig 4. Broido Method: Mo (VI)-[DHBHPO] complex (Step-II)

IR Spectra: Chelate shows weak band around 3475 cm^{-1} in comparisons to the ligand molecule. The weak band due to ν (O-H) of Oximino group was found to 3363 cm^{-1} in ligand was observed at nearly the same position in the complex. (C=N) stretching band observed at 1492 cm^{-1} in ligand was shifted to 1440 cm^{-1} in chelate, indicating that nitrogen is co-ordinately bonded with metal ion and covalently bonded with oxygen atom.

APPLICATIONS

Determination of Molybdenum in Ferro-Molybdenum Alloy: Molybdenum has been accurately determined in ferro-molybdenum alloy (The Preanalyzed sample of ferro-molybdenum alloy obtained from National Metallurgical Laboratory, Jamshedpur) at the above pH value at 420 nm. Percentage of molybdenum obtained agrees with the reported value.

For the determination exactly weighed alloy was dissolved in mixture of conc. HNO_3 and conc. HCl (1:3) by heating on a sand-bath. Excess nitric acid was evaporated and the solution was diluted to 250ml. A known volume of alloy solution (1.0mL) was taken. Fe (III) was masked by adding sodium fluoride. The pH of the solution was adjusted to 2.5 and the color of the complex was developed by adding reagent DHBHPO (0.05M, 5.0mL). The insoluble complex precipitated was extracted in chloroform using three 5.0 mL portion of chloroform and final volume of the extract was adjusted to 25 mL. Absorbance was measured at 420nm. The findings are given below.

• Weight of ferro molybdenum alloy	: 0.3471 g
• Absorbance of the solution (average of three determination)	: 0.172
• Mo (VI) ppm found (from graph)	: 35.30 ppm
• Mo (VI) ppm taken	: 35.74 ppm
• Total amount of Mo (VI) in sample	: 223.35 mg
• %age of Mo (VI) found	: 63.56
• %age of Mo (VI) reported	: 64.35
• Error	: -1.23%

CONCLUSIONS

In the present investigation, 1:1 stoichiometry of Mo (VI)-DHBHPO complex has been established. From the micro analytical data of the solid complex, gravimetric and spectrophotometry studies, it is found that the complex formed is $(\text{C}_{12}\text{H}_{15}\text{O}_3\text{NBr})\text{Mo}$. TG curves shows that thermal stability of complex is fairly good. Broido method, Job's method and Mole ratio method confirms the stoichiometry. 2, 4-Dihydroxy-5-Bromo Hexaphenone Oxime [DHBHPO] gave satisfactory results in evaluating metal content in ores and alloys.

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