

A sensitive and selective chromogenic reagent using 2-hydroxy 3, 5-dimethoxy benzaldehyde thiosemicarbazone (HDMBTSC) for direct and derivative spectrophotometric determination of Molybdenum (VI)

¹M.Hymavathi, ²N.Devanna, ³C.Viswanatha

Department of Chemistry, J. N.T.University, Anantapur-515002, A.P, India.
Prof of chemistry, J.N.T.U.A- OTRI, Anantapuramu-515002, A.P, India.

Abstract: 2-hydroxy 3, 5-dimethoxy benzaldehyde thiosemicarbazone (HDMBTSC) used as a novel chromogenic organic reagent for the determination of Molybdenum (VI) with spectrophotometry. The novel chromogenic reagent 2-hydroxy 3,5-dimethoxy benzaldehyde thiosemicarbazone (HDMBTSC) form green coloured complex with Molybdenum(VI). The colour complex shows maximum absorption at λ_{\max} 406 nm. The beer's law validity range is 0.3838 to 2.399 ($\mu\text{g/ml}$) and optimum concentration range is 0.5757 to 2.0151 ($\mu\text{g/ml}$). The molar absorptivity and sandell's sensitivity $2.93 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$ and $0.00326 \mu\text{g/cm}^2$ respectively. The Molybdenum(VI) forms M:L(I:I) colour complex with HDMBTSC and stability constant of the complex was found to be 2.17×10^6 . This developed method was applied for the determination of Molybdenum(VI) in pharmaceutical samples with good results as compared with certified reference results.

Keywords: Novel chromogenic organic reagent, derivative spectrophotometry, Mo (VI) and pharmaceutical samples.

I. INTRODUCTION

Molybdenum has very adaptable applications not only in metallurgy but also in paints, pigments, dyes, ceramic, electroplating, industrial catalyst, industrial lubricants and organo metallic chemistry. Very low concentrations of Molybdenum and vanadium are present in various matrices such as plants, soil and sea water etc. Therefore, it is very important from the analytical point of view to develop sensitive, selective, rapid and economical methods for their simultaneous determination even when present in trace amounts.

A number of novel chromomeric organic reagents were reported for the spectrophotometric determination of the molybdenum ion. For the determination of molybdenum(VI) at minute levels, there several frequently adopted methods using analytical techniques such as AAS, polography, spectrophotometric and other techniques. Among them, spectrophotometric methods are preferred because they are low cost instrument and high sensitivity.

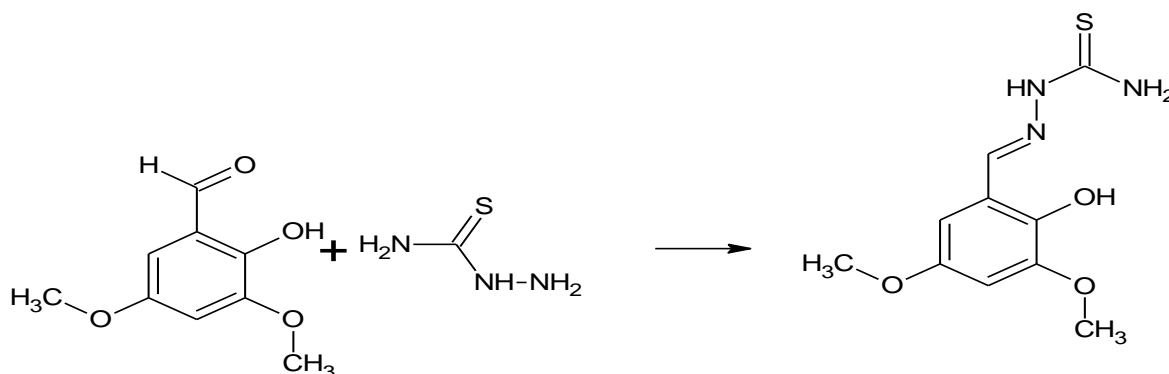
II. EXPERIMENTAL

Spectrophotometric measurements were made in a shimadzu 160 a microcomputer based UV-Visible spectrophotometer equipped with 1.0 cm quartz cells, an ELICO LI- 120 digital pH meter. All reagents used were of analytical reagent (AR) grade unless otherwise stated.

III. REAGENT

Synthesis of 2-hydroxy 3, 5-dimethoxy benzaldehyde thiosemicarbazone (HDMBTSC)

2-hydroxy 3,5- dimethoxybenzaldehyde (0.4554 g, 0.01 mole) dissolved in hot ethanol, hot ethanolic solution of thiosemicarbazide (0.2275 g, 0.01 mole) were taken in a 250-ml round bottom flask. The contents in flask were refluxed for 45 minutes using a water condenser. On cooling the reaction mixture, Light yellow coloured product was separated out. It was collected by filtration and washed several times with hot water and cold ethanol. This compound was recrystallised and dried in vacuo.



Analytical properties of HDMBTSC:

The reactions of some important metal ions were tested at various pH values. The characteristics of the most important metal complexes are presented in Table:1. The samples were prepared with the addition 3 ml of buffer (pH 1.0-11), 0.5 ml of metal ion (1×10^{-3} M) and 0.5 ml of (1×10^{-2} M) HDMBTSC solutions in 10 ml standard flask and it is diluted up to the mark. The absorbance were measured in wavelength region 300 to 800nm against reagent blank.

Table: 1 Characteristics of HDMBTSC complexes in solution

Metal ion	λ_{\max} (nm)	pH	Molar absorptivity ($\text{l.mol}^{-1}.\text{cm}^{-1}$)	Stability constant
Cu(II)	397	9.0	3.06×10^4	1.72×10^6
Mo(VI)	406	4.0	2.93×10^4	2.17×10^6
Zn(II)	416	5.0	1.83×10^4	1.19×10^6

IV. RECOMMENDED PROCEDURE

Estimation of Molybdenum (VI) (zero order)

An aliquot of the solution containing 0.3838 to 2.399 $\mu\text{g/ml}$ of Molybdenum (VI), 3 ml of buffer solution pH 3.0 to 5.0 and 0.5 ml of (1×10^{-2} M) HDMBTSC reagent were taken in a 10ml standard volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 406 nm in a 1.0 cm cell against corresponding reagent blank prepared in the same way but without Molybdenum (VI) metal solution. The absorption spectra of HDMBTSC and its Mo (VI) complex under the optimum conditions are shown in fig no:1. The Mo (VI)-HDMBTSC complex shows the maximum absorbance at 406 nm, whereas the reagent blank does not absorb appreciably.

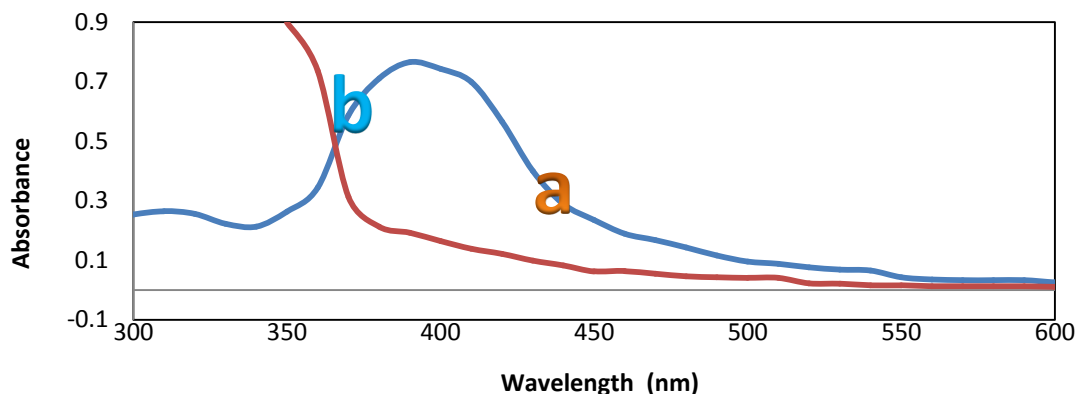


Fig no. 1: Absorption spectra

(a). [Mo (VI)-HDMBTSC] complex Vs reagent blank (b). HDMBTSC Vs buffer blank.

V. RESULTS AND DISCUSSION

2-hydroxy 3,5-dimethoxy benzaldehyde thiosemicarbazone (HDMBTSC) reagent is a blend of a carbonyl compound and a thiosemicarbazide. The reagent solution is stable for more than 20 hrs. in buffer medium. The ligand presumably coordinates the metal ions to give a neutral water soluble complex.

Determination of Molybdenum (VI) using HDMBTSC:

Molybdenum (VI) reacts with HDMBTSC in acidic medium to give green coloured water-soluble complex. The colour reaction between Molybdenum (VI) and HDMBTSC are instantaneous even at room temperature in the pH range 3.0 to 5.0 and Triton X-100 (5%) solution. The absorbance of the green coloured species remains constant for two hours. The maximum colour intensity is observed at pH 4.0. A 10-fold molar excess of reagent is adequate for full colour development. The order of addition of buffer solution, metal ion and reagent has no adverse effect on the absorbance. The complex formation reaction between Molybdenum (VI) and HDMBTSC has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Important physico-chemical and analytical characteristics of Molybdenum (VI) and HDMBTSC are incorporated in table-2

Table-2: Physico-Chemical and analytical characteristics of [Mo(VI) – HDMBTSC] complex

Characteristics	Results
Colour	Green
λ_{max} (nm) (zero order)	406
pH range (optimum)	3.0 to 5.0
Mole of reagent required per mole of metal ion for full colour development	10 – folds
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	2.93×10^4
Sandell's sensitivity ($\mu g.cm^{-2}$)	0.00326
Beer's law validity range ($\mu g/ml$)	0.3838 to 2.399
Optimum concentration range ($\mu g/ml$)	0.5757 to 2.0151
Composition of complex (M:L) obtained in Job's and mole ratio method	1: 1
Stability constant of the complex (jobs method)	2.17×10^6
Relative standard deviation (%)	0.02
Regression coefficient	0.998

The first order derivative spectra were shown in fig no-2. From this shows that the derivative amplitudes measured at 438 nm for first order and found to be proportional to the amount of Molybdenum(VI) respectively.

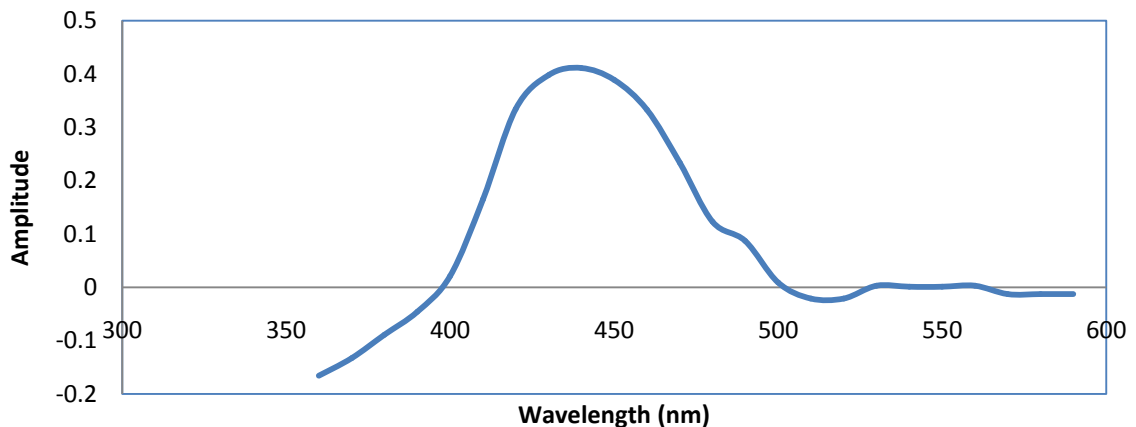


Fig no-2: First derivative spectra of [Mo(VI)-HDMBTSC] Vs reagent

VI. EFFECT OF FOREIGN IONS

Derivative spectrophotometry is a very useful technique in the sense that it decreases the interference, i.e., increases the tolerance limit value of foreign ions of metal ions having overlapping spectra. The recommended procedures have been employed for the spectrophotometric determination of Molybdenum (VI). The effect of various diverse ions in the determination of Molybdenum (VI) was studied to find out the tolerance limit of foreign ions in the present method. The results are given in Table-3.

Table-3: Tolerance limit of foreign ions in the determination of 0.9596 µg/ml of Molybdenum (VI)

Ion Added	Tolerance Limit(µg/ml)	Ion Added	Tolerance Limit(µg/ml)
Sulphate	3663	Pb(II)	49
Bromide	69	Au(III)	65
Urea	218	Zr(IV)	42
Iodide	658	Zn(II)	23
Tartar ate	431	Sn(II)	39
Thiourea	48	Cr(VI)	25
Phosphate	133	W(VI)	16
Acetate	65	Co(II)	1.9
Nitrate	48	Ti(IV)	13
Fluoride	11	Ni(II)	14
Ascorbic acid	265	Bi(III)	13
Citrate	33	Cu(II) ^a	3.93
Pd(II)	4.63	V(V)	11
Ru (III)	2.9	Cd (II)	6
Hg(II)	4.1	Fe(III) ^b	3.613

a. Masked with thiourea 132 µg/ml.

b. Masked with phosphate 186 µg/ml.

VII. APPLICATIONS

Analysis of pharmaceutical sample:

About 3g of sample (Pantobionta) was heated after treating it with 15 ml of 1 N HNO₃. Then 15 ml 1:1 mixture of HNO₃ and HClO₄ were added and the solution was heated until dryness. The residue was dissolved in hot distilled water and 15 ml of 2 M HCl were added. The solution was filtered and diluted to 50 ml with distilled water. The results are presented in table-4

Table 4: Determination of Mo (VI) in pharmaceutical samples

Pharmaceutical sample	Certified value	Amount of Molybdenum (VI) Found	Error (%)
Pantobionta	2.0	1.96	-2.0

*Average of best three determinations

VIII. CONCLUSION

2-hydroxy 3,5-dimethoxy benzaldehyde thiosemicarbazone (HDMBTSC) has been proven a sensitive and selective novel chromogenic organic reagent for the determination of Molybdenum (VI). Molar absorptivity of the colour complex was $2.93 \times 10^4 \text{ L.mole}^{-1} \text{ cm}^{-1}$. The proposed method was especially sensitive and selective with respect to metals, which commonly seriously interfere with the determination of Molybdenum performed by literature methods. The proposed method can be successfully applied to the determination of Molybdenum (VI) in pharmaceutical samples. The number of chromogenic reagents available for the determination of Molybdenum is relatively small. Some of the spectrophotometric methods¹⁻²² proposed for the determination of Molybdenum (VI) was reviewed.

ACKNOWLEDGEMENT

The authors are thankful to the Jawaharlal Nehru Technological University, Anantapur, Anthapuramu, A.P, India, for providing research facilities to carry out my present work.

REFERENCES

- [1] Chandrasekhar L.P. and Mishra R.K., J. Indian Chem., Soc., LXIII, 1986 .920.
- [2] Alkan M., Kharun M. and Chmielecnclo F., Talanta, 59, 2003,605.
- [3] Filik H., Tutem E. and Apak R., Anal. Chim. Acta, 505, 2004, 77.
- [4] Hoshi S., Konuma K., Sugawara K., Uto M. and Akatsuka, K., Talanta, 44, 1997,1473.
- [5] Baranowska I. and Baraszczewska K., Talanta, 39, 1992, 1205.
- [6] Tarek M., Zaki M., Abdel-Kadar A.K. and Abdella M.M., Talanta, 37, 1990,1091.
- [7] Sato S., Iwamoto M. and Uchikawa S., Talanta, 34, 1987,419.
- [8] Thimmaiah K.N., Llyod W.D. and Chandrappa G.T., Microchem. J., 32, 1985, 281.
- [9] Bermejo-Barera, P., Vazquez-Gonazlez, J., Pazos-Naveria, M.C., and Bermejo-Martinez, F., Analyst, 112, 1987,477.
- [10] Kania, K. and Buhl, F., Chem. Anal. (Warsaw), 38, 1993,613.
- [11] Agarwal, Y.K. and Paghavan, T.N.V., Indian J. Technol., 20, 1982 ,498.
- [12] Peshkova, V.M., Ivanova, E.K. and Memon, S.D., Anal. Khim., 35, 1980,486. Chem. Abstr., 93, 1980,604.
- [13] Lahiri, S. and Ghosh, M., Indian J. Chem., 30(A), 1991,989.
- [14] Junwei, Di, and Yifeng Tu, Talanta, 55, 2001,783.

- [15] Dimitrov, Atanas, N., Lekovg, Vania, D., Gavazov, Kiril, B., Boyanov, Boyan, S., Central European J. Chem., 3, 2005,747.
- [16] Li Zaijun, A., Yang, Yulingb, Tang Jiana and Pan Jiaomaic, Journal of Food Composition and Analysis, 18, 2005,561.
- [17] Martinez V.J.L., and Fernandez A.A.R., Analyst. 115, 1990,329.
- [18] Venkata Narayana, B., Srinivas, J., and Suryanarayana Rao, V. Res. J. Chem. Environ. 10 (3), 2006,67.
- [19] Yoshiaki Sasaki, Shoji Tagashira, Yoshiko Murakami and Masafumi Ichikawa, Anal Sci., 14, 1998,603.
- [20] Thanikachalam V., Subramani P., Jayabharathi J., Manivarman S., and Sureshkumar G., Asian J. Chem., 16 (2), 2004,675.
- [21] Ahmed, M.J., Haque. M.E., Anal. Sci., 18 (4), 2002,433.
- [22] Malik A.K., Sharma V., Nijhawan M., and Rao A.L., Ann.Chim., 92 (1-2), 2002,115.