

# Analytical Chemistry of Tungsten: Method of Trace Determination of Tungsten (VI) Using 6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4H-1-benzopyran as an Analytical Reagent

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**Abstract:** A binary complex of tungsten (VI) with 6-chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (CHMTB) is produced from hydrochloric acid medium and studied spectrophotometrically. The 1:3 (M: L) complex is quantitatively extracted into dichloromethane and absorbs light intensity in the range 410-418 nm. Beer's law as shown by the calibration curve holds good in the W(VI) concentration range of 0-1.6  $\mu\text{g ml}^{-1}$  in the measured solution ( $r = 0.9998$ ). The molar annihilation coefficient and Sandell's sensitivity are calculated to be  $9.93 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.00185 \mu\text{g cm}^{-2}$ , respectively at 415 nm. The proposed method offers advantage of a quick, cheap, reproducible, sensitive and selective technique and has been successfully used in the determination of tungsten in spiked samples like flue dust and water with satisfactory results.

**Keywords:** 6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4H-1-benzopyran, Determination, Extraction, Spectrophotometry, Tungsten

## INTRODUCTION

Although some spectrophotometric methods for trace determination of W(VI) using 4H-1-benzopyran derivatives have been explored in the past, sensitivity of the methods are poor and establishment of a new determination system is still required to widen the scope of applicability. In continuation with the previous studies, in the present correspondance, the complexation propensity of another benzopyran derivative has been investigated and reached out over to the assurance of W(VI) utilizing one of the subsidiaries as 6-chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (CHMTB;  $\text{C}_{17}\text{H}_9\text{O}_3\text{SCl}$ ; Fig. 1). The proposed investigation is found to be much more fruitful enhancing sensitivity of the binary complex thus formed to a much larger value as compared to the existing similar methods carried out in the same lab and updated in the review article [1].

## EXPERIMENTAL

### Reagents and Solutions

#### 1) W(VI) Solutions

The standard stock solutions of W(VI) containing  $1 \text{ mg ml}^{-1}$  of metal ion was prepared by dissolving the precisely gauged accessible salt, the sodium tungstate,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (CDH, 'AR') in doubly deionized water and standardized as per the reported method [2]. At the  $\mu\text{g ml}^{-1}$  level, lower concentrations were prepared by appropriate dilutions.

The other metal ions were brought into solutions at  $\text{mg ml}^{-1}$  level by dissolving their commonly available sodium or potassium salts in doubly distilled water or mineral acids. Dilution was done as per the requirements.

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## 2) CHMTB Solution

6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4H-1-benzopyran(CHMTB); molar mass = 292.5 g mol<sup>-1</sup>, melting point = 207°C was synthesized by the prior reported method [3] and a 0.1% (m/v) solution was set up by dissolving a measured sample in acetone.

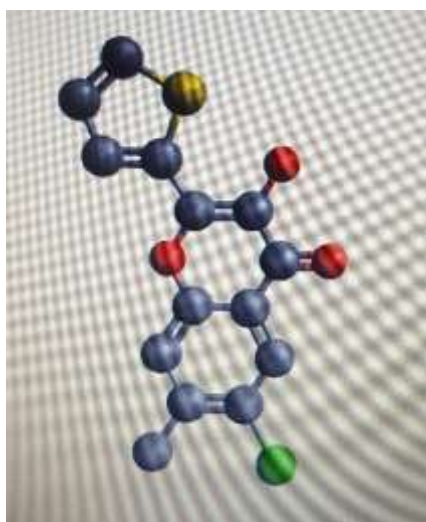


Fig. 1: 6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)- 4-oxo-4H-1-benzopyran (CHMTB).

## 3) HCl Solution

Concentrated hydrochloric acid (CDH 'AR'; 11.3 M) was diluted to produce a 2 M working HCl solution. Dichloromethane (CDH 'AR') was utilized as extractant.

### Equipment

An Electronics India - 2375 UV-VIS spectrophotometer with 10 mm coordinated quartz cells was utilized for absorbance estimations and spectral investigations.

### Samples

#### 1) Synthetic Samples

Synthetic samples (some of them comparable to the technical samples like minargent, platinoid, tungsten alloy, heat resistant steel, high speed steel and stellite) were set up by blending solutions of W(VI) with the solutions of other metal ions in reasonable extents as mentioned in (Table 1).

#### 2) Spiked Samples

Technical spiked samples including reverberatory flue dust and water (from different sources) were brought into arrangements according to the existing system [4]. 1 and 0.5 ml portions were examined for tungsten determination by the proposed method as given in (Table 1).

### Spectrophotometric Determination

0.5 ml of 2 M HCl and 1.0 ml of 0.1% (m/v) CHMTB solution alongwith the sample solution containing  $\leq 16 \mu\text{g}$  of W(VI) and appropriate amount of doubly deionized water were brought together into solution in a 125 ml separatory funnel to make-up the volume of aqueous phase 10 ml. The mixed aqueous volume was equilibrated once for 30 s. by extracting out with 10 ml of dichloromethane. After clear phase partition, the light yellow coloured organic phase containing complex was filtered through a Whatman filter paper (No. 41, 9 cm diameter, preprocessed with the solvent) to annihilate any traces of water left in the extract. At 415 nm, the analytical signals for absorbance of the light yellow complex were observed against likewise treated reagentblank and from the standard curve thus obtained, concentration of the metal ion can be interpolated under identical conditions.

However, for the samples containing Ce(IV), Cr(VI), Mo(VI), Fe(III) and V(V) change in the methodology is required to maintain a strategic distance from co-extraction of these metals. In their respective specimens, masking or complexing agents were added to avoid the obstruction caused by the mentioned elements. For each of 0.4 mg Ce(IV), 5 mg of fluoride; for 0.1 mg Cr(VI), 0.1 mg of Fe(III) and 0.01 mg of Mo(VI), 20 mg of ascorbic acid and for 0.1 mg of V(V), 10 mg disodium 'EDTA' were added preceding use of the ideal conditions intended for formation of the complex.

Table 1: Analysis of synthetic and technical samples by the proposed method

S. No.	Composition of sample		W(VI) found ( $\mu\text{g}$ )**
	Matrix*	W(VI) added ( $\mu\text{g}$ )	
1	Cu(0.1), Ni(0.1), Pb(0.06) <sup>a</sup>	10	9.92
2	Cu(0.8), Ni(0.16), Zn(0.32) <sup>a</sup>	12	12.31
3	Cu(0.15), Zn(0.075), Al(1.2) <sup>a</sup>	15	15.03
4	Fe(0.06), Cr(0.01), Co(0.01), Mn(0.01), Ni(0.01) <sup>a,b</sup>	10	9.92
5	Fe(0.05), Cr(0.003), V(0.001) <sup>a,b,c</sup>	8	7.90
6	Co(0.06), Cr(0.06), Fe(0.03) <sup>a,b</sup>	10	9.88
7	Mg(2), Ba(4), Sn(0.01)	6	6.02
8	Co(3), Hg(2), Ba(4)	5	5.20
9	Zr(0.1), Au(0.01), Ir(0.01)	10	9.94
10	Cu(2), Ni(4), Ba(2)	14	14.07
11	Co(2), Cr(0.05), Fe(0.03) <sup>b</sup>	5	5.37
12	Co(3), Mg(3), Mn(5)	12	12.05
13	Ce(0.05), Zn(5), Pb(3) <sup>d</sup>	15	14.94
14	Water samples : Tap	5	4.97
	Well	5	5.19
15	Reverberatory flue dust	10	10.19
		5	5.13

\*figure in bracket indicates the amount of metal ion in mg/10 ml.

\*\*Average of duplicate analyses.

<sup>a</sup>Composition analogous to minargent, platinoid, tungsten alloy, heat resistant steel, high speed steel and stellite, respectively.

<sup>b</sup>In the presence of 20 mg ascorbic acid, <sup>c</sup>In the presence of 10 mg disodium 'EDTA',

<sup>d</sup>In the presence of 10 mg sodium fluoride.

## RESULTS AND DISCUSSION

Like other benzopyran derivatives, CHMTB strongly reacts with W(VI) to produce an extractable stable (> 2 h) yellow coloured system under acidic conditions that appears to be the most sensitive ( $\epsilon = 9.93 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) visible range spectrophotometric method proposed so far for the binary systems of W(VI) (Fig. 2). The effect of different acids on the colour intensity of W(VI) complex is studied at 0.1 M acidity and is found that absorbance decreases in the order;  $\text{HClO}_4 > \text{HCl} > \text{H}_2\text{SO}_4 > \text{CH}_3\text{COOH} > \text{H}_3\text{PO}_4$ . Though absorbance is maximum using  $\text{HClO}_4$ , the colour of complex is not stable at all in it. Therefore, HCl is chosen for further studies giving a constant absorbance for more than 2 h.

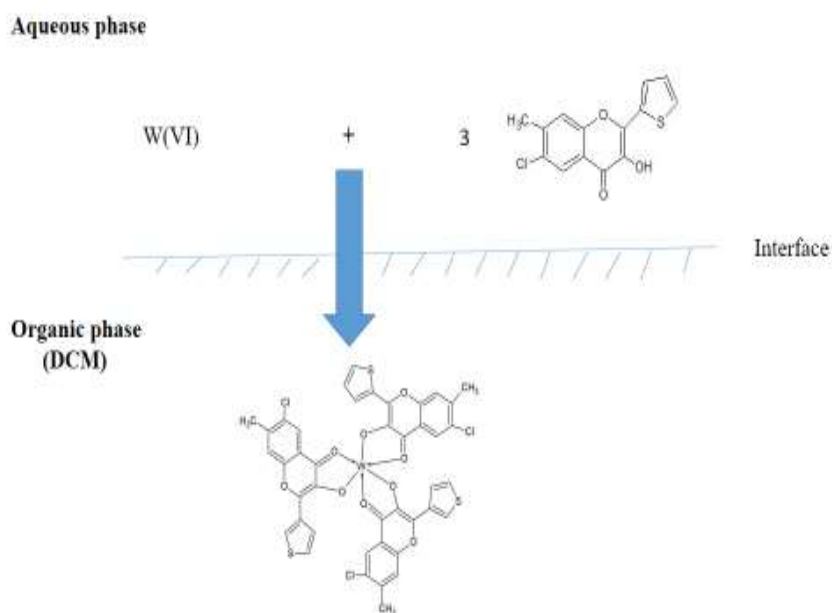


Fig. 2: Extraction system for W(VI)-CHMTB complex.

### 1) Choice of Extractant

Different non-aqueous organic solvents have been utilized to assess the extraction behaviour of the coloured complex (Bar chart 1) but dichloromethane has been found to be the most effective to assure maximum extraction, sensitivity and stability. Consequently, dichloromethane exhibiting greatest and considerable optical density have been picked up as the most reasonable extractant for the spectrophotometric determination of W(VI)-CHMTB complex. A solitary equilibration of the aqueous phase with equivalent volume (10 ml) of the solvent under optimum conditions give quantitative (100 %) recovery of the complexes. The other experimental conditions being kept up while studying different physical specifications in a steady progression are as appeared in Table 2.

Table 2: Effect of physical parameters on the absorbance of W(VI) – 6 chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4H-1-benzopyran complex

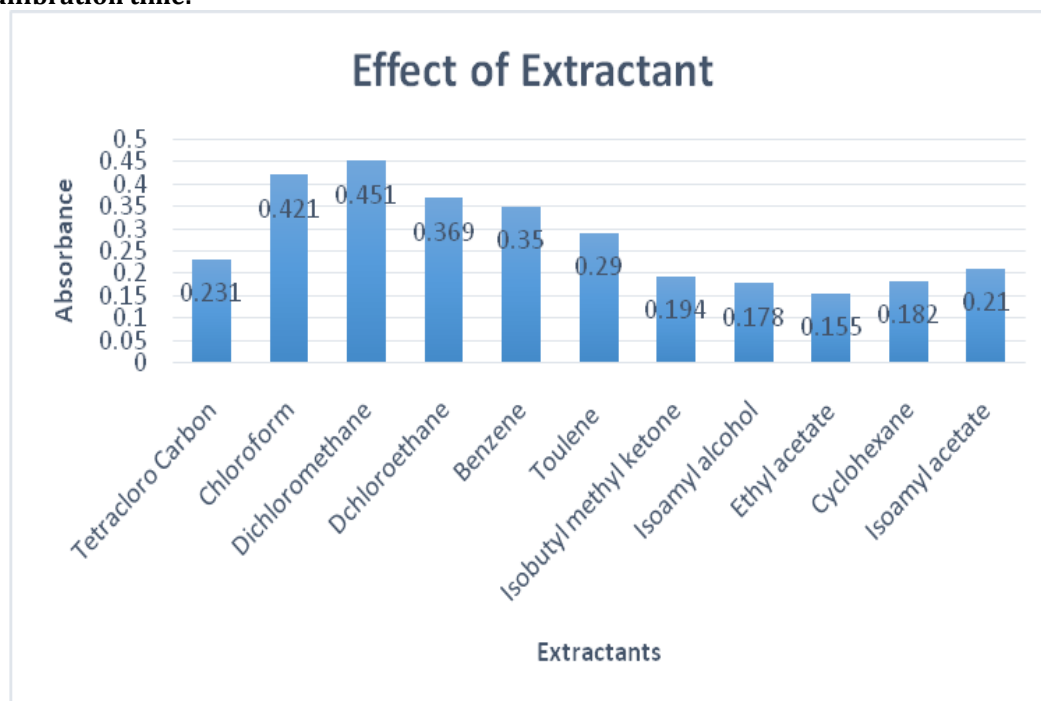
<b>HCl(M)<sup>a</sup></b>	0.02	0.04	0.06-0.18	0.2	0.24	0.30		
<b>Absorbance</b>	0.370	0.400	0.440	0.420	0.405	0.360		
<b>CHMTB (ml)<sup>b</sup></b>	0.1	0.3	0.4	0.5	0.7	0.8-1.4	1.5	2.0
<b>Absorbance</b>	0.135	0.240	0.380	0.440	0.480	0.540	0.520	0.470
<b>Equilibration time(s)<sup>c</sup></b>	0	2	10-120					
<b>Absorbance</b>	0.280	0.485	0.540					

Conditions :<sup>a</sup>W(VI) = 10 µg; HCl = variable; CHMTB [ 0.1% (m/v) in acetone ] = 0.5 ml ; aqueous volume= solvent volume = 10 ml; solvent = Dichloromethane ; equilibration time = 30 seconds;  $\lambda_{\max}$  = 415 nm

<sup>b</sup>HCl = 0.1M; remaining parameters same as in (a) except for the variation in CHMTB

concentration;CHMTB=6-Chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4H-1-benzopyran

<sup>c</sup>CHMTB [0.1% (m/v) in acetone] = 1.0 ml; remaining conditions same as in (b) excepting variation in equilibration time.



Bar Chart 1: Effect of Extractants on the absorbance of W(VI)-CHMTB complex

### 2) Effect of Foreign ions

Under the ideal states of the proposed strategy, 16 µg concentration of W(VI) in a complete 10 ml aqueous volume all through is taken and impact of different anions or complexing agents and the cations on the extraction and assurance of W(VI) have been explored to assess selectivity of the proposed method and set up together in Tables 3 and 4. The tolerance limit was adjusted as the amount of diverse ion causing an error < 1% in the extraction recovery of W(VI).The impact of different anions and cations is studied by carrying out determination of W(VI) in presence of anion and cation in aqueous phase where addition of anion and cation is done before including the reagent solution. Citrate and oxalate interfere with the determination of W (VI) reducing absorbance value to a much lower extent than the normal.

Table 3: Effect of anions / complexing agents on the absorbance of W(VI)-CHMTB complex

S.No	Anion or complexing agent	W(VI)-CHMTB complex	
		Tolerance limit (mg/10ml)	Absorbance
1	None	-	0.540
2	Thiourea	100	0.540
3	Sulphate, Carbonate	80	0.540
4	Hydrazine sulphate, Chloride, Acetate	50	0.540
5	Nitrate	50	0.540
6	Sulphite	40	0.540
7	Bromide	20	0.540
8	Ascorbic acid	20	0.540
9	Phosphate	10	0.540
10	Disodium 'EDTA', Nitrite, Thiocyanate	10	0.540
11	Fluoride	5	0.540
12	Sodium dithionite	0.5	0.540
13	Tartrate	0.5	0.540
14	H <sub>2</sub> O <sub>2</sub> (30 %)*	0.1	0.540

\*Amount added in ml.

Table 4: Effect of cations on the absorbance of W(VI)-CHMTB complex

S.No	Cation	W(VI)-CHMTB complex	
		Tolerance limit (mg/10ml)	Absorbance
1	None	-	0.540
2	Co(II), Hg(II), Ba(II), Ca(II), Al(III)	10	0.540
3	Mg(II)	10	0.540
4	Sr(II)	10	0.540
5	Zn(II)	10	0.540
6	Cu(II)	10	0.540
7	Ni(II), Mn(II), Pb(II),	8	0.540
8	Ru(III), Zr(IV)	1	0.540
9	Th(IV)	1	0.540
10	Ag(I)	1	0.540
11	Pd(II)	1	0.540
12	Au(III), Os(VIII)	0.5	0.540
13	Se(IV)	0.5	0.540
14	Pt(IV)	0.5	0.540
15	Ir(III)	0.5	0.540
16	Ce(IV)	0.4	0.540 <sup>a</sup>
17	Cr(VI)	0.1	0.540 <sup>b</sup>
18	Fe(III)	0.1	0.540 <sup>b</sup>
19	V(V)	0.1	0.540 <sup>c</sup>
20	Sn(II)	0.01	0.540
21	Mo(VI)	0.01	0.540 <sup>b</sup>

<sup>a</sup>In the presence of 5 mg fluoride; <sup>b</sup>In the presence of 20 mg ascorbic acid ; <sup>c</sup>In the presence of 10 mg EDTA

### 3) Photometric Parameters and Correlation Data

The absorption spectra of W(VI)-CHMTB complex in the visible region of electromagnetic spectrum is shown in figure 3. The spectrum of W(VI)-CHMTB complex in dichloromethane against reagent blank shows a broad maximum in the range 414-422 nm ( Fig. 3, Curve A). The spectrum of reagent blank prepared in an analogous manner against pure solvent indicates that the reagent also absorbs negligibly at this wavelength ( Fig. 3, Curve B). The concentration range obeyed as determined by Beer's law is 0.0-1.6  $\mu\text{g W(VI) ml}^{-1}$  and the optimum concentration range with minimum photometric analysis error as evaluated from Ringbom plot [5] is 0.38-1.46  $\mu\text{g ml}^{-1}$ . Molar absorptivity and Sandell's sensitivity of the complex are calculated to be  $9.93 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.00185 \mu\text{g cm}^{-2}$ , respectively at 415 nm. Using statistical methods, the values for other optical and statistical parameters are evaluated and summarized

in Table 5. The data indicated that the proposed method is highly sensitive, reproducible and can affectively analyze tungsten at trace levels.

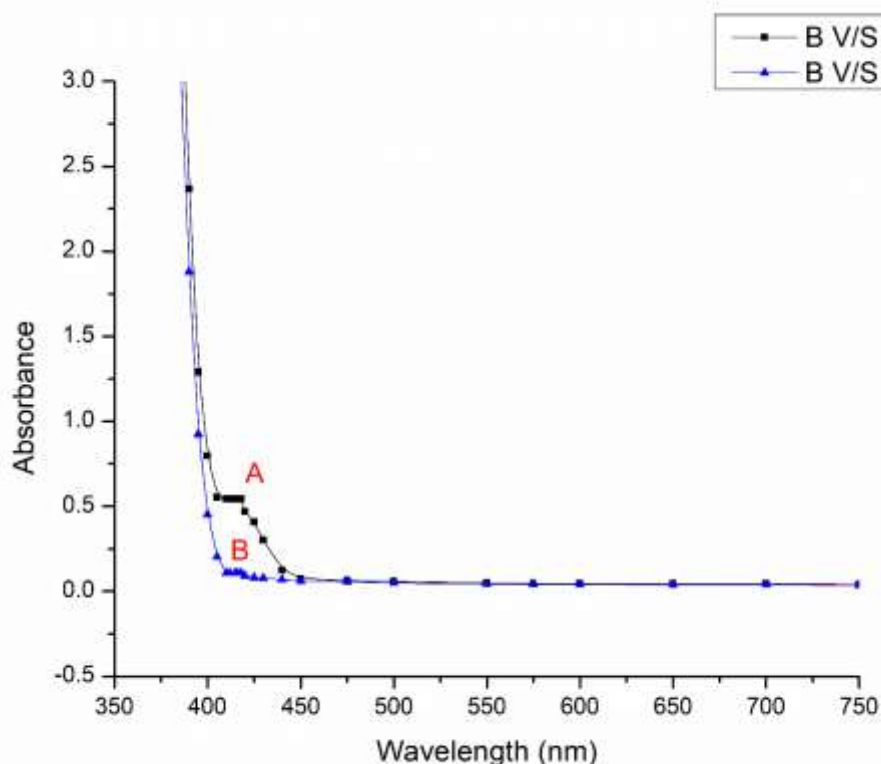


Fig. 3: Absorption spectra of W(VI)-CHMTB complex

#### 4) Geometry of W(VI)-CHMTB Complex

Job's continuous variations method [6] as modified by Vosburgh and Cooper [7], mole ratio [8] and equilibrium shift [9] methods are employed for the M:L stoichiometric ratio determination of W(VI)-CHMTB complex. The maximum absorbance as observed by the continuous variations method of the complex was at the mole fraction of 0.27 of W(VI) corresponding to a 1:3 ratio of W(VI)-CHMTB.

Table 5: Photometric characteristics, precision and accuracy data

S. No.	Parameter	Value W(VI)-CHMTB
1	$\lambda_{max}$ (nm)	410 - 418
2	Beer's law limits ( $\mu\text{g ml}^{-1}$ )	0 - 1.6
3	Optimum range of determination ( $\mu\text{g ml}^{-1}$ )	0.32- 1.46
4	Molar absorptivity ( $\text{l mol}^{-1} \text{cm}^{-1}$ )	$9.93 \times 10^4$
5	Sandell's sensitivity ( $\mu\text{g cm}^{-2}$ )	0.00185
6	Correlation coefficient (r)	0.9998
7	Regression equation (Y) *	$Y = 0.533 X + 0.006$
8	Slope (b)	0.533
9	Intercept (a)	0.006
10	Standard deviation	$\pm 0.0025$
11	Relative standard deviation (%)	0.46
12	Limit of detection ( $\mu\text{g ml}^{-1}$ )	0.038
13	Stability constant	$3.572 \times 10^{-11}$

Validity of the result is supported by the mole ratio and equilibrium shift methods where the slope of 2.6 by the equilibrium shift method ( Fig. 4) confirmed 1:3 ratio of the formed complex.

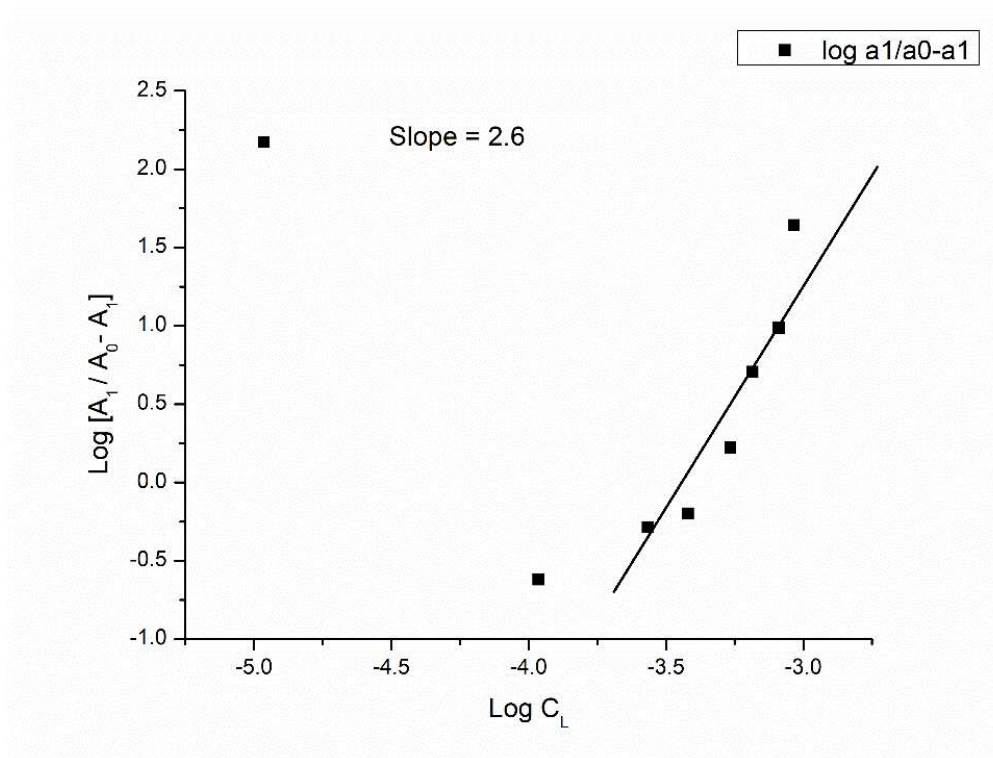


Fig. 4: Equilibrium shift method

Hence, from the stoichiometric evaluation, the following structure is proposed for the complex:

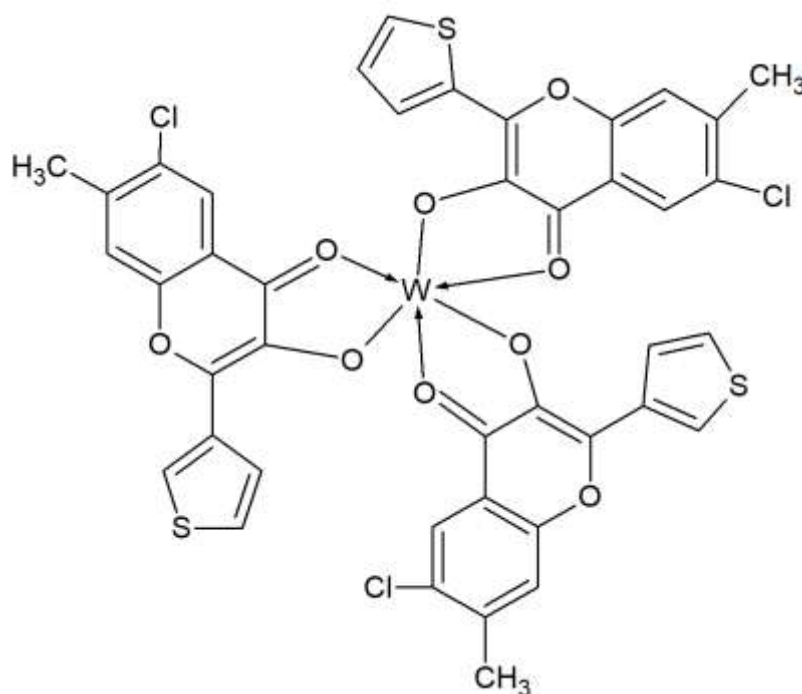


Fig. 5: W(VI)-CHMTB complex

### 5) Structural Elucidation

Useful resource of Avogadro 1.01 program [10] is applied for structural modelling and optimization of W(VI)-CHMTB complex. The energy of optimized complex after carrying out 500 cycles of optimization is observed to be  $4363.28 \text{ K J mol}^{-1}$ , however that of the unoptimized complex was  $4363.90 \text{ K J mol}^{-1}$ . The shape of the optimized complex is octahedral. The optimized metal - oxygen bond length is between  $2.055 \text{ \AA}$  -  $2.084 \text{ \AA}$  whereas the ideal bond length was  $1.347 \text{ \AA}$ . Various optimized properties of the complex are calculated and shown in Table 6. Hence, the optimized octahedral structure of the complex is shown as:

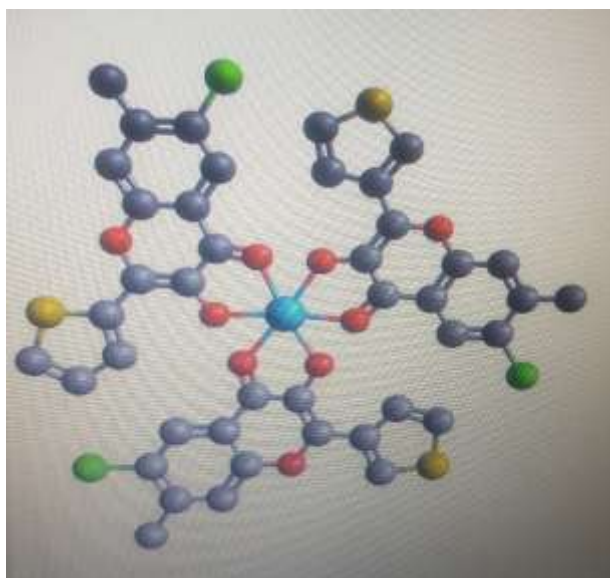


Fig. 6: Optimized structure of W(VI)-CHMTB complex

Table 6: Computational Parameters of W(VI)-CHMTB complex

S. No.	Atom Type	Bond length (Å <sup>o</sup> )	Atom type	Bond angle (°)
1	W-O(1)	2.057	O(1)-W-O(2)	66.8
2	W-O(2)	2.081	O(2)-W-O(3)	53.0
3	W-O(3)	2.055	O(3)-W-O(4)	66.8
4	W-O(4)	2.083	O(4)-W-O(5)	53.3
5	W-O(5)	2.055	O(5)-W-O(6)	66.8
6	W-O(6)	2.082	O(6)-W-O(1)	53.4

### APPLICATIONS

The W(VI)-HCl-CHMTB-H<sub>2</sub>O-DCM system for the determination of traces of tungsten is rapid, sensitive and selective and is applied satisfactorily for the determination of W(VI) in different spiked samples like water and flue dust. The proposed system produces satisfactory and reliable results (Table 1) and could compete successfully with the existing methods for determination of tungsten in terms of sensitivity which is observed to be exceptionally high for the proposed binary liquid-liquid extraction system (Table 7).

### CONCLUSION

A new binary W(VI)-CHMTB complex system was studied after its extraction into dichloromethane from HCl medium containing up to 16 µg W(VI) and CHMTB (acetic solution) in 10 ml water phase. The method finds highly accurate and precise (RSD= 0.46% ) application for trace determination of the metal from several synthetic and natural samples including flue dust, tap water and well water.

Table 7: Comparison of analytical characteristics of the proposed method with other methods

S.No.	Aqueous conditions	$\lambda_{\text{max}}$ (nm), Solvent	Molar absorptivity (l mol <sup>-1</sup> cm <sup>-1</sup> )	Reference
1	W(VI), 3-hydroxy-2-(2'-furyl)-4-oxo-4H-1-benzopyran, 0.06-1 M HCl	410, dichloromethane	4.88 × 10 <sup>4</sup>	[11]
2	W(VI), 3-hydroxy-2-(3'-methyl-2'-thienyl)-4-oxo-4H-1-benzopyran, 2 M HClO <sub>4</sub>	420, dichloromethane	5.80 × 10 <sup>4</sup>	[12]
3	W(VI), 6-chloro-3-hydroxy-2-[2'-(5'-methylfuryl)]-4H-chromen-4-one, 0.18-0.32 M HClO <sub>4</sub>	435, Chloroform	2.16 × 10 <sup>4</sup>	[13]
4	W(VI), 3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran, HCl medium	415, dichloromethane	6.45 × 10 <sup>4</sup>	[14]
5	W(VI), 6-chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4H-1-benzopyran, 0.2 M HCl	420, dichloromethane	2.2 × 10 <sup>4</sup>	[15]
6	W(VI), 6-chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran, 0.16-0.32 M HCl	420, chloroform	4.05 × 10 <sup>4</sup>	[16]
7	W(VI), 6-chloro-3-hydroxy-2-phenyl-4-oxo-4H-1-benzopyran, 0.04-0.32 M HCl	420, Chloroform	3.125 × 10 <sup>4</sup>	[17]
8	W(VI), 6-chloro-3-hydroxy-7-methyl-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (CHMTB), 0.06-0.18 M HCl	415, dichloromethane	9.93 × 10 <sup>4</sup>	Proposed method



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