



Extraction, Spectrophotometric Determination of Tungsten(VI) with 3-Hydroxy-2-[1'-phenyl-3'-(*p*-methylphenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran as Chelating Agent and its *in situ* Computational Studies

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A simple, fast, selective and sensitive method is developed for the microdetermination of tungsten(VI) with 3-hydroxy-2-[1'-phenyl-3'-(*p*-methylphenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPPB). The reagent forms a 1:4 (M:L) yellow complex in HCl medium which is extractable into chloroform and exhibits maximum absorbance at 415-430 nm. The Beer's law holds good in tungsten(VI) concentration range of 0.0-2.0 $\mu\text{g mL}^{-1}$ with molar extinction coefficient and Sandell's sensitivity of $9.936 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.0019 \mu\text{g W cm}^{-2}$, respectively at 420 nm. The proposed method is free from the interference of a large number of analytically important elements and shown to give satisfactory results in the analysis of various synthetic and industrial samples of varying composition.

Keywords: Tungsten, Extraction, Spectrophotometry, Benzopyran.

INTRODUCTION

Tungsten and its alloys find numerous applications in various fields including incandescent light bulb filaments, X ray tubes, electrodes in welding and radiation shielding, in penetrating projectiles and also as an industrial catalysts [1]. Tungsten is the only element known to occur in biomolecules in a few species of bacteria and archaea. The element is the heaviest known essential metal to the living organisms [2] and the element interferes with Mo and Cu metabolism and is somewhat toxic to animal life [3,4].

Tungsten is determined in environmental samples by using a number of techniques such as AAS [5], NAA [5], ICP-AES [6], etc. The methods though sensitive are found to be disadvantageous in respect of cost, instrumentation, lack of selectivity and above all lacking of simplicity. Keeping in mind the drawbacks associated with the above mentioned methods, spectrophotometric determination of tungsten is found to be highly fruitful in the past [7-12]. Several organic reagents have been employed for spectrophotometric determination of the elements but suffering from time consumption, less sensitive, less selective and less stable in nature. Therefore, in order to overcome the mentioned problems associated with the earlier methods, in

the proposed investigation, it is observed that a newly synthesized organic reagent, 3-hydroxy-2-[1'-phenyl-3'-(*p*-methylphenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPPB), possesses a better complexing and chelating ability with respect to W(VI).

EXPERIMENTAL

A UV-VIS spectrophotometer (2375; Electronics, India) with 10 mm matched quartz cells is used for absorbance measurements and spectral studies.

Stock and working solutions of W(VI) and other metal ions are prepared as reported earlier [13]. 3-Hydroxy-2-[1'-phenyl-3'-(*p*-methylphenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPPB, m.p. 221-224 °C, m.f. $\text{C}_{25}\text{H}_{18}\text{N}_2\text{O}_3$) is synthesized by the literature method [14,15] and dissolved in acetone to produce 0.2 % (w/v) solution.

A 2 M hydrochloric acid (AR, CDH, India) is prepared by diluting 11.3 M acid with deionized water. Chloroform (AR, CDH, India) is distilled and the fraction distilling at 60-61 °C is used for extraction.

Synthetic samples: Synthetic samples (some of them analogous to technical samples such as minargent, platinumid,

W-alloy, heat resistant steel and high speed steel) are prepared by mixing solutions of W(VI) with the solutions of other metal ions in suitable proportions to give the composition as shown in Table-1.

TABLE-1
ANALYSIS OF VARIOUS SAMPLES BY
THE PROPOSED METHOD

Composition of sample*	W added (µg)	W found (µg)**
Cu(0.5), Zn(0.2), Ni(0.1) ^a	10	9.91
Cu(0.1), Zn(0.05), Al(0.8) ^a	10	10.00
Fe(0.03), Cr(0.005), Co(0.005), Mn(0.005), Ni(0.005) ^a	4	3.94
Cu(0.1), Ni(0.1), Pb(0.01) ^a	10	10.37
Fe(0.08), Cr(0.003), V(0.002) ^{a,b}	15	14.44
Se(2), Ba(5), Co(2)	5	4.94
Mo(0.01), Fe(0.1), Ba(1) ^c	5	5.27
Ce(0.1), Cr(0.1), Mg(1) ^{d,e}	10	10.09
Reverberatory flue dust (100)	10	10.00
	5	4.94
Tap water sample	10	10.06

*Figure in parentheses indicates the amount of metal ion in mg.

**Average of triplicate analysis.

^aSample number 1-5 analogous to minargent, platinumoid, W- alloy, heat resistant steel and high speed steel

^bIn the presence of 20 mg ascorbic acid.

^cIn the presence of 20 mg sodium dithionite.

^dIn the presence of 30 mg ascorbic acid.

^eIn the presence of 40 mg ascorbic acid.

Technical samples: Technical samples including reverberatory flue dust and tap water from different sources are brought into solution as per the reported procedure [13]. In suitable aliquots, tungsten is then analyzed by the proposed method.

Extraction and spectrophotometric determination: An aliquot of sample solution containing upto 20 µg of tungsten(VI) is placed in a 125 mL separating funnel and to the solution is added 0.5 mL of 2 M HCl followed by 1.2 mL of 0.2 % (w/v) acetic solution of reagent. The whole mixture thus obtained is diluted to 10 mL with deionized water so as to bring the final acidity of aqueous phase to 0.1 M. The contents are mixed gently and equilibrated once with an equal volume (10 mL) of chloroform for 30 s. After separation, organic phase is filtered into a 10 mL standard volumetric flask through a dry Whatman filter paper (No. 41, 9 cm diameter) and diluted to the mark. Absorbance of yellow extracted solution is measured against a similarly prepared reagent blank at 420 nm in a pair of 10 mm cuvettes.

The samples containing other metal ions involved appropriate additions of masking or complexing agents before addition

of HPMPPB as modified procedure as: 1 mg of V(V) in presence of 20 mg ascorbic acid, 0.3 mg of Ce(IV) with 30 mg of ascorbic acid, 0.1 mg Cr(VI) with 40 mg ascorbic acid and 0.1 mg of Mo(VI) is masked with 20 mg of sodium dithionite.

RESULTS AND DISCUSSION

Similar to various flavonol derivatives, 3-hydroxy-2-[1'-phenyl-3'-(*p*-methyl-phenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPPB) also reacts strongly with W(VI) in HCl medium to produce a yellow coloured stable complex which is quantitatively extracted into chloroform. The colour of complex is comparatively less intense in other acids such as perchloric acid, sulphuric acid, acetic acid and phosphoric acid with a lower value of absorbance in the same order. Therefore, HCl showing a maximum and constant absorbance is selected for further studies.

In order to provide optimum values of other parameters found for achieving maximum and constant absorbance of the complex containing 10 µg tungsten per 10 mL aqueous solution, 0.04 - 0.16 M HCl and 1.0-1.4 mL of 0.2 % HPMPPB solution in acetone are added in the same order (Table-2). The mixture is extracted with 10 mL of chloroform once over a period of 10-120 s. The extraction behaviour of W(VI)-HPMPPB complex is studied into various water immiscible organic solvents where absorbance of complex decreases in the order: chloroform > carbon tetrachloride > dichloromethane > benzene > 1,2-dichloroethane > toluene > isobutyl methyl ketone > amyl acetate > cyclohexane. The absorbance is found to remain unchanged for more than 1 h in chloroform and hence, chloroform is preferred as an extractant for the metal complex. The coloured complex formed at 0.1 M HCl concentration is completely transferred into the organic chloroform layer in one extraction step.

Effect of foreign ions: The effect of various diverse ions on the determination of W(VI)-HPMPPB complex is studied to estimate the tolerance levels of these diverse ions as described in Tables 3 and 4. Large number of commonly associated anions/complexing agents and cations do not interfere in the determination. The tolerance limit of a foreign ion is taken in the quantities as maximum amounts causing an error in the absorbance value by ± 1 %.

Optical characteristics, precision and accuracy: Absorption spectrum of yellow W(VI)-HPMPPB complex in chloroform indicates that the maximum lies in the range 415-430 nm where the reagent blank absorbs negligibly. The correlation between the measured sample absorption and concentration

TABLE-2
EFFECT OF PHYSICAL PARAMETERS ON THE ABSORBANCE OF W(VI)-HPMPPB COMPLEX

HCl (M) ^a	0.01	0.02	0.03	0.04-0.16	0.18	0.20	0.24	0.28	
Absorbance	0.280	0.400	0.430	0.478	0.460	0.411	0.350	0.320	
HPMPPB (mL) ^b	0.1	0.2	0.3	0.5	0.8	0.9	1.0-1.4	1.5	1.6
Absorbance	0.103	0.231	0.296	0.478	0.500	0.520	0.540	0.519	0.410
Equilibration time (S) ^c	0	2	5	10-120					
Absorbance	0.050	0.150	0.530	0.540					

Conditions: ^aW(VI) = 10 µg; HPMPPB [0.1 % (W/V) in acetone] = 1 mL; aqueous volume = solvent volume = 10 mL; solvent = chloroform; equilibration time = 30 s; λ_{max} = 420 nm; ^bHCl = 0.1 M; other conditions are the same as in (a) excepting variation in HPMPPB concentration; HPMPPB = 3-Hydroxy-2-[1'-phenyl-3'-(*p*-methyl phenyl)-4'-pyrazolyl]-4-oxo-4*H*-1-benzopyran (HPMPPB); ^cHPMPPB [0.2% (W/V) in acetone] = 1.2 mL; other conditions are the same as in (b) excepting variation in equilibration time.

TABLE-3
EFFECT OF ANIONS AND COMPLEXING AGENTS ON
THE ABSORBANCE OF W(VI)-HPMPPB COMPLEX

Anion/Complexing agent added	Amount (mg/10 mL)	Absorbance
None	00	0.540
Chloride, bromide, iodide	100	0.540
Sulphate, bicarbonate, EDTA disodium salt, acetate	90	0.540
Sulphite, thiocyanate, hydrazine sulphate	50	0.540
Ascorbic acid	40	0.540
Sodium citrate	30	0.540
Glycerol*	0.5	0.540
H ₂ O ₂ (6 % w/v)*	0.1	0.540

Conditions: As mentioned in the procedure. *Added in mL

TABLE-4
EFFECT OF CATIONS ON THE
ABSORBANCE OF W(VI)-HPMPPB COMPLEX

Cation added	Amount (mg/10 mL)	Absorbance
None	00	0.540
Ni(II), Cu(II), Zn(II), Sr(II), Al(III)	10	0.540
Bi(III), Ba(II), Ca(II), Mn(II), Mg(II), Pb(II), Hg(II)	8	0.540
Co(II), Cd(II), Be(II), Se(IV)	5	0.540
Ru(III), Fe(III), Os(VIII), V(V) ^a	1	0.540
Ce(IV) ^b	0.3	0.540
Zr(IV)	0.2	0.540
Pd(II), Th(IV), Cr(VI) ^c , Mo(VI) ^d	0.1	0.540

Conditions: As mentioned in the procedure.
^aIn presence of 20 mg ascorbic acid.
^bIn presence of 30 mg ascorbic acid.
^cIn presence of 40 mg ascorbic acid.
^dIn presence of 20 mg sodium dithionite.

of W(VI) is estimated using regression analysis. The calibration graph is found to obey Beer's law in the concentration range 0-2.0 $\mu\text{g W(VI) mL}^{-1}$. However as evaluated from Ringbom plot [16], the optimum range for accurate determination of tungsten is 0.36-1.58 ppm. The other analytical characteristics and statistical parameters are also calculated by applying various statistical methods and shown in Table-5.

Stoichiometry of complex: Stoichiometry of HPMPPB-W(VI) complex is established by Job's method of continuous

TABLE-5
OPTICAL CHARACTERISTICS, PRECISION
AND ACCURACY DATA

Parameter	Value
λ_{max} (nm)	415-430
Beer's law limits ($\mu\text{g mL}^{-1}$)	0-2.0
Molar absorptivity ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	9.936×10^4
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0019
Correlation coefficient (r)	0.9978
Regression equation (Y)*	$Y = 0.509 X + 0.011$
Slope (b)	0.509
Intercept (a)	0.011
Standard deviation	± 0.0016
Limit of detection ($\mu\text{g mL}^{-1}$)	0.140

* $Y = bX + a$; where Y = absorbance and X = Concentration of W(VI) in $\mu\text{g mL}^{-1}$

variations [17] as modified by Vosburgh and Cooper [18] and confirmed by mole ratio method [19].

Job's continuous variations method: Equimolar solutions ($1.63 \times 10^{-3} \text{ M}$) of tungsten and HPMPPB are mixed together so that mole fraction of W(VI) varies from 0 to 1 keeping the concentration of two variables equal at two different wavelengths *i.e.* 400 and 420 nm. Under optimum conditions of the proposed procedure, the organic layer is separated and absorbance is measured against a reagent blank obtained by carrying out extraction under similar conditions. The plot of absorbance against mole fraction indicates 1:4 (M:L) composition of extracted complex.

Mole ratio method: The metal to ligand ratio is further confirmed by mole ratio method where in concentration of tungsten is kept constant ($1.63 \times 10^{-3} \text{ M}$) and that of reagent is varied. The absorbance is measured at two different wavelengths 400 and 420 nm and the variation of absorbance against mole ratio of two components show a clear break at 1:4 metal to HPMPPB ratio. Thus, the probable structure of obtained yellow coloured W(VI)-HPMPPB complex is assigned in Fig. 1.

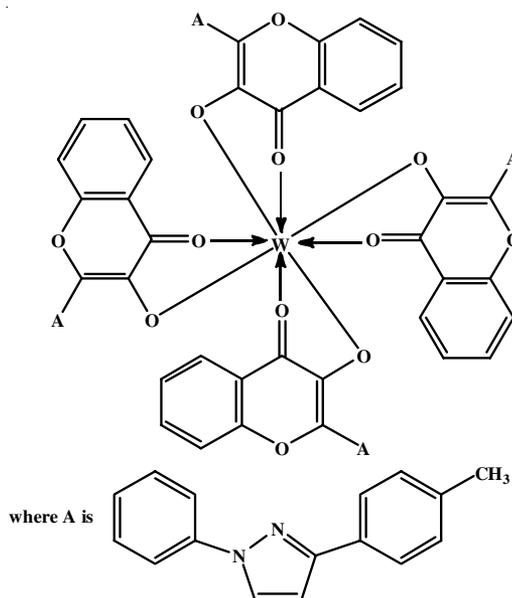


Fig. 1. Probable structure of [W(VI)-HPMPPB complex]

Structural elucidation: The metal complex is modelled with the aid of Avogadro 1.01 program [20]. The complex is optimized using molecular mechanics. Several cycles of optimization are carried out. The energy of unoptimized complex is found to be 6179.6 KJ/mol, which is optimized to 3157.51 KJ/mol after several cycles of optimization. The structure of optimized form is cubic. The optimized metal-oxygen bond length is found to be in the range 2.011-2.089 Å, whereas the ideal bond length was 1.978 Å. Various optimized bond lengths and bond angles are also calculated and shown in Table-6. The optimized structure is shown in Fig. 2.

Analytical applications: The proposed method for micro determination of W(VI) is extremely sensitive ($\epsilon = 9.936 \times 10^4 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), simple, rapid, selective and applicable to various synthetic, natural and industrial tungsten containing materials. Proposed method for determination normally takes 2-3 min for a single operation and gives reproducible and

TABLE-7
COMPARISON OF THE PROPOSED METHOD WITH REPORTED METHOD

Aqueous conditions	Solvent (λ_{\max} , nm)	Sandell's Sensitivity, $\mu\text{g cm}^{-2}$ (Molar absorptivity, $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	Interfering metal ions	Ref.
W(VI), H ₂ SO ₄ , 4-nitro catechol and thiazolyl blue	Chloroform (415)	0.0066 (2.8×10^4)	Al(III), Cr(III,VI), V(IV,V), Mo(VI), Mn(VII)	[7]
W(VI), 0.04-0.32 M HCl, 6-chloro-3-hydroxy-2-phenyl-4-oxo-4H-1-benzopyran in acetone	Chloroform (420)	0.0029 (3.125×10^4)	–	[8]
W(VI), 10 M HCl, SnCl ₂ , NH ₄ SCN, 15 min	Chloroform (404)	0.0200 (1.74×10^4)	–	[9]
Standing time, ethopropazinehydrochloride, W(VI), 2 M HCl, 6-chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran	Chloroform (420)	0.0045 (4.05×10^4)	–	[10]
W(VI), 0.2 M HCl, 3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran	Dichloromethane (415)	0.0029 (6.45×10^4)	–	[11]
W(VI), 0.2 M HCl, 6-chloro-3-hydroxy-2-(2'-furyl)-4-oxo-4H-1-benzopyran	Dichloromethane (420)	0.0083 (2.2×10^4)	–	[12]
W(VI), 0.1 M HCl, 3-hydroxy-2-[1'-phenyl-3'-(p-methylphenyl)-4'-pyrazolyl]-4-oxo-4H-1-benzopyran (HPMPPB)	Chloroform (420)	0.0019 (9.936×10^4)	26 metal ions do not interfere	Proposed method

TABLE-6
COMPUTATIONAL PARAMETERS OF
W(VI)-HPMPPB COMPLEX

Atom type	Bond length (Å)	Atom type	Bond angle (°)
W-O(1)	2.081	O(1)-W-O(2)	80.9
W-O(2)	2.073	O(2)-W-O(3)	65.9
W-O(3)	2.103	O(3)-W-O(4)	76.0
W-O(4)	2.037	O(4)-W-O(5)	137.2
W-O(5)	2.089	O(5)-W-O(6)	75.2
W-O(6)	2.011	O(6)-W-O(7)	137.3
W-O(7)	2.040	O(7)-W-O(8)	76.1
W-O(8)	2.043	O(8)-W-O(1)	71.4

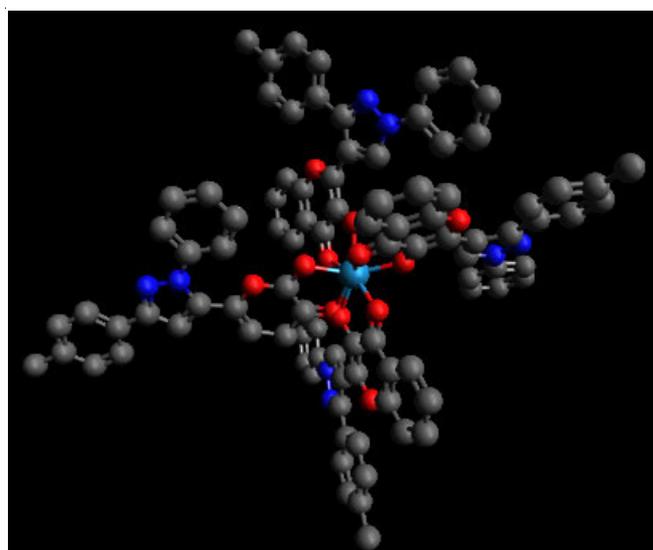


Fig. 2. Optimized structure of W(VI)-HPMPPB complex

satisfactory results with the standard deviation of ± 0.0016 for 10 replicates containing $1 \mu\text{g W(VI) mL}^{-1}$. The proposed method is found to be superior in comparison to various existing methods in respect of rapidity, sensitivity and selectivity (Table-7).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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