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# Spectrophotometric determination of tungsten (VI) after extraction of its 6chloro-3-hydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran complex into chloroform

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## ABSTRACT

6-chloro-3-hydroxy-2-phenyl-4-oxo-4H-1-benzopyran CHPB) has been used for the first time as an analytical reagent for the spectrophotometric determination of tungsten. The yellow colored W (VI) – CHPB complex has  $\lambda_{max}$  at 420 nm, is extractable into chloroform from 0.04 – 0.32 M HCl medium containing 0.6 – 1.6 mL of 0.1% CHPB (in acetone). Tungsten (VI) in presence of several cations, anions and complexing agents forms a yellow 1: 2 complex with CHPB which is stable for about 20 h in organic extract. The molar absorptivity and Sandell's sensitivity of the complex at 420 nm are calculated to be  $3.125 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> and 0.00294 µg W cm<sup>-2</sup>, respectively. Beer's law is obeyed over the concentration range 0 – 2.9 µg W(VI) mL<sup>-1</sup>. However, the optimum range of determination of tungsten from Ringbom's curve at 420 nm is 0.9–3.1 µg mL<sup>-1</sup>. For 2 µg W mL<sup>-1</sup>, the standard deviation is 0.000726 and relative standard deviation of ± 0.21% absorbance unit. The method is simple, selective, rapid and precise and has been applied to the determination of tungsten in synthetic and standard samples.

Keywords: Spectrophotometric method, tungsten, Beer's law

## INTRODUCTION

Spectrophotometric methods [1-5] are among the most precise instrumental methods of analysis for the determination of elements in trace amounts. These methods are remarkable for their versatility, sensitivity and precision. In these methods, a very extensive range of concentrations may be covered for the trace analysis of the elements.

There are various spectrophotometric methods which suffer from low sensitivity, non-selectivity and complexity in the procedures for the determination of tungsten in trace amounts using thiocyanate, vanadophosphoric acid as ligands [6-8]. Many chromone derivatives have been used as analytical reagents for spectrophotometric determination of tungsten but most of these are not suitable for routine analysis of the metal ion due to one or more of the above drawbacks [9-12]. This has appreciated to search for new better methods and accordingly, 6-chloro-3-hydroxy-2-phenyl-4-oxo-4H-1-benzopyran (CHPB) has been used as a complexing agent for tungsten (VI) in the spectrophotometric determination of metal ion to meet the above requirements.

## MATERIALS AND METHODS

#### Apparatus and reagents:

Visible Double Beam spectrophotometer (Cat No. 1203, Make Systronics) with 10 mm matched quartz cells has been used for routine absorbance measurements and spectral studies.

Tungsten Solution: A standard stock solution (100 mL) of tungsten (VI) containing 1 mg mL<sup>-1</sup> of the metal ion is prepared by dissolving an accurately weighed amount (0.179g) of sodium tungstate (A.R) in distilled water. Lower concentrations at  $\mu$ g mL<sup>-1</sup> (10, 20, 50 and 100) level are prepared by suitable dilution there from.

Stock solutions of other metal ions are prepared at mg mL<sup>-1</sup> level by dissolving their commonly available pure grade sodium or potassium salts in deionized water or dilute acid. They are suitably diluted to give  $\mu$ g mL<sup>-1</sup> level concentration of the metal ions. Chloroform is used for extraction of W(VI) - CHPB complex. CHPB is prepared by reported methods [13, 14] as follows.

*Preparation of CHPB*: To a solution of 5-chloro-2-hydroxyacetophenone (3.42, 0.02 mol) and NaOH (1.6 g, 0.04 mol) in ethanol, benzaldehyde (2.12 g, 0.02 mol) is added at 0-5°C. The reaction mixture is stirred for 3 - 4 h at room temperature. The 1-(2'-hydroxy-5'-chlorophenyl)-3-phenylprop-2-en-1-one, thus obtained is neutralized with 0.2 M HCl, washed with water and crystallized from ethanol-water mixture. Solution of the compound 1-(2'-hydroxy-5'-chlorophenyl)-3-phenylprop-2-en-1-one (2 g in 20 mL methanol), NaOH (10 mL of 20% methanol) and H<sub>2</sub>O<sub>2</sub> (10 mL 30%) are mixed, stirred (2h, below 10°C) and neutralized with acetic acid. The yellow compound, so obtained after crystallization from ethanol and water, is CHPB (m.pt. 168-170°C). The molecular formula of CHPB is  $C_{15}H_9O_3Cl$ . 0.1 % w/v solution of reagent (CHPB) is prepared in acetone.



#### Samples:

*i)* Synthetic samples: Synthetic samples (some of them analogous to stellite no. 2, cooperite, Duke's metal, heat resistant steel, complex English metal, minargent, arkit and silchrome wire) are prepared by mixing a tungsten (VI) solution with solutions of other metal ions in suitable proportions as shown in Table-10.

*ii) Reverberatory flue dust*: Reverberatory flue dust sample (0.1g) from the copper manufacturing unit without tungsten is mixed with a solution of known tungsten content (0.015 mg) in a silica crucible and dried in an oven. It is then fused with sodium peroxide. The fused mass is cooled and then treated with 0.1 g sodium potassium tartarate, neutralized with concentrated HCl and adjusted to 1M acidity in a final volume. Tungsten is then analyzed by the proposed method by taking suitable aliquots.

#### **Procedure:**

To the sample solution containing  $\leq 29 \ \mu g$  tungsten (VI) and other ions taken in a 100 mL separatory funnel are added 1mL of 1M hydrochloric acid, 0.1% (w/v) CHPB in acetone (1mL) and sufficient deionized water to make up the volume to 10 mL. It is then equilibrated once with an equal volume (10 mL) of chloroform for 20 s. After phase separation, the organic extract is passed through Whatman no. 41 filter paper pretreated with the solvent to remove water droplets if any. Finally the absorbance of the light yellow extract is measured at 420 nm against a similarly

prepared reagent blank using 10 mm matched quartz cells. Amount of tungsten in the samples is computed from a calibration curve prepared under identical conditions of the procedure.

*Modification when Pt and Mo are present*: To the samples containing above mentioned elements, the optimum amounts of masking agents added before the addition of CHPB are: 50 mg sodium phosphate for Pt (IV) up-to 600  $\mu$ g and 0.05 mL 6 % (w/v) H<sub>2</sub>O<sub>2</sub> for Mo (VI) up-to 200  $\mu$ g are added to the solution before extraction.

## **RESULTS AND DISCUSSION**

Tungsten (VI) reacts with CHPB giving a light yellow color in neutral medium which intensifies in acidic medium. The effect of variables and diverse ions on W (VI) – CHPB absorbance, the spectral characteristics, stoichiometry of the complex and applications of the system are discussed below:

#### Effect of varying experimental conditions

*i)* Choice of the solvent: The complex is quantitatively extracted in a single extraction with equal volume (10 mL) each of chloroform, dichloromethane, carbon tetra chloride, 1, 2-dichloroethane, benzene, isobutyl methyl ketone, toluene, iso amyl alcohol, ethyl acetate, iso amyl acetate and cyclohexane in the decreasing order of absorbance. In each case, the aqueous phase after extraction is free from tungsten. A single extraction with equal volume (10 mL) of chloroform is sufficient to give quantitative extraction. As chloroform gives maximum absorbance with a rapid and clear phase separation, it is chosen as the most suitable extractant. The absorbance of the complex remains practically constant for about 20 h in chloroform at 420 nm.

*ii) Effect of acidity*: The absorbance of the W (VI) - CHPB complex in chloroform is greatly influenced by the nature of acids. The complex gives very low absorbance in the neutral medium. From 1 M acidity fixed in each case, the absorbance is found to decrease in the order:  $HCl > H_2SO_4 > HNO_3 > HClO_4 > CH_3COOH > H_3PO_4$ . Therefore HCl medium is preferred for further studies. The optimum values of acid parameter found for achieving maximum and constant absorbance is: 0.04 - 0.32 M HCl (Fig.1, Curve a) for  $\leq 29 \ \mu g$  W(VI) per 10 ml aqueous volume. Therefore, the aqueous phase is adjusted to be 0.1 M HCl in each case for further studies.

*iii)* Effect of reagent concentration: It is observed that the maximum and constant absorbance is obtained for 0.6 - 1.6 mL of 0.1 % CHPB (w/v) in acetone (Fig.1, Curve b). The extract shows no absorbance in absence of CHPB. It starts forming colored species on addition of the reagent. Higher concentrations (>1.6 mL) of the reagent resulted in the lowering of absorbance values. Hence, 1.0 mL of 0.1% (w/v) CHPB is used for further investigations.

*iv)* Effect of equilibration time: After complexation under optimum conditions, the extraction of W (VI) – CHPB complex into chloroform is very fast and no change in the absorbance is observed when shaking time is varied from 8 to 240 seconds (Fig.-1, Curve c). The optimum equilibration time adopted is 20 seconds. Thus the data obtained above concludes that for the spectrophotometric determination of 20  $\mu$ g of tungsten (VI), 0.1 M HCl and 1 mL of 0.1% CHPB (in acetone) in the order as described above in 10 mL aqueous volume are sufficient to give maximum and constant absorbance. Equalibration is done with equal volume (10 mL) of chloroform for 20 seconds; metal ligand complex is quantitatively transferred into the solvent, whose absorbance is measured at 420 nm as described in procedure.

### Effect of diverse ions:

The effect of diverse ions is studied by carrying out determination of  $20 \ \mu g$  of tungsten in presence of each of these ions (mg amount in parentheses) added to the aqueous phase (10 mL) before the addition of CHPB. The following ions do not interfere: Sodium chloride, bromide, iodide, acetate, nitrate, dithionite and thiourea (100 each); phosphate and ascorbic acid (90 each); sodium sulphite and sulfosalicylic acid (60 each); sodium sulphate, hydrazine sulphate and sodium nitrite (40 each); EDTA 'disodium salt' and sodium potassium tartarate (10 each); sodium citrate (2); sodium oxalate (0.5); glycerol (0.2 mL) and  $H_2O_2$  (6% w/v) does not interfere up to 0.05 mL. (Table-1).



Fig. 1- Effect of varying experimental conditions

Table-1: Effect of various anions/ complexing agents on the absorbance of the W (VI) - CHPB

Anions/complexing agent	Amount (mg/10 mL)	Abs.
None		0.340
Sodium chloride, Potassium bromide, Potassium iodide, Sodium acetate, Sodium nitrate and Sodium dithionite	100	0.340
Sodium phosphate and ascorbic acid	90	0.340
Sodium sulphite and sulfosalicylic acid	60	0.330
Sodium sulphate, hydrazine sulphate and nitrite	40	0.335
Disodium EDTA and sodium potassium tartarate	10	0.340
Sodium citrate	2	0.340
Sodium oxalate	0.5	0.340
Glycerol <sup>a</sup>	0.2	0.335
Hydrogen peroxide <sup>a</sup> (6% w/v)	0.05	0.340

Conditions: As given in the Procedure. <sup>a</sup>Amount added in mL.

In 10 mL aqueous phase, the cations such as Ni(II), Zn(II), Mg(II), Ca(II), Mn(II) and Co(II) (10 mg each); Ba(II), Hg(II) and Pb(II) (8 mg each); Al(III) and Sr(II) (6 mg each); Se(IV), Cr(III) and Fe(III) (4 mg each); Be(II) and Bi(III) (2 mg each); Cu(II), As(V) and Zr(IV) (0.8 mg each); Sn(II) and Pt(IV) (0.6 mg each); Ce(IV), Ta(V) and Pd(II) (0.4 mg each); Ag(I), Mo(VI) and Ti(IV) (0.2 mg each); Ru(III) and Th(IV) (0.06 mg each); V(V) (0.03 mg); Ir(III) and Au(III) (0.01 mg each) do not interfere. Pt (IV) and Mo(VI) require respective masking agents as described under the procedure (Table-2).

## Spectral characteristics, Beer's law range and sensitivity:

The absorption spectrum of yellow W(VI) – CHPB complex against reagent blank in chloroform at optimum conditions shows an absorption maximum at 420 nm (Fig. 2, Curve A). The spectrum of reagent blank against pure solvent (Fig. 2, Curve B) shows that the reagent practically does not absorb above 410 nm. Beer's law is obeyed over the concentration range  $0 - 2.90 \,\mu g \, W(VI) \, mL^{-1}$  (Fig. 3).

Cation <sup>a</sup>	Amount (mg/10 mL)	Abs.
None		0.340
Ni(II), Zn(II), Mg(II), Ca(II), Mn(II) and Co(II)	10	0.340
Ba(II), Hg(II) and Pb(II)	8	0.345
Hg(II), Al(III) and Sr(II)	6	0.340
Se(IV), Cr(III) and Fe(III)	4	0.335
Be(II) and Bi(III)	2	0.335
Cu(II), As(V) and Zr(IV)	0.8	0.340
Sn(II) and Pt(IV) <sup>b</sup>	0.6	0.330
Ce(IV), Ta(V) and Pd(II)	0.4	0.340
Ag(I), Mo(VI) <sup>c</sup> and Ti(IV)	0.2	0.340
Ru(III) and Th(IV)	0.06	0.335
V(V)	0.03	0.340
Ir(III) and Au(III)	0.01	0.340

Table-2: Effect of cations on the absorbance of W (VI) -CHPB complex

<sup>a</sup>Initial oxidation state shown in parentheses. <sup>b</sup>In presence of 50 mg of sodium phosphate. <sup>c</sup>In presence of 0.05 mL of  $H_2O_2$  (6% w/v).



However the optimum range for accurate determination of tungsten as obtained from Ringbom's curve [15] at 420 nm is  $0.9 - 3.1 \ \mu\text{g} \text{ mL}^{-1}$  (Fig. 4). The molar absorptivity and Sandell's sensitivity of the complex at 420 nm are calculated to be  $3.125 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  and  $0.00294 \ \mu\text{g} \text{ W} \text{ cm}^{-2}$ , respectively. Ten replicate determinations containing 2  $\mu$ g W cm<sup>-3</sup> in each case give mean absorbance of 0.338 with a standard deviation of 0.0007262 and relative standard deviation of  $\pm 0.2136$  % absorbance unit.



Fig.-4: Ringbom plot for W (VI) - CHPB complex in Chloroform at 420 nm

#### Stoichiometry of the complex:

The stoichiometry of W (VI) – CHPB complex is established by Job's method of continuous variations [16, 17] for the two phase system and by mole ratio method [18]. The details of the concentrations used in respective methods are given below:

*i)* Job's method of continuous variations: Equimolar solutions  $(5.43 \times 10^{-4} \text{ M})$  of tungsten and CHPB are mixed so that the mole fraction of tungsten (VI) varies from 0 to 1 keeping the concentrations of the two variables i.e. 420 and 435 nm. To the mixture, 1 ml of 1 M HCl is added and the complex is extracted from 10 ml aqueous phase with 10 ml chloroform after shaking for 20 seconds. The organic layer is separated and the absorbance is measured against a reagent blank obtained by carrying out the extraction under similar conditions. The curves in the Fig.5 indicate 1:2 stoichiometry in the extracted species.



*ii)* Mole-ratio method: The concentration of one component (metal ion) is fixed at  $5.43 \times 10^{-4}$  M and that of the other component (reagent) is varied. The absorbance is measured at 420 and 435 nm (Fig. 6) keeping other conditions same as given in the procedure. The clear breaks in the curves corresponding to mole ratio 2 suggest metal to ligand stoichiometry to be 1: 2.



On the basis of the above stoichiometry, the most probable structure of the complex may be shown as:



Structure of W (VI) - CHPB Complex

#### Applications

The wide applicability of the proposed method has been tested by the satisfactory analysis of flue dust, steel and various synthetic samples containing tungsten up to  $28 \ \mu g$  in the aliquot (Table-3). This method is quite selective for the determination of tungsten in the presence of large number of elements especially nickel, zinc, magnesium, berelium, copper, uranium, selenium, cerium, arsenic, osmium, tin, titanium, palladium, chromium, platinum, ruthenium, rhenium, iridium, tantalum, gold, zirconium, iron, vanadium and molybdenum which seriously interfere in most of the existing methods of tungsten determination. The method is found to be more sensitive than those reported earlier for tungsten complex with chromone derivatives and other reagents (Table-4). Thus the proposed method offers the advantage of better sensitivity, selectivity and wider Beer's law range, applicability to samples containing several interfering elements in concentrations higher than normally met with and is simple, rapid, precise and accurate. The method is simple and takes about 5 minutes for a single determination.

Table-3: Analysis of sample solutions	
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Sr. No.	Composition of Sample Matrix*	Tungsten added(µg)	Tungsten found**
1.	[Fe(0.025), Co(0.15), Cr(0.10)]	25.0	24.92
2.	[Ni(0.160), Zr(0.012)]	28.0	27.98
3.	[Fe(4.05), Cr(0.6), C(0.075), Co(0.2), Si(0.03), Mn(0.01)]	20.0	20.09
4.	[Fe(0.10), Co(0.02), Mn(0.02), Cr(0.02), Ni(0.02)]	16.0	15.91
5.	[Sn(0.87), Sb(0.06), Ni(0.02), Cu(0.02), Zn(0.01), Bi(0.05)]	15.0	14.89
6.	[Cu(0.10), Pb(0.06), Ni(0.10)]	10.0	9.94
7.	[Cr(0.015), Co(0.019), Ni(0.005), Mo(0.002) <sup>a</sup> , C(0.001)]	8.0	7.91
8.	[Fe(0.03), Cr(0.03), Si(0.005), C(0.005)]	5.0	5.03
9.	Zr(0.02), Nb(0.02), Ta(0.02)	12.0	11.89
10.	Tap water	8.0	7.98
11.	$Pt(0.1)^{b}, Pd(0.01), Ru(0.05)$	25.0	25.04
12.	Reverberatory flue dust(100)	15.0	15.09
12.	Reverberatory flue dust(100)	15.0	15.09

\*Figure in the bracket indicates the amount of metal ion per sample in milligrams; \*\* Average of triplicate analysis.

Compositions (1-8) corresponds to Stellite No. 2, Cooperite, Duke's metal, Heat resistant steel, Complex English metal, Minargent, Arkit and Silchrome wire, respectively.

<sup>a</sup>In presence of 0.05 ml of  $H_2O_2$  (6 % w/v). <sup>b</sup>In presence of 10 mg of sodium phosphate.

### Table-4: Comparison of the proposed method with the existing methods

Sr. No.	Aqueous conditions	Solvent/ (λmax,nm)	Sandell's Sensitivity (µg cm <sup>-2</sup> ) Molar Absorptivity (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> )	Interfering metal ions
1.	W(VI), conc.HCl, SnCl <sub>2</sub> , 0.5% dithiol (in amyl acetate), heat to $80^{\circ}$ C, wash the extract with conc. HCl, time consuming <sup>a</sup>	Amyl acetate/640	0.006 (1.92×10 <sup>4</sup> )	Mo(VI) separated by extraction as dithiolate from 1.9 M HCl before determination of W(VI)
2.	W(VI), 10 M HCl, 25% KSCN, 30% SnCl <sub>2</sub> , 0.5% quinaldic acid, heat to 80°C, colour development time 10 minute <sup>b</sup>	Isoamyl acetate/405	0.012 (1.51×10 <sup>4</sup> )	Pd((II), Ti(IV), Re(VII), V(V), Pt(IV), Mo(VI)
3.	W(VI), pH 0.8-2.4; 2,4-dihydroxybenzenethiol <sup>c</sup>	Isoamyl Alcohol/490	0.046 (0.40×10 <sup>4</sup> )	Not known
4.	Proposed method	Chloroform/ 420	0.00294 (3.125×10 <sup>4</sup> )	39 metal ions do not interfere
	${}^{a}Ref = [7], {}^{b}Ref = [9], {}^{c}Ref = [12]$			

### CONCLUSION

The proposed method for the determination of micro-amounts of tungsten has been found free from interference of large number of metal ions. The method is found to be more sensitive than those reported earlier for tungsten complex with chromone derivatives and other reagents (Table-4). The wide applicability of the proposed method has been tested by the satisfactory analysis of flue dust, steel and various synthetic samples containing tungsten up to 28

 $\mu$ g in the aliquot. The proposed method is rapid, simple, sensitive, selective and precise for the determination of tungsten.

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