Extractive Spectrophotometric Determination of Tungsten(VI) as Its 6-Chloro-3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran Complex

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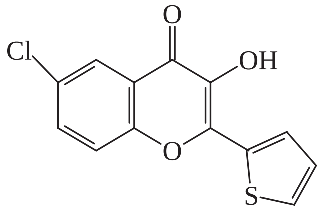
An extractive spectrophotometric method was developed for the trace determination of tungsten in an acidic medium. A yellow-colored 1:3 complex of tungsten(VI) and 6-chloro-3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHTB), prepared in 0.16–0.32 mol dm^{-3} hydrochloric acid medium, was quantitatively extracted into chloroform. The complex had a maximum absorbance at 417–423 nm. The method obeyed Beer's law in the range of 0–3.0 µg cm^{-3} W^{VI}; the correlation coefficient was $r = 0.9902$. The molar absorptivity and Sandell's sensitivity of the complex were 4.05×10^4 dm^3 mol^{-1} cm^{-1} and 0.0045 µg of W^{VI} cm^{-2}, respectively, at 420 nm. Various metals, including Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ta, Mo, U, Zr, Th, Ce, Re, and various platinum metals did not interfere in the extraction, and this procedure was satisfactorily applied to the analysis of tungsten in various synthetic, technical and natural samples, including reverberatory flue dust and water.

The existing methods of spectrophotometric determination of tungsten[1,2] using binary complexes are generally time consuming, less sensitive, non-selective and thus have limited applications due to the complexity of procedures involved. Various organic reagents,[3–6] utilized recently for this purpose, have similar disadvantages. To overcome these difficulties, we developed a new method by using 6-chloro-3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHTB) as a complexing agent, which not only enhances the selectivity but also gives a more sensitive, simple, and rapid method of spectrophotometric determination of tungsten in trace amounts.



(CHTB)

Chart 1.

Experimental

Apparatus. A UV–visible 140-02 spectrophotometer (Shimadzu, Japan) with 1 cm matched glass cuvettes was used for spectral studies and absorbance measurements.

Reagents and Solutions. A standard stock solution (100 cm^3) of tungsten(VI) containing 1 mg cm^{-3} of the metal ion was prepared by dissolving an accurately weighed amount (0.179 g) of sodium tungstate (LR, CDH) in deionized water and standardized by using the oxine method.[1] Lower concentrations at 1 µg cm^{-3} level were prepared by diluting the stock solution. Stock solutions of other metal ions were prepared at 1 mg cm^{-3} level by dissolving their commonly available sodium or potassium salts in deionized water or dilute acids. They were then diluted to obtain lower concentrations of the metal ion at <1 µg cm^{-3} level. Two molar hydrochloric acid was prepared by diluting conc. Hydrochloric acid (11.3 mol dm^{-3}). 6-Chloro-3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHTB; mp 202 °C) was synthesized by using a previously reported literature method[7] and dissolved in acetone to give a 0.1% (w/v) solution. The chemical composition of CHTB is $C_{13}H_7ClO_3S$, and its structure is shown in Chart 1. Chloroform (RANBAXY) was distilled, and the fraction that distilled at 60–61 °C was used for extraction.

Synthetic Samples. Synthetic samples (some of them analogous to minargent, platinoid, W-alloy, heat resistant steel, high speed steel and stellite No. 2) were prepared by mixing the solution of tungsten(VI) with solutions of various metal ions in suitable proportions so as to give the compositions as shown in Table 1.

Reverberatory Flue Dust. Flue dust sample (0.1 g) from a copper manufacturing unit containing no tungsten was mixed with a solution of known tungsten content (1 mg) and dried in an oven at 110–120 °C. After fusion of the dried dust sample with sodium peroxide (0.8 g), the mass was leached with 25–30 mL of hot water containing 0.9 g sodium potassium tartrate, neutralized with concentrated HCl and adjusted to 2 mol dm^{-3} and a final volume of 100 cm^3. Aliquots (1.5 and 2.0 cm^3) were taken for the determination of tungsten by the proposed method after adding 50 mg ascorbic acid in each case to mask the iron present in the dust sample.

Water Samples. Water sample (1000 cm^3) from tap and well was spiked with 250 µg of W^{VI}, evaporated to about 25 cm^3, treated with 6% H_2O_2 (w/v) (1–2 cm^3) in an ammoniacal medium and heated to dryness. The residue was dissolved in 2 mol dm^{-3} HCl to give a total 25 cm^3 volume of the solution. Tungsten was determined in the aliquots (1 and 0.5 cm^3) by the proposed method after masking the iron with 50 mg ascorbic acid in each case.

Procedure. To the sample solution containing $\leq$30 µg of tungsten(VI) (taken in a 100 cm^3 separatory funnel) were added 1 cm^3 of 2 mol dm^{-3} HCl, 0.5 cm^3 of 0.1% (w/v) CHTB and sufficient amount of deionized water to make the final aqueous

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Table 1. Analysis of Samples by the Proposed Method

Sr. No.	Composition of sample: Matrix a)	W added /μg	W found b) /μg
1	Cu(0.2), Ni(0.2), Pb(0.12) c)	20	19.8 ± 0.79
2	Cu(0.6), Zn(0.25), Ni(0.15) c)	10	10.1 ± 0.88
3	Cu(0.15), Zn(0.08), Al(0.12) c)	15	14.9 ± 0.64
4	Fe(0.15), Cr(0.03), Co(0.03), Mn(0.01), Ni(0.01) c),d)	20	19.7 ± 0.93
5	Fe(0.15), Cr(0.005), V(0.003) c),d)	25	25.2 ± 0.63
6	Co(0.06), Cr(0.04), Fe(0.01) c)	10	9.9 ± 0.88
7	Fe(0.1), Ba(1), Mg(2) d)	15	14.9 ± 1.24
8	Hg(2), Co(2), Nb(0.5) e)	5	5.0 ± 0.00
9	Sr(5), Pd(0.05), Pt(0.1)	10	10.2 ± 1.46
10	Ru(0.01), Re(0.01), Au(0.01)	20	20.1 ± 0.48
11	Mo(0.01), Sn(0.05), Th(0.1) f)	25	25.3 ± 0.73
12	Cr(1), Zr(0.05), Ce(0.5) g)	10	9.9 ± 0.88
13	U(1), Se(1), Ti(0.01)	10	10.1 ± 0.88
14	Reverberatory flue dust (100) d)	15	15.2 ± 1.06
		20	19.9 ± 0.48
15	Tap Water	5	5.08 ± 1.75
		10	9.9 ± 0.88
16	Well Water	5	5.1 ± 1.75
		10	10.0 ± 1.46

a) Figure in parentheses indicates the amount of metal ion in mg. b) Average of triplicate analyses; Mean ± % RSD. c) Compositions of sample Nos. 1–6 correspond to minargent, platinoid, W-alloy, heat resistant steel, high speed steel, and stellite No. 2, respectively. d) In presence of 50 mg ascorbic acid. e) In presence of 9 mg sodium potassium tartrate. f) In presence of 50 mg sodium dithionite and 100 mg Na_2H_2edta·$2H_2O$. g) In presence of 90 mg sodium phosphate.

volume 10 cm^3. The mixture was then extracted with equal volume (10 cm^3) of chloroform after equilibrating once for 30 s. The yellow solvent layer was passed through Whatman filter paper (No. 41, 9 cm diameter, pretreated with chloroform) to remove water droplets, if any, and the absorbance of the extract was measured at 420 nm against a similarly treated reagent blank. The tungsten content was determined from the calibration curve prepared under identical conditions of the procedure.

Results and Discussion

Absorption Spectra. Tungsten(VI) formed a yellow complex with 6-chloro-3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran (CHTB) under acidic conditions, which could be quantitatively extractable into chloroform. The absorption spectrum of the W^{VI}–CHTB complex extracted from 0.2 mol dm^{-3} HCl in chloroform showed a maximum in the region of 417–423 nm, where the reagent blank had minimal absorbance (Fig. 1).

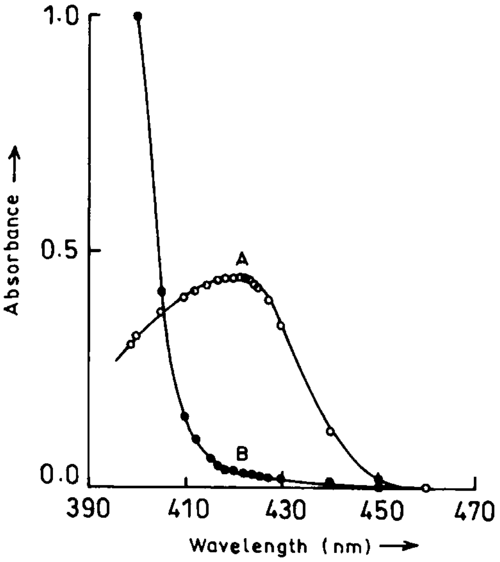

Fig. 1. Absorption spectra of W^{VI}–CHTB complex in chloroform. Curve A: complex studied against reagent blank, curve B: reagent blank against pure chloroform, 2 μg of W cm^{-3}, [HCl] = 0.2 mol dm^{-3}, [CHTB (0.1%)] = 0.5 cm^3.

Selection of Experimental Conditions. The absorbance of the W^{VI}–CHTB complex in chloroform was influenced by the nature and concentration of the acids. From 0.2 M acidity in each case, the absorbance was found to decrease in the order: HCl = H_2SO_4 > H_3PO_4 > $HClO_4$ > CH_3COOH. Though H_2SO_4 medium showed same absorbance as that of HCl, HCl medium was used for further studies as the reagent blank showed minimal absorbance.

In order to achieve an optimum and constant absorbance of the complex containing ≤30 μg of tungsten in 10 cm^3 of aqueous phase, 0.16–0.32 mol dm^{-3} HCl and 0.4–0.7 cm^3 of 0.1% (w/v) acetonic CHTB solution were added in the same order as per the proposed procedure (Table 2). Then, the mixture was equilibrated only once with 10 cm^3 of chloroform for 7–75 s. The investigated complex could be easily extracted into various other water immiscible solvents, such as dichloro-

Table 2. Effect of Various Parameters on the Absorbance of W^{VI}–CHTB Complex

HCl/mol dm^{-3} a)	0.04	0.08	0.12	0.14	0.16–0.32	0.40	0.50
Absorbance	0.270	0.330	0.350	0.375	0.395	0.365	0.345
CHTB b) (0.1% in acetone, cm^3)	0.1	0.3	0.4–0.7	0.8	1.0	1.5	2.0
Absorbance	0.115	0.420	0.440	0.420	0.395	0.370	0.290
Equilibration time c)/s	0	5	7–75	90	120		
Absorbance	0.050	0.420	0.440	0.375	0.325		

Conditions: a) W^{VI} = 20 μg, HCl = variable, the volume of the 0.1% CHTB solution = 1 cm^3, equilibration time = 30 s, solvent = chloroform, absorbance measured at 420 nm against reagent blank. b) HCl = 0.2 mol dm^{-3}, other conditions being the same as in (a) except for the variation in CHTB concentration. c) 0.1% CHTB in acetone = 1 cm^3, other conditions being the same as in (b) except for the variation in equilibration time.

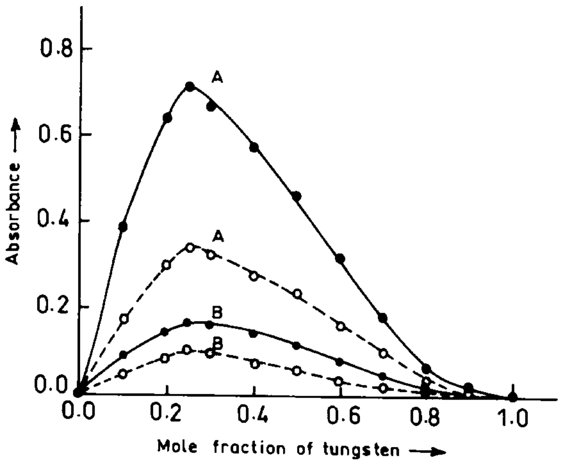

Fig. 2. Job's method of continuous variations. Total concentrations: ●——● [W] + [CHTB] = 1.086×10^{-3} mol dm^{-3}, ○- - - -○ [W] + [CHTB] = 5.43×10^{-4} mol dm^{-3}. Curves A = 420 nm, Curves B = 440 nm, [HCl] = 0.2 mol dm^{-3}.

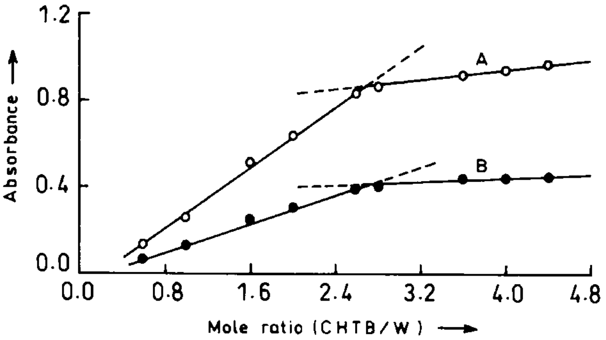

Fig. 3. Mole ratio method. Total concentration of metal ion fixed, [W] = 5.43×10^{-4} mol dm^{-3}, curve A = 420 nm, curve B = 435 nm, [HCl] = 0.2 mol dm^{-3}.

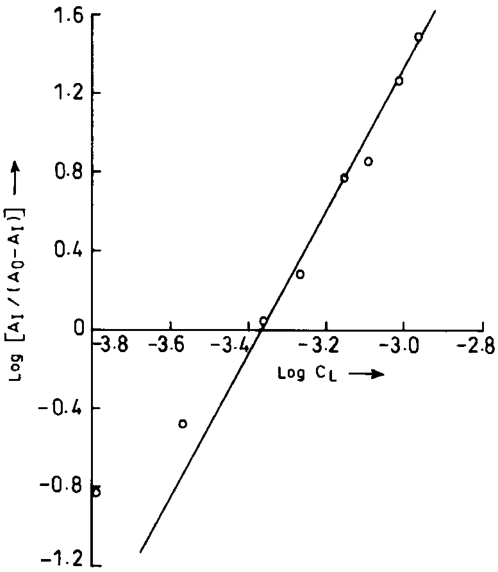

Fig. 4. Equilibrium shift method. A_I = Absorbance at a reagent concentration C_L; A_0 = absorbance at complete formation of the complex; C_L = total concentration of the reagent added. Conditions: Concentration of W^{VI} = 5.43×10^{-4} mol dm^{-3}, concentration of CHTB = 1.629×10^{-4}–1.195×10^{-3} mol dm^{-3}, 0.2 mol dm^{-3} HCl, aqueous volume = solvent volume = 10 cm^3, solvent = chloroform, λ_{max} = 420 nm.

methane, 1,2-dichloroethane, toluene, benzene, carbon tetrachloride, ethyl acetate, amyl alcohol, amyl acetate, and cyclohexane. However, chloroform was found to be the most suitable solvent, since it provided maximum and highly stable (>2 days) absorbance of the complex. A single equilibration with 10 cm^3 of chloroform caused the quantitative transfer of the W^{VI}–CHTB complex into the organic phase. The complete absence of tungsten in the raffinate was verified by using the more sensitive 3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran method.[4]

Composition of the Complex. The stoichiometric ratio of W^{VI} and CHTB in the extracted species was determined to be 1:3 by using Job's method of continuous variations as modified by Vosburgh and Cooper for a two phase system[8,9] by taking equimolar solutions of tungsten(VI) and CHTB reagent with two different concentrations (1.086×10^{-3} and 5.43×10^{-4} mol dm^{-3}). The absorbance values were measured at two different wavelengths, 420 and 440 nm (Fig. 2). The 1:3 ratio was confirmed by using mole ratio method[10] (Fig. 3) by taking the concentration of tungsten as 5.43×10^{-4} mol dm^{-3} and varying the reagent concentration from 1.629×10^{-4} to 1.195×10^{-3} mol dm^{-3} and measuring the absorbance again at two different wavelengths, 420 and 435 nm. The composition of the complex was further verified by using equilibrium shift method[11] at 5.43×10^{-4} mol dm^{-3} tungsten and in the CHTB concentration range of 1.629×10^{-4}–1.195×10^{-3} mol dm^{-3}, which gave a slope of the curve of 2.7 (Fig. 4), confirming the 1:3 ratio of the extracted species. Other conditions were the same as per the proposed procedure in all of the above methods. From the mole ratio method, the stability constant was estimated to be 7.34×10^{11}.

Analytical Characteristics. Under optimum conditions, Beer's law was obeyed in the range of 0–3.0 µg of W^{VI} cm^{-3} of the solvent phase. However, from the Ringbom plot,[12] the accurate range for determining the tungsten content was determined to be 0.5–2.88 µg cm^{-3}. The molar absorptivity and Sandell's sensitivity of the complex at 420 nm were 4.05×10^4 dm^3 mol^{-1} cm^{-1} and 0.0045 µg of W^{VI} cm^{-2}, respectively. For 20 µg of W^{VI} taken in pure solutions, the relative standard deviation of ten replicate determinations was 0.409%. The linear regression equation was $Y = 0.187X + 0.059$ (Y = absorbance; X = W^{VI} concentration), and the correlation coefficient was $r = 0.9902$.

Interference Studies. Under optimum conditions of the procedure and in a solution with a volume of 10 cm^3, the following did not affect the determination: chloride, bromide, iodide, sulphate, thiocyanate, and EDTA "disodium salt" (100 mg each); sulphite, phosphate, thiourea, carbonate, and sulfosalicylic acid (90 mg each); nitrate (70 mg); nitrite, ascorbic acid, dithionite, and hydrazine sulphate (50 mg each); acetate (20 mg); tartrate (9 mg); citrate (5 mg); glycerol (0.8 cm^3) and H_2O_2, 6% (w/v) (0.5 cm^3). However, oxalate and fluoride seriously interfered. The following cations caused $\leq$1% error:

Table 3. Comparison of the Proposed Method with the Existing Ones

Sr. No.	Aqueous Conditions	Solvent ($\lambda_{\max}$, nm)	Sandell's sensitivity, $\mu g\,cm^{-2}$ (Molar absortivity, $dm^3\,mol^{-1}\,cm^{-1}$)	Interfering metal ions	Reference
1	W^{VI}, 20% KSCN, 40% $SnCl_2$, 8–9 mol dm^{-3} HCl, color development time 5–15 min	Isoamyl alcohol (403)	0.012 (1.56×10^4)	Hg^{II}, Au^{III}, Pt^{IV}, Cr^{VI}, Ni^{II}, Co^{II}, As^{V}, V^{V}	1,2
2	W^{VI}, conc. HCl, $SnCl_2$ 0.5% dithiol (in amyl acetate), heat to 80 °C, wash the extract with conc. HCl, takes longer time	Amyl acetate (640)	0.0096 (1.92×10^4)	Mo^{VI} separated by extraction as dithiolate from 1.9 mol dm^{-3} HCl before detn of W^{VI}	2
3	W^{VI}, 10 mol dm^{-3} HCl, 25% KSCN, 30% $SnCl_2$, 0.5% quinaldic acid, heat to 80 °C color development time 10 min	Isoamyl acetate 405	0.012 (1.51×10^4)	Mo^{VI}, Pd^{II}, Ti^{IV}, Re^{VII}, V^{V}, Pt^{IV}	3
4	W^{VI}, 0.2 mol dm^{-3} HCl, 0.6–2.1 cm^3 of 0.1% 3-hydroxy-2-(2′-thienyl)-4-oxo-4*H*-1-benzopyran in ethanol, takes longer time	Dichloromethane (415)	0.0029 (6.45×10^4)	Mo^{VI} separated by extraction as thiocyanate complex in presence of NaF before detn. Of W^{VI}	4
5	W^{VI}, pH 0.8–2.4, 2,4-dihydroxybenzenethiol	Isoamyl alcohol (490)	0.046 (0.04×10^4)	Not known	5
6	W^{VI}, 0.16–0.32 mol dm^{-3} HCl, 0.4–0.7 cm^3 of 0.1% acetonic CHTB soln.	Chloroform (420)	0.0045 (4.05×10^4)	38 metal ions do not interfere	Proposed method.

Ca^{II}, Pb^{II}, Sr^{II}, Mn^{II}, Al^{III}, and As^{V} (10 mg each); Zn^{II}, Co^{II}, Ni^{II}, Ba^{II}, Hg^{II}, and Mg^{II} (8 mg each); Cr^{VI} (5 mg); U^{VI} and Cr^{III} (4 mg each); Se^{IV} (3 mg); Os^{VIII} (2 mg); Ce^{IV}, Ag^{I}, and Cu^{II} (1 mg each); Th^{IV} and Cd^{II} (0.5 mg each); Pt^{IV} (0.4 mg); Pd^{II}, Re^{VII}, Ir^{III}, Au^{III}, Ta^{V}, and Ru^{III} (0.1 mg each) and Ti^{IV} (0.03 mg). The interference due to Fe^{III} (1.5 mg) could be eliminated by adding 50 mg ascorbic acid and that from Bi^{III} (1 mg), Sb^{III} and V^{V} (0.5 mg each), and Mo^{VI} (0.1 mg) were masked with sodium dithionite (50 mg). That from Nb^{V} (1 mg) was masked with sodium potassium tartrate (9 mg) and that from Zr^{IV} and Sn^{II} (0.2 mg each) were masked by adding sodium phosphate (90 mg) and EDTA "disodium salt" (100 mg), respectively. The masking agents were added to the sample solution prior to the addition of CHTB to suppress the coextraction of metal ion complexes.

Conclusion

The proposed method is simple, rapid (takes 2–3 min for a single determination), sensitive, reproducible and highly selective as it is free from the interference of a large number (38) of metal ions, including platinum metals. The wide applicability of the method was tested by analyzing several synthetic, technical and natural samples with satisfactory results (Table 1). The proposed method is better than the existing methods (Table 3) particularly with respect to sensitivity, selectivity and rapidity.

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