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3-Hydroxy-2-(3'-methyl-2'-thienyl)-4-oxo-4*H*-1-benzopyran as an Analytical Reagent for the Spectrophotometric Determination of Tungsten(VI)

R. Agnihotri, N. Agnihotri, Raj Kamal and Jaswant R. Mehta*
Department of Chemistry, Kurukshetra University
Kurukshetra-136 119, India
E-mail: rajniv@sify.com

An extractive spectrophotometric method is developed for the trace determination of tungsten. Tungsten(VI) forms a yellow (1:4) complex with 3-hydroxy-2-(3'-methyl-2'-thienyl)-4-oxo-4*H*-1-benzopyran (HMTB) in perchloric acid medium. The coloured species is quantitatively extracted into dichloromethane and shows maximum absorbance at 415-423 nm. The method obeys Beer's law up to 3.6 µg W mL^{-1}, having molar absorptivity, Sandell's sensitivity and correlation coefficient of 5.80×10^4 dm^3 mol^{-1} cm^{-1}, 0.0032 µg W cm^{-2} and 0.9963, respectively at 420 nm. The method is free from the interference of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Ta, Mo, U, Zr, Th, Ce, Se, Re, platinum metals and many other analytically important elements. The method has good reproducibility and can be satisfactorily applied to the determination of tungsten in several samples of varying complexity.

Key Words: Tungsten, Extraction, 3-Hydroxy-2-(3'-methyl-2'-thienyl)-4-oxo-4*H*-1-benzopyran, Spectrophotometry.

INTRODUCTION

The existing methods of spectrophotometric determination of tungsten[1-4] using binary complexes are generally time consuming, less sensitive, non-selective and thus have limited applications due to more complexity of procedures. Some mixed ligand complexes of tungsten though show high value of sensitivity yet lack selectivity[5-9] due to the non-extractability of the complexes into organic solvents. In view of the above observations, it is considered of interest to study the complex formation reaction of tungsten(VI) with 3-hydroxy-2-(3'-methyl-2'-thieny1)-4-oxo-4*H*-1-benzopyran which not only gives a more rapid and highly reproducible method but also provides a highly selective and sensitive extractive spectrophotometric determination of tungsten in trace amounts.

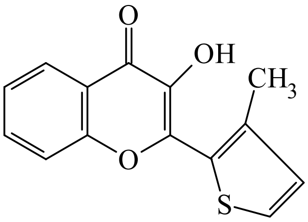
EXPERIMENTAL

Tungsten(VI) solution: A standard stock solution (100 mL) of tungsten(VI) containing 1 mg mL^{-1} of the metal ion is prepared by dissolving an accurately weighed amount (0.179 g) of sodium tungstate (CDH, India) in deionized water and standardized by the oxine method[10]. Lower concentrations at µg mL^{-1} level are prepared by suitable dilution therefrom.

Solutions of other ions are prepared at mg mL^{-1} level by dissolving their sodium or potassium salts in deionized water or dilute acids. They are also suitably diluted to obtain lower concentrations of the metal ions at µg mL^{-1} level.

Perchloric acid (Qualigens excela R) 2 M is prepared by diluting 70 % (11.6 M) acid with deionized water.

3-Hydroxy-2-(3'-methy1-2'-thieny1)-4-oxo-4*H*-1-benzopyran (HMTB, m.p. 190 ºC, m.f. $C_{14}H_{10}O_3S$) is synthesized by the literature method[11,12] and dissolved in acetone to get 0.02 % (w/v) solution.



3-Hydroxy-2-(3'-methy1-2'-thieny1)-4-oxo-4*H*-1-benzopyran (HMTB)

Synthetic and technical samples: Synthetic samples (some of them analogous to technical samples such as minargent, platinoid, W alloy, heat resistant steel, high speed steel and stellite No. 2) are prepared by adding the solutions of various metal ions to tungsten solution in suitable proportions, as shown in Table-1.

Reverberatory flue dust sample (100 mg) from copper manufacture unit containing no tungsten is mixed with a solution of known tungsten content (1 mg) and dried in an oven at 110-120 ºC. After fusion of the dried dust sample with sodium peroxide (0.8 g) and dissolution of the fused mass in 25-30 mL hot water, the leach is treated with 100 mg sodium potassium tartrate, neutralized with concentrated $HClO_4$ and adjusted to 1 M acidity in 100 mL final volume. Aliquots (1 and 2 mL) are analyzed for tungsten by the proposed method.

Water samples (1000 mL) from tap and well are spiked with 250 µg W (VI). Each sample is evaporated to about 25 mL, treated with 6 % H_2O_2 (w/v) (1-2 mL) in ammonical medium and again heated to dryness. The residue is dissolved in 1 M $HClO_4$ to give a total 25 mL volume of the solution.

TABLE-1
ANALYSIS OF SAMPLES BY THE PROPOSED METHOD

S. No.	Composition of sample Matrix	Tungsten	
		Added (μg)	Found** (μg)
1	Cu (0.3), Ni (0.3), Pb (0.2)[a]	30	29.91 ± 0.43
2	Cu (0.12), Sn (0.5), Ni (0.3)[a]	20	20.09 ± 0.33
3	Cu (0.15), Sn (0.08), Al (0.12)[a]	15	15.06 ± 1.13
4	Fe (0.075), Cr (0.02), Co (0.02), Mn (0.01), Ni (0.01)[a]	10	9.78 ± 0.64
5	Fe (0.10), Cr (0.004), V (0.002)[a]	20	20.00 ± 0.56
6	Co (0.12), Cr (0.08), Fe (0.02)[a]	20	19.78 ± 0.65
7	Nb (0.01), Be (0.5), Ba (1.0)	10	10.06 ± 1.24
8	As (1.0), Mo (0.1), Se (1.0)[b]	10	9.91 ± 0.65
9	Pt (0.1), Pd (0.1), Ti (0.1)	20	19.84 ± 0.56
10	Sn (0.05), Th (0.01), Rh (0.1)[c]	5	4.94 ± 1.27
11	Zr (0.05), Hg (2.0), Mg (2.0)[d]	30	29.75 ± 0.22
12	Reverberatory flue dust (100)	20	20.22 ± 0.65
		10	10.25 ± 1.24
13	Tap water	5	4.94 ± 1.27
		10	9.91 ± 0.64
14	Well water	5	4.91 ± 1.27
		10	10.00 ± 1.06

*Figure in parentheses indicates the amount of metal ion in mg.
**Average of five replicate analyses; Mean ± % RSD.
[a] Compositions of sample Nos. 1-6 correspond to minargent, platinoid, W-alloy, heat resistant steel, high speed steel and stellite No. 2, respectively.
[b] In presence of 10 mg sodium dithionite.
[c] In presence of 1 mg sodium fluoride.
[d] In presence of 10 mg EDTA disodium salt.

Aliquots (0.5 and 1 mL) are taken for the determination of tungsten by the proposed method.

For an absorbance measurement and spectral studies, a UV-Visible 140-02 spectrophotometer (Shimadzu, Japan) is used.

Procedure: To an aliquot of the sample solution containing ≤ 36 μg W (VI) and other metal ions in a 100 mL separatory funnel are added 0.5 mL of 2 M $HClO_4$, 1 mL of 0.02 % HMTB in acetone and enough deionized water to make the final aqueous volume 10 mL. The mixture is then equilibrated with equal volume (10 mL) of dichloromethane once for 30 s. The yellow coloured organic phase is passed through Whatmann filter paper (No. 41, 9 cm diameter, pretreated with dichloromethane) to remove water droplets, if any and the absorbance of the extract is measured at 420 nm against a similarly treated reagent blank. The tungsten content is determined from the calibration curve prepared under identical conditions of the procedure.

In the samples containing 0.3 mg V(V) and 0.2 mg Mo (VI), 10 mg sodium dithionite is added in each case to mask them. Similarly, up to 0.8 mg Bi(III), 0.1 mg Zr(IV) and 0.08 mg Sn(II) are masked with 100 mg of sodium iodide, 10 mg of EDTA disodium salt and 1 mg of sodium fluoride, respectively, when added in a 10 mL aqueous volume prior to the addition of the reagent.

RESULTS AND DISCUSSION

A yellow complex of tungsten(VI) is formed with 3-hydroxy-2-(3'-methyl-2'-thienyl)-4-oxo-4*H*-1-benzopyran (HMTB) in acidic medium, which is quantitatively extracted into dichloromethane. The absorbance of the W(VI)-HMTB complex in dichloromethane is influenced by the nature and concentration of acids. From 0.2 M acidity in each case, the absorbance decreases in the order: HCl > $HClO_4$ > H_2SO_4 > CH_3COOH > H_3PO_4. Though, HCl shows higher value of absorbance, yet $HClO_4$ medium is preferred for further studies as the reagent blank shows zero absorbance in it. The absorption spectrum of the complex against a reagent blank in dichloromethane indicates that the maximum lies at 415-423 nm in the visible region, where the reagent blank shows no absorbance at all (Fig. 1).

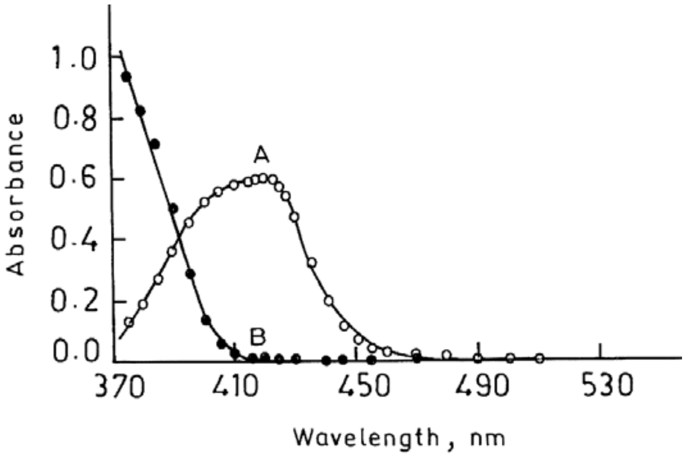


Fig. 1. Absorption spectrum of W (VI)-HMTB complex in dichloromethane
(A) 2.0 μg mL^{-1} of tungsten measured against reagent blank
(B) reagent blank measured against dichloromethane

The investigated complex can be easily extracted into various water immiscible solvents with the absorbance decreasing in the order: dichloromethane, 1,2-dichloroethane, chloroform, toluene, benzene, carbon tetrachloride, isobutyl methyl ketone, isopentyl acetate, isopentyl alcohol, ethyl acetate and cyclohexane. Hence dichloromethane showing maximum and stable absorbance (> 2 d) is selected for further studies. A single equilibration with 10 mL of dichloromethane quantitatively transfers the W(VI)-HMTB complex into organic phase. The complete absence of tungsten in the raffinate is tested by the more sensitive 3-hydroxy-2-(2'-thienyl)-4-oxo-4*H*-1-benzopyran method[12,13].

Other operative parameters which affect the absorbance of the metal complex (molarity of $HClO_4$, HMTB concentration and equilibration time) are given in Table-2. From this data, the experimental conditions are chosen as described in present investigation.

TABLE-2
EFFECT OF VARIOUS PARAMETERS ON THE ABSORBANCE OF THE TUNGSTEN-COMPLEX

$HClO_4$(M)[a]	0.02	0.04	0.06-0.14	0.16	0.20	0.24
Absorbance	0.490	0.530	0.630	0.620	0.600	0.560
0.02% HMTB (mL)[b]	0.2	0.6	0.8	0.9-2.0	2.1	2.5
Absorbance	0.190	0.500	0.600	0.630	0.620	0.570
Equilibration time (s)[c]	0	2	3	5-300		
Absorbance	0.100	0.600	0.620	0.630		

Conditions: [a]W(IV) = 20 µg, $HClO_4$ = variable, 0.02 % HMTB = 1 mL, equilibration time = 30 s, solvent = dichloromethane, aqueous volume = solvent volume = 10 mL, λ_{max} = 420 nm; [b]$HClO_4$ = 0.1 M, other conditions being the same as in (a) except for the variation in HMTB concentration, also (b) 3-hydroxy-2-(3'-methyl-2'-thienyl)–4-oxo-4*H*-1-benzopyran (HMTB); [c]0.02 % HMTB in acetone = 1.0 mL, other conditions being the same as in (b) except for the variation in equilibration time.

Effect of diverse ions: Under the optimum conditions of the procedure, the ions and/or complexing agents added as their sodium or potassium salts in the aqueous phase (mg/10 mL amounts in parentheses) such as chloride, iodide, sulfate, sulfite, thiourea, sulfosalicylic acid (100 each), bromide, nitrate (80 each), phosphate, carbonate, acetate, hydrazine sulfate (50 each), thiocyanate, ascorbic acid, dithionite, EDTA disodium salt (10 each), fluoride, tartrate (1 each), citrate (0.5), glycerol (0.5 mL) and H_2O_2 (6 % w/v) (0.05 mL) cause ≤ 1 % error. However, oxalate interferes seriously even in traces.

Among the cations (mg/10 mL amounts in parentheses), Co(II), Ni(II), Ca(II), Hg(II), Ba(II), Zn(II), Sr(II), Mg(II), Mn(II), Cd(II) (10 each), Pb(II), As(V), Al(III) (5 each), Se(IV), U(VI) (4 each), Os(VIII) (3), Cu(II), Be(II) (1 each), Rh(III), Cr(III) (0.5 each), Ti(IV), Pt(IV) (0.3 each), Pd(II) (0.2), Ag(I), Fe(III), Au(III), Ce(IV) (0.1 each), Th(IV), Ta(V), Cr(VI) (0.05 each), Ru(III), Nb(V) (0.02 each) and Ir(III) (0.01) have no effect on the absorbance of the complex. V(V), Mo(VI), Bi(III), Zr(IV) and Sn(II) do not interfere in the presence of respective masking agents as described in present studies.

Analytical characteristics: Beer's law is obeyed in the range 0.0-3.6 µg W mL^{-1}. However, the optimum range for the determination of tungsten, as evaluated from a Ringbom plot[14], is calculated to be 0.34-3.16 ppm. The molar absorptivity and Sandell's sensitivity of the complex at 420 nm are: 5.80×10^4 dm^3 mol^{-1} cm^{-1} and 0.0032 µg cm^{-2}, respectively. For 20 µg W (VI) taken in pure solutions, the relative standard deviation of ten replicate determinations is 0.78 %. The linear regression equation is $Y = 0.295 X + 0.040$ (Y = absorbance, X = µg W mL^{-1}) and the correlation coefficient, r = 0.9963.

Stoichiometry of the complex: Two sets of equimolar solutions of tungsten and HMTB reagent (1.086×10^{-3} M and 1.629×10^{-3} M) are utilized to determine the metal to ligand ratio by Job's method of continuous variations as modified by Vosburgh and Cooper[15,16]. The absorbance values are measured at two different wavelengths, 420 and 435 nm. The obtained curves are indicative of 1:4 stoichiometry in the extracted species. This is further confirmed by the mole ratio method[17] by taking two different concentrations (1.629×10^{-3} M and 5.43×10^{-4} M) of tungsten and measuring the absorbance in each case at two wavelengths, 420 and 435 nm. The composition of the complex is further verified by the equilibrium shift method[18] at 1.629×10^{-3} M tungsten and 3.258×10^{-4}–6.516×10^{-3} M reagent concentrations, which gives the slope of the curve to be 3.7 (Fig. 2) confiming the 1:4 composition of the metal-ligand complex. By the mole ratio method the stability constant is calculated to be 5.938×10^9.

Applications: 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 interferences of a large number of metal ions especially Ti, Cr, Co, Ni, Cu, Mo, V, U, Zr, Nb, Re, Fe, platinum metals as well as many other important elements. The wide applicability of the method is further tested by analyzing several synthetic, technical and natural samples of varying compositions satisfactorily. The reproducibility of the method is tested by performing ten sets of experiments while keeping the same (2.0 µg W mL^{-1}) amount of the metal ion each time. The relative standard deviation is 0.78 %.

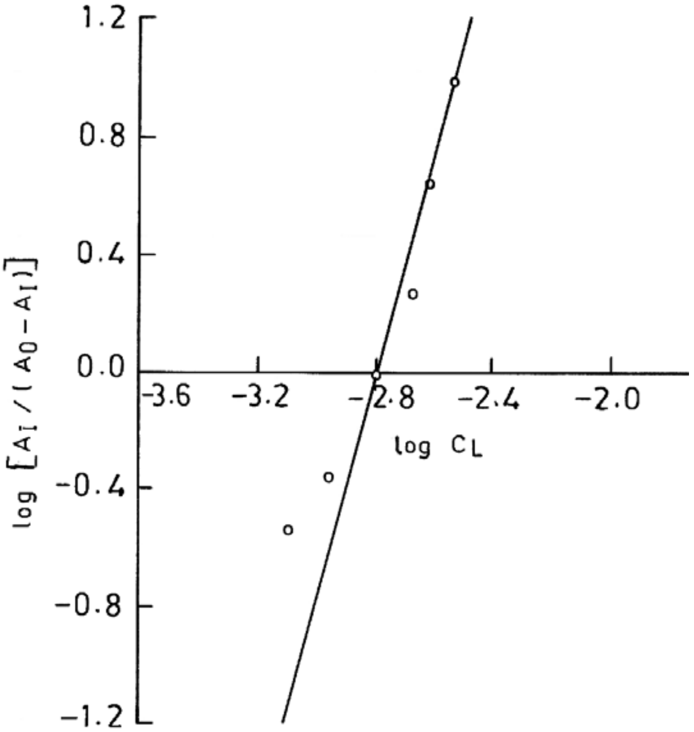


Fig. 2. Equilibrium-shift method showing a plot of log [$A_I/(A_0-A_I)$] *vs.* log C_L A_I = absorbance at a reagent concentration C_L, A_0 = absorbance at complete formation of the complex and C_L = total concentration of the reagent added
Conditions: conc. of W (VI) = 1.629×10^{-3} M; conc. of HMTB = 3.258×10^{-4}–6.516×10^{-3} M; 0.1 $HClO_4$; aqueous volume = solvent volume = 10 mL; solvent = dichloromethane; λ_{max} = 420 nm; HMTB = 3-hydroxy-2-(5´-methyl-2´-thienyl)-4-oxo-4*H*-1-benzopyran

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