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Research Article

SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF TRACE AMOUNT OF TUNGSTEN (VI) IN ALLOY SAMPLES USING 4-HYDROXYBENZALDEHYDETHIOSEMICARBAZON

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ABSTRACT

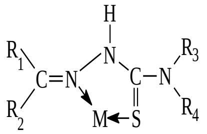
A simple ultra-sensitive non extractive spectrophotometric method for the determination of tungsten (VI) using the reagent 4-hydroxybenzaldehyde thiosemicarbazone (**4-HBTS**). The reagent 4-HBTS gives Yellow color with tungsten (VI) solution of weak acidic medium p H 6.0 and the maximum absorbance was observed at 365 nm, Beer's law is obeyed in the range.0.7354 to 7.354 µg/ml. The linear plot can be fitted into the equation $A_{356} = 0.0186C + 0.0149$. The molar absorptivity and Sand ell's sensitivity values are 1.4×10^4 L mol^{-1} cm^{-1} and 0.00128µg/cm^2 respectively. The stability constant of 1:1 tungsten (VI) - 4-HBTS complex is calculated and is found to be 6.7×10^6. The influence of interferences on the proposed method was studied and presented. The procedure was successfully applied for the determination of tungsten in different alloy samples.

Keywords: Tungsten (VI), 4-hydroxybenzaldehydethiosemicarbazone, Spectrophotometry, Alloy sample

1. INTRODUCTION

Tungsten as its oxide WO_3 was discovered in 1781 by Scheele, in the mineral then known as "tungstein" and now called Scheelite. Because of its occurrence in tungsten and in wolframite, the element was given both the names tungsten and wolfram. In German nomenclature, the element has retained the name of wolfram. English and French usage has adopted the name tungsten. Tungsten is used in high temperature applications due to its high melting point. Its use as afilament in incandescent lamps is well known. Tungsten steels are also used in springs, valves, magnetos, contact points, spark plugs and numerous other products where strength, hardness, resistant to corrosion and a high melting point are essential.

The chemical determination of tungsten is more difficult than that of many other transition metals, particularly in trace levels. It has been determined by neutron activation analysis [1], ICP-AES [2], anion exchange-ICP [3], ICP-MS [4], XRF [5, 6], voltammetry [7], electron Auger spectroscopy [8], polarography [9], differential pulse polarography [10] and AAS [11]. However, these methods are dis advantageous in terms of cost and the instruments used in routine analysis. AAS is often lacking in sensitivity and is affected by the matrix conditions of samples, such as salinity.As a result, the trace analysis of tungsten is carried out by spectrophotometric methods. Several analytical reagents have been reported for its spectro photometric determination [12-14]. Thiosemicarbazones contain nitrogen as well as sulphur. Thiosemicarbazones are good analytical reagents [15-22]. Thiosemicarbazones contain azomethine nitrogen atom and thioamide group. These reagents act as good chelating agents and form complexes with various metal ions by bonding through thioketosulphur and hydrazino- nitrogen atom.



A good number of thiosemicarbazone ligands have been derived by simply condensing aliphatic, aromatic or heterocyclic aldehydes or ketones with thiosemicarbazide.

2. EXPERIMENTAL

The absorbance and pH measurements were made on a Shimadzu UV-Visible spectrophotometer (model UV-160A) fitted with 1.0cm quartz cells and Elico digital pH meter (modelLI20) respectively.

2.1. Preparation and characterization of 4-hydroxy benzaldehydethiosemicarbazone

The reagent was prepared by simple condensation of 1 mole of 4-hydroxy-benzaldehyde(1.22gm) with 1 mole (0.92gm) of thiosemicarbazide in a clean 250ml round bottomed flask 4-hydroxybenzaldeyde was dissolved in 100ml of methanol and thiosemicarbazide was dissolved in hot water. The solutions were mixed and refluxed for two hours. On cooling brown colored product was formed which was collected by filtration. It was recrystalized using methanol and dried in vacuum.

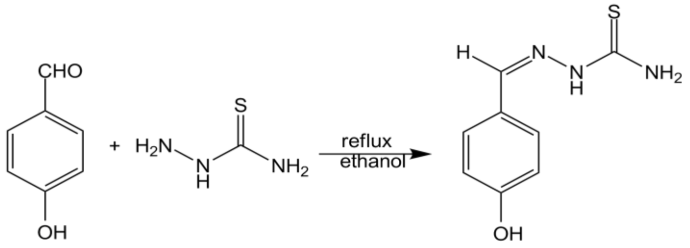


Fig-1: 4-hydroxy Thiosemicarbazide 4-HBT Benzaldehyde

The yield was 80% by weight. and the M.P. was 207-209^{0}C. The structure of the compound was established using IRspectra and NMR spectra,

2.2. Characterization

The IR spectrum of the compound was recorded using Perkin-Elmer 137 IR spectrometer in KBr. The peaks observed at 3458cm^{-1} and 3342^{-1} may be assighned to symmetric and assymetric (–N-H) steching frequency of primary amino group. The peak observed at 3028cm^{-1} may be assighned to Ar-H stretching frequency of aromatic proton, and that observed at 1595cm^{-1} to C=N stretching frequency of azomethine. The peak observed at 3218-3092 for –OH group. A strong peak observed at 1056cm^{-1} may be assigned to C=S stretching frequency. The peaks observed in the range of 1530-1360cm^{-1}frequency were charecteristic aromatic ring stretching frequency.

The ^{1}H-NMR spectrum of the compound was recorded with DRX300 NMR spectrometer in DMF solvent. The peak observed at δ value 10.74(H) was charecterstic of phenolic –OH group. The peak found at δ value 7.86(4H) may be due to aromatic protons, the peak observed at δ value 6.8 (2H) may be due to –NH_2 protons attached to thionylgroup (C=S) and the peak observed at δ value 9.0 is due to aldehydic proton. The peak at δ value 11.5 may be due to –NH proton (azomethine).

2.3. Preparation of the solutions

W (VI) solution: 0.4596gm. of sodium tungstate (AR, BDH, India) was dissolved in doubly distilled water in a 250 ml volumetric flask to get 1 x 10^{-2} M solution and standardized. The stock solution was suitably diluted to get the required concentration

Stock solution of the reagent: 0.195 g of recrystallized sample of the reagent 4-hydroxybenzaldehyde thiosemicarbazone was dissolved in DMF in a 100 ml volumetric flask to obtain the stock solution (0.1 M), and it was suitably diluted to get the required concentration. Fresh reagent solutions were prepared as and when required.

Buffer solutions: The buffer solutions are prepared by mixing 1M hydrochloric acid and 1M Sodium acetate (pH 1.0-3.0) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0). Exact pH of the solution was measured using a pH meter.

1 ml of 1 x 10^{-3} M sodium tungstate solution, 10 ml of buffer solution of required pH, 1 ml of 1 x 10^{-2} M 4-hydroxy benzaldehydethiosemicarbazone are taken in a 25 ml standard flask. The contents of the flask are made up to the mark with double distilled water. The solution is shaken well for uniform concentration. The blank solution is also prepared on the same lines but without containing the metal ion. The spectrum of the experimental solution is recorded in the wavelength range 350 to 700 nm against the respective blank solution.

3. RESULTS AND DISCUSSIONS

W (VI) reacts with 4-HBTS in weak acidic pH to give a yellowcoloured water soluble species. The colour reaction between W (VI) and 4-HBTS is instantaneous even at room temperature. The maximum absorbance λ_{max} of the yellow coloured species (complex) was observed at 365 nm which remains constant for 24 hours. Studies on the effect of pH on the absorbance revealed that the maximum colour was formed in a solution of pH 6. A tenfold excess of the reagent is adequate for complete colour development. Addition of excess of reagent has no adverse effect on absorbance.

The studies relating to the effect of W (VI) revealed that a linear relationship (Fig. 2) exists between metal ion concentration and the absorbance in the range .0.7354 to 7.354 µg/mL.

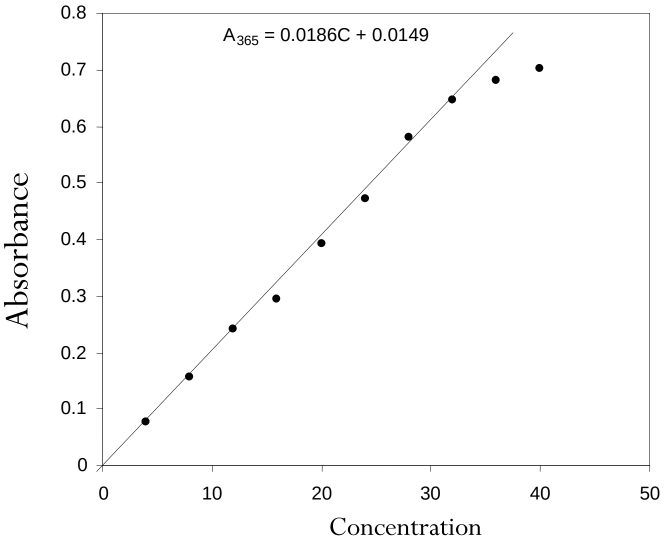


Fig 2: Effect of metal ion concentration (Beer's law)

[4-HBTS] = 1.6 x 10^{-3} M
pH = 6
λ_{max} = 365

The molar absorptivity and sandell's sensitivity are 1.2x10^{4}L.mol $^{-1}$cm^{-1} and 1.64x10^{-3}µg / cm^2 respectively. The effect of the reagent on absorbance is also studied, no linear relationship is found between the reagent and the absorbance. As the metal ion W (VI) forms a coloured complex with reagent, an attempt is made to determine the composition and the stability of the complex. Job's method (Fig. 3) and mole ratio method are conducted to make these determinations. The stability constant of 1:1 tungsten (VI) - 4-HBTS complex is calculated and is found to be 6.7×10^6.

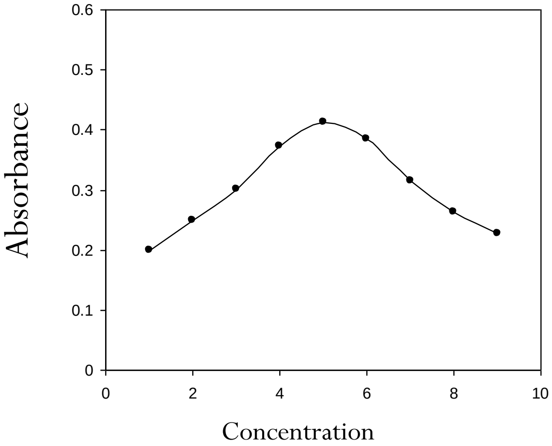


Fig 3: Job's continuous variation method

[W (VI)] = 2×10^{-4} M
[4-HBTS] = 2×10^{-4} M
PH = 6
λ_{max} = 365nm

Table-1Physico-chemical and analytical characterstics of W (VI)- 4-HBTS

Chareacteristics	Results
λ_{max} (nm)	365
p^H range (optimum)	5-6
Moles of the reagent required per mole of metal ion for complete colour development	10 folds
Molar absorptivity (Lmole $^{-1}$cm $^{-1}$)	1.4×10^4 L mol^{-1} cm^{-1}
Sandell's sensitivity(μg/cm^2)	0.00128μg/cm^2
Composition of the complex (M:L ratio)	1:1
stability constant of the complex	6.7×10^6
Standard deviation	0.000252
RSD	0.00685%

Table 2: Tolerance limit of foreign ions in the determination of tungsten (VI)

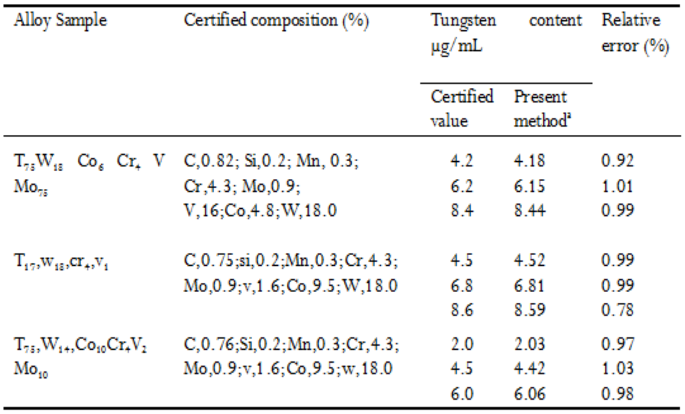
Ion added (Anions)	Tolerance limit (μg/ml)	Ion added (Cations)	Tolerance limit (μg/ml)
Chloride	141	Vanadium(IV)	24.45
Bromide	319	Cobalt(II)	4.71
Iodide	761	Molybdenum(VI)	3.07
Nitrate	496	Chromium(VI)	1.03
Acetate	472	Manganese(II)	2.19
Urea	720	Nickel(II)	4.22
Thio Urea	365	Silver(I)	6.47
Tartarate	1104	Cadmium(II)	8.99

[W (VI)] = 4×10^{-5} M
[4-HBTS]=8×10^{-4}
pH = 6
λ_{max} =365 nm

Applications of the method

The applicability of the proposed method was studied by extending it for the analysis of various tungsten alloys. The results presented in table 3 compare favorably with the certified values.

Table 3: Determination of tungsten in tungsten steels



Alloy Sample	Certified composition (%)	Tungsten content μg/mL		Relative error (%)
		Certified value	Present method^a	
T_{75},W_{18} Co_6 Cr_4 V Mo_{75}	C,0.82; Si,0.2; Mn, 0.3; Cr,4.3; Mo,0.9; V,16;Co,4.8;W,18.0	4.2	4.18	0.92
		6.2	6.15	1.01
		8.4	8.44	0.99
T_{17},w_{18},cr_4,v_1	C,0.75;si,0.2;Mn,0.3;Cr,4.3; Mo,0.9;v,1.6;Co,9.5;W,18.0	4.5	4.52	0.99
		6.8	6.81	0.99
		8.6	8.59	0.78
T_{75},W_{14},$Co_{10}$$Cr_4$$V_2$ Mo_{10}	C,0.76;Si,0.2;Mn,0.3;Cr,4.3; Mo,0.9;v,1.6;Co,9.5;w,18.0	2.0	2.03	0.97
		4.5	4.42	1.03
		6.0	6.06	0.98

4. CONCLUSIONS

A new spectrophotometric method is reported for the determination of micro gram levels of W (VI). W (VI) forms a 1:1 stable Yellow coloured complex with 4-Hydroxy benzaldehydethiosemicarbazone. The Stability constant of the complex is 6.7×10^6. Themolar absorptivity and Sandell's sensitivity are 1.4×10^4 L mol^{-1} cm^{-1} and0.00128μg/cm^2 respectively. In comparison with many expensiveinstrumental techniques and the procedures which usually require prior separation and pre concentration process and time sensitive procedures, the present method is a new, rapid, simple, sensitive and selective method for the micro determination of tungsten (VI) in the range of0.7354 to 7.354μg/mL.The method has been applied for the analysis of W (VI) in tungsten alloys.

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