

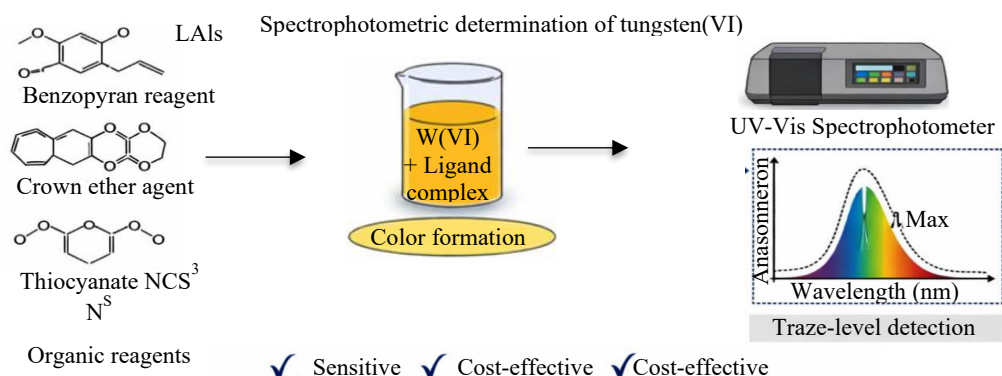
Modern Trends in Tungsten(VI) Analysis: From Smart Organic Reagents to High-Sensitivity Spectrophotometry

Parveen Kumar^{1,*}, Karan Bhola²

Abstract

The present review focuses on the spectrophotometric determination of tungsten(VI) using a wide range of organic reagents and their derivatives. Organic ligands have gained considerable importance in analytical chemistry due to their strong ability to form stable and highly colored complexes with tungsten(VI), which enhances the sensitivity and selectivity of spectrophotometric analysis. Various chromogenic reagents reported in the literature for tungsten(VI) determination have been critically examined and compared on the basis of their analytical performance and applicability. The review discusses important experimental variables affecting complex formation, including pH, acidity, solvent medium, reagent concentration, extraction conditions, and reaction time. Significant analytical parameters such as Beer's law range, molar absorptivity, Sandell's sensitivity, detection limits, precision, accuracy, and tolerance toward interfering ions have also been evaluated systematically. In addition, the coordination behavior of tungsten(VI) with different organic ligands, along with factors influencing the stability and absorbance characteristics of the resulting complexes, has been discussed in detail.

Graphical abstract



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INTRODUCTION

Tungsten, a member of the third transition series with atomic number 74, predominantly exists in its most stable oxidation state, +6. It is a greyish-white, lustrous metal that remains solid under ambient conditions. Owing to its exceptionally high melting point and remarkable thermal stability, tungsten is extensively used in high-temperature applications.

It serves as a crucial material in incandescent lamp filaments and is widely incorporated into alloys used in valves, electrical contact points, spark plugs, springs, and magnetos. These applications exploit its superior mechanical strength, hardness, and corrosion resistance properties. Furthermore, tungsten has been identified in certain biomolecular systems, where it plays a functional role in specific microorganisms, particularly in some bacteria and archaea [1–6].

Various advanced analytical techniques have been employed for the determination of tungsten, including neutron activation analysis, inductively coupled plasma atomic emission spectroscopy (ICP-AES), anion exchange ICP methods, inductively coupled plasma mass spectroscopy, polarography, differential pulse polarography, and atomic absorption spectroscopy (AAS), along with UV–visible spectrophotometry for tungsten–ligand complexes [7–10].

Among these techniques, spectrophotometric methods continue to attract considerable attention for trace-level analysis because of their inherent advantages, including operational simplicity, high sensitivity, and satisfactory precision. While most instrumental techniques require sophisticated, high-cost equipment and specialized operational expertise, spectrophotometry offers a comparatively economical and accessible alternative to other analytical techniques. Moreover, it enables the analysis of tungsten over a broad concentration range with acceptable accuracy. Consequently, UV–visible spectrophotometry remains the preferred analytical approach, particularly for routine and large-scale analyses, owing to its simplicity, rapid response, sensitivity, and selectivity [11–13].

Spectrophotometric Determination of Tungsten(VI)

Various spectrophotometric methods have been reported for the determination of trace amounts of tungsten using different organic reagents (ligands). However, many of these methods suffer from limitations such as low sensitivity, poor selectivity, and procedural complexity [14–17].

Preparation of Stock Solution

A standard stock solution (100 mL) of tungsten(VI), containing 1 mg mL⁻¹ of the metal ion, was prepared by dissolving an accurately weighed amount (0.179 g) of analytical-grade sodium tungstate in distilled water. The solution was then standardized using the oxine method. Working solutions at the µg mL⁻¹ level were obtained by appropriate dilution of the stock solution [18–22].

Stock solutions of other metal ions were prepared at the mg mL⁻¹ level by dissolving their respective high-purity sodium or potassium salts in deionized water or dilute acid. These solutions were further diluted as required to obtain concentrations in the µg mL⁻¹ range [23–30].

Spectrophotometric Determination of Tungsten(VI) Using Organic Reagents

The complexation behavior of tungsten(VI) with 2-hydroxy-5-chlorothiophenol (HCTP) in the presence of hydrophobic amines has been extensively investigated using spectrophotometry [31]. Hydrophobic amines, such as aniline, N-methylaniline, and N,N-dimethylaniline, facilitate the formation of mixed ligand complexes. In weakly acidic media (pH 4.2–5.4), stable ternary complexes were formed with a stoichiometric ratio of W(VI):HCTP:amine = 1:2:2. These complexes exhibited maximum absorbance in the range of 465–475 nm, with molar absorptivity values of $(2.4\text{--}2.6) \times 10^4$ L mol⁻¹ cm⁻¹. The method has been successfully applied to determine tungsten in steel samples.

3-Hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (HTB) has been reported as an efficient analytical reagent for the determination of tungsten(VI) [32]. The reagent forms a 1:2 (metal:ligand) complex that is extractable into dichloromethane from a 0.2 M HCl medium. Beer's law is obeyed up to 2.8 µg mL⁻¹ of tungsten. The molar absorptivity and Sandell's sensitivity at 415 nm were 6.45×10^4 L mol⁻¹ cm⁻¹ and 0.0029 µg cm⁻², respectively.

Dibenzo-18-crown-6 has also been used for the spectrophotometric determination of tungsten(VI) under acidic conditions [33]. The method involves complexation and extraction using crown ether

systems, with an emphasis on the influence of multivalent metal ions. Beer's law was valid over the concentration range of 0.18–18.3 $\mu\text{g mL}^{-1}$, with a molar absorptivity of $1.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 415 nm. The detection and quantification limits were reported to be 0.7–1.8 $\mu\text{g cm}^{-3}$. This method has been successfully applied to high-speed steel samples.

6-chloro-3-hydroxy-2-phenyl-4-oxo-4H-1-benzopyran (CHPB) has been proposed as a sensitive analytical reagent for the determination of tungsten(VI) [34]. The reagent forms a yellow 1:2 (metal:ligand) complex in a hydrochloric acid medium (0.04–0.32 M HCl), which is extractable into chloroform. The complex exhibited a maximum absorbance at 420 nm and remained stable for approximately 20 h in the organic phase. The molar absorptivity and Sandell's sensitivity were $3.125 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.00294 $\mu\text{g cm}^{-2}$, respectively, as shown in Figure 1. Beer's law was obeyed in the concentration range of 0–2.9 $\mu\text{g mL}^{-1}$.

4-Hydroxybenzaldehyde thiosemicarbazone (4-HBTS) has been used as a reagent for the determination of tungsten(VI) [35]. In a weakly acidic medium (pH 6.0), it forms a yellow-colored complex with a maximum absorbance at 365 nm. Beer's law was valid over the concentration range of 0.7354–7.354 $\mu\text{g mL}^{-1}$, with a calibration equation of $A = 0.0186C + 0.0149$. The molar absorptivity and Sandell's sensitivity were $1.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.00128 $\mu\text{g cm}^{-2}$, respectively. The stability constant of the 1:1 complex was 6.7×10^6 . The method showed good tolerance toward interfering ions and has been successfully applied to alloy samples.

Ethopropazine hydrochloride has also been reported to be an effective reagent for the determination of tungsten(VI) [36]. The formed complex was extractable into chloroform and exhibited a maximum absorbance at 404 nm. Beer's law was obeyed in the concentration range of 1–15 $\mu\text{g mL}^{-1}$, with an optimum working range of 2.3–12.9 $\mu\text{g mL}^{-1}$. The influence of foreign ions was systematically investigated, demonstrating the acceptable selectivity of the method.

4-Hydroxybenzaldehyde thiosemicarbazone (4-HBTS) [37] has been effectively employed as an analytical reagent for the spectrophotometric determination of tungsten(VI). In a weakly acidic medium (pH 6.0), the reagent forms a stable yellow complex that exhibits a maximum absorbance at 365 nm. Beer's law was obeyed over the concentration range of 0.7354–7.354 $\mu\text{g mL}^{-1}$. The calibration plot followed the linear equation $A_{365} = 0.0186C + 0.0149$. The molar absorptivity and Sandell's sensitivity were determined to be $1.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.00128 $\mu\text{g cm}^{-2}$, respectively. The stability constant of the 1:1 (W(VI):4-HBTS) complex was calculated to be 6.7×10^6 . The method demonstrated good tolerance toward interfering ions and was successfully applied to the determination of tungsten in alloy samples, as shown in Figure 2.

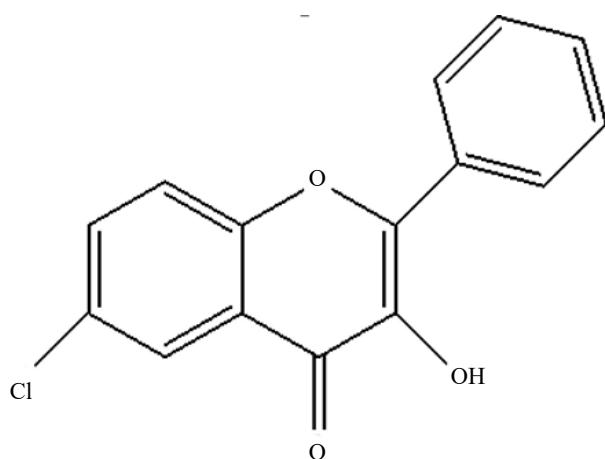


Figure 1. Chemical structure of 6-chloro-3-hydroxy-2-phenyl-4H-chromen-4-one.

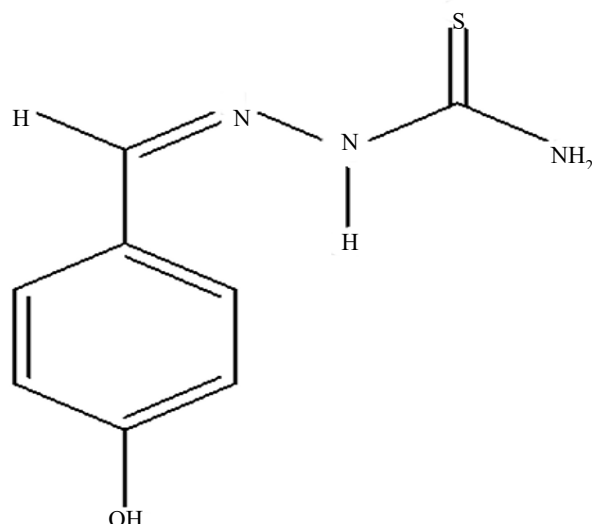


Figure 2. Chemical structure of (4-hydroxybenzylidene)thiosemicarbazide.

3,4-dihydroxybenzaldehyde isonicotinoylhydrazone (3,4-DHBINH) has also been reported as a suitable chromogenic reagent for tungsten(VI), forming a green-colored complex with a maximum absorbance at 374 nm, indicating its potential for analytical applications.

6-chloro-3-hydroxy-2-[2-(5-methylfurfural)]-4-oxo-4H-1-benzopyran (CHMFB) [38] has been used as an analytical reagent for the determination of tungsten(VI). In perchloric acid medium, it forms a yellow complex that can be quantitatively extracted into chloroform. The complex exhibited maximum absorbance in the range of 429–437 nm. The stoichiometry of the complex was found to be 1:2 (metal:ligand), with molar absorptivity and Sandell's sensitivity values of $2.16 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0085 \mu\text{g W cm}^{-2}$, respectively. Beer's law was valid over the concentration range of 0–2.6 $\mu\text{g mL}^{-1}$.

The reagent 3-hydroxy-2-(4-methoxyphenyl)-4-oxo-4H-1-benzopyran (HMPB) (Fig. 3 B) [39] forms a yellow complex with tungsten(VI) in a perchloric acid medium with a stoichiometric ratio of 1:4. The complex was extracted into dichloromethane and exhibited a maximum absorbance in the range of 403–411 nm. Beer's law was obeyed up to 3.8 $\mu\text{g mL}^{-1}$. The molar absorptivity and Sandell's sensitivity were $3.78 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0049 \mu\text{g W cm}^{-2}$, respectively.

Similarly, 6-chloro-3-hydroxy-2-(2-thienyl)-4-oxo-4H-1-benzopyran (CHTB) (Figure 3.C) [40] has been proposed for spectrophotometric determination. The reagent forms a yellow complex with tungsten(VI) in a hydrochloric acid medium (1:3 ratio), which is extractable into chloroform and exhibits maximum absorbance at 417–423 nm. Beer's law was valid up to 3.0 $\mu\text{g mL}^{-1}$, with a molar absorptivity of $4.05 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of $0.0045 \mu\text{g W cm}^{-2}$.

3-Hydroxy-2-(3-methyl-2-thienyl)-4-oxo-4H-1-benzopyran (HMTB) [41] forms a colored complex with tungsten(VI) in a perchloric acid medium, which is extractable into dichloromethane and shows maximum absorbance in the range of 415–423 nm. Beer's law was valid up to 3.6 $\mu\text{g mL}^{-1}$. The molar absorptivity and Sandell's sensitivity were $5.80 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0032 \mu\text{g W cm}^{-2}$, respectively.

6-Chloro-3-hydroxy-2-(4-methoxyphenyl)-4-oxo-4H-1-benzopyran (CHMPB) [42] also produces a colored complex with tungsten(VI) in a hydrochloric acid medium. The complex was extracted into dichloromethane and exhibited a maximum absorbance at 415 nm. Beer's law was valid up to 2.09 $\mu\text{g mL}^{-1}$, with a molar absorptivity of $6.08 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of $0.0030 \mu\text{g W cm}^{-2}$.

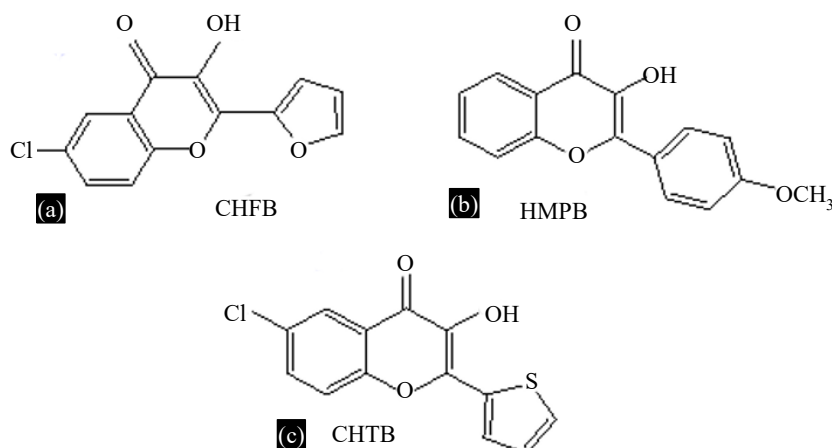


Figure 3. Chemical structures of synthesized flavonoid derivatives: (a) CHFB, (b) HMPB, and (c) CHTB.

The reagent 3-hydroxy-2-[1'-phenyl-3'-(p-chlorophenyl)-4'-pyrazolyl]-4-oxo-4H-1-benzopyran (HPCPB) [43] forms a 1:4 colored complex with tungsten(VI) in a perchloric acid medium. The complex was extracted into chloroform and exhibited maximum absorbance in the range of 403–407 nm. Beer's law was valid up to $1.3 \mu\text{g mL}^{-1}$, with a molar absorptivity of $5.709 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of $0.0032 \mu\text{g W cm}^{-2}$.

6-Chloro-3-hydroxy-2-(2-furyl)-4-oxo-4H-1-benzopyran (CHFB) (Figure 3(a)) [44] forms a light yellow 1:2 complex with tungsten(VI) in a hydrochloric acid medium. The complex was quantitatively extracted into dichloromethane and exhibited a maximum absorbance in the range of 414–422 nm. Beer's law was valid up to $2.0 \mu\text{g mL}^{-1}$. The molar absorptivity and Sandell's sensitivity were $2.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0083 \mu\text{g W cm}^{-2}$, respectively.

Pyrocatechol violet (PCV) forms both binary and ternary complexes with W (VI). In acidic medium (pH 1–4), a 1:1 complex is formed, whereas in the presence of cetylpyridinium bromide (CPBr), a ternary ion-association complex with a stoichiometry of 1:1:2 is obtained. These systems exhibit enhanced molar absorptivity ($\epsilon \approx 6.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at 670 nm), improved sensitivity, and extended linear ranges for the determination of tungsten.

Preconcentration techniques have significantly enhanced the sensitivity of spectrophotometric analysis. For instance, tungsten(VI) has been preconcentrated as its thiocyanate complex using Amberlite XAD-1180 resin [45], followed by spectrophotometric determination using potassium thiocyanate and stannous chloride. The method demonstrated excellent recoveries ($>95\%$) and low detection limits ($\sim 12 \mu\text{g L}^{-1}$).

Similarly, nanostructured titanium dioxide (TiO_2) has been employed for the selective adsorption and preconcentration of tungsten(VI), followed by spectrophotometric determination [46]. This approach provided a significant enrichment factor (≈ 50), low detection limit (1.2 ng mL^{-1}), and high precision ($\text{RSD} \approx 2.3\%$).

A systematic assessment of thiocyanate-based spectrophotometric methods [47] for the determination of Mo and W has been undertaken within the broader context of trace metal ion analysis. The investigation confirmed that Mo underwent a two-electron reduction in the presence of stannous chloride and revealed the formation of multiple species in different oxidation states. The specific oxidation state responsible for the observed color development was identified, and various limitations associated with the color formation process were critically discussed. When properly controlled, these procedures demonstrate enhanced selectivity, sensitivity, and analytical reliability compared to conventional methods for thiocyanate detection.

The extraction characteristics of tungsten as its α -benzoinoxime complex in chloroform were examined with respect to reagent concentration and acidity. Optimal extraction efficiency was achieved in hydrochloric acid media within the acidity range of 0.01–1 M, with particularly favorable results at 0.5 M HCl. This approach enables the effective separation of tungsten from iron and most other interfering elements. However, molybdenum is co-extracted quantitatively with tungsten, allowing their simultaneous determination using the thiocyanate method. The absorbance in the isopropyl ether phase was measured at 405 nm and 490 (or 475) nm to facilitate accurate quantification. Under optimized conditions, tungsten can be determined at levels as low as 1 μg in the presence of 10 μg of molybdenum without requiring prior separation.

Further advancements include ion exchange preconcentration methods [48]. A preconcentration method using Amberlite XAD-7 resin was developed for the spectrophotometric determination of trace tungsten. This method is based on the adsorption of tungsten as a reduced W(V)–thiocyanate complex formed with tin(II) chloride. It shows high selectivity, with negligible interference from common ions such as Ca^{2+} , Mg^{2+} , Na^+ , SO_4^{2-} , F^- , NO_3^- , Cu^{2+} , Fe^{3+} , and Mo^{6+} . The procedure was successfully applied to hot spring water, providing recoveries above 95% with good precision and accuracy (RSD < 5%, error < 3%).

A ternary ion-association complex of tungsten(VI) with 4-nitrocatechol and thiazolyl blue (MTT) [49] was developed using an extraction–spectrophotometric approach. The complex, with a stoichiometric ratio of 1:2:2 (W:NC:MTT), exhibits maximum absorbance at 415 nm with a molar absorptivity of $2.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and follows Beer's law up to 8.8 $\mu\text{g cm}^{-3}$ concentration. The method showed good sensitivity, with detection and quantification limits of 0.27 $\mu\text{g cm}^{-3}$ and 0.92 $\mu\text{g cm}^{-3}$, respectively. It demonstrates high precision and accuracy (RSD 0.53%, error 0.2%) and has been successfully applied to the determination of W in ferrous metallurgical samples.

A combined ion-exchange–spectrophotometric method [50] was developed for the simultaneous determination of Mo and W in silicate rocks. Following sample decomposition using a mixture of sulfuric, nitric, and hydrofluoric acids, the analytes were selectively separated by anion exchange in an acidic sulfate medium containing hydrogen peroxide. The retained species were subsequently eluted using a sodium hydroxide–sodium chloride solution. This adsorption–desorption process enables effective preconcentration and separation, facilitating simultaneous determination using a dithiol reagent. The method has been validated using standard reference materials, demonstrating good accuracy and reliability, and has been successfully applied to complex matrices such as geological and metallurgical samples.

Other notable tungsten can be determined spectrophotometrically in spongy zirconium using zinc bithiomol [51], which forms a blue-green complex that is extractable into chloroform. The method follows Beer's law in the concentration range of 0.5–20 $\mu\text{g mL}^{-1}$, indicating good linearity and applicability for quantitative analysis.

2,4-Dihydroxybenzenethiol [52] has been employed as an analytical reagent for the spectrophotometric determination of W (VI). It forms a violet-colored complex at pH 1.5, which is extractable into isoamyl alcohol and exhibits a maximum absorbance at 490 nm. The complex remained stable for up to 1.5 h at room temperature and demonstrated a Sandell's sensitivity of 0.046 $\mu\text{g W cm}^{-2}$ and a molar absorptivity of $0.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

In polyoxometalate systems, tungsten(VI) has been determined spectrophotometrically using tiron (disodium 1,2-dihydroxybenzene-3,5-disulfonate) [53], with absorption in the wavelength range of 352–400 nm. Additionally, tungsten(VI) forms a red-colored complex with 2,3,7-trihydroxy-9-(3,5-dichloro-4-hydroxyphenyl) fluorone in the presence of cetyltrimethylammonium bromide (CTMAB) in 0.6 M hydrochloric acid medium, exhibiting maximum absorbance at 536 nm with a high molar absorptivity of $1.28 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and adherence to Beer's law up to 0.4 $\mu\text{g mL}^{-1}$.

Similarly, 2,3,7-trihydroxy-9-(2,5-dibromo-o-nitrophenyl) fluorone [54], in the presence of CTMAB, has been utilized as a sensitive spectrophotometric reagent, forming a red complex with a maximum absorbance at 537 nm. The method showed a high molar absorptivity of $5.64 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and a detection limit of $4.12 \mu\text{g mL}^{-1}$.

3-Hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (HTB) [32] has been employed as an effective reagent for the extractive spectrophotometric determination of tungsten(VI). The method is based on the formation of a 1:2 (metal:ligand) complex, which is extracted into dichloromethane from a 0.2 M hydrochloric acid medium. The complex exhibits maximum absorbance at 415 nm and obeys Beer's law up to $2.8 \mu\text{g mL}^{-1}$, with a molar absorptivity of $6.45 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of $0.0029 \mu\text{g cm}^{-2}$. The method shows high selectivity with minimal interference from a wide range of coexisting ions and is suitable for the analysis of complex sample matrices.

A spectrophotometric method for the determination of tungsten(VI) has been developed using 2,6-dithiol-4-methylphenol in the presence of hydrophobic amines such as aniline, N-methylaniline, and N,N-dimethylaniline. The mixed complex was formed in a weakly acidic medium (pH 3.2–4.5) with a stoichiometric ratio of W(VI):DTMF:Am = 1:2:2. The complex exhibited maximum absorbance in the range of 480–490 nm, with a molar absorptivity of $(2.6\text{--}2.8) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Based on these findings, the method was successfully applied for the spectrophotometric determination of tungsten in soil samples.

A catalytic spectrophotometric method based on the thiocyanate-activated tungsten-catalyzed malachite green–Ti(III) [55] reaction allows determination at 616 nm, with linear ranges of 1.2–10 and 10–80 ng mL^{-1} , a detection limit of 0.15 ng mL^{-1} , and an RSD of 1.8%. Another method based on molybdenum-tungsten isopoly anion–malachite green association in the presence of a non-ionic surfactant shows linearity in the range of $10^{-6}\text{--}10^{-5} \text{ mol L}^{-1}$ with a molar absorptivity of $7.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and tolerates over 100-fold excess of molybdenum.

Table 1. Comparison of spectrophotometric methods for tungsten(VI) determination (ascending order of molar absorptivity).

S.N.	Reagent/ligand	λ_{max} (nm)	Beer's law range ($\mu\text{g mL}^{-1}$)	Molar absorptivity ϵ ($\text{L mol}^{-1} \text{ cm}^{-1}$)	Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	Remarks	Ref .
1	2,4-Dihydroxybenzenethiol	490	Not specified	0.4×10^4	0.046	Low sensitivity, violet complex	[52]
2	Ethopropazine hydrochloride	404	1–15	Not specified	20.03	Moderate sensitivity	[36]
3	CHMFB	429–437	0–2.6	2.16×10^4	0.0085	Extractive method	[38]
4	CHFB	414–422	0–2.0	2.2×10^4	0.0083	Light yellow complex	[44]
5	HCTP + amines	465–475	Not specified	$(2.4\text{--}2.6) \times 10^4$	-	Mixed ligand system	[31]
6	CHPB	420	0–2.9	3.125×10^4	0.00294	Stable complex (20 h)	[34]
7	HMPB	403–411	0–3.8	3.78×10^4	0.0049	Good selectivity	[39]
8	CHTB	417–423	0–3.0	4.05×10^4	0.0045	Extractive method	[40]
9	HTB	415	Up to 2.8	6.45×10^4	0.0029	High sensitivity	[32]
10	HMTB	415–423	Up to 3.6	5.80×10^4	0.0032	Good precision	[41]
11	CHMPB	415	Up to 2.09	6.08×10^4	0.0030	Highly sensitive	[42]
12	HPCPB	403–407	Up to 1.3	5.709×10^4	0.0032	Selective method	[43]
13	PCV–CPBr (ternary)	670	0.2–23	6.1×10^4	-	Enhanced sensitivity	-
14	Fluorone derivative (CTMAB)	536–537	Up to 0.4	1.28×10^5	-	Very high sensitivity	[54]

Advanced analytical strategies, such as microwave-assisted digestion, have been applied for the determination of tungsten in ores using thiocyanate spectrophotometry. The digestion was carried out with 40 mL of NaOH solution (25 g L^{-1}) at medium-high microwave power for 30 min. The method showed a detection limit of $0.5 \mu\text{g mL}^{-1}$ and good precision ($\text{RSD} < 2.3\%$), with results consistent with those of conventional sample preparation techniques.

Additionally, a spectrophotometric method [56] combined with artificial neural networks was developed for the simultaneous determination of Mo (VI) and W (VI) in polyoxometalates, providing improved analytical performance. MALDI-TOF and LDI-TOF mass spectrometry techniques were also evaluated, with LDI-TOF MS proving effective for the rapid determination of the Mo:W ratio in polyoxometalates, as shown in Table 1.

Similarly, 3-hydroxy-2-(2'-furyl)-4-oxo-4H-1-benzopyran [57] forms a yellow complex with tungsten(VI), which is extractable into dichloromethane with a maximum absorbance at 410 nm. The method follows Beer's law up to $2.8 \mu\text{g W mL}^{-1}$, with a molar absorptivity of $4.88 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity of $0.0038 \mu\text{g cm}^{-2}$.

CONCLUSION

This review provides a systematic overview of the spectrophotometric determination of tungsten(VI) using different organic chromogenic reagents and their derivatives. The reported methods have considerable analytical significance owing to their simplicity, sensitivity, selectivity, rapidity, and cost-effectiveness for routine analysis. Various classes of organic ligands, such as benzopyran derivatives, thiosemicarbazones, hydrazones, fluorones, and sulfur-containing reagents, have been successfully utilized to form stable and intensely colored tungsten(VI) complexes with favorable spectrophotometric characteristics. Extractive spectrophotometric procedures and preconcentration techniques considerably improved the analytical sensitivity and selectivity for trace and ultra-trace determination of tungsten(VI). Furthermore, the development of ternary complex systems, ion-association complexes, and catalytic and kinetic spectrophotometric methods has enhanced the overall analytical applicability of these procedures. However, certain limitations, including interference from foreign ions, dependence on toxic organic solvents, and difficulties associated with complex sample matrices, persist.

Future research should therefore be directed towards the development of environmentally benign reagents, green analytical methodologies, solvent-free systems, nanostructured materials, and chemometric approaches to improve the analytical accuracy, selectivity, sensitivity, and automation of tungsten(VI) determination.

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