Liquid-Liquid Extraction- Spectrophotometric Investigation of Three Ternary Complex Of Tungsten

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ABSTRACT

Complex formation and liquid-liquid extraction were studied in 9 different systems, containing tungsten(V), o-hydroxythiophenol derivative (HTPDs) {2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HITP)}, and an - hydrophobic amines (AP) {As hydrophobic amine 2(N, N-dimethylaminomethyl)-4-chlorphenol (AP1) and 2(N, N-dimethylaminomethyl)-4-bromphenol (AP2), 2 (N, N-dimethylaminomethyl) - 4-yodophenol (AP3) were used}. The absorption maxima (λ_{max}) of the ternary W(V)- HTPDs-AP complexes lie in the range of 461-490 nm. Molar coefficients of absorption make (2.0-2.8)×104 L mol^{-1} cm^{-1}.Concentration of the reagents {HTPDs (1.2 ×10-3 M) and AP (2 × 10–3 M)}, pH of the aqueous(pH 3.5-5.5) medium, and shaking time (5-8 minutes) were subjects of optimization experiments. Formation of ternary complexes with a composition of 2:2:2 was demonstrated by a set of different methods. Some key characteristics concerning the analytical application of the studied liquid-liquid extraction-chromogenic systems were established as well.

The proposed method were applied to the determination of tungsten in steel and samples of soil.

KEYWORDS: Ttungsten, liquid-liquid extraction, ion-association; 2:2:2 complex, o-hydroxythiophenol.

1. Introduction

A great variety of photometric reagents is known for the determination of tungsten. However, the studies aiming to find and investigate new photometric reagents with different functional groups are still going on. The very sensitive, fairly selective direct spectrophotometric method for the determination of trace amount of W(V) with Toluene-3,4-dithiol has been developed. The method was successfully applied in the determination of tungsten in environmental, and biological samples [1-3].

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 [1,3]. Many organic reagents 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 [1,3,6]. This has appreciated to search for new better methods and accordingly,we have synthesized several very effective reagents - o-hydroxythiophenol derivative (HTPDs, L) {2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-

bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HITP)} has been used as a complexing agent for tungsten (VI) in the spectrophotometric determination of metal ion to meet the above requirements.

In the present paper, we report results from liquid-liquid extraction-spectrophotometric experiments on 9 different systems, each of which containing W(VI), a HTPDs and an - aminophenols (AP) {As aminophenole 2(N, N-dimethylaminomethyl)-4-chlorphenol (AP1) and 2(N, N-dimethylaminomethyl)-4-bromphenol (AP2), 2 (N, N-dimethylaminomethyl) -4-yodophe-nol (AP3) were used}. We propose new procedures for determining molybdenum in soils and plants.

2. Materials and Methods

2.1. Reagents and instrumentation

A stock solution containing 1 $mgmL^{-1}$ of tungsten was used. A weighed portion (1.7941 g) of sodium tungstate $Na_2WO_4 \cdot 2H_2O$ (reagent grade) was dissolved in a 0.5 M NaOH solution. The concentration of the tungsten solution was adjusted gravimetrically by sedimenting tungsten in the form of H_2WO_4 and weighing WO_3 [2, 7]. Working solutions with the tungsten concentration of 0.1 mg/mL were prepared by diluting the stock solution. Stock solutions of other metal ions are prepared at mg mL^{-1} level by dissolving their commonly available pure grade sodium or potassium salts in deionized water or dilute acid. They are suitably diluted to give μg mL^{-1} level concentration of the metal ions.

Chloroform is used for extraction of W(VI) – HTPDs-AP complex. HTPDs is prepared by reported methods [8] as follows.

An optimum acidity was created by means of 0.01 M HCl or an ammonium acetate buffer solution and controlled using an I-120.2 potentiometer equipped with a glass electrode. The absorbance of the extracts was measured using a KFK-2 photocolorimeter (USSR), a SF-26 spectrophotometer (USSR), equipped with 5 and 10 mm pathlength cells. Muffle furnace was used for dissolution of the samples.

2.2. Procedure for determining the optimum conditions

Portions of a working tungsten solution, 0.1 to 0.8 mL with an increment of 0.1 mL, 1.0-2,0 mL of 0.01 M HCl, and 0.3-0.5 mL of a 0.01 M HTPDs solution were placed in calibrated test tubes with ground stoppers. The mixture was stirred thoroughly for 5 min to reduce tungsten, and 2.0-3.0 mL of a 0.01 M solution of AP was added. The volume of the organic phase was adjusted to 5 mL with chloroform, and the volume of the aqueous phase was brought to 20 mL with distilled water. After the formation of the hydroxythiophenolate complex of tungsten, it was extracted, and the absorbance of extracts was measured by a KFK-2 photoelectrocolorimeter at 490 nm.

2.3. Studies on the oxidation state of tungsten

In acidic medium, HTPDs exhibit reducing properties [9-11]. Hence, in the complex formation with HCTP, tungsten (VI) is reduced to tungsten (V) by the reagent itself. This fact was confirmed by ESR spectrometry [11].

2.4. Charge of the complex tungsten

The present study is concerned with the investigation of W (V) interaction with HTPDs, resulting in the formation of colored complexes insoluble in nonpolar solvents. To determine the sign of the complex charge, ion exchange chromatography was used: AV-17 anion exchanger in chloroform absorbs a part of solution; the chromatographic column is colored in orange, and tungsten is not detected in the filtrate. The anion complex is extracted in the presence of a hydrophobic amine, wherein the complex stability increases, and the color becomes more saturated. To neutralize the charge of the anion complex, aminophenol is used as a hydrophobic amine, which transforms into a aminophenol ion in acidic medium.

Complexing agents may be a dibasic (HCTP, HBTP, HITP, H_2L) weak acid, and depending on pH of the medium may be in molecular and anionic forms.

The synthesized compounds were characterized by physicochemical methods: IR [16] and NMR spectroscopy (Table 2).

2.5. Determination of tungsten in different objects

2.5.1. Determination of tungsten in steels

0.1 g weighed sample of steel [composition steel EU-45 (0.24% of C, 0.60% of Mn, 0.03% of Si, 3.30% of Cr, 0.50% of Ni, 0.50% of W, 0.50% of Mo, 0.30% of V, and the rest of Fe)] was dissolved under heating in 4 mL of freshly prepared mixture of HCl and HNO3 (3: 1) in the presence of a few drops of HF. After dissolution, 0.5 mL of HCOOH is added, and the mixture is

Table 2. Results of studies of IR and NMR spectroscopy HTPDs

Reagent	IR (KBr) [16]	1H NMR (300.18 MHz, C_6D_6)
HCTP	3460 см$^{-1}$ ν (OH), 2570см$^{-1}$ ν(SH), 1580 см$^{-1}$ ν(C6H5)	δ 5.70 (s, 1H- OH), δ 3.40(s, 1H - SH), δ 7.05 (s, 2H Ar-H), δ 6.25 (s, 2H Ar-H).
HBTP	3458 см$^{-1}$ ν(OH), 2568 см$^{-1}$ ν(SH), 1550 см$^{-1}$ ν(C6H5)	δ 5.60 (s, 1H- OH), δ 3.35(s, 1H- 1SH), δ 6.85 (s, 1H Ar-H), δ 7.15 (s, 2H Ar-H)
HITP	3456 см$^{-1}$ ν(OH), 2578 см$^{-1}$ ν(SH), 1570 см$^{-1}$ ν(C6H5)	δ 5.55 (s, 1H- OH), δ 3.32(s, 1H- 1SH), δ 6.80 (s, 1H Ar-H), δ 7.30 (s, 2H Ar-H)

heated until the decomposition of HNO_3 occurs. After cooling, the mixture is transferred to a 50 mL volumetric flask and diluted up to the mark with water. An aliquot portion of the resulting solution is transferred to a separatory funnel; 3.0 mL of 0.01 M HCl and 0.3-0.5 mL of a 0.01 M HTPDs solution were added, and, after thorough mixing, 2.0-3.0 mL of a 0.01 M AP solution was added. The volume of the organic phase was adjusted to 5 mL with chloroform, and the volume of the aqueous phase was brought to 20 mL with distilled water. The mixture is shaken for 5-8 min. After layering of the phases, the absorbance of extracts is measured using a KFK-2 photocolorimeter at 490 nm in cuvettes of 0.5 cm in thickness. The tungsten concentration is found from the calibration curve. The results of the determination of tungsten in steel demonstrate the reliability of the proposed procedure. The analysis of this steel by the proposed method, the concentration of tungsten is found to be 0.497± 0.009% ($n = 9$, $P = 0.95$, RSD = 4.7%).

2.5.2. Determination of tungsten in soils

The proposed procedures for the determination of tungsten were applied to its determination in light-chestnut soil from the Caspian zone. A 0.5 g weight was finely ground in an agate mortar and calcined in muffle furnace for 3 h. After cooling, the sample was treated and dissolved in a graphite cup in a mixture of 16 mL of HF (conc.), 5 mL of HNO_3 (conc.), and 15 mL of HCl (conc.) at 50-60°C to remove excess hydrogen fluoride. A further 8 mL portion of HNO_3 (conc.)

was added triply to the solution that was each time evaporated to 5-6 mL. After that, the solution was transferred into a 100 mL volumetric flask and its volume was brought to the mark with distilled water. Tungsten was determined in aliquot portions of the solution using the proposed procedures.

3. Results and Discussion

3.1. The Choice of the Extractant

For the extraction of complexes, we used $CHCl_3$, $C_2H_4Cl_2$, CCl_4, C_6H_6, C_6H_5-CH_3, C_6H_5Cl, *iso*-C_4H_9OH, *iso*-$C_5H_{11}OH$, *n*- C_4H_9OH and their mixes. Extractability of complexes was estimated in coefficient of distribution (D) and extent of extraction (R%) [9]. Chloroform, dichloroethane and chlorobenzene appeared to be the best extractants. Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. After a single extraction with chloroform about 96.2-98.8% of tungsten was extracted as an ion associate. Further researches were conducted with chloroform. The concentration of tungsten in the organic phase was determined with toluene-3,4-dithiol by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference.

3.2. Influence of the pH of the Aqueous Phase

Studying of dependence of a complex formation from pH showed that, the exit of complexes of tungsten is maximum at pH 4.5-5.5. Extraction of W (V) enhanced with the increase in the acidity of the initial solution but further increase in acidity lead to the gradual decrease of recovery, which was obviously associated with a decrease in the concentration of the ionized form of o-hydroxythiophenol derivatives. Probably, it is present in the solution in the non-dissociated state. At pH≥7.1 the complexes were hardly extracted, obviously because of the decrease in the degree of AP protonation. The effect of pH on the intensity of the colour reaction is shown in the Fig.1 (Table 1).

Fig. 1. *Absorbance of W(V)-HTPDs-AP complexes in chloroform vs. pH of the aqueous phase.* $C_W = 1.09 \times 10^{-5}$ mol L^{-1}, HTPDs = $(2.2-2.8) \times 10^{-3}$ mol L^{-1}, $C_{AP} = (2.0-2.5) \times 10^{-3}$ mol L^{-1}, λ=490 nm, SF-26, ℓ=1.0 cm

It could be seen that W(V)- HCTP-Am species are extracted in a great extent at pH values in the range 2.5-7.1 (with AP1), 2.3-6.9 (with AP2) or 2.1-6.8 (with AP3). W-HBTP-Am complexes are

extracted at low pH: 2.2-6.9 (with AP1), 2.0-6.8 (with AP2) or 1.7-6.7 (with AP2). W- HITP-Am complexes are extracted at lower pH: 2.0-6.6 (with AP1), 1.8-6.4 (c AP2) or 1.5-6.2 (with AP3). Existence of one maximum peak of absorbance in the specified limits of pH confirms the assumption of formation of one complex connection. The nature of acids (HCl, H_2SO_4) almost does not influence a complex formation of tungsten with o-hydroxythiophenol derivatives and AP.

3.3. Electronic Absorption Spectra

The absorption maxima (λ_{max}) of the ternary W(V)- HTPDs-AP complexes lie in the range of 461-490 nm (Fig. 2, Table 1). All colour reactions were very contrast since the initial solutions are colourless (λ_{max} (HTPDs) = 283-290 nm). Thus, bathochromic shift makes 171-207 nm. Close values of maxima of light absorption allow to draw a conclusion that the formed complexes were ionic associates. Contrast of reactions was high i.e. initial reagents are colourless while complexes are intensively painted. Molar coefficients of absorption make (2.0-2.8)×104 L $mol^{-1}.cm^{-1}$.
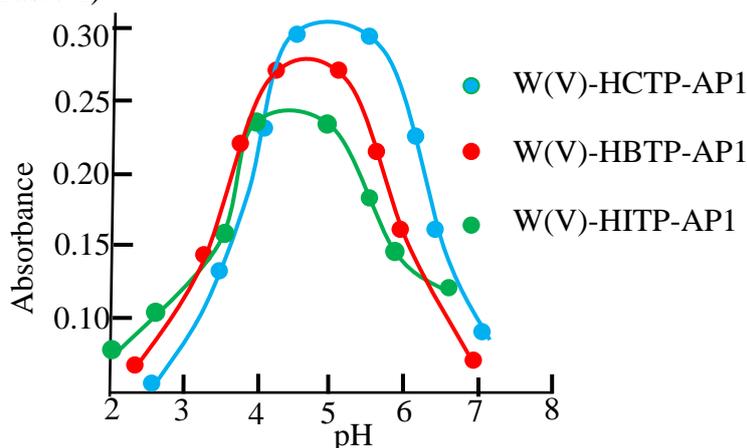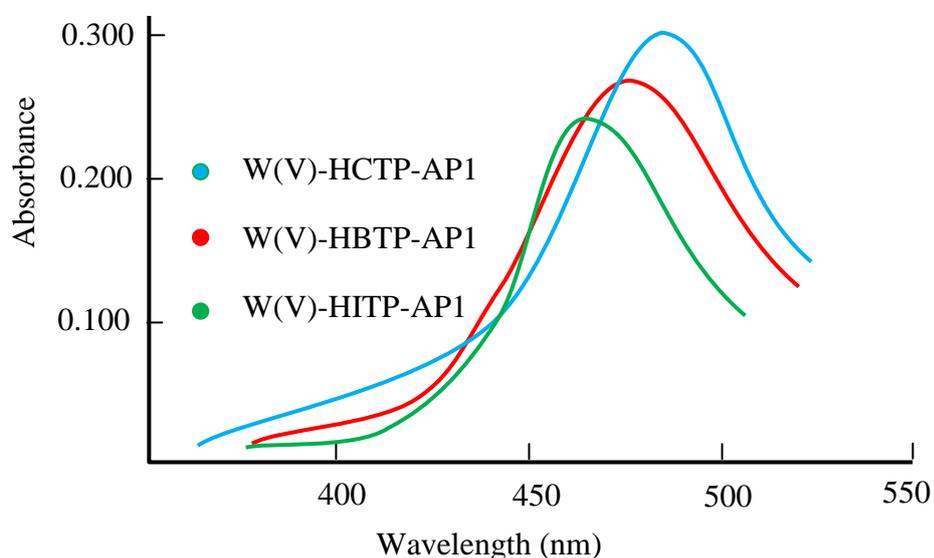

Fig.2. *Absorbance of Mo(V)-o-HTPh-Am complexes in chloroform vs. pH of the aqueous phase*. $C_W = 1.09 \times 10^{-5}$ mol L^{-1}, HTPDs = (2.2-2.8)×10^{-3}mol L^{-1}, C_{AP} = (2.0-2.5)×10^{-3} mol L^{-1}, pH 4.5-5.5, SF-26, ℓ=1.0 cm

3.4. Reagent Concentration and Incubation Time Influence

The effect of the concentration of HTPDs on the completeness of complexation was studied at the optimum pH and at a constant concentration of tungsten and AP. The optimum amount of AP for the maximum binding of the anionic hydroxyl thiophenolate complex of tungsten [W (V)–HTPDs] into an ionic associate was determined by varying the quantity of AP added. For the formation of mixed-ligand complex (MLC) W(V)–HTPDs–AP, the concentration of 1.2×10^{-3} M of HTPDs and 2×10^{-3} M of AP in the solution is required.

MLC of W(V)–HTPDs–AP were stable in aqueous and organic solvents and did not decompose for three days, and after extraction, more than a month. The maximum absorbance is reached within 5-8 minutes.

3.5. Stoichiometry of the Complexes and the Mechanism of Complexation

The ratio of components in the complex corresponds to W (V) : HTPDs : AP = 1 : 2 : 2; it was determined by the methods of straight line, equilibrium shift, and the relative yield [12] (Fig.3).
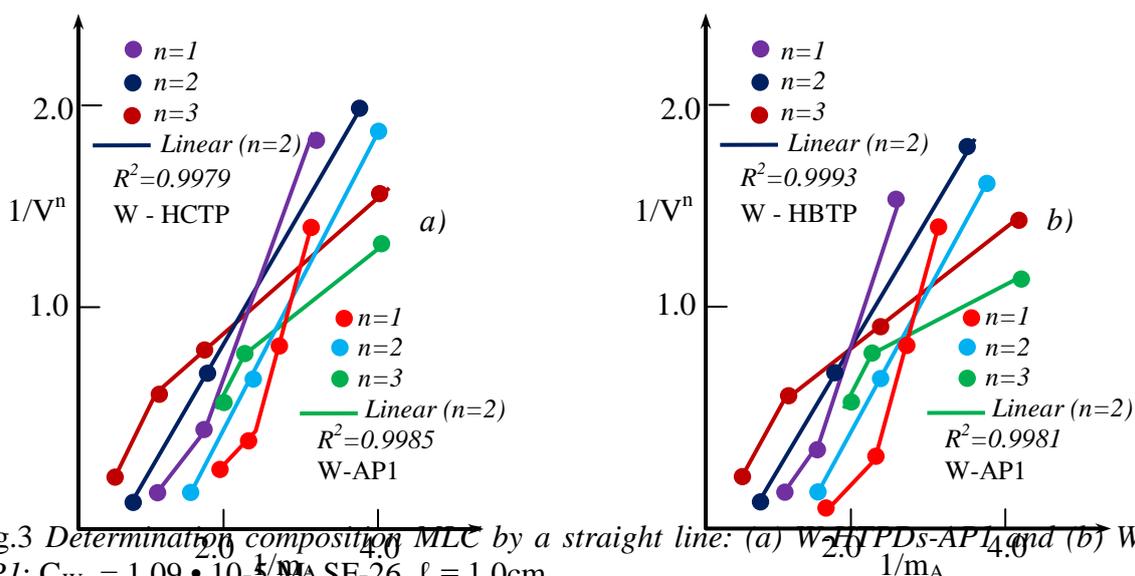

Fig.3 *Determination composition MLC by a straight line: (a) W-HTPDs-AP1 and (b) W-HCTP-AP1*; C_W = 1.09 • 10^{-5} M, SF-26, ℓ = 1.0cm.

Additional experiments by the Akhmedly's method [13] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 0.95-1.09). The stability constant determined by crossed lines method. The stability constant of W(V)-HTPDs-AP complexes was calculated and found to be lgβ= 7.19-11.25 at room temperature. The sizes of equilibrium constant K_e calculated on a formula $lgK_e = lg\, D − 2lg\, [AmH^+]$ were presented in table 4.

The IR spectra of the complexes W-HCTP- AP1, in the field of 780-810 cm^{-1}, there is an intensive strip of absorption caused by valent vibration of group $[O=Mo-Cl]^{2+}$ [14]. The disappearance of a distinct strip at 2580 sm^{-1}, observed in ranges HCTP and shows that sulfhydryl groups participates in formation of a complex. Observed reduction of intensity of a strip of absorption in area of 3200-3600 sm^{-1}, with a maximum at 3455 sm^{-1}, emergence of a wide strip in area 3050-3150 sm^{-1} shows that the hydroxyl group takes part in formation of Coordination communication in the ionized state. Detection of strips of absorption at 2385 cm^{-1} indicates availability of the protonated AP1 [15].

In a highly acidic medium, there are various cationic forms of tungsten (V) in the solution, with dominating WO^{3+} ion. In hydrochloric acid solutions, this ion can react with Cl$^−$ to form complexes and $WOCl^{2+}$, similarly to molybdenum [10]. The number of protons replaced by tungsten in one HTPDs molecule appeared to be two. Given the found component ratio in the complex and an ionic state of tungsten, it was assumed that upon complexation, the following reactions proceed (scheme):

Cl

Scheme. Chemical mechanism of the process

From Eqs (1) and (2), one can judge the reaction mechanism: tungsten (VI) is reduced by o-hydroxythiophenol derivative in a hydrochloric acid medium to tungsten (V), and the latter in the form of a chloride complex cation interacts with excess HTPDs. The resulting anionic complex $[WOClR_2]^{2-}$ is reacted with AP, which the acidic solution is in the protonated state (APH^+).

3.6. Influence of Interfering Ions

The selectivity for the spectrophotometric determination of tungsten in the form of the complex described above is presented in Table 3. It is determined that large amounts of alkali, alkaline earths, and rare earth metals and fluorides, chlorides, and sulfates do not interfere with the determination of tungsten. The interfering effect of Fe (III) was eliminated by introducing a 20% solution of $SnCl_2$ before the addition of the reagent; the effect of Ti (IV) was removed by adding ascorbic acid, and Cu (II), by thiourea. Mo (VI) is acidic medium is reduced with HCTP to Mo (V), which is masked by the addition of EDTA. Because tungsten forms a complex in a more acidic medium than vanadium, tungsten can be determined the presence of large amounts (50 μg) of vanadium.

Table 3. Influence of interfering ions on the determination of tungsten (V) as MLC with HCTP and AP1 (30,0 μg of W added, *n*=9, *P*=95%)

Ion	Molar excess of the ion	Masking agent	Found W, μg	RSD,%
Thiourea	25		30.0	3

Cu(II)	78	Thiourea	30.1	6
Zr(IV)	75	NaF	30.2	4
Cd(II)	90		29.3	6
Fe(III)	80		29.4	3
Fe(II)	80		30.1	2
Al(III)	200		30.0	5
Ni(II)	80	EDTA	30.2	6
Co(II)	67	EDTA	29.6	2
Ti(IV)	10	Ascorbic acid	29.5	5
Mn(II)	60		29.7	4
U(VI)	40	CH_3COO^-	30.0	6
Mo(VI)	20		30.2	3
Cr(III)	45		29.6	2
V(IV)	90		30.0	6
Ta(V)	50		30.2	4
Nb(V)	50		30.2	5
Pt(II)	70	$Na_2C_4H_4O_6$	30.1	3
Pd(II)	70		29.6	6
Ascorbic acid	130		30.2	4
Tartaric acid	130		30.0	6
Oxalate	17		29.6	3
Fluoride	12		29.8	2
Phosphoric acid	30		29.7	5

In conclusion the analytical parameters pertaining to the proposed method are given in Table 4.

Table 4. Optical characteristics, precision and accuracy of the spectrophotometric determination of W(V) with HTPDs and AP

Analytical characteristics	HCTP			HBTP			HITP		
	AP1	AP2	AP3	AP1	AP2	AP3	AP1	AP2	AP3
pH[1]	2.5-7.1	2.3-6.9	2.1-6.8	2.2-6.9	2.0-6.8	1.7-6.7	2.0-6.6	1.8-6.4	1.5-6.2
pH[2]	4.5-5.5	4.1-5.3	4.0-5.1	4.3-5.2	4.1-5.0	3.9-4.8	4.0-5.0	3.7-4.8	3.5-4.6
R[3]/ %	96.2	98.8	96.7	97.4	98.1	98.5	97.2	98.0	96.5
λ_{max} / nm	490	485	483	480	476	472	470	465	461
$\Delta\lambda_{max}$ / nm	207	202	200	194	190	186	180	175	171
Ma[4] /$Lmol^{-1}cm^{-1}$	2.8	2.7	2.6	2.4	2.3	2.3	2.2	2.1	2.0
Cp[5]/ γ	1.01	0.95	1.03	1.05	1.06	1.07	1.09	0.99	1.02
Ec[6]/ lgK_e	6.45	6.87	7.24	8.13	8.61	8.72	9.43	9.66	9.89
Sc[7]/ $lg\beta$	7.19	7.36	7.68	8.73	8.97	9.05	10.57		11.25
Wr[8] / $\mu g\ cm^{-3}$	0.5-95	0.5-90	0.5-95	0.5-90	0.5-85	0.5-80	0.5-85	0.5-80	0.5-80

Note: 1- pH range complexation;2- The pH range of maximum extraction, 3- Degree of extraction; 4-Coefficient polymerization; 5- Molar absorptivity; 6- Equilibrium constant; 7- Stability constant; 8- Working range

3.7. Effect of tungsten (V) Concentration

The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. Beer's law is obeyed over the concentration range $0.04 - 3.8$ µg W(V) mL^{-1} (Fig. 4). Table 5 summarises the calibration characteristics obtained with HTPDs and AP.

Table 5. Analytical characteristics of some ternary complexes of W with HTPDs and AP

Compound	SS*(µg cm^{-2})	Beer's law range (µg· mL^{-1})	LOD*, ng mL^{-1}	LOQ*, ng mL^{-1}	The equation of calibration curves	Cc*
W-HCTP-AP1	0.0033	0.05-3.8	11	36	0.032+0.25x	0.9987
W-HCTP-AP2	0.0034	0.04-3.6	12	40	0.027+0.24x	0.9974
W-HCTP-AP3	0.0035	0.05-3.8	11	36	0.045+0.22x	0.9931
W-HBTP-AP1	0.0038	0.04-3.6	12	40	0.039+0.21x	0.9981
W-HBTP-AP2	0.0040	0.04-3.4	15	50	0.015+0.20x	0.9891
W-HBTP-AP3	0.0040	0.05-3.3	14	45	0.014+0.20x	0.9956
W-HITP-AP1	0.0044	0.04-3.4	10	33	0.031+0,18x	0.9989
W-HITP-AP2	0.0046	0.05-3.2	12	40	0.024+0.16x	0.9975
W-HITP-AP3	0.0050	0.05-3.2	9	29	0.023+0.15x	0.9991

Note: SS- Sandell's sensitivity; LOD- Limit of detection; LOQ- Limit of quantificat ion; Cc- Correlation coefficient.
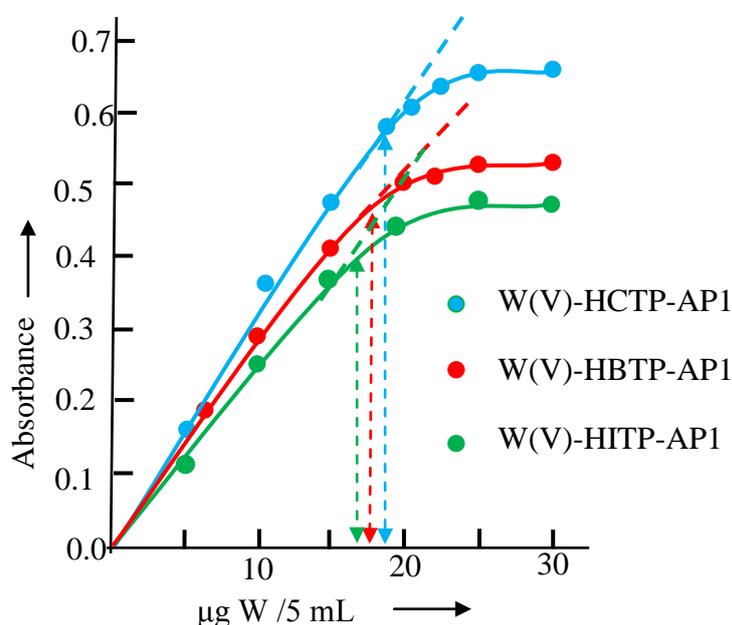

Fig.4. *Beer's law range of W (V)- HTPDs-AP complex in Chloroform at 470-490 nm.*

The proposed method compares favourably with the existing ones (Table 5) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity [1-3,6,5].

Table 5. Comparative characteristics of tungsten determination methods

Reagent	pH (solvent)	λ, nm	$\varepsilon \times 10^{-4}$	Beer's law range ($\mu g \cdot mL^{-1}$)	Sandell's Sensitivity ($\mu g\ cm^{-1}$)	[Ref.]
HCTP-AP1	4.5-5.5 (CHCl$_3$)	490	2.8	0.05-3.8	0.0033	Proposed method
HBTP-AP1	4.3-5.2 (CHCl$_3$)	480	2.4	0.04-3.6	0.0038	
HITP-AP1	4.0-5.0 (CHCl$_3$)	470	2.2	0.04-3.4	0.0044	
Toluene-3,4-dithiol	1.5-2.0 (CHCl$_3$)	640	1.92	-	0.0060	[1-3]
8- Mercaptoquinoline	0.5-3.0 (isobutanol – chloroform (1:1))	412	0.367	≤ 4	Not known	[1,2,6]
8 - Hydroxyquinoline	4.4 (CHCl$_3$)	363	0.64	-		[2,6]
KSCN	10M HCl (isoamyl acetate)	405	1.51	-	0.0120	[5]

3.8. Analytical Applications

The proposed method were applied to the determination of tungsten in steel and samples of soil. The accuracy of the results was checked by three independent methods. The results are listed in Table 6.

Table 6. Tungsten content in steel (EU-45: 0.50% W) and samples soil determined by different methods (n=5, P=95%)

Method		Tungsten content in steel		Tungsten content in soil	
		$\overline{X}$, %	RSD,%	$\times 10^4$,%	RSD,%
Proposed method	HCTP-AP1	0.47	3.5	4.85	3.2
	HBTP-AP1	0.51	3.5	4.49	5.1
	HITP-AP1	0.48	3.4	4.71	4.6
Toluene-3,4-dithiol		0.48	3.4	4.65	3.6
8- Mercaptoquinoline		0.52	3.2	4.53	3.9
8 - Hydroxyquinoline		0.51	3.6	4.92	4.5

4. CONCLUSION

1. Mixed-ligand complexes of tungsten (V) with HTPDs and AP have been studied by spectrophotometry. Extraction of mixed ligand complexes is maximal at pH 3.5-5.5. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found.

2. The molar ratio of the reacting W(V), HTPDs and AP species is 1:2:2. The general formula of the mixed-ligand complexes is $[WOCl(HTPDs)_2](APH)_2$. They can be regarded as ion-associates between doubly charged anionic chelates $[WOCl(HTPDs)_2]^{2-}$ and protonated AP species.

3. The developed method retains specific interaction of tungsten (V) with HTPDs and AP to form a colored complex and has good sensitivity. The proposed method has significant advantage over the other spectrophotometric methods in terms of simplicity and sensitivity.

4. In the complex formation with HCTP, tungsten (VI) is reduced to tungsten (V) by the reagent itself. This fact was also confirmed by ESR Spectrometry.

5. $CHCl_3$, CCl_4, $C_2H_2Cl_2$, benzene, toluene, isopentanol, nhexanol, and their mixtures were tested as extractants. $CHCl_3$ demonstrated the best result; it was used in further experiments.

6. Beer's law is obeyed over the concentration range 0.04 – 3.8 μg W(V) mL^{-1}. The proposed method were applied to the determination of tungsten in steel and samples of soil.

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