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Liquid-liquid extraction-chromogenic systems containing tungsten (VI), 2-Hydroxy-5-Chlorothiophenol and Diphenylguanidine

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Abstract
The complexation of tungsten (VI) with 2-hydroxy-5-chlorothiophenol in the presence of diphenylguanidine is studied by spectrophotometry. Optimal conditions for the formation and extraction of the complex are determined. It is found that a mixed-ligand complex is formed at pH 5–6. Chloroform and dichloroethane are the best extractants. Some physicochemical characteristics of the mixed-ligand complex are determined; the molar absorption coefficient at 480 nm is 5.6×10^4. The molar ratio of components in the complex is 1: 2: 2.

Keywords: complexation, extraction, tungsten, 2-hydroxy-5-chlorothiophenol, diphenylguanidine

1. Introduction
Thio- and dithiophenols constantly attracted the attention of researchers as analytical reagents [1–14]. For the photometric determination of tungsten, derivatives of *o*-diphenols or *o*-thiophenols are used [15]. It was previously found that at pH 1.5–2.0, tungsten (VI) reacts with 2-hydroxy-5-chlorophenol (HCTP) yielding a chelate compound extractable with chloroform [14]. At pH 5–6, the formed tungsten complex of a brown color is not extracted with inert organic solvents, including chloroform and dichloroethane. However, with the addition of diphenylguanidine (DPG) into the solution, an orange mixed-ligand complex is formed that is well extracted by some organic solvents. The use of this complex for the extraction photometric determination of tungsten greatly increases the sensitivity of the method.

2. Experimental
2.1. Reagents and instrumentation
A stock solution containing 1 mg/mL 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 solu- tion. The concentration of the tungsten solution was adjusted gravimetrically by sedimenting tungsten in the form of H_2WO_4 and weighing WO_3 [16, 17]. Working solutions with the tungsten concentration of 0.1 mg/mL were prepared by diluting the stock solution.
We used a 0.01 M HCTP solution and a 0.025 M DPG solution in chloroform. HCTP was synthesized by the procedure proposed in [18]. and its purity was checked by determining its melting point and paper chromatography. 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. Chloroform was purified by washing with conc. H_2SO_4 and shaking with distilled water followed by washing with a 5% solution of NaOH. 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 mL of 0.01 M HCl, and 0.3 mL of a 0.01 M HCTP solution were placed in calibrated test tubes with ground stoppers. The mixture was stirred thoroughly for 5 min to reduce tungsten, and 2 mL of a 0.025 M solution of DPG 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

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water. After the formation of the hydroxythiophenolate complex of tungsten, it was extracted, and the absorbance of extracts was measured by a KFK-2 pho- toelectrocolorimeter at 490 nm.

2.3. Studies on the oxidation state of tungsten
In acidic medium, HCTP exhibit reducing properties. It is known that only tungsten (V) forms a colored compound with dithiol, while tungsten (VI) is reduced by the reagent itself [15]. The question arises: Does the valence of tungsten change in the interaction with HCTP? To answer this question, two series of experiments were conducted: (1) reaction of tungsten (V), obtained by reduction of $SnCl_2$ and KI in a hydrochloric acid solution, with HCTP and (2) the same reaction without use of additional reducing agents. Both compounds had maximum in absorbance at 480 nm. Hence, 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. The results of the studies are presented in Figure 1.
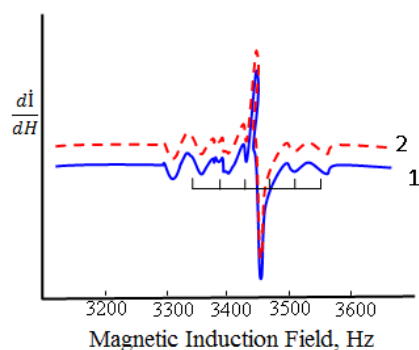

Fig 1: Hyperfine Splitting of the Paramagnetic Resonance Line in Solutions: (1) Mo (V)- HCTP - DPG and (2) Mo(VI)- HCTP - DPG

2.4. Charge of the complex tungsten
It was previously found that at pH 1.5–2.0, tungsten (VI) reacts with HCTP with the formation a chelate compound that is readily extracted with chloroform [14]. At pH 5–6, the complex of tungsten is not extracted by inert organic solvents. To determine the sign of the complex charge, ion exchange chromatog raphy was used: AV-17 anion exchanger in chloro Form 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, diphenylguanidine is used as a hydrophobic amine, which transforms into a diphenylguadininic ion in acidic medium that is (scheme 1):
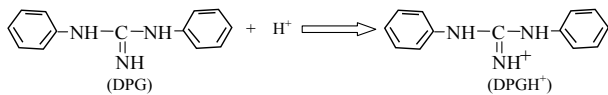
Scheme 1: Protonation molecule of diphenylguanidine.

2.5. Determination of tungsten in different objects
2.5.1. 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 soil sample (15 g) collected from depths of 25 - 30 cm was subjected to available tungsten extraction procedure [19] with an oxalate buffer of pH 3.3. Then the procedure [19] was followed: An aliquot of the obtained soil

extract (50-100 mL) was placed in a quartz beaker and evaporated to dryness on a hot plate. For dehydration of the residue and partial sublimation of the oxalates, the beaker was left on the plate for 30 more minutes. The beaker was transferred in a cold muffle furnace. The temperature was raised to 500 °C and held for 1 hour. After cooling 2 mL of perchloric acid were added for complete destruction of the organic matter. The content was heated to near dryness on a hot plate and the beaker was placed again in the muffle furnace. The temperature was raised to 500 °C and held for 15-20 minutes. The residue was cooled and then dissolved in 25 mL of 14% hydrochloric acid under heating. Aliquots of thus obtained filtrate were used to determine the tungsten content. Tungsten was determined in aliquot portions of the solution using the proposed procedures.

2.5.2. Determination of tungsten in steels
A weighed sample of steel (0.1 g) was dissolved under heating in 4 mL of freshly prepared mixture of HCl and HNO_3 (3: 1) in the presence of a few drops of HF. After dissolution, 0.5 mL of HCOOH is added, and the mixture is 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 mL of a 0.2 M HCTP solution were added, and, after thorough mixing, 2 mL of a 0.025 M DPG 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 min. After layering of the phases, the absorbance of extracts is measured using a KFK-2 photoelectrocolorimeter at 490 nm in cuvettes of 0.5 cm in thickness. The tungsten concentration is found from the calibration curve.

The tungsten concentration in 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) is certified to be 0.50%. In the analysis of this steel by the proposed method, the concentration of tungsten is found to be $0.497\pm 0.009\%$ ($n = 9$, $P = 0.95$, RSD = 4.7%). The results of the determination of tungsten in steel demonstrate the reliability of the proposed procedure.

2.5.3. Determination of tungsten in plants
15 g of the powdered plant material (seeds of pea) were soaked in 50 mL of 96 % ethanol for 48 h. The sample was dried and carefully carbonized in a quartz beaker on a hot plate. The beaker was placed into a cold muffle furnace and its temperature was slowly increased (at a rate of 100 °C per hour) up to 450°C. The sample was dry-ashed for 10-15 h. The obtained gray ash was cooled and moistened with a few drops of nitric acid (1:1). Then the ash was heated to dryness on a water bath and placed into the muffle furnace. The temperature was raised to 300°C and held for 30 minutes. This cycle was repeated several times until white ash was obtained. Then, several drops of bidistilled water and 2 mL of perchloric acid were added. The beaker was heated on a hot plate until smoking ceased and transferred in a cold muffle furnace. The temperature was raised to 500 °C and held for 15 minutes. After cooling, 25 mL of 14% hydrochloric acid were added and the beaker was kept in a boiling water bath for 10-20 min. The obtained solution was quantitatively transferred to a volumetric flask of 50 mL [19]. Tungsten was determined in aliquot portions of the Solution using the proposed procedures.

## 3. Results and Discussion

3.1. Choice of organic solvent

$CHCl_3$, CCl_4, $C_2H_2Cl_2$, benzene, toluene, isopentanol, *n*-hexanol, and their mixtures were tested as extractants. $CHCl_3$ demonstrated the best result; it was used in further experiments. The concentration of tungsten in the organic phase was determined photometrically by using dithiol after reextraction, and in the aqueous phase, its concentration was found by the difference. Extractable complexes evaluated coefficient distribution bution (D) and the Extraction ratio (R, %) [20].

$$D = \frac{[W]_{org}}{[W]_{aq}} \; ; \qquad R = \frac{100 \times D}{D + \frac{V_{aq}}{V_{org}}}$$

At the optimum conditions this solvent provides degrees of extraction R=98.6%.

3.2. Effect of solution pH

It is found that to form a mixed_ligand compound of tungsten(V) and its extraction, 0.2–0.3 mL of 0.01 M HCl per 25 mL of solution is required (Fig. 2). With further increase in the acidity of the aqueous phase, the recovery of tungsten decreases. This is because with increasing acidity, the concentration of the cationic reactive form of tungsten decreases. At pH $\geq$ 8, the extraction of the complex is practically not observed, which is probably because a decrease in the degree of protonation of DPG.
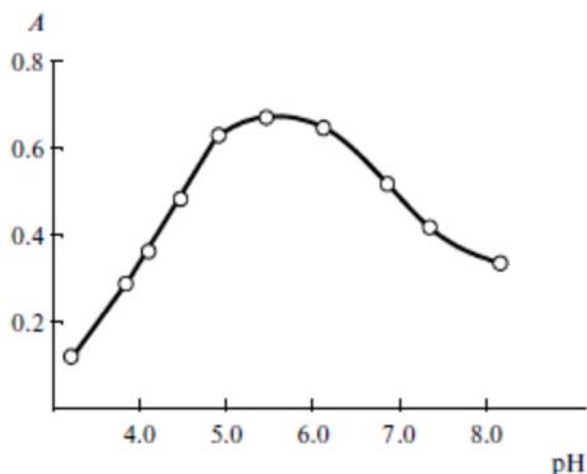
Fig 2: Effect of pH on the light absorption of the complex of tungsten with HCTP and DPG; $c_{W (V)} = 1.08 \times 10^{-5}$ M, $c_{HCTP} = 1.2 \times 10^{-2}$ M, $c_{DPG} = 3 \times 10^{-3}$ M; 440 nm, KFK-2, $l = 0.5$ cm.

3.3. Effect of the concentrations of reagents and incubation time

The effect of the concentration of HCTP on the completeness of complexation was studied at the optimum acidity and at a constant concentration of tungsten and DPG. The optimum amount of DPG for the maximum binding of the anionic hydroxyl thiophenolate complex of tungsten [W (V)–HCTP] into an ionic associate was determined by varying the quantity of DPG added. For the formation of mixed-ligand complex W (V)–HCTP–DPG, the concentration of 1.2×10^{-3} M of HCTP and 2×10^{-3} M of DPG in the solution is required (Fig. 3).
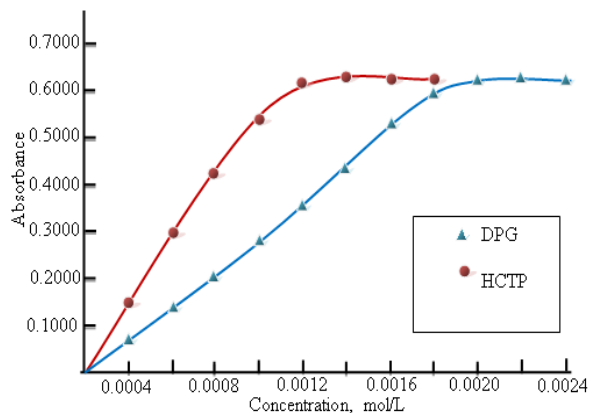
Fig 3: Absorbance of W (V) extracts with HCTP and DPG concentration of the reagent plots. $c_{W(V)} = 1.08 \times 10^{-5}$ M, pH KFK-2, 440nm, ℓ=0.5 mm.

The mixed-ligand complex is almost completely transferred into the organic phase by shaking the mixture for 5 min. The complex is stable in the chloroform extract, and its absorbance did not change over time.

3.4. Absorption spectra and molar absorptivitie

The absorption maximum of the mixed-ligand complexes is observed at 480 nm. 2-Hydroxy-5-chlorothiophenol absorbs light in the ultraviolet region (280 nm). Thus, the complexation is accompanied by a bathochromic shift of the maximum by 200 nm. The electronic absorption spectrum of the extract of the tungsten complex indicates the formation of only one complex. The molar coefficient of light absorption is 5.6×10^4.

3.5. Stoichiometry of the ternary complexes and general formula

The ratio of components in the complex corresponds to W (V) : HCTP : DPG = 1 : 2 : 2; it was determined by the methods of straight line[21], equilibrium shift[21], and the relative yield[21] (Fig. 4).
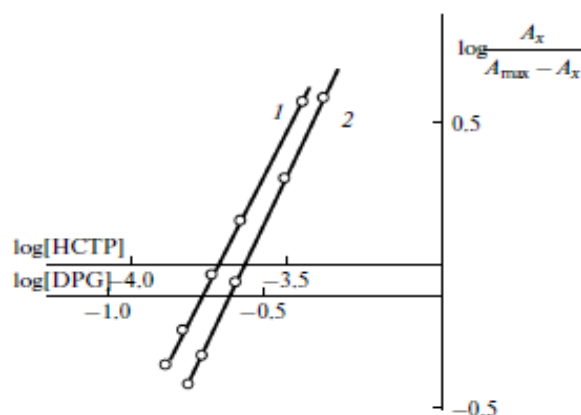
**Fig 4:** Composition of the complex of tungsten with HCTP and DPG: (*1*) W (V): HCTP and (*2*) W (V): DPG; $c_{W(V)} = 1.08 \times 10^{-5}$ M, pH 5.5, SF-26, $l = 1.0$ cm.

Additional experiments by the Akhmedly's method [22]. showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 1.11).

3.6. Chemical mechanism of the process

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 [5]. The number of protons replaced by tungsten in one HCTP 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 2):

(1)

(2)
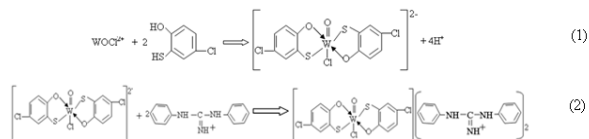
Scheme 2: chemical mechanism of the process

From Eqs. (1) And (2), one can judge the reaction mechanism: tungsten (VI) is reduced by 2-hydroxy-5-chlorothiophenol in a hydrochloric acid medium to tungsten (V), and the latter in the form of a chloride complex cation interacts with excess HCTP. The resulting anionic complex $[WOClR_2]^{2-}$ is reacted with DPG, which the acidic solution is in the protonated state ($DPGH^+$). The IR spectra of the complexes W-HCTP- DPG, in the field of 780-810 cm-1, there is an intensive strip of absorption caused by valent vibration of group $[O=Mo-Cl]^{2+}$. 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 DPG [23, 24]. (Fig.5).

3.7. Equilibrium constant.

Using Eq. (2), the equilibrium constant can be calculated by equation $\log K_e = \log D - 2\log [DPGH+]$. The data for calculating $\log K_e$ of the complex are given in Table 1; the average value of the logarithm of the equilibrium constant is 6.2 ± 0.4.

Table 1: Equilibrium constant of the reaction of complex formation of W (V)–HCTP–DPG (Amax = 0.61)

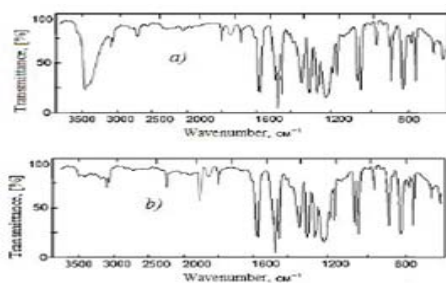| $\log c_{DPG}$	A_x	$\log D$	$\log K_e$
-2.92	0.31	0.01	5.85
-2.89	0.38	0.22	6.00
-2.82	0.46	0.49	6.13
-2.77	0.54	0.89	6.43
-2.70	0.58	1.28	6.68
			$\log K_e =6.2\pm0.4$

Fig 5: IR spektrums of HCTP (*a*) and the W-HCTP- DPG (*b*)

3.8. Effect of foreign ions.

The selectivity for the spectrophotometric determination of tungsten in the form of the complex described above is presented in Table 2. It is determined that large amounts of

Table 2: Effekt of foreign ions the determination of tungsten (V) (30 µg of tungsten added, *n*=9, *P*=95%)

| Foreign ion	Multiple molar excess	Masking agent	Found W, µg	RSD,%
Co(II)	70	EDTA	30.0	1.5
Ni(II)	70	EDTA	30.0	1.5
Fe(II)	200	Do not interfere	29.7	2.4
Fe(III)	90	SnCl$_4$	29.6	2.3
Cr(VI)	60	Do not interfere	29.8	2.5
Cd(II)	80	-	29.9	2.4
Zr(IV)	80	NaF	29.7	2.4
Cu(II)	140	Thiourea	30.5	4.2
Al(III)	350	Do not interfere	29.8	2.6
Mo(VI)	20	EDTA	30.5	4.2
Nb(V)	50	Do not interfera	29.8	2.6
V(V)	50	-	29.8	2.6
PO$_4^{3-}$	200	-	30.2	4.0
SO$_4^{2-}$	180	-	29.9	2.4
F$^-$	1500	-	30.0	1.5
Cl$^-$	1500	-	30.0	1.5
NO$_3^-$	1200	-	30.0	1.5

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.

3.9. Calibration graphs and analytical characteristics

In conclusion the analytical parameters pertaining to the proposed method are given in (Table 3). The Beer's law holds in the concentration range of tungsten of 0.2–20 µg/mL in chloroform. The equation of the calibration curve is $y = 0.01 + 0.008x$, where x is the tungsten concentration, µg. The pertaining calibration graph is shown in the Fig. 6.

Table 3: Optical characteristics, precision and accuracy of the spectrophotometric determination of W (V) with HCTP and DPG.

Parameter	Value
Color	orange
The pH range of education and extraction	3.1-8.0
The pH range of maximum extraction	5.0-6.0
Concentration of HCTP: mol· L^{-1}	1.2×10^{-3}
Concentration of DPG: mol· L^{-1}	2.0×10^{-3}
Organic solvent	CHCl$_3$
Extraction time	5 min
λ_{max} (nm)	480
Molar absorptivity (L· mol^{-1} cm^{-1})	5.6×10^4
Sandell's sensitivity (µg· cm^{-2})	0.025
R,%	98.6
The equation of calibration curves	$y = 0.01 + 0.008x$
Correlation coefficient	0.9973
Beer's law range (µg· mL^{-1})	0.2–20
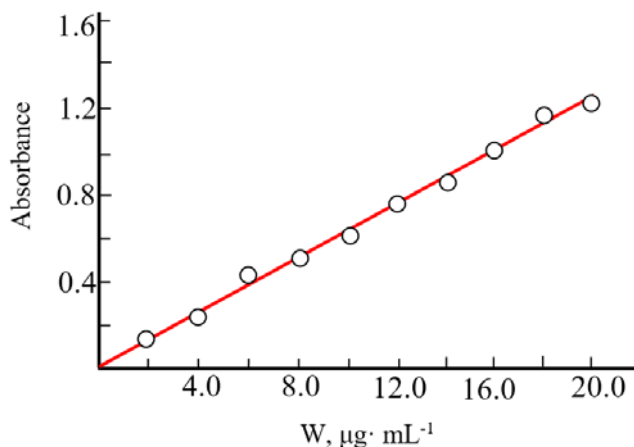
Fig 6: Analytical Determination of W (V) with HCTP and DPG. $c_{HCTP} = 1.2 \times 10^{-2}$ M, $c_{DPG} = 3 \times 10^{-3}$ M, pH 5-6, KFK-2, 480nm, ℓ=10 mm

The proposed method compares favourably with the existing ones (Table 4) and offers the advantages of better simplicity, Rapidity, sensitivity and selectivity [25-31].

Table 4: Comparative Characteristics of the Procedures for Determining Tungsten

Reagent	pH, c mol/L	Solvent	λ, nm	$\varepsilon \cdot 10^{-4}$, L·mol^{-1}· cm^{-1}	Beer's Law Range, µg ·ml^{-1}	[Ref.]
8- mercaptoquinoline	0.5-3.0	isobutanol-chloroform (1:1)	412	0,367	$\leq$4	[25]
8 - hydroxyquinoline	4.4	chloroform	363	0,64	-	[25]
Toluene-3,4-dithiol	1.5-2.0	chloroform	640	1,92	-	[26]
Thiocyanate + DB-18-C-6	2.5-4.2 mol/L HCl	chloroform	415	1,6	0,18-18,3	[27]
Thiocyanate + ЕПХ	≈4 mol/L HCl	chloroform	404	1,74	1,0-15,0	[28]
4-nitrocatechol + 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide	1.2-3.6	chloroform	415	2.8	0.9-8.8	[29]
3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-enzo-pyran	0.2 mol/L HCl	dichlorethane.	415	6,45	0-2,8	[30]
HCTP + DPG	3.1-8.0	chloroform	480	5.6	0.2-20.0	Proposed method

3.10. Analytical Applications
The proposed method were applied to the determination of tungsten in steel, samples of soil and pea. The accuracy of the results was checked by three independent methods. The results are listed in Table 5.

Table 5: Tungsten content in steel, soil and pea samples determined by different methods (n=5, P=95%).

Method		Tungsten content in steel		Tungsten content in soil		Tungsten content in pea	
		X⁻,%	RSD,%	×10⁴,%	RSD,%	×10⁴,%	RSD,%
Present method	HCTP+DPG	0.51	3.5	3.21	2.2	4.87	3.0
8- mercaptoquinoline		0.50	5.0	3.29	3.4	4.91	3.2
8 - hydroxyquinoline		0.49	4.3	3.22	2.9	4.82	3.6
Toluene-3,4-dithiol		0.51	5.0	3.26	2.5	4.75	3.4

4. Conclusion
1. The complexation of tungsten (VI) with 2-hydroxy-5-chlorothiophenol in the presence of diphenylguanidine is studied by spectrophotometry.
2. Hence, 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.
3. $CHCl_3$, CCl_4, $C_2H_2Cl_2$, benzene, toluene, isopentanol, n-hexanol, and their mixtures were tested as extractants. $CHCl_3$ demonstrated the best result; it was used in further experiments.
4. Optimal Conditions for the formation and extraction of the complex are determined. It is found that a mixed-ligand complex is formed at pH 5–6. Chloroform and dichloroethane are the best extractants. Some physicochemical characteristics of the mixed-ligand complex are determined; the molar absorption coefficient at 480 nm is 5.6×10^4.
5. The molar ratio of components in the complex is 1: 2: 2. The average value of the logarithm of the equilibrium constant is 6.2±0.4.
6. The Proposed Method Were applied to the determination of tungsten in steel, samples of soil and pea.

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