



SPECTROSCOPIC INVESTIGATION COMPLEX FORMATION OF TUNGSTEN WITH 2, 6-DITHIOL-4-METHYLPHENOL IN THE PRESENCE OF AMINOPHENOLS

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Abstract

The mixed-ligand complexes of tungsten (VI) with 2, 6-dithiol-4-methylphenol (DTMP) in the presence of hydrophobic amines have been investigated by spectrophotometric method. The condition of complexing and extraction, physical-chemical and analytical characteristics of this complex have been found. From aminophenol 2(N, N-dimethylaminomethyl)-4-methylphenol (AP₁), 2(N,N-dimethylaminomethyl)-4-chlorophenol (AP₂) and 2(N, N-dimethylaminomethyl)-4-bromophenol (AP₃), were used.. It has been found that mixed-ligand complex were formed in weakly acidic medium (pH 3.9 – 5.2). Maximum of light absorption observed at 476-480 nm. The calculated molar absorptivities (ϵ_{\max}) belong to the interval $(2.73-2.92) \times 10^4$. The extraction-photometric methods of tungsten determination have been worked out. The influence of diverse ions on determination of tungsten has been studied. The proposed methods have been successfully applied to determination of tungsten in steel, soil and plant samples.

KEYWORDS: Tungsten, 2,6-dithiol-4-methylphenol, aminophenols, mixed-ligand complexes, extraction - photometric method, determination

Introduction

Tungsten is used in high temperature applications due to its high melting point. Its use as a filament 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.

Tungsten is able to replace molybdenum in animals and plants, as well as in bacteria, while inhibiting the activity of molybdenum-dependent enzymes, for example, xanthine oxidase. With excessive intake of tungsten in plants, the symptoms of molybdenum insufficiency develop: a large number of nitrates accumulate, chlorosis develops - first at the edges of the leaves, and then between the veins, which is accompanied by brown necrosis; while the tips of the leaves are twisted, the petioles are also bent.

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], polarography [8] and AAS [9]. However, these methods are disadvantageous 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 spectrophotometric determination [10]. Thiosemicarbazones contain nitrogen as well as sulphur. Thiosemicarbazones are good analytical reagents [11,12].

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 [13].

In the present paper was studied the complex formation in a liquid-liquid extraction system containing W(VI), dithiolphenols and hydrophobic amines (Am), and show the potential of this system for determination of W(VI) in real samples. Dithiophenolate complexes of metals are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [14, 15, 16].

In this respect, a very promising reagent is (2, 6-dithiol-4-methylphenol (DTMP), which contains one hydroxyl and two sulfohydriyl groups and is a sulfur-containing analogue of mononuclear polyphenols with two oxygen atoms replaced with sulfur atoms.

The real work is devoted to studying of reaction of a complex formation of tungsten (VI) with 2,6-dithiol-4-methylphenol (DTMP) and aminophenols (AP). From aminophenols 2(N, N-dimethylaminomethyl)-4-methylphenol (AP₁), 2(N,N-dimethylaminomethyl)-4-chlorophenol (AP₂) and 2(N, N-dimethylaminomethyl)-4-bromophenol (AP₃), were used.

Materials and Methods

Reagents and solutions

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 (A.R) in distilled water. The solution is diluted with water in a volumetric flask to 100 mL. Concentration of solution of Tungsten was established gravimetric [17]. Working solution with concentration of 0.1 mg/ml was prepared by dilution of stock with deionized water.

Solutions of DTMP and AP in chloroform (0.01M) were used. DTMP their purity was verified by paper chromatography and melting point determination. AP was used after purification by recrystallization. As an extract the cleared chloroform was applied.

The ionic strength of solutions was maintained constant ($\mu = 0.1$ M) by adding the calculated quantity of KCl solution. To create the optimal acidity, 1M solutions of KOH and HCl were used.

Instruments

The absorbance of the extracts was measured using a KFK-2 photocolormeter and an SF-26 spectrophotometer; the equilibrium value of the pH of aqueous phase was measured using a I-120.2 potentiometer with a glass electrode. IR - spectra were recorded on a spectrophotometer Specord M80.

All specified devices passed state check. All measurements was carried out at $20 \pm 1^\circ \text{C}$.

Procedure

General procedure for the determination of Tungsten

Portions of stock solutions of tungsten (VI) varying from 0.1 to 1.0 mL with a 0.1mL step, a 2.5 mL portion of a 0.01 M solution of DTMP, and a 2.0 mL portion of a 0.01M solution of Am were placed in to calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding 0.1M HCl. The volume of the aqueous phase was increased to 20 mL using distilled water. In 10 minute after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 590 nm ($l = 0.5$ cm).

Determination of Tungsten in the steel

A 0.5-0.6 g sample of steel was carefully dissolved in 10 ml of H_2SO_4 (1: 4). 2 ml of mix (1:3) conc. HCl and HNO_3 was added and heated to release of nitrogen oxides. Filtered insoluble precipitate and a filtrate transferred into a 50 mL volumetric flask. After cooling, the solution was diluted

with water to a mark. Select aliquot portions of the received solution, transfer to a in a separator funnel, the required value of pH was adjusted by adding 0.1M HCl. 2.0 ml 0.01 M of DTMP and 2.3 ml 0.01M AP was added. The volume of an organic phase adjusted to 5 ml chloroform, and total amount - to 25 ml the distilled water. After 10 min. of shaking, a portion of the organic extract was transferred through a filter paper into a cell and the absorbance was read at $\lambda = 540$ nm against chloroform. The tungsten content was found from a calibration graph.

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 an graphite cup in a mixture of 16 mL of conc. HF, 5mL of conc. HNO_3 , and 15 mL of conc. HCl at 50-60 $^\circ\text{C}$. to remove excess hydrogen fluoride, a 8 mL portion of conc. HNO_3 was added triply to the solution that was each time evaporated to 5-6mL. 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.

Preparation of plant samples

A wet ash method was employed in the preparation of the sample solution. 0.5 g of the sample was dissolved in a 1:1 mixture of nitric acid and perchloric acid. The solution was evaporated to dryness, and the residue was ashed at 300 $^\circ\text{C}$. The ash was dissolved in 2 mL of 1M sulphuric acid and made up to the volume in a 25 mL standard flask with distilled water. Tungsten was determined in aliquot portions of the solution using the proposed procedures.

Results and discussion

DTMP were synthesized according to the procedure [18]. The reagent was characterized by taking the elemental analysis, NMR and IR spectra (Table 1; fig.1 and fig.2) [19, 20, and 21].

IR (KBr), cm^{-1}	^1H NMR (300.18 MHz, C_6D_6)
3460 ν (OH), 3050 ν (CH), 2570 ν (SH), 2962 and 2872 ν ($-\text{CH}_3$), 1555 δ (C_6H_5), 1390 δ_{as} ($-\text{CH}_3$)	δ 5.24 (s, 1H- OH), δ 3.32(s, 2H - 2SH), δ 7.11 (s, 2H Ar-H), δ 2.38 (s, 3H $-\text{CH}_3$)

Table 1. The research results of IR and NMR spectroscopy

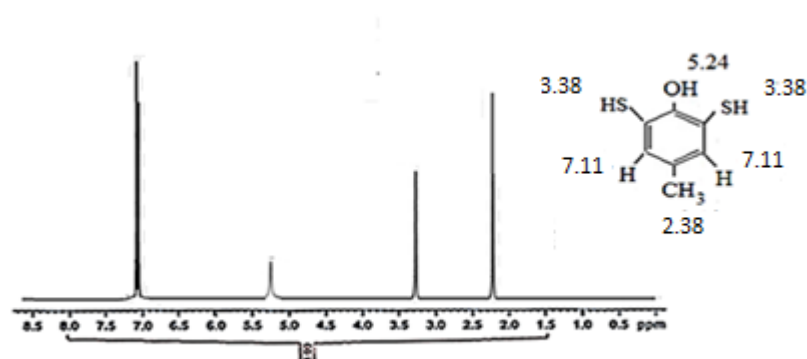


Figure 1. ^1H NMR –spectrum of DTMP

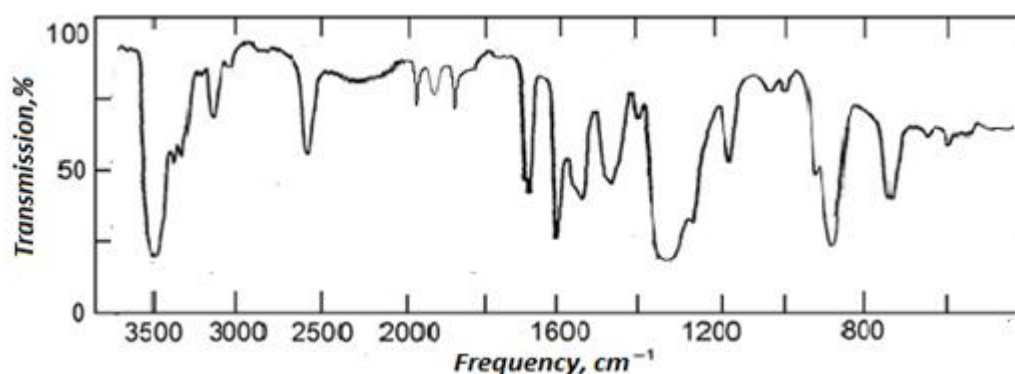


Figure 2. IR spectrum of the DTMP

The present study is concerned with the investigation of W(VI) interaction with DTMP and its derivatives, resulting in the formation of colored complexes insoluble in nonpolar solvents. Experiments on electro-migration in a U-shaped tube and on sorption on EDE-10P (EDE-ethylenediamine, epichlorohydrin; 10- serial

number of the brand: P- means that the matrix has a macroporous structure) anion exchangers have demonstrated the anionic nature of single-ligand complexes, in the electro-migration study of the complexes, it was found that the orange colored binary dithiophenolate complexes of tungsten (VI) moved to the cathode. When the sign of the

charge of the single-ligand complexes was determined by ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. When AP were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. On the basis of the obtained data new selective and highly sensitive procedures were developed for the extraction-spectrophotometric determination of small amount of tungsten in the steel of various brands, soils and food samples.

It is known that dithiophenols have reducing properties in acidic medium. To elucidate the oxidation state of tungsten in MLC, we conducted two series of experiments. In the first series we used W(VI), while in the second series we used W(V) obtained by addition of a supplementary reducing agent (SnCl_2 or KI). It was found that the spectrophotometric characteristics of the MLC of W(VI) and W(V) were identical, i.e., in the interaction with DTMP, W(VI) was reduced to W(V).

The choice of the extracting

The extraction of the complex has been tried with several solvents: chloroform,

1, 2-dichloroethane, tetra-chloromethane, dichloromethane, benzene, chlorobenzene, toluene, *o*-xylene, isobutanol, isoamyl alcohol, cyclohexane, ethyl acetate, 1-butanol, isoamyl acetate and their mixes. Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. The extraction decreases in the order: chloroform > carbon tetrachloride > 1,2-dichloroethane > chlorobenzene > toluene > benzene > ethyl acetate > n-butanol > isoamyl alcohol > benzoyl alcohol (Figure 3). Thus basicity of amines has no noticeable impact on conditions and extraction of complexes. 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, 99.2-99.6% of tungsten was extracted as an ion associate (in a case the dichloromethane and carbon tetrachloride was removed 96.0-97.4 % of tungsten). Further researches were conducted with chloroform. The concentration of vanadium (IV) in the organic phase was determined photometrically by using 8-hydroxyquinoline [13] after re-extraction, and in the aqueous phase, its concentration was found by the difference.

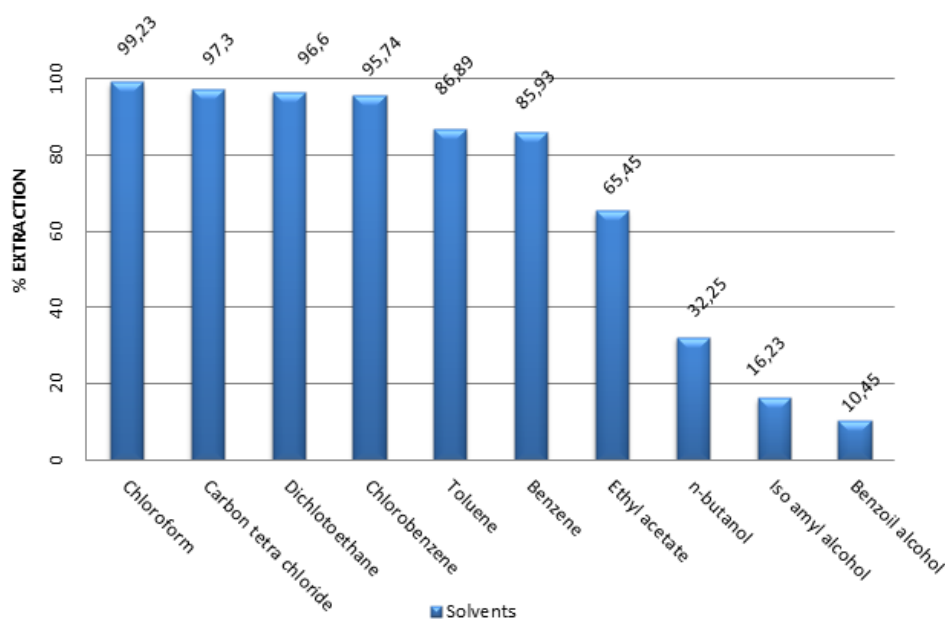


Figure 3. Effect of solvents on extraction of W (V) as W-DTMP-AP₂

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 3.9-5.2. Extraction of W (V) enhanced with the increase in the acidity of the initial solution; the 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 DTMP. Probably, it is

present in the solution in the non-dissociated state. At $\text{pH} \geq 7$, the complexes were hardly extracted, obviously because of the decrease in the degree of Am protonation. The effect of pH on the intensity of the color reaction is shown in the Figure 4. Existence of one maximum of absorbance in the specified limits pH confirms the assumption of formation of one complex compound.

The nature of acids (HCl , H_2SO_4) almost does not influence a complex formation of Tungsten with DTMP and AP.

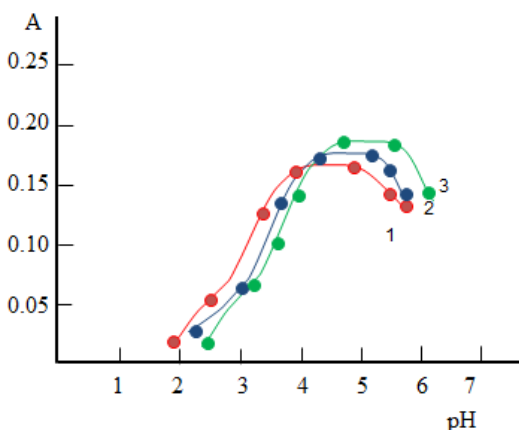


Figure 4. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase.

1. W(V)-DTMP-AP₁; 2. W(V)-DTMP-AP₂; 3. W(V)-DTMP-AP₃

$C_W = 1.09 \times 10^{-5} \text{ M}$, $C_{\text{DTMP}} = 8.0 \times 10^{-4} \text{ M}$, $C_{\text{AP}} = 0.92 \times 10^{-4} \text{ M}$, $\text{pH} = 4$, KFK-2, 490 nm, $\ell = 0.5 \text{ cm}$.

Electronic absorption spectra

The absorption maxima (λ_{max}) of the ternary W (V) - DTMP-AP complexes lie in the range of 476-480 nm (Table 2, Figure 5). All color reactions were very contrast since the initial solutions are colorless (λ_{max} (DTMP) = 274 nm). Thus, bathochromic shift makes 202-206 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: initial reagents - are colorless, and complexes – are intensively colored. Molar coefficients of absorption make $(2.73\text{-}2.92) \times 10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

Influence of reagent concentration and incubation time

The studies of the effect of concentration of the reagent revealed that a reagent excess of

40-fold was optimum for the complex formation. Hence, a 30-40 fold reagent excess was adopted for further investigations. However, the presence of excess of the reagent solution does not interfere with the color reaction. The optimal concentration of DTMP and Am for formation of the complex was found to be $8.0 \times 10^{-4} \text{ M}$ and $9.2 \times 10^{-4} \text{ M}$, respectively.

We investigated dependence of absorbance of extracts on time at excess of reagents and at an optimum pH. MLC of tungsten with DTMP and Am 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 minutes. At weak heating (to 30 °C) coloring develops instantly.

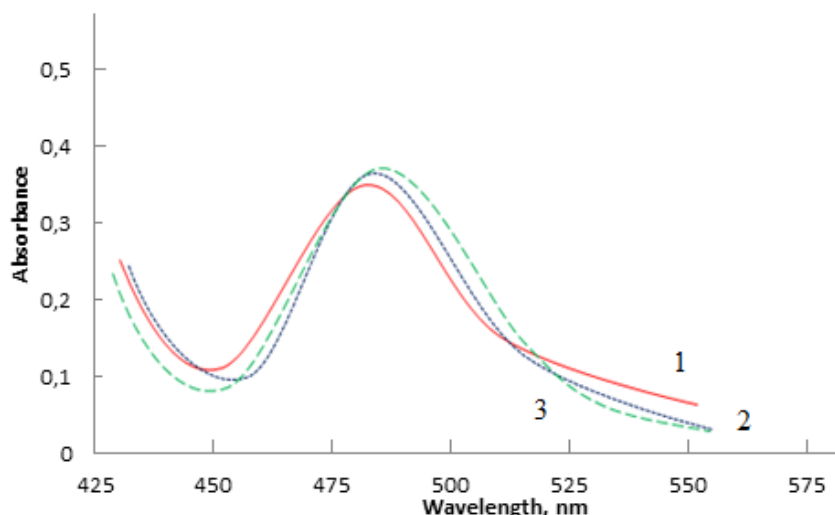


Figure 5. Absorption of mixed-ligand complexes

1. W(V)-DTMP-AP₁; 2. W(V)-DTMP-AP₂; 3. W(V)-DTMP-AP₃

$C_W = 1.09 \times 10^{-5} \text{ M}$, $C_{\text{DTMP}} = 8.0 \times 10^{-4} \text{ M}$, $C_{\text{AP}} = 0.92 \times 10^{-4} \text{ M}$, pH=4, Shimadzu 1240, $\ell = 1 \text{ cm}$.

Stoichiometry of the complexes and the mechanism of complexation

The stoichiometric coefficients of the reaction were determined by the Asmus method, by the relative yield method and by the equilibrium shift method [22]. The formation of MLC can be presented in the following way. When tungsten ion interact with two molecules of dithiophenols, they

Form doubly-charged anionic complexes, which were extracted with two molecules of protonated AP (Figure 6).

It was found using the Nazarenko method that W(V) in the complexes was present in the double charging cation $\text{WO}(\text{OH})^{2+}$. The number of protons replaced by Tungsten in one DTMP molecule appeared to be one [23, 24].

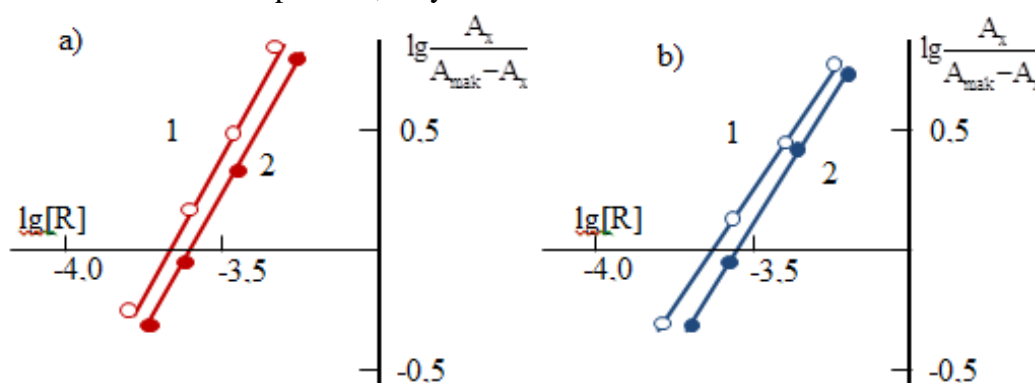


Figure 6. Determination of the ratio of components by the equilibrium shift method for (a) W(V)-DTMP-AP₂ and (b) W(V)-DTMP-AP₃. 1- W : DTMP; 2- W : AP.

$C_W = 1.09 \times 10^{-5} \text{ M}$, $C_{\text{DTMP}} = 8.0 \times 10^{-4} \text{ M}$, $C_{\text{AP}} = 0.92 \times 10^{-4} \text{ M}$, pH=4, Shimadzu 1240, $\ell = 1 \text{ cm}$.

In the IR spectra of the complex W-DTMP-AP₁ in the field of 860-810 cm^{-1} there is an intense absorption band caused by valent vibration of group $\text{WO}(\text{OH})^{2+}$. The disappearance of a distinct strip at 2570 cm^{-1}

¹, observed in ranges DTMP and emergence spectrum of complexes of two bands of absorption one of which is displaced towards smaller frequencies, says that one of the sulfhydryl groups participates in

formation of a complex. The disappearance of the pronounced absorption bands in the 3600-3200 cm^{-1} with a maximum at 3450 cm^{-1} observed in the spectrum of DTMP, says that the -OH group is involved in the formation of the complex. Detection of

bands of absorption at 2375 cm^{-1} indicates availability of the protonated aminophenol [20, 21].

Structure extractable complexes can be represented as in Figure 7.

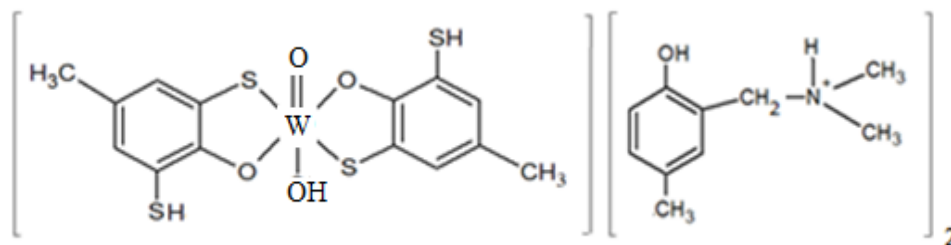
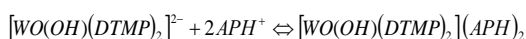
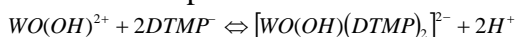


Figure 7. Structure of complex $[\text{WO}(\text{OH})(\text{DTMP})_2](\text{AP}_1\text{H})_2$

Ions of tungsten at interaction with two molecules of DTMP, form doubly charged anionic complex, which were extracted with two molecules of protonated AP. The composition of the extractable complexes can be represented by the formula $[\text{WO}(\text{OH})(\text{DTMP})_2](\text{APH})_2$.

It is assumed that at a complex formation there are processes:



The sizes of equilibrium constant K_e calculated on a formula $\lg K_e = \lg D - 2\lg[\text{APH}^+]$ were presented in Table 2.

$$D = \frac{\{[\text{WOOH}(\text{DTMP})_2](\text{APH})_2\}_o}{\{[\text{WOOH}(\text{DTMP})_2]^{2-}\}_a}$$

The distribution constant KD was calculated from the absorption values obtained after single and double extraction as described above. The extraction constant K_{ex} was calculated by the formula $K_{\text{ex}} = KD \beta$.

Calculation of extent of polymerization of complexes was carried out on the equation [25]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form (degree of polymerization $\gamma = 1.05-1.18$).

The limit of photometric determination of tungsten in the form of ionic associates was counted on the equation [33].

Chemical-analytical parameters pertaining to the proposed methods are given in table 2.

Compound	pH_{opt}	Grade of extraction R	λ , nm	$\Delta\lambda$, nm	Molar absorptivity 10^4 ($\text{L mol}^{-1} \text{cm}^{-1}$)	Equilibrium constant $\lg K_e$	Stability constant $\lg \beta$	Extraction constant $\lg K_{\text{ex}}$
W(V)-DTMP-AP ₁	4.0-5.1	99.20	476	202	2.73	6.5	9.82	12.86
W(V)-DTMP-AP ₂	4.2-5.2	99.23	479	205	2.83	6.6	9.78	12.79
W(V)-DTMP-AP ₃	3.9-5.1	99.60	480	206	2.92	6.7	9.89	12.75

Table 2. Some chemical-analytical parameters of W (V)-DTMP- AP complexes

The effect of non-target species

Influence of a number of cations and anions on the accuracy of determination of W(V) was studied. Experiments were performed according to the recipe, by which established calibration curves, with the only

difference that a solution other than W (V) injected a certain amount of the corresponding ions. The selectivity of the photometric determination of W with dithiol phenols and Am is demonstrated in Table 3.

Non-target species	Tolerance ratio non-target species / Mo (w/w)	Masking agent	Found W, µg	Relative Standard Deviation RSD(%)	Non-target species	Tolerance ratio non-target species / Mo (w/w)	Masking agent	Found W, µg	Relative Standard Deviation RSD(%)
Co(II)	20	Potassium cyanide	29.8	4.2	UO_2^{2+}	50	Acetylacetone	30.2	3.9
Ni(II)	20	Potassium cyanide	29.7	5.5	Citric acid	15		30.3	3.6
Fe(II)	34	Potassium cyanide	30.2	4.5	Oxalic acid	20		29.6	3.9
Cd(II)	200	Potassium cyanide	30.2	5.3	Wine acid	15		30.2	4.2
Al(III)	180		29.8	4.4	EDTA	25		29.8	3.7
Fe(III)	60	EDTA	29.6	3.7	NH_4F	250		30.1	4.5
Zr(IV)	50		29.8	4.4	Bromide	300		30.1	4.8
Cu(II)	25	Thiourea	29.8	4.3	Nitrate	480		30.2	3.9
Hg(II)	40	$Na_2S_2O_3$	29.7	5.5	Urea	720		30.3	3.6
Ti(IV)	30	Ascorbic acid ($C_6H_8O_6$)	30.2	4.5	Thiourea	356		29.6	3.9
V(IV)	25		30.3	4.8	Acetate	480		30.2	4.2
Mo(VI)	10	EDTA	29.6	3.9	Thiocyanate	400		29.8	3.7
Mn(II)	18				Chloride	145		30.5	4.5
Cr(III)	120		30.2	3.8	Phosphate	90		30.1	4.8
Cr(VI)	8		29.8	4.2	Fluoride	300		30.2	3.9
Nb(V)	50	$C_2O_4^{2-}$	29.8	4.9	Iodide	450		30.3	3.6
Ta(V)	50	Ascorbic acid ($C_6H_8O_6$)	30.1	4.8	Sulphate	350		29.6	3.9
Pd(II)	40		29.6	5.1	Citric acid	15		30.3	3.6
Pt(II)	30		29.7	4.7	Oxalic acid	20		29.6	3.9

Table 3. The effect of non-target species on the determination of W(V) as MLC with DTMP and AP_2 (50.0 µg W added) n=5, p = 0.95.

Large amounts of alkali and alkaline-earth metals and rare earth elements, F^- , Cl^- , Br^- , SO_3^{2-} , SO_4^{2-} , $C_2O_4^{2-}$, F^- and Cl^- do not interfere with the determination of Tungsten.

Selectivity of definition significantly increases in the presence of the masking substances. The interference of Fe (III) and Ti(IV) was eliminated with ascorbic acid, Cu(II) – thiourea and Nb(V) – oxalate anion. When using a 0.01M EDTA solution, do not interfere with the determination Ti (IV), V (IV), Nb (V), Ta (V), Mo(VI) and Fe (III).

Pt(IV) and Mo(VI) require respective masking agents as described under the procedure. 50 mg sodium phosphate for Pt (IV) up-to 600 μg and 0.05 mL 6 % (w/v) H_2O_2 for Mo (VI) up-to 200 μg are added to the solution before extraction.

Table 4 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of Tungsten with the earlier known procedures [26].

Reagent	pH (solvent)	λ , nm	$\epsilon \times 10^{-4}$	Beer's law range, μg	References
Toluene-3,4-dithiol	1.5-2.0 (chloroform)	640	1.92	0.1-2.0	
8-Mercaptopoquinoline	0.5-3.0 (изобутанол- chloroform (1:1))	412	0,367	≤ 4	
8 - Hydroxyquinoline	4.4(chloroform)	363	0,64		
3,5-dinitropyrocatechin + 2,3,5-triphenyl-2H-tetrazolium	0.25-0.4M H_2SO_4 (chloroform)	400	2.12	0.5-7.4	27,28
2,3-dihydroxynaphthalene + 2,3,5-triphenyl-2H-tetrazolium	50.4-1.8 MH_2SO_4 (chloroform)	420	2.12	0.7-7.4	28
2-hydroxy-5-thiophenol + aniline	4.2-5.4 (chloroform)	465	2.4		29
6-chloro-3-hydroxy-2-phenyl-4-oxo-4H-1-benzopyran (CHPB)	0.04 – 0.32 M HCl	420	3.125	0 – 2.9	30
SCN^- ethopropazine hydrochloride	4MHCl(chloroform)	404	1.74	1.0-15.0	31
DTMP+AP ₁	4.0-5.1(chloroform)	476	2.73	0.4-16	
DTMP+AP ₂	4.2-5.2(chloroform)	479	2.83	0.4-20	
DTMP+AP ₃	3.9-5.1(chloroform)	480	2.92	0.4-20	

Table 4. Comparative characteristics of the procedures for determining tungsten
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. A linear calibration graph drawn between absorbance and the metal ion concentration indicates

that W(V) may be determined in the range 0.4-20 $\mu g/ml$. Table 5 summarizes the calibration characteristics obtained with DTMP+AP₁ and DTMP+AP₂ and DTMP+AP₃[32]. The pertaining calibration graph is shown in the Figure 8.

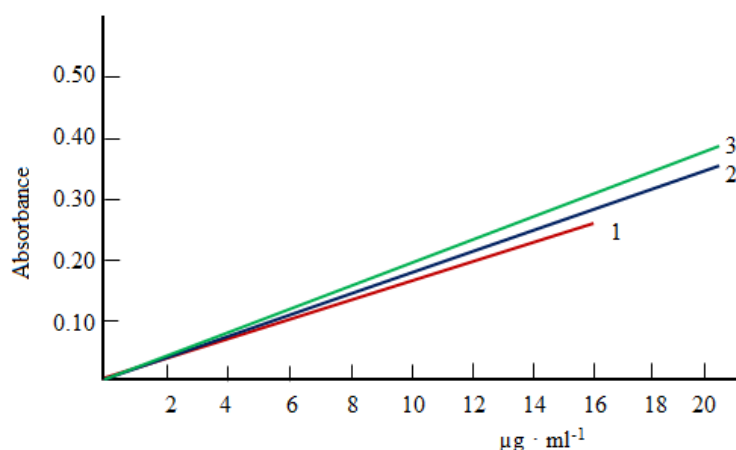


Figure 8. Analytical determination of W(V) with DTMP and hydrophobic amines
 1-W-DTMP-AP₁; 2-W-DTMP-AP₂; 3-W-DTMP-AP₃
 $C_W = 1.09 \times 10^{-5} \text{ M}$, $C_{\text{DTMP}} = 8.0 \times 10^{-4} \text{ M}$, $C_{\text{AP}} = 0.92 \times 10^{-4} \text{ M}$, KFK-2, 490 nm, $l = 0.5 \text{ cm}$.

Parameter	AP ₁	AP ₂	AP ₃
The equation of calibration curves	$0.030 + 0.0119x$	$0.022 + 0.0133x$	$0.019 + 0.0139x$
Correlation coefficient (9 standards used)	0.9970	0.9965	0.9976
Linear calibration range / $\mu\text{g} \cdot \text{cm}^{-3}$	0.4-16	0.4-20	0.4-20
Limit of detection (LOD) / $\text{ng} \cdot \text{cm}^{-3}$	12	11	11
Limit of quantification (LOQ) / $\text{ng} \cdot \text{cm}^{-3}$	38	36	35
Sandell's sensitivity / $\text{ng} \cdot \text{cm}^{-2}$	6.73	6.5	6.3

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

Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of W(V) in steel, soil and plant samples. The usefulness of the method is tested by analyzing satisfactorily a wide variety of samples. In addition, the method has a wider Beer's law range, better precision and accuracy, and free from the interference of a large number of metal ions of great analytical importance.

It is quite simple, rapid, and takes less than 15 minutes for a single determination, and also has an edge over some of the existing methods of tungsten determination in trace amounts. The proposed procedures for determining tungsten in steel, soils and plant samples were verified by 8-hydroxyquinoline and dithiole methods [13]. The results of the analysis are listed in Table 6, 7 and 8 indicate the successful applicability of the proposed method to real sample analysis.

Method	Found W, %	Standard Deviation	Relative Standard Deviation RSD	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Toluene-3,4-dithiol	0.186	0.011	0.06	0.186±0.012
DTMP +AP ₂	0.182	0.009	0.05	0.182±0.009
DTMP +AP ₃	0.181	0.007	0.04	0.181±0.008

Table 6. Correctness and reproducibility of determination of tungsten in steel (steel 339, W-0,183%). number of parallel experiment n=5, Student's coefficient P=0.95.

Method	Found W, % (10 ⁻⁴)	Standard Deviation 10 ⁻⁴	Relative Standard Deviation RSD, %	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
<i>Standard method</i>				
Toluene-3,4-dithiol	2.95	0.148	5	(2.95±0.18)
8 - Hydroxyquinoline	3.02	0.151	5	(3.02±0.19)
<i>Proposed method</i>				
DTMP+AP ₁	2.87	0.087	3	(2.87±0.11)
DTMP +AP ₂	2.85	0.114	4	(2.85±0.14)
DTMP +AP ₃	2.92	0.145	5	(2.92±0.18)

Table 7. Correctness and reproducibility of determination of tungsten in soil. n=5, P=0.95.

	Method	Found W, mg/kg	Standard Deviation	Relative Standard Deviation RSD	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
White cabbage	Toluene-3,4-dithiol	0.139	0.0061	0.044	0.139±0.0064
	8 – Hydroxyquinoline	0.141	0.0070	0.050	0.141±0.0074
	DTMP+AP ₁	0.140	0.0046	0.033	0.140±0.0048
	DTMP +AP ₂	0.134	0.0033	0.025	0.134±0.0033
	DTMP +AP ₃	0.142	0.0060	0.042	0.142±0.0063
Red cabbage	Toluene-3,4-dithiol	0.84	0.047	0.056	0.84±0.05
	8 - Hydroxyquinoline	0.85	0.038	0.045	0.85±0.04
	DTMP+AP ₁	0.86	0.030	0.035	0.86±0.031
	DTMP +AP ₂	0.82	0.023	0.028	0.82±0.024
	DTMP +AP ₃	0.86	0.027	0.032	0.86±0.029

Table 8. The results of determination of tungsten in plant. n=5, P=0.95.

4. Conclusions

1. Mixed-ligand complexes of tungsten (V) with 2, 6-dithiol-4-methylphenol and aminophenols have been investigated by spectrophotometric method.
2. Extraction of mixed ligand complexes is maximal at pH 3.9-5.2. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components in the complexes have been determined.
3. The Beer's law was applicable in the range of 0.4-20 µg/ml. A simple, rapid and sensitive methods proposed for the determination of trace amounts of tungsten.
4. The proposed method has been applied to determine tungsten in steel, soil and plant samples with good results. The proposed method is simple and more sensitive than other methods commonly used at microgram level, in addition to lower tolerance limits.

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