EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF TANTALUM (V) WITH 2-HYDROXYTHIOPHENOL AND ITS DERIVATIVES IN THE PRESENCE OF HYDROPHOBIC AMINES

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Mixed-ligand complexes of Tantalum (V) with thiocatecholic compounds (TCs){2-hydroxy-thiophenol (HTP), 2,4-dihydroxythiophenol (DHTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP) and 2-hydroxy-5-iodothiophenol (HITP)} in the presence of hydrophobic amines (Am) have been studied by spectrophotometry. As hydrophobic amine were used aniline (An), N-methylaniline (MAn), N, N-dimethylaniline (DAn), aminopyridine (APy), dipyridyl (DiPy), guanidine (Gu), diphenylguanidine (DPG), and triphenylguanidine (TPG). Extraction of mixed ligand complexes is maximal at pH 2.4-6.8. The best organic solvent was chloroform. Under the optimum conditions, the molar absorptivities (emax) and the degrees of Tantalum extraction (R%) in this solvent were in the ranges $(1.60\text{-}3.94)\times10^4$ L $mol^{-1}cm^{-1}$ and (98.1-98.6)%, respectively. The molar ratio of the reacting species was 1:2:2 (Ta:TCs:Am). If APy and DiPy molar ratio is 1: 2: 1. The Beer's law was applicable in the range of 1.0-100 µg· ml^{-1}. The method is free from common interferences. A procedure has been developed for extraction – spectrophotometric determination tantalum in steel.

Keywords: Tantalum, solvent extraction, spectrophotometry, ion-associate

1. Introduction

A great variety of photometric reagents is known for the determination of tantalum [1]. However, the studies aiming to find and investigate new photometric reagents with different functional groups are still going on .

Micro amounts of tantalum can be determined directly by spectrophotometry with 4, 5-dibromo-*o*-nitrophenylfluorone, citric acid, hydrogen peroxide and Triton X-100 in 0.5–5 mol L^{-1} sulphuric acid. The synthesis of the complexing agent is described [2].

A rapid and sensitive method for the extraction and spectrophotometric determination of tantalum in presence of niobium with N-p-chlorophenylbenzohydroxamic acid has beendescribed. The tantalum-N-p-chlorophenylbenzohydroxamic acid complex is extractable into toluene or benzene in HCl media [3].

Tantalum (V)-2-(2-thiazolylazo)-5-dimethylaminophenol chelate anion is extracted quantitatively into benzyl alcohol with 1, 3-diphenylguanidine to form a ternary complex [4]. Mixed-ligand complexes of Tantalum (V) with dithiolphenol and its derivatives in the presence of hydrophobic amines have been studied by spectrophotometry [5].

An extraction-spectrophotometric method for the determination of microgram amounts of tantalum (V) based on the extraction of the tantalum-*N*-4-chlorophenyl-3, 4, 5- trimethoxycin-namohydroxamic acid complex from HCI medium into toluene is described. Brilliant Green is added to the organic phase containing the binary complex and the absorbance of the ternary system is measured the method has been applied to the determination of tantalum in the presence of niobium (V) and tantalum in standard samples [6].

A method for determining ~ 0.001% or more of tantalum in ores and mill products is described. After fusion of the sample with sodium carbonate, the cooled melt is dissolved in dilute sulphuric-hydrofluoric acid mixture and tantalum is separated from niobium and other matrix elements by methyl isobutyl ketone extraction of its fluoride from 1M hydrofluoric acid- 0.5M sulphuric acid [7].

The real work is devoted to studying of reaction of a complex formation of Tantalum (V) with thiocatecholic compounds (TCs, H_2L) {2-hydroxythiophenol (HTP), (2,4-dihydroxythiophenol (DHTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP) and 2-hydroxy-5-iodothiophenol (HITP)} in the presence of hydrophobic amines (Am). As hydrophobic amine aniline (An), N-methylaniline (MAn), N, N-dimethylaniline (DAn), aminopyridine (APy), dipyridyl (DiPy), guanidine (Gu), diphenylguanidine (DPG), and triphenylguanidine (TPG) were used.

Some of the mentioned reagents have been recently applied for spectrophotometric determination of various elements in real samples [8-14].

2. Experimental

2.1. Reagents and apparatus

Standard solution of Ta (V) (1mg L^{-1}) were prepared by fusing 0,123g Ta_2O_5 with 4 g $K_2S_2O_7$ in a quartz or platinum crucible. The melt is dissolved in a hot 4% solution of ammonium oxalate, cooled and diluted with a solution ammonium oxalate to 100 ml in a volumetric flask. Working solutions were prepared by appropriate dilution of standard solution 2% solution of ammonium oxalate [14]. The concentration of the niobium solution standardized gravimetrically with N-benzoil-N-phenylhydroxylamine [1]. Working solutions (0.1mg mL^{-1}) were prepared by appropriate dilution of the stock solutions.

Chloroform solutions (1.3×10–2 mol L^{-1}) of the reagents TCs and Am were used. Am (97-99% purity) were purchased from Sigma-Aldrich. TCs were synthesized according to the procedure of Kuliev et al. [15]. Their purity was verified by melting point determination and paper chromatography.

The acidity was adjusted by adding HCl and NaOH solutions (0.1 mol L^{-1}). pH was measured using an I-120.2 potentiometer with a glass electrode. The absorbance was recorded with a KFK-2 photocolorimeter (USSR) and a SF-26 spectrophotometer (USSR). Glass cells with optical path of 5 or 10 mm were used.

For the determination of the composition of the synthesized reagents for the NMR spectroscopy method withdrawn by their 1H nuclear spectra. Spectra were recorded on Fure spectrometer ("Bruker", Germany) at 300,18 MHz operating ranges that were at room temperature in a solution of benzene deuterium (C_6D_6).

IR - spectra were recorded on a spectrophotometer UR-20.

2.2. General Procedure for the Determination of Tantalum (V)

Portions of stock solutions of Tantalum (V) varying from 0.1to 1.0 mL with a 0.1mL step, a 2.5 mL portion of a 0.01 M solution of TCs, and a 2.2 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 0.1 M HCl. The volume of the aqueous phase was increased to 20 mL using distilled water. In 8-15 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 440 nm (ℓ=5mm).

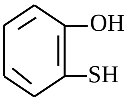
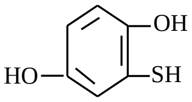
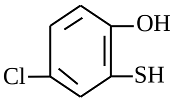
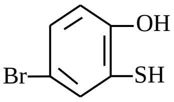
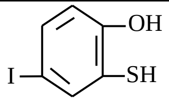
2.3. Determination of Tantalum (V) in steel

A weighed sample of 0.2 g was dissolved in 20 ml of H_2SO_4(1: 1) was oxidized with a few drops of concentrated nitric acid and evaporated twice lo vapor SO_3. The precipitated salt was dissolved in 20 ml of 15% tartaric acid under heating, the solution was cooled, adjusted with water to 100 ml in a volumetric flask, stirred and filtered. An aliquot of 5 ml was put into a separatory funnel, was added 1 ml of 10% hydroxylamine solution, 1 ml of 3% ascorbic acid and was determined tantalum using the proposed procedures.

3. Results and Discussion

The present study is concerned with the investigation of Ta (V) interaction with thiocatecholic compounds, resulting in the formation of colored complexes insoluble in nonpolar solvents. Experiments on electromigration 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 electromigration study of the complexes, it was found that the yellow green thiocatecholic complexes of Tantalum (V) 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 hidrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. Complexing agents may be a dibasic (HTP, HCTP, HBTP, HITP, H_2L) and tribasic weak acid (DHTP, H_3L), and depending on pH of the medium may be in molecular and anionic forms. Some characteristics of the reagents studied are presented in Table 1.

Table 1. **Some characteristics of the studied reagents**

Reagent	Structural formula	The composition of the neutral form	pK_1	pK_2	pK_3	pH neutral form of existence
HTP		H_2L	5.80	10.9	-	0-3.7 (λ=278 nm)
DHTP		H_3L	6.33	8.96	12.78	0-4.0 (λ=281 nm)
HCTP		H_2L	5.10	10.6	-	0-3.5 (λ=283 nm)
HBTP		H_2L	5.05	10.4	-	0-3.3 (λ=286 nm)
HITP		H_2L	5.00	10.2	-	0-3.2(λ=290 nm)

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

3.1. The Choice of the Extractant

For the extraction of complexes we used chloroform, tetrachloromethane, benzene, toluene, xylene, isobutanol, isopentanol, and dichlorethane. The extractivity of the complexes was estimated by the distribution coefficient and recovery. Chloroform, dichloroethane, and chlorobenzene appeared to be the best extractants. All the further investigations were carried out with chloroform. The concentration of

Tantalum in the organic phase was determined with methyl red [17] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference. The basicity of Am hardly influences the recovery of tantalum. After a single extraction with chloroform, 98.1-98.6% of tantalum was extracted as an ion associate.

Table 2. Results of studies of IR and NMR spectroscopy

TCs	IR (KBr) [16]	1H NMR (300.18 MHz, C_6D_6)
HTP	3470 см$^{-1}$ ν (OH), 2580 см$^{-1}$ ν(SH), 3050 см$^{-1}$ ν(CH), 1580 см$^{-1}$ ν(C_6H_5)	δ 5.58 (s, 1H - OH), δ 3.35 (s, 1H - SH), δ 7.06 (s,1H-Ar-H), δ7.25 (s, 2H Ar-H), δ 7.41(s, 2H Ar-H)
DHTP	3470 см$^{-1}$ ν (OH), 2580 см$^{-1}$ ν(SH), 3050 см$^{-1}$ ν(CH), 1580 см$^{-1}$ ν(C_6H_5)	δ 5.48 (s, 2H - OH), δ 3.47 (s, 1H - SH), δ 7.28 (s, 2H Ar-H), δ 6.95 (s, 1H - Ar-H)
HCTP	3460 см$^{-1}$ ν (OH), 2570см$^{-1}$ ν(SH), 1580 см$^{-1}$ ν(C_6H_5)	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(C_6H_5)	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(C_6H_5)	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)

3.2. Influence of the pH of the Aqueous Phase

Extractable ternary complexes are formed in acidic and weakly acidic medium (pH 1.5-7.8). The course of all pH curves supports the assumption that only one complex is formed in each of the extraction-chromogenic systems (Fig. 1). At pH values higher than pH_{opt}, the extraction efficiency reduces most likely due to a decrease of degree of Am protonation. At pH values lower than pH_{opt} (2.8-6.5), the concentration of the anionic TCs species is insufficient for quantitative complex formation.

3.3. Incubation Time and Influence of Reagent Concentration

Unlike single-ligand complexes, MLC of Ta (V) with TCs and Am were stable in aqueous and organic solvents and did not decompose for two days, or over a month after extraction. The required duration of the phase contact was 8-15 min. For the formation and extraction of MLC, a 26-39-fold excess TCs and 20-28 -fold excess Am is required. It was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction.

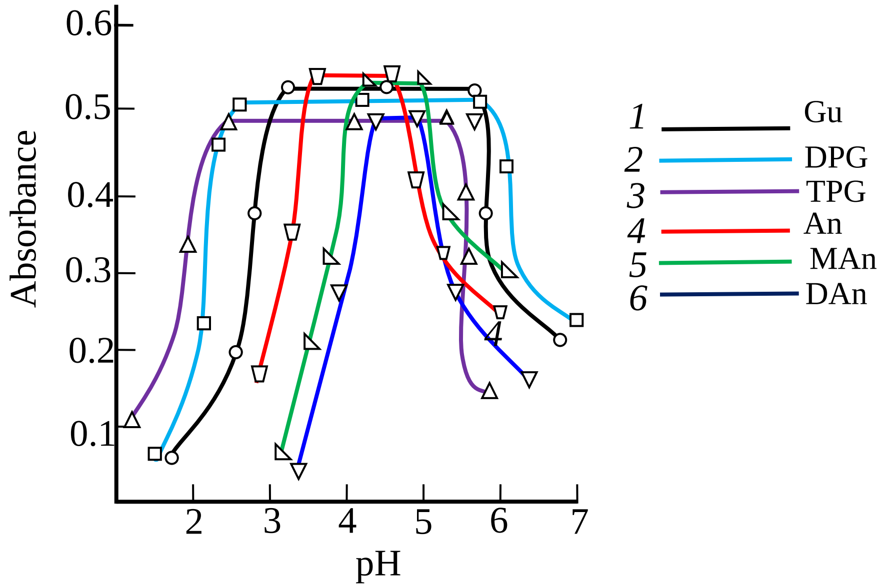


Fig. 1. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase 1.Ta(V)-HBTP-Gu; 2.Ta(V)-HBTP-DPG; 3.Ta(V)-HBTP-TPG; 4.Ta(V)-DHTP-An; 5. Ta(V)-DHTP-Man; 6. Ta(V)-DHTP-DAn.

$C_{Ta(V)}$= 3.31·10^{-5} mol L^{-1}, C_{TCs}=(0.88-1.3)· 10^{-3} mol L^{-1}, C_{AM}= (6.8-9.2)·10^{-4} mol L^{-1}, КФК-2, λ=490 nm, ℓ = 0.5cm.

3.4. Electronic Absorption Spectra

The absorption maxima (λ_{max}) of the ternary Ta:TCs:Am complexes lie in the range of 418-470 nm (Table 4). All colour reactions are very contrast since the initial solutions are colourless (λ_{max} TCs = 278-290 nm). The calculated molar absorptivities (λ_{max}) belong to the interval (1.60-3.94)×10^4 L mol^{-1} cm^{-1}.

3.5. Stoichiometry of the Complexes and the Mechanism of Complexation

The molar ratios between the components of the ternary complex were found by several methods [18] (Starik-Barbanel relative yield method, straight line method, equilibrium shift method and crossed lines method). The results suggest the complex composition of 1:2:2 (Ta: TCs: Am). The formation of MLC can be presented in the following way. When tantalum ion interact with two molecules of TCs, they form doubly-charged anionic complexes, which are extracted with two molecules of protonated Am (Fig. 2). APy and DiPy are part of the complex in the double-protonated form. Therefore, in the case of APy and DiPy molar ratio is 1: 2: 1.

It was found using the Nazarenko method that Ta (V) in the complexes was present in the form of $Ta(OH)_3^{2+}$. The number of protons replaced by tantalum in one TCs molecule appeared to be 1[19].

The disappearance of the pronounced absorption bands in the 3200-3600 cm-1 with a maximum at 3460 sm^{-1} observed in the spectrum of DTP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2580 sm^{-1} shows that -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1380 cm-1 indicates the presence of a protonated aniline [16].Structure extractable complexes can be represented as in Figure 3.

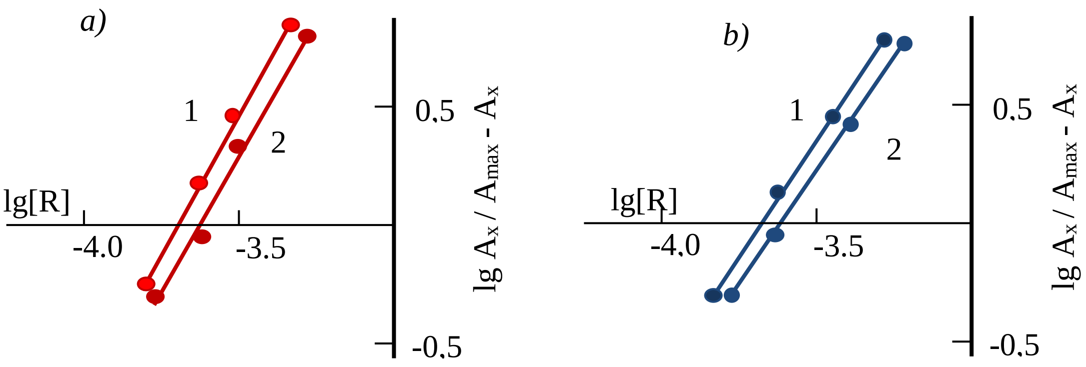


Fig. 2. Determination of the ratio of components by the equilibrium shift method for (a) Ta(V)- DHTP-An and (b) Ta(V)-DHTP-MAn. 1. Nb:DHTP; 2.Nb : Am.

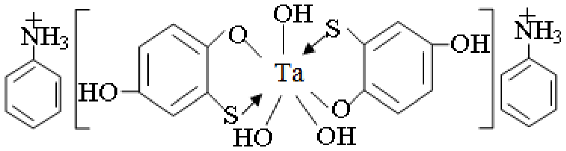


Fig. 3. Structure of complex

3.6. Calculation of the degree of polymerization, the stability constant and the equilibrium constant

Calculation of extent of polymerization of complexes was carried out on the equation [20]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form (γ =1.07-1.12).

The stability constant determined by crossed lines method (Fig. 3). The stability constants of the complex were calculated by the formula [18]

$$\beta = \frac{C_{comp}}{(C_{Ta} - C_{comp})(C_R - nC_{comp})^n}$$

3.7. Influence of Interfering Ions

To evaluate the complex applicability for photometric determination of tantalum, we examined the influence of foreign ions and reagents. The results showed that great excesses of alkali, alkali earth, and rare earth elements, as well as NO_3^-, ClO_4^-, CH_3COO^-, F^-, Cl^-, Br^-, SO_3^{2-}, SO_4^{2-} and $C_2O_4^{2-}$ do not interfere with determination. The influence of Fe(III) was eliminated by thioglycolic acid; Ti(VI), by ascorbic acid; Cu(II), by thiourea; and Mo(VI) and Nb(V), by oxalate. If a 0.01 mol L^{-1} solution of EDTA was used, Ti(IV), V(IV), Nb(V), Mo(VI) and Fe(III) exhibited no interference. The results are summarized in Table 3.

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

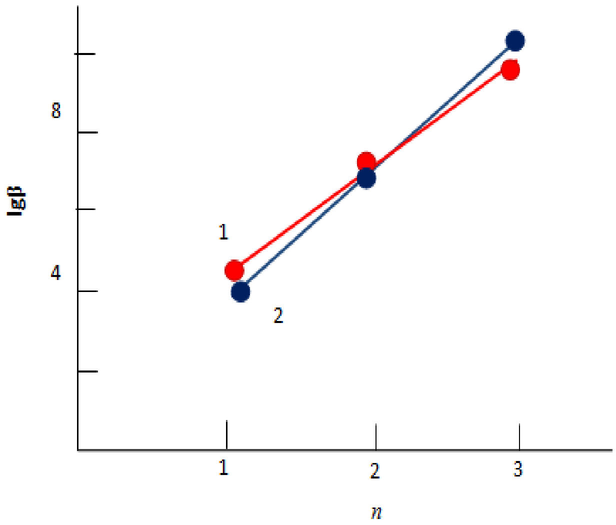


Fig. 3. Determination of the two phase stability constant by the crossed curves method C_{Ta}=3.31·10^{-5} mol L^{-1}, C_{An}= 6.8·10^{-4} mol· L^{-1}, pH=3.5.
1-C_{HTP}=2,4 ·10^{-4} mol· L^{-1}, C_{comp}=9.8 ·10^{-6}mol· L^{-1}; 2-C_{HTP}=4,8 ·10^{-4}mol·L^{-1}, C_{comp}=1,94 ·10^{-5} mol

The sizes of equilibrium constant (K_e) calculated on a formula $\lg K_e = \lg D - 2\lg\left[AmH^+\right]$ were presented in table 4.

Table 3. Influence of interfering ions on the determination of Ta(V) as MLC with DHTP and Am (30.0 µg Ta added).

Ion	Molar excess of the ion	Masking agent	Found Ta, µg (*RSD*,%)				
			DHTP-An	HTP-An	HCTP-Gu	HCTP-DPG	HBTP-DPG
Co(II)	60		30.2 *(4)*	30.0 *(0)*	30.2 *(4)*	29.5 *(4)*	30.2 *(4)*
Ni(II)	55		30.6 *(5)*	30.5 *(3)*	30.2 *(3)*	29.7 *(4)*	30.2 *(3)*
Fe(II)	55		30.5 *(3)*	30.5 *(4)*	30.2 *(2)*	29.7 *(3)*	29.8 *(4)*
Fe(III)	50	$SnCl_2$	30.2 *(6)*	30.1 *(3)*	30.2 *(4)*	30.0 *(0)*	29.8 *(5)*
Cd(II)	190		30.2 *(4)*	29.5 *(4)*	30.2 *(4)*	29.5 *(4)*	30.2 *(6)*
Al(III)	160		30.4 *(4)*	29.6 *(2)*	30.2 *(3)*	29.7 *(4)*	30.2 *(3)*
Mo(VI)	35	T.A.*	30.2 *(4)*	29.5 *(4)*	30.0 *(0)*	29.6 *(2)*	30.0 *(0)*
Zr(IV)	55		29.8 *(4)*	30.5 *(3)*	29.8 *(4)*	30.5 *(3)*	30.0 *(0)*
Cu(II)	40	T.*	30.6 *(5)*	30.5 *(3)*	30.2 *(2)*	29.7 *(3)*	30.4 *(4)*
Hg(II)	40		30.2 *(3)*	29.7 *(3)*	30.2 *(6)*	30.1 *(3)*	30.2 *(4)*
Ti(IV)	40		30.0 *(0)*	29.8 *(3)*	29.6 *(4)*	30.0 *(0)*	30.2 *(4)*
V(IV)	40		30.2 *(2)*	29.7 *(3)*	29.8 *(4)*	30.5 *(3)*	29.8 *(4)*
V(V)	55	EDTA	30.2 *(4)*	30.0 *(0)*	30.6 *(5)*	30.5 *(3)*	29.8 *(4)*
W(VI)	30	T.A.*	29.6 *(4)*	29.7 *(3)*	30.4 *(4)*	30.4 *(4)*	29.6 *(2)*
Cr(III)	130		30.2 *(2)*	29.7 *(3)*	30.0 *(0)*	29.8 *(3)*	30.6 *(5)*
Nb(V)	30	T.A.*	30.2 *(3)*	29.8 *(5)*	29.9 *(4)*	30.0 *(0)*	29.7 *(3)*
UO_2^{2+}	50	T.A.*	30.6 *(5)*	30.5 *(3)*	30.1 *(3)*	30.2 *(3)*	30.2 *(6)*
Cr(VI)	50	T.*	30.4 *(4)*	30.0 *(0)*	30.2 *(4)*	30.0 *(0)*	29.9 *(4)*
Mn(VII)	50	T.*	30.2 *(2)*	29.7 *(3)*	29.6 *(4)*	29.8 *(5)*	30.1 *(3)*

Mn(II)	50		30.5 *(3)*	30.2 *(2)*	29.6 *(4)*	30.2 *(3)*	29.6 *(4)*
Cl^-	60		30.0 *(0)*	29.7 *(3)*	29.6 *(4)*	30.2 *(2)*	30.2 *(2)*
Br^-	60		30.0 *(0)*	30.0 *(0)*	29.6 *(2)*	30.2 *(2)*	29.7 *(3)*
NO_3^-	120		30.0 *(0)*	30.2 *(3)*	29.9 *(4)*	30.2 *(2)*	30.2 *(6)*
SO_4^{2-}	130		29.8 *(5)*	30.0 *(0)*	30.1 *(3)*	30.2 *(4)*	30.0 *(0)*
PO_4^{3-}	130		30.0 *(0)*	30.2 *(3)*	29.7 *(3)*	29.6 *(4)*	30.2 *(3)*
$C_2O_4^{2-}$	70		30.4 *(5)*	30.3 *(4)*	29.9 *(6)*	30.2 *(5)*	29.9 *(2)*
SCN^-	70		30.5 *(3)*	30.2 *(6)*	30.1 *(3)*	30.2 *(2)*	29.7 *(3)*
NO_2^-	140		29.6 *(2)*	29.6 *(2)*	30.2 *(3)*	29.7 *(3)*	30.2 *(2)*
$S_2O_3^{2-}$	90		30.2 *(4)*	30.0 *(0)*	30.2 *(4)*	30.0 *(0)*	29.9 *(4)*
S^{2-}	30		29.8 *(5)*	29.6 *(4)*	30.0 *(0)*	30.2 *(3)*	30.1 *(3)*
$P_2O_7^{4-}$	100		29.8 *(3)*	29.8 *(4)*	30.5 *(3)*	30.2 *(2)*	29.7 *(3)*
CO_3^{2-}	70		30.2 *(6)*	30.1 *(3)*	30.0 *(0)*	29.8 *(5)*	29.8 *(4)*
T.A.- Tartaric acid; T.- Thiourea							

3.8. Effect of Tantalum (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 Ta (V) may be determined in the range 0.04-4.00 gml^{-1}. The pertaining calibration graph is shown in the Fig. 4.

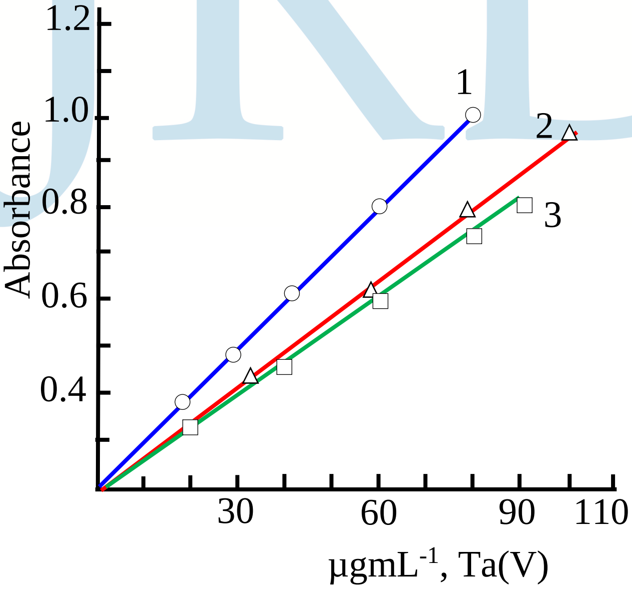


Fig. 4: Analytical determination of Ta (V).

C_{TCs}=(0.88-1.3)· 10^{-3} mol L^{-1}, C_{AM}= (6.8-9.2)·10^{-4} mol L^{-1}, pH = 3.5, SF-26, λ=490 nm, ℓ = 1.0 cm. 1.Ta(V)-HDTF-An; 2. Ta(V)-HTF-An; 3. Ta(V)-HYTF-An

Analytical characteristics ternary complexes Ta (V) with 2-hydroxythiophenol and its derivatives in the presence of hydrophobic amines are given in Table 5.

Table 4. Optical characteristics, precision and accuracy of the spectrophotometric determination of Ta (V) with 2-hydroxythiophenol and its derivatives in the presence of hydrophobic amines

Compound	pH*	λ_{max}, nm	*$\varepsilon \cdot 10^{-4}$	*$\lg K_e$	*$\lg K_{ex}$	*$\lg \beta_k$	*R,%	Working range / $\mu g \cdot cm^{-3}$
Ta-DHTP-An	3.6-4.6	418	3.30	2.71	8.32	6.84	98.5	0.20-16
Ta-DHTP-MAn	3.1-6.2	423	3.62	2.68	8.54	6.46	98.3	0.20-16
Ta-DHTP-DAn	3.2-6.5	428	3.94	2.63	8.67	6.12	98.2	0.20-16
Ta-HTP-AmPy	1.8-5.0	453	2.00	8.58	12.61	7.42	98.1	0.48-20
Ta-HTP-Dipy	1.9-6.0	465	2.20	8.73	12.93	7.37	98.2	0.36-18
Ta-HTP-An	2.0-6.1	440	3.00	2.68	8.65	8.19	98.3	0.2-20
Ta-HCTP-Gu	2.0-7.8	436	3.00	8.93	12.78	6.29	98.4	0.84-18
Ta-HCTP-DPG	1.9-7.5	440	3.30	8.87	13.54	6.07	98.6	0.72-19
Ta-HCTP-TPG	1.7-7.4	447	3.32	8.79	14.95	5.94	98.5	0.76-20
Ta-HBTP-Gu	1.8-6.6	435	3.24	8.82	12.33	5.93	98.3	0.32-20
Ta-HBTP-DPG	1.5-7.0	442	3.09	8.79	13.85	5.80	98.3	0.40-16
Ta-HBTP-TPG	1.5-5.9	451	2.95	8.91	14.92	5.72	98.6	0.60-18
Ta-HITP-AmPy	1.2-5.2	460	1.60	8.86	14.67	5.61	98.6	0.60-20
Ta-HITP-Dipy	1.5-5.4	470	1.70	8.77	12.83	5.49	98.5	0.52-20
Ta-HITP-An	1.7-5.8	450	2.50	2.73	8.85	5.64	98.3	0.56-18

Note: *pH- The pH range of maximum extraction; ε- Molar absorptivity (L·mol^{-1}cm-^{1}); lgK$_e$- equilibrium constant; lgK$_{ex}$-extraction constant; lgβ$_k$-stability constant; R,%- degree of extraction.*

Table 5. Analytical characteristics ternary complexes Ta (V) with 2-hydroxythiophenol and its derivatives in the presence of hydrophobic amines

Compound	1*	2*	3*	4*	5*	6*
Ta-DHTP-An	0.0055	0.20-16	14	45	0.075+0.0063x	0.9854
Ta-DHTP-MAn	0.0050	0.20-16	13	42	0.007+0.016x	0.9923
Ta-DHTP-DAn	0.0046	0.20-16	12	40	0.075+0.013x	0.9847
Ta-HTP-AmPy	0.0091	0.48-20	15	50	0.0027+0.053x	0.9775
Ta-HTP-Dipy	0.0082	0.36-18	13	42	0.0019+0.095x	0.9931
Ta-HTP-An	0.0060	0.2-20	12	40	0.012+0.018x	0.9866
Ta-HCTP-Gu	0.0060	0.84-18	11	36	0.035+0.061x	0.9648
Ta-HCTP-DPG	0.0055	0.72-19	15	50	0.0063+0.063x	0.9651
Ta-HCTP-TPG	0.0055	0.76-20	14	45	0.015+0.078x	0.9877
Ta-HBTP-Gu	0.0056	0.32-20	13	42	0.0075+0.012x	0.9783
Ta-HBTP-DPG	0.0059	0.40-16	12	40	0.078+0.041x	0.9954
Ta-HBTP-TPG	0.0061	0.60-18	13	4	0.037+0.053x	0.9762
Ta-HITP-AmPy	0.0011	0.60-20	10	33	0.0075+0.063x	0.9985
Ta-HITP-Dipy	0.0011	0.52-20	10	33	0.075+0.027x	0.9748
Ta-HITP-An	0.0072	0.56-18	14	45	0.0038+0.037x	0.9634

Note: *1*- Sandell's sensitivity (μg· cm^{-2}); 2*- Beer's law range (μg· ml^{-1}; 3*-Limit of detection(LOD): ng ·mL^{-1}; 4*- Limit of quantification (LOQ): ng ·mL^{-1}; 5*- The equation of calibration curves; 6*-Correlation coefficient.*

The proposed method compares favourably with the existing ones (Table 6) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity [1,4-6,17].

Table6. Comparative characteristics of the procedures for determining tantalum

Reagent	pH (solvent)	λ, nm	$\varepsilon \cdot 10^{-4}$	Beer's law range ($\mu g \cdot ml^{-1}$)	Ref.
Pyrogallol	4 M HCl	335	0.24	0-16	[1]
2-(2-thiazolylazo)-5- dimethylaminophenol + diphenylguanidine	4.1–4.9	605	4.10	2–18	[4]
2, 6-dithiolphenol + N-methylaniline	3.1 -4.0 ($CHCl_3$)	435	2.31	0.05-3.2	[5]
2, 6-dithiol-4-ethylphenol + diphenylguanidine	4.1-5.6 ($CHCl_3$)	448	3.49	0.04-3.8	[5]
2, 6-dithiol-4-*tert*-buthylphenol + N,N -dimethylaniline	3.6-4.9 ($CHCl_3$)	455	3.17	0.04-3.8	[5]
N-4-chlorophenyl-3,4,5-trimethoxycin-namohydroxamic	3.1-5.7	385	2.90	-	[6]
N-4-chlorophenyl-3,4,5-trimethoxycin-namohydroxamic + Brilliant Green	3.1-4.8	635	2.30	0.7-4.8	[6]
Methylviolet	2.1-2.3	605	7.50	-	[17]
Dimethylfluoran	0.1 M HCl	500	4.20	0-5	[17]
2,4-dihydroxythiophenol + aniline	3.6-4.6	418	3.30	0.20-16	Proposed method
2,4-dihydroxythiophenol+ N-methylaniline	3.1-6.2	423	3.62	0.20-16	
2,4-dihydroxythiophenol+ N, N-dimethylaniline	3.2-6.5	428	3.94	0.20-16	

3.9. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Ta (V) in steels of different brands. The results presented in table 7 indicate the successful applicability of the proposed method to real sample analysis.

Table 7. Determination of Tantalum in steel (*n*=5, *P*=0.95)

Steel	Prosedure	$\bar{X}$, %	*RSD,%*
CBT-1 (0.012 % Ta)	DHTP+An	0.0127±0.042	2.4
	DHTP+MAn	0.0123±0.018	2.8
	DHTP+DAn	0.0118±0.031	2.0
CBT-3 (0.029 % Ta)	DHTP+An	0.0294±0.015	2.3
	DHTP+MAn	0.0283±0.026	2.5
	DHTP+DAn	0.274±0.042	2.3
CBT-6 (0.147 % Ta)	DHTP+An	0.148±0.032	2.6
	DHTP+MAn	0.146±0.027	2.7
	DHTP+DAn	0.148±0.029	2.2

4. Conclusion

1. Mixed-ligand complexes of Tantalum (V) with thiocatecholic compounds and hydrofob amins have been studied by spectrophotometry.
2. Extraction of mixed ligand complexes is maximal at pH 1.5-7.8. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found.
3. The molar ratio of the reacting Ta (V), TCs and Am species is 1:2:2 (If APy and DiPy molar ratio is 1: 2: 1). The general formula of the ternary complexes is $[Ta(OH)_3(TCs)_2](AmH)_2$. They can be regarded as ion-associates bet-ween doubly charged anionic chelates $[Ta(OH)_3(TCs)_2]^{2-}$ and protonated Am species.
4. The molar absorptivities (ε_{max}) belong to the interval $(1.60\text{-}3.94)\times10^4$ L mol^{-1} cm^{-1} for the complexes of NbV . The highest molar absorptivity can be achieved with the couple DHTP-DAn.
5. A procedure has been developed for extraction spectrophotometric determination tantalum in steels of different brands.

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