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Spectrophotometric determination of trace amounts of tantalum (V) with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines

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Abstract

Mixed-ligand complexes of Tantalum (V) with dithiolphenol (DP) {2, 6-dithiolphenol (DTP) and its derivatives (2, 6-dithiol-4-methylphenol (DTMP), 2, 6-dithiol-4-ethylphenol (DTEP), 2, 6-dithiol-4-propylphenol (DTPP), 2, 6-dithiol-4-*tert*-butylphenol (DTBP)} in the presence of hydrophobic amines (Am) have been studied by spectrophotometry. As hydrophobic amine were used aniline (An), N-methylaniline (MAAn), N, N-dimethylaniline (DAn), aminopyridine (APy), dipyridyl (DiPy), diphenylguanidine (DPG), and triphenylguanidine (TPG). The best organic solvent was chloroform. Extraction of mixed ligand complexes is maximal at pH 2.9-6.0. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components I the complexes have been determined. The Beer's law was applicable in the range of 0.03-3,8µg/ml. 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

Tantalum in nuclear energy is used primarily as a construction material, in particular in equipment designed for the chemical processing of nuclear fuel. Tantalum carbide is part of some brands of super-hard and refractory alloys and cast carbide. Tantalum produce anodes, grid, indirectly heated cathodes and other parts for vacuum tubes [1].

A great variety of photometric reagents is known for the determination of niobium. 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. Results obtained by applying the proposed method to niobium oxide, ferroniobium, nickel-base alloy and a mineral are satisfactory. The synthesis of the complexing agent is described [2].

A method for tantalum (V) spectrophotometric determination in a non-aqueous phase is proposed. Tantalum (V) is extracted with N-phenylbenzohydroxamic acid into toluene from a 5M hydrochloric acid solution. The colour is then developed by addition of 4-(2-pyridylazo)-resorcinol (PAR) solution in N, N-dimethylformamide and pyridine to an aliquot of the extracted phase. The method has been applied to the selective determination of tantalum in ores with good accuracy and precision [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. In the organic phase, the complex has an absorption maximum at 605 nm. The optimum pH range for the extraction is 4.1–4.9 and the ternary complex is stable for at least 50 min [4].

The mixed micellar media of hexadecyltrimethylammonium bromide as a cationic surfactant and poly (oxyethylene) - cetyler (Brij 35) as a nonionic surfactant was used for a highly sensitive spectrophotometric determination of tantalum with *o*-hydroxyhydroquinonephthalein at strong acidic media [5].

A rapid and sensitive method for the extraction and spectrophotometric determination of Tantalum in presence of niobium with N-p-chlorophenylbenzohydroxamic acid has been

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described. The tantalum-N-p-chlorophenylbenzohydroxamic acid complex is extractable into toluene or benzene in HCl media [6].

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 HCl medium into toluene is described. Brilliant Green (BG) 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 [7].

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. [8].

Hydroxyphenolate complexes of tantalum are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines easily dissolve in various organic solvents [25]. 29 liquid-liquid extraction-chromogenic systems containing M^V (M=Nb or Ta), thiocatecholic compounds and hydrophobic amines were studied. The following TCs were used: 2, 4-dihydroxythiophenol, 2-hydroxythiophenol, 2-hydroxy-5-chlorothiophenol, 2-hydroxy-5-bromothiophenol, and 2-hydroxy-5-iodothiopheno [9].

In this respect, a very promising reagent is 2, 6-dithiolphenol (DTP), which contains one hydroxyl and two sulfhydryl groups and is a sulfur-containing analogue of mononuclear poly-phenols with two oxygen atoms replaced with sulfur atoms. The real work is devoted to studying of reaction of a complex formation of Tantalum (V) with 2, 6-dithiolphenol (DTP) and its derivatives {(2, 6-dithiol-4-methylphenol (DTMP) 2, 6-dithiol-4-ethylphenol (DTEP), 2, 6-dithiol-4-propylphenol (DTPP) and 2, 6-dithiol-4-*tert*-butylphenol (DTBP)} in the presence of hydrophobic amines (Am). As hydrophobic amine aniline (An), N-methylaniline (MAN), N, N-dimethylaniline (DAn), aminopyridine (APy), dipyrindyl (DiPy), 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 [10-13].

2. Experimental

2.1. Reagents and apparatus

Standard solution of Ta (V) (1mg / L) were prepared by fusing 0,123g Ta₂O₅ with 4 g K₂S₂O₇ 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].

Solutions of DTP and Am in chloroform (0.01M) were used. Their purity was verified by melting point determination and paper chromatography. To create the optimal acidity, 0.1M solutions of KOH and HCl were used. The extractant was purified chloroform.

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 an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples.

2.2. General Procedure

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

Portions of stock solutions of Tantalum (V) varying from 0.1 to 1.0 mL with a 0.1-mL step, a 2.5 mL portion of a 0.01 M solution of DP, and a 2.8 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 1M HCl. The volume of the aqueous phase was increased to 20 mL using distilled water. In 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=0.5cm).

2.2.2. Determination of Tantalum (V) in steel

A weighed sample of 0.2 g was dissolved in 20 ml of H₂SO₄ (1: 1) was oxidized with a few drops of concentrated nitric acid and evaporated twice to vapor SO₃. 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 dithiolphenol (DP), 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 blue-green dithiophenolate 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 hydrophob amin (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 (DTP, DTMP, DTEP, DTPP and DTBP) are weak tribasic acid (H₃R) and depending on the pH of the medium may be in molecular and sushestvovat two anionic forms. Reagents were synthesized by the known procedure [15]. The synthesized compounds were characterized by physicochemical methods: IR and NMR spectroscopy. 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	pH neutral form of existence
2,6 dithiolphenole (DTP)		H ₃ R	6,30	0-6,3 (λ=270 nm)
2,6-dithiol-4-methylphenole(DTMP)		H ₃ R	6,84	0-6,9 (λ=274 nm)
2,6-dithiol-4-ethylphenole(DTEP)		H ₃ R	6,92	0-6,9 (λ=276 nm)
2,6-dithiol-4-propylphenole(DTPP)		H ₃ R	6,72	0-6,7 (λ=278 nm)
2,6-dithiol-4-tert-butylphenole(DTBP)		H ₃ R	6,98	0-7,0 (λ=280 nm)

3.1. The Choice of the Extractant

For the extraction of complexes we used chloroform, tetrachloromethane, benzene, toluene, xylene, isobutanol, isopentanol, and dichloroethane. 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 ^[14] 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, 96.9-98.8% of tantalum was extracted as an ion associate.

3.2. Influence of the pH of the Aqueous Phase

The effect of pH on the intensity of the color reaction is shown in the Fig. 1. The absorbance was found to be maximum in the pH range 2, 9-6, 0. Hence further analytical investigations were carried out in media of pH 3. Extraction of Ta (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 DTP. Probably, it is present in the solution in the non-dissociated state. At pH ≥ 7, the complexes were hardly extracted, obviously because of the decrease in the degree of Am protonation.

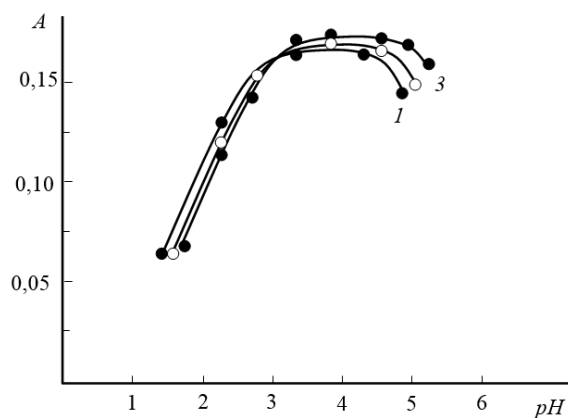


Fig 1: Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase.

1. Ta (V)-DTBP-*An*; 2. Ta (V)-DTBP-*mAn*; 3. Ta (V)-DTBP-*dAn*.
 $C_{Ta}=1.104 \times 10^{-5}$ M, $C_{DTP}=1.0 \times 10^{-3}$ M, $C_{Am}=1.12 \times 10^{-3}$ M, KFK-2, 440nm, $l=0.5$ cm.

3.3. Influence of Reagent Concentration and Incubation Time

For the formation and extraction of MLC, a 20-25-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by 1.0×10^{-3} M DP and 1.12×10^{-3} M Am. A large excess of hydrophob amin interferers with the determination. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. Unlike single-ligand complexes, mixed-ligand complexes of Ta (V) with DP 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 10 min.

3.4. Electronic Absorption Spectra

Neither the metal ion nor the reagent has appreciable absorbance at specified wave-lengths. Hence further studies were carried out at 435-440 nm (fig.2). The Komar method [16] also allows to calculate the true molar absorptivity of the complex: $\epsilon = (2.1-2.4) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.

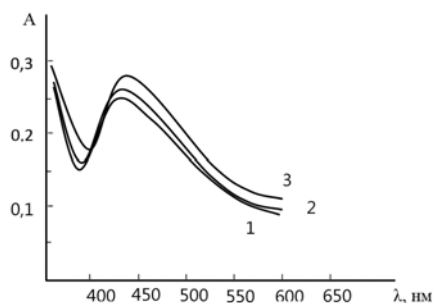


Fig 2: Absorption of mixed-ligand complexes

1. Ta (V)-DTP-*An*; 2. Ta (V)-DTP-*mAn*; 3. Ta (V)-DTP-*dAn*.
 $C_{Ta}=1.104 \times 10^{-5}$ M, $C_{DTP}=1.0 \times 10^{-3}$ M, $C_{Am}=1.12 \times 10^{-3}$ M, KFK-2, 440nm, $l=1$ cm.

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: Starik-Barbanel relative yield method [16], straight line method [16], equilibrium shift method [16] and crossed lines method [16]. The results

suggest the complex composition of 1:2:2 (Ta: DP: Am). The formation of MLC can be presented in the following way. When tantalum ion interact with two molecules of DP, they form doubly-charged anionic complexes, which are extracted with two molecules of protonated Am. (Fig. 2). Formed ion-association complex between anionic chelates of tantalum (V) with DP and hydrophobic aromatic amines. It was found using the Nazarenko method that Ta (V) in the complexes was present in the form of $Ta(OH)_5^{2+}$. The number of protons replaced by tantalum in one DP molecule appeared to be 1 [17, 18].

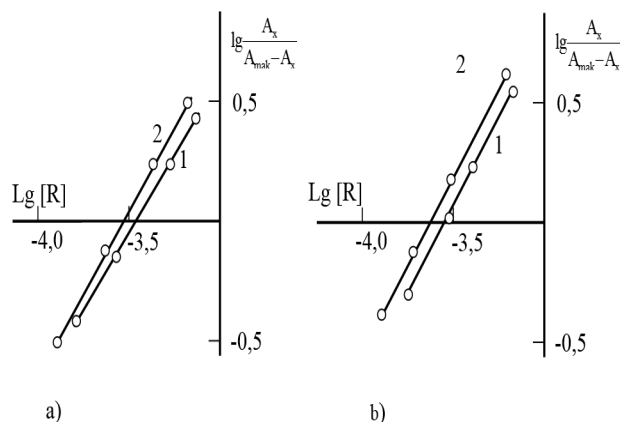


Fig 3: Determination of the ratio of components by the equilibrium shift method

a) Ta-DTEP-AmPy; b) Ta-DTEP-DPG

1- Ta-DTEP; 2- Ta-Am
 $C_{Ta}=1,104 \cdot 10^{-5} \text{ mol L}^{-1}$, $pH=3$.

The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3460 cm^{-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 cm^{-1} shows that one of the -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 [19, 20].

Structure extractable complexes can be represented as in Figure 4.

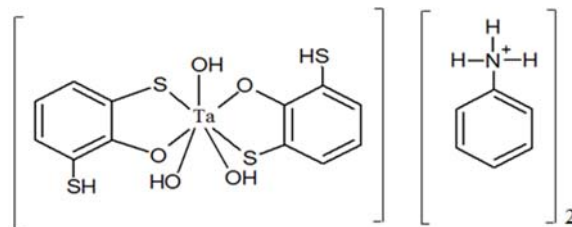


Fig 4: Structure of complex

The stability constant determined by crossed lines method. The sizes of equilibrium constant K_e calculated on a formula $\lg K_e = \lg D - 2 \lg [AmH^+]$ were presented in table 3.

Calculation of extent of polymerization of complexes was carried out on the equation [21]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma = 1, 07-1, 12$).

3.6. 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^- , SO_4^{2-} and CH_3COO^- do not interfere

determination of tantalum with DTP and Am. Interference of most cations masked by the addition of complexone III. Tartrate mask the milligram quantities of Ta, Ti, W and Mo. Zr fluorides should mask, and copper-thiourea. The results are summarized in Table 2.

Table 2: Influence of interfering ions on the determination of tantalum (V) as MLC with DTP and an (30, 0 μg Ta added)

Ion	Molar excess of the ion	Masking agent	Found Ta, μg	RSD, %
Ascorbic acid	100		30,0	3
Tartaric acid	100		30,2	3
Oxalate	5		30,7	4
Fluoride	1,5		29,6	4
Phosphoric acid	30		30,0	3
Thiourea	20		31,2	6
Co(II)	120		30,0	3
Ni(II)	120		30,2	3
Al(III)	190		30,8	4
Fe(II)	80		29,6	4
Fe(III)	80		30,2	4
Cd(II)	200		30,2	3
Zr(IV)	75	NaF	30,5	5
Cu(II)	35	$\text{SC}(\text{NH}_2)_2$	29,7	5
Ti(IV)	5	Ascorbic acid	29,6	5
Mn(II)	50		29,5	3
W(VI)	8		29,8	4
Mo(VI)	15		29,6	5
Cr(III)	30		30,2	2
V(IV)	10		30,2	6
Nb(V)	5	NaF	30,2	5
Pt(II)	50		29,2	5
Pd(II)	50		30,4	6
UO_2^{2+}	40	CH_3COO^-	29,3	4

In conclusion the analytical parameters pertaining to the proposed method are given in Table 3.

Table 3: Optical characteristics, precision and accuracy of the spectrophotometric determination of Ta (V) with DP and Am

Compound	The pH range of maximum extraction	R, %	λ_{max} (nm)	Molar absorptivity ($\text{L} \cdot \text{mol}^{-1} \text{cm}^{-1}$) $\epsilon \cdot 10^{-4}$	$\lg K_e$	$\lg \beta$	$\lg K_{\text{ex}}$	Working range / $\mu\text{g} \cdot \text{cm}^{-3}$
Ta-DTP-An	2,9-3,7	97.5	430	2.09	5.04	6.89	9.28	0.5-16
Ta-DTP-mAn	3,1-4,0	97.8	435	2.31	5.22	7.10	9.42	0.5-16
Ta-DTP-dAn	3,3-4,3	98.0	438	2.45	5.35	7.25	9.46	0.5-18
Ta-DTP-AmPy	3,6-4,8	96.9	445	2.48	5.34	7,16	9.31	0.5-18
Ta-DTP-DPG	3,9-5,4	97.9	440	2.95	5.42	7.40	10.06	0.5-19
Ta-DTP-DiPy	3,7-4,9	97.8	438	2.34	5.36	8.31	9.95	0.5-16
Ta-DTMP-An	3,2-4,4	97.6	425	2.29	5.65	10.28	11.08	0.4-16
Ta-DTMP-mAn	3,3-4,6	97.9	435	2.44	5.72	10.32	11.20	0.5-17
Ta-DTMP-dAn	3,5-4,7	98.1	440	2.53	5.83	10.53	11.32	0.5-17
Ta-DTMP-DPG	4,3-5,8	98.9	445	3.32	5.82	9.40	10.06	0.5-19
Ta-DTMP-TPG	3,6-5,5	97.8	445	3.05	5.62	9.10	10.02	0.5-16
Ta-DTEP-An	3,9-5,3	98.3	448	2.48	5.53	9.94	11.25	0.4-16
Ta-DTEP-mAn	3,8-5,1	98.4	450	2.65	5.65	10.06	11.05	0.5-17
Ta-DTEP-dAn	3,6-5,0	98.4	445	2.77	5.68	10.25	10.83	0.5-17
Ta-DTEP-AmPy	2,9-4,2	97.8	445	2.84	5.55	9.24	10.33	0.5-16
Ta-DTEP-DPG	4,1-5,6	98.0	448	3.49	5.86	9.35	10.48	0.5-18
Ta-DTEP-DiPy	3,3-4,5	98.2	450	2.56	5.92	10.50	10.55	0.5-17
Ta-DTPP-An	3,9-5,3	98.4	450	2.68	5.42	9.25	10.85	0.4-18
Ta-DTPP-mAn	3,8-5,1	98.5	454	2.84	5.55	10.60	10.75	0.4-18
Ta-DTPP-AmPy	3,6-5,0	98.6	455	2.95	5.63	10.50	10.63	0.5-17
Ta-DTPP-DPG	4,9-6,0	98.0	460	3.57	5.65	10,46	10.08	0.5-19
Ta-DTPP-TPG	3,3-4,2	98.0	455	3.32	5.72	9.41	10.26	0.5-18

Ta-DTBP-An	3,3-4,6	98.2	450	2.87·	5.78	10.65	11.60	0.5-17
Ta- DTBP-mAH	3,5-4,8	98.4	455	3.03·	5.82	10.79	11.75	0.5-17
Ta- DTBP-dAH	3,6-4,9	98.5	455	3.17·	5.86	10.85	11.87	0.4-18
Ta- DTBP -AmPy	4.0-5.1	98.2	460	3.24	5.87	10.90	11.90	0.4-19

3.7. 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 0.04-3.8 $\mu\text{g/ml}$. The pertaining calibration graph is shown in the Fig. 5.

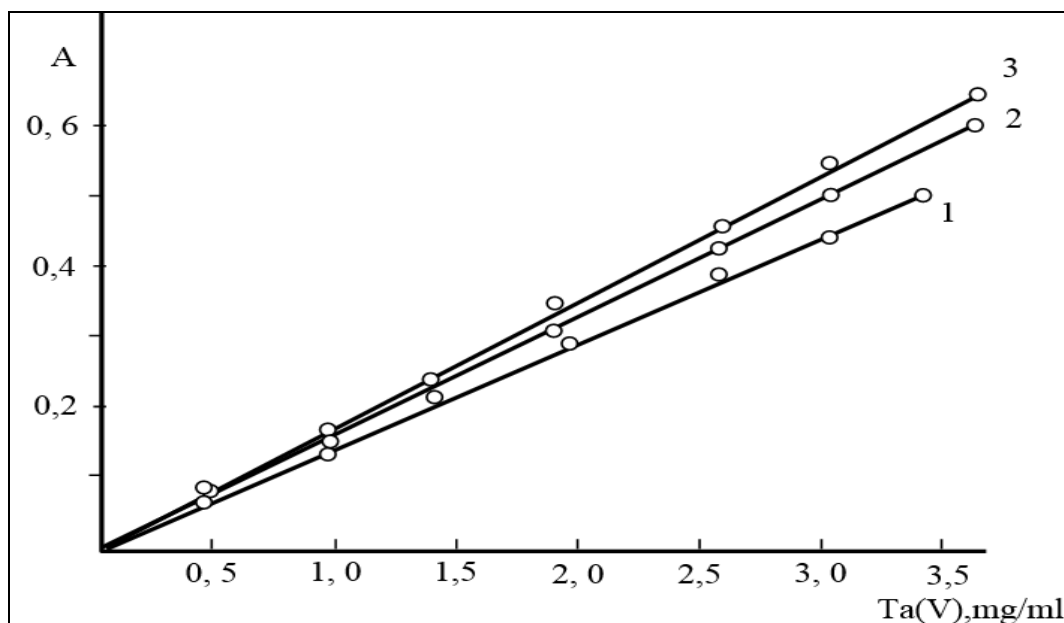


Fig 5: Analytical determination of Ta (V); $C_{DTP} = 1 \times 10^{-3} \text{ M}$; $C_{Am} = 1.12 \times 10^{-3} \text{ M}$; $\text{pH} = 3$; $\lambda = 440 \text{ nm}$, $l = 0.5 \text{ cm}$.
1- Ta-DTEP-An 2- Ta- DTEP-mAH 3- Ta- DTEP -dAH

Table 4: Analytical characteristics of some ternary complexes of Ta with 2, 6-Dithiolphenol and its Derivatives in the Presence of Hydrophobic Amines

Compound	Sandell's sensitivity ($\mu\text{g} \cdot \text{cm}^{-2}$)	Beer's law range ($\mu\text{g} \cdot \text{mL}^{-1}$)	Limit of detection (LOD): $\text{ng} \cdot \text{mL}^{-1}$	Limit of quantification (LOQ): $\text{ng} \cdot \text{mL}^{-1}$	The equation of calibration curves	Correlation coefficient
Ta-DTP-An	0.00854	0.05-3.2	15	50	$0.011+0.11x$	0.9863
Ta- DTP-mAH	0.00783	0.05-3.2	14	45	$0.021+0.12x$	0.9875
Ta- DTP -dAH	0.00739	0.05-3.6	14	45	$0.015+0.14x$	0.9938
Ta-DTP-AmPy	0.00730	0.05-3.6	13	42	$0.016+0.14x$	0.9921
Ta-DTP-DPG	0.00613	0.05-3.8	12	40	$0.023+0.15x$	0.9911
Ta-DTP-DiPy	0.00773	0.05-3.2	13	42	$0.018+0.12x$	0.9982
Ta-DTMP-An	0.00790	0.05-3.2	14	45	$0.034+0.11x$	0.9865
Ta-DTMP-mAn	0.00742	0.05-3.4	13	42	$0.012+0.13x$	0.9911
Ta-DTMP-dAn	0.00715	0.04-3.4	12	40	$0.010+0.14x$	0.9838
Ta-DTMP- DPG	0.00545	0.04-3.6	11	36	$0.016+0.18x$	0.9854
Ta-DTMP- TPG	0.0060	0.05-3.2	12	40	$0.038+0.15x$	0.9874
Ta-DTEP-An	0.0074	0.05-3.2	11	36	$0.052+0.12x$	0.9738
Ta- DTEP-mAH	0.0069	0.05-3.4	12	40	$0.038+0.14x$	0.9673
Ta- DTEP -dAH	0.0066	0.05-3.6	11	36	$0.027+0.15x$	0.9871
Ta- DTEP -AmPy	0.0066	0.04-3.2	11	36	$0.014+0.16x$	0.9933
Ta-DTEP-DPG	0.0052	0.04-3.8	10	33	$0.014+0.18x$	0.9643
Ta-DTEP-DiPy	0.0071	0.04-3.4	10	33	$0.033+0.11x$	0.9974
Ta-DTPP-An	0.0065	0.04-3.4	11	36	$0.046+0.13x$	0.9938
Ta-DTPP-mAn	0.0063	0.05-3.5	10	33	$0.031+0.14x$	0.9931
Ta-DTPP- AmPy	0.0061	0.04-3.4	10	33	$0.019+0.16x$	0.9970
Ta-DTPP- DPG	0.0051	0.05-3.8	9	29	$0.017+0.19x$	0.9936
Ta-DTPP- TPG	0.0054	0.04-3.5	10	33	$0.031+0.17x$	0.9822
Ta-DTBP-An	0.0061	0.04-3.2	10	33	$0.029+0.15x$	0.9772
Ta- DTBP -mAH	0.0060	0.04-3.6	9	29	$0.018+0.16x$	0.9630
Ta- DTBP -dAH	0.0057	0.04-3.8	10	33	$0.023+0.16x$	0.9744
Ta- DTBP -AmPy	0.0056	0.05-3.6	12	40	$0.019+0.17x$	0.9676

With the increase of the basic amine (pK_a) complexes improved analytical parameters ($\text{pK}_a(\text{An})=4,58$, $\text{pK}_a(\text{mAn})=4,85$, $\text{pK}_a(\text{dAn})=5.06$).

The proposed method compares favourably with the existing ones (Table 4) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity [1, 14].

Table 4: Comparative characteristics of the procedures for determining tantalum

Reagent	pH (solvent)	λ , nm	$\epsilon \cdot 10^{-4}$	Beer's law range ($\mu\text{g} \cdot \text{ml}^{-1}$)
Pyrogallol	4MHCl	335	0.24	0-16
Methyl violet	2.1-2.3(benzen)	605	7,5	
Dimethyl fluoran	0.1MHCl	500	4.2	0-5
DTP+mAn	3,1 -4,0 (CHCl ₃)	435	2.31	0.05-3.2
DTEP- DPG	4,1-5,6(CHCl ₃)	448	3.49	0.04-3.8
DTBP -dAn	3,6-4,9(CHCl ₃)	455	3.17	0.04-3.8

3.8. 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 5 indicate the successful applicability of the proposed method to real sample analysis.

Table 5: Determination of Tantalum in steel (n=5, P=0.95)

Prosedure	\bar{X} , %	RSD, %
<i>CBT-3(0,029%Ta)</i>		
<i>Standard method</i>		
Pyrogallol	$(2.94 \pm 0,30) \cdot 10^{-2}$	2.9
Bromopyrogallol red	$(3.10 \pm 0,27) \cdot 10^{-2}$	3.1
<i>Proposed method</i>		
DTP+An	$(2.84 \pm 0,24) \cdot 10^{-2}$	1.8
DTP+dAn	$(2.85 \pm 0,24) \cdot 10^{-2}$	1.9
<i>CBT-6(0,0147%Ta)</i>		
<i>Standard method</i>		
Pyrogallol	$(1.49 \pm 0,25) \cdot 10^{-2}$	3.8
Bromopyrogallol red	$(1.50 \pm 0,29) \cdot 10^{-2}$	4.1
<i>Proposed method</i>		
DTPP+DPQ	$(1.46 \pm 0,21) \cdot 10^{-2}$	2.7
DTPP+dAn	$(1.45 \pm 0,19) \cdot 10^{-2}$	2.1

3.9. Correlation between Properties of the Reagents and Complexes

To establish relationships between the acid-base properties of the sulfhydryl group (pK_{SH}) and some properties of the ternary complexes (ΔpH_{50} and $\text{lg}\beta$) we constructed Fig. 6. The pH_{50} values were determined graphically from the dependence $A=f(\text{pH})$ (see Fig. 1) for absorbance of 50% (Tabl. 6). $\Delta\text{pK}_{\text{SH}}$ values in Fig. 6 and Fig. 7 are the differences between pK_{SH} of the unsubstituted reagent (DP; X=H) and pK_{SH} of its substituted analogues (X=-CH₃, -C₂H₅, -C₃H₇ and -C(CH₃)₃). ΔpH_{50} in Fig. 6. Is the corresponding difference between the pH_{50} values for DTP and DTMP, DTEP, DTPP or DTBP ($R^2=0.9675$).

Table 6: Analytical characteristics of some ternary complexes of Ta with 2, 6-Dithiolphenol and its Derivatives in the Presence of An.

H ₃ R	pK_{SH}	$\Delta \text{pK}_{\text{SH}}$	pH_{50}	ΔpH_{50}	$\text{lg}\beta$	σ_n
H	6.30	0.0	2.21	0.00	6.89	0
-C ₃ H ₇	6.72	-0.42	2.62	-0.41	9.25	-0.126
-C ₂ H ₅	6.84	-0.54	2.70	-0.49	9.94	-0.151
-CH ₃	6.92	-0.62	2.75	-0.54	10.28	-0.170
-C(CH ₃) ₃	6.98	-0.68	2.86	-0.58	10.65	-0.197

$$\Delta\text{pH}_{50} = 0,803 \times \Delta\text{pK}_{\text{SH}} + 0,08$$

$$\Delta\text{pK}_{\text{SH}} = \frac{\Delta\text{pH}_{50} + 0,08}{0,803}$$

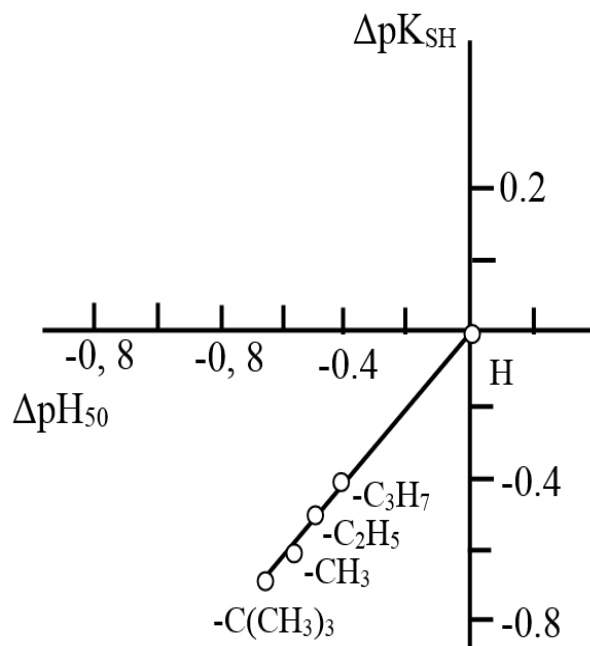


Fig 6: Correlation between the acidic properties of DP ($\Delta\text{pK}_{\text{SH}}$) and ΔpH_{50} for the Ta (V)-DP-An complexes

The relationship between pK_{SH} and $\text{lg}\beta$ can be described by a linear regression type equation (Fig. 7). ($R^2=0.9985$). $\text{pK}_{\text{SH}}=5,1+0,176\text{lg}\beta$

$$\text{pK}_{\text{SH}} = 5.1 + 0.176 \text{lg}\beta$$

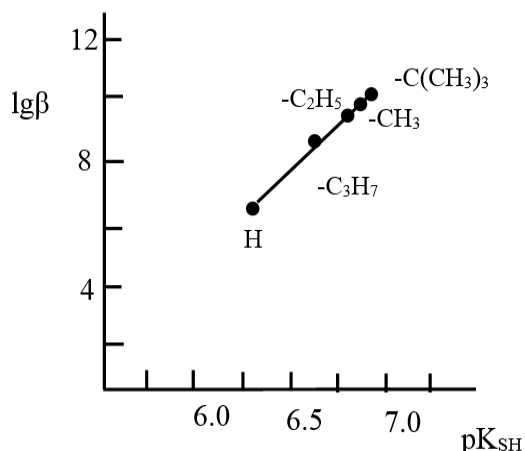


Fig 7: Correlation between the acidic properties of DP (pK_{SH}) and $\text{lg}\beta$ for the Ta (V)-DP-An complexes

It was found that increasing the molar mass of the substituent (X) is the molar absorbance coefficient of ionic association increased (Fig. 8).

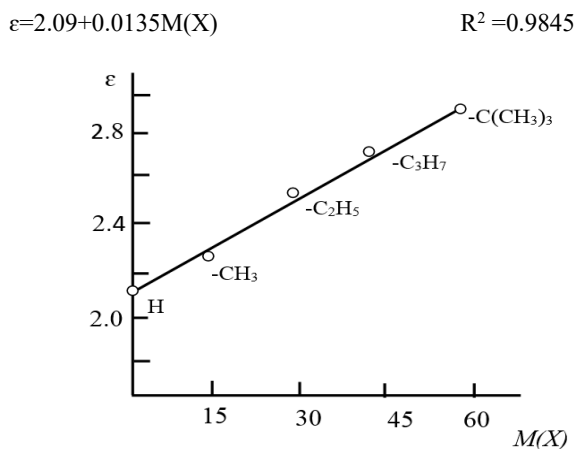


Fig 8: Correlation between the molar mass ($M(X)$) and molar absorptivity of the Ta (V)-DP-An complexes

Also, there is a correlation between pH_{50} and σ_n , and between pK_{SH} and σ_n . Correlation expressed by the equation:
 $\text{pH}_{50} = 0.045 + 3.38\sigma_n$ ($r = 0.98$)
 $\text{pH}_{\text{SH}} = 0.038 + 3.46\sigma_n$ ($r = 0.98$)

4. Conclusion

- Mixed-ligand complexes of Tantalum (V) with dithiophenols and hydrofob amins have been studied by spectrophotometry.
- Extraction of mixed ligand complexes is maximal at pH 2.9-6.0. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found.
- The molar ratio of the reacting Ta (V), DP and Am species is 1:2:2. The general formula of the ternary complexes is $[\text{Ta}(\text{OH})_3(\text{DP})_2](\text{AmH})_2$. They can be regarded as ion-associates between doubly charged anionic chelates $[\text{Ta}(\text{OH})_3(\text{DP})_2]^{2-}$ and protonated Am species.
- A procedure has been developed for extraction-spectrophotometric determination Tantalum in steels of different brands.
- Relationships exist between the acid-base properties of the sulfhydryl group of DP (pK_1) and some characteristics of the ternary complexes. The relationship between $\Delta\text{pK}_{\text{SH}}$ and ΔpH_{50} for the Ta (V) complexes can be adequately described by a straight-line equation ($\Delta\text{pH}_{50} = 0.809 \times \Delta\text{pK}_1 - 0.08$). The relationship between $\Delta\text{pK}_{\text{SH}}$ and ϵ_{max} for the same complexes can be described by a linear regression equation ($\epsilon = 2.09 + 0.0135M(X)$).

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