

Spectrophotometric Determination of Trace Amounts of Niobium (v) with 2, 6-Dithiolphenol and Its Derivatives In The Presence Of Hydrophobic Amines

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ABSTRACT

Mixed-ligand complexes of Niobium (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. Extraction of mixed ligand complexes is maximal at pH 2.9-5.3. 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. The Beer's law was applicable in the range of 0.03-4.2 μ g/ml. The method is free from common interferences. A procedure has been developed for extraction – spectrophotometric determination Niobium in steel.

Key words: niobium, solvent extraction, spectrophotometry, ion-associate

1. INTRODUCTION

Among the refractory metals and alloys, niobium alloys are used in variety of high temperature applications ranging from light bulbs to rocket engines because of its high melting and boiling point, lower density, good ductility at room temperature and high corrosion resistance. Niobium is widely used for the fabrication of steels and superalloys, special materials for microelectronics and optics, superconductors, refractory materials and catalysts [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.

A method of flotation separation with subsequent sensitive spectrophotometric determination of niobium is developed. In the presence of oxalate, niobium and 3,5-dinitrocatechol form an anionic complex able to associate with Rhodamine B [2].

The application of ternary and multicomponent complexes in spectrophotometric and spectrofluorimetric determination of trace elements is reviewed. Newer types of colour systems employing mixed ligand, surfactant sensitized, ion-association, flotation, derivative and FIA systems are described. Separate sections are devoted to advances in both spectrophotometric and

spectrofluorimetric determination of individual elements. Future trends in spectrophotometric and spectrofluorimetric analysis are discussed [3].

The chelator 2-[2-(5-bromoquinolinylazo)]-5-diethylaminophenol (5-Br-QADEAP) was synthesized. A method was developed for the simultaneous determination of vanadium, niobium and tantalum as metal-5-Br-QADEAP chelates using rapid column high performance liquid chromatography along with an on-line enrichment technique. Vanadium, niobium and tantalum were precolumn derivatized with 5-Br-QADEAP to form colored chelates [4].

For determination of niobium in the steel proposed several methods based on the use of complexes of Nb (V) c TS and polyphenols (4-nitropirotechin, 2,3-dihydroxynaphthalene and pyrocatechol [5]

The formation and solvent extraction of new ion-association complexes between anionic chelates of niobium (V) with nitroderivatives of catechol {NDC: 3,5-dinitrocatechol (3,5-DNC) and 4-nitrocatechol (4-NC)} and tetrazolium cations {2,3,5-triphenyl-2H-tetrazolium (TT⁺) and 3,3'-[3,3'-dimethoxy(1,1'-biphenyl)-4,4'-diyl]-bis[2,5-diphenyl-2H-tetrazolium] (Blue Tetrazolium, BT²⁺)} were studied [6]

The complex formation and liquid-liquid extraction in the niobium(V)-4-nitrocatechol (4-NC) – Thiazolyl Blue Tetrazolium (MTT) – water – organic solvent system was studied [7]

Niobium was determined by flow injection spectrophotometry at 393 nm after extraction of ethylene-bis(triphenylphosphonium) thiocyanatoniobate (V) into chloroform. The effects of diverse ions are reported. The system has been applied to the determination of niobium in steels by the method of standard additions [8].

The colour reaction of niobium (V) with the four kinds of hydroxamic acids in the presence of thiocyanate was examined. The results showed that *N*-cinnamoyl-*N*-2,3-xilylhydroxylamine (CXHA) was the most suitable reagent for the spectrophotometric determination of small amounts of niobium [9].

Color reactions studied of niobium and tantalum with certain heterocyclic azoreagent group PAN(1-(2-pyridylazo)-2-naphthol)- PAR (4-(2-pyridylazo) resorcinol): 2-(2-pyridylazo)-5-aminophenol, 2-(3,5-dibromo-2-pyridylazo)-5-aminophenol and 2-(3,5-dibromo-2-pyridylazo)-5-diethylaminophenol. The quantitative characteristics of reactions and found the conditions determining both small and large amounts of niobium and tantalum in the mutual presence with a reagent 3,5-dibromo-PADAP [10].

Investigated complex formation of niobium and tantalum with 2,3,4-dihydroxyphenylazo 5-sulfonaphthalene in the presence of cetyltrimethylammonium bromide [11]

Has a high sensitivity method for determination of niobium with sulfonitrofenole M. Among other reagents recommended for the determination of niobium, -sulfonitrazo E [12] azoderivatives 8-hydroxyquinoline [13] phenylfluorone, on-nitrofenilfluoron [14, 15, 16]. Very sensitive technique based on the formation of mixed complexes of niobium with o-nitrofenilfluoron and DAM [17]. Still higher sensitivity achieved using salitsilfluorona surfactant and SAS [18, 19]. Other organic reagents for determination of niobium include 8-hydroxyquinoline-5-sulfonic acid [20], 5,7-dichloro-8-hydroxyquinoline [21], 5-chloro-7-iodo-8-hydroxyquinoline [22], lyumogallion [23] and thioglycolic acid [24]

Oxyphenolate and dithiophenolate complexes of niobium are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [25, 26].

In this respect, a very promising reagent is dithiolphenols (DP), which contains one hydroxyl and two sulphohydril 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 Niobium (V) with dithiolphenols (DP) in the presence of hydrophobic amines (Am). From dithiolphenols 2, 6-dithiolphenol (DTP), 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) were used. in the presence of hydrophobic amines (Am). As hydrophobic amine aniline (An), N-methylaniline (mAn), N, N-dimetilaniline (dAn), aminopyridine (APy) and aminophenole (2(N, N-dimethylaminomethyl)-4-methylphenol (AP₁), 2(N, N-dimethylaminomethyl)-4-chlorphenol (AP₂), 2(N, N-dimethylaminomethyl)-4-bromphenol (AP₃)) were used.

2.EXPERIMENTAL

2.1. Reagents and apparatus

Standard solution of Nb (V) (1mg / L) were prepared by fusing 0,1430g Nb₂O₅ with 4 g K₂S₂O₇ in a quartz or platinum crucible. The melt is dissolved in a hot 5% solution of tartaric acid, cooled and diluted with a solution of tartaric acid to 100 ml in a volumetric flask. Lower concentrations of the metal ion are obtained by suitable dilution of the stock solution. The concentration of the niobium solution was adjusted gravimetrically [27].

Solutions of DP and Am in chloroform (0.01M) were used. DP were synthesized according to the procedure [28] Their purity was verified by melting point determination and pa-

per 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 a 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 Niobium (V)

Portions of stock solutions of Niobium (V) varying from 0.1 to 1.0 mL with a 0.1-mL step, a 2.2 mL portion of a 0.01 M solution of DP, and a 2.5 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 minnute 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 ($l=0.5\text{cm}$).

2.2.2. Determiation of Niobium (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 niobium using the proposed procedures.

3.RESULTS AND DISCUSSION

Nb (V) reacts with dithiolphenols (DP)and gives a yellow colored complexes. These complexes are insoluble in non-polar 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 demonstratedthe anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the yellow dithiophenolate complexes of Niobium (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 hydrophobic amines (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed

3.1. The Choice of the Extractant

For the extraction of complexes we used CHCl_3 , CCl_4 , C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_4(\text{CH}_3)_2$, $\text{C}_2\text{H}_4\text{Cl}_2$, isobutanol and isopentanol. 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 Niobium in the organic phase was determined with bromopyrogallol red [29] 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 niobium. After a single extraction with chloroform, 98.2-98.8% of niobium was extracted as an ion associate.

3.2. Influence of the pH of the Aqueous Phase

The effect of pH on the formation of Nb(V)-DP-Am complex was studied, in order to find a suitable pH that can be adopted in the determination of niobium(V) (Fig. 1). The absorbance was found to be maximum in the pH range 2.9-4.2. Hence further analytical investigations were carried out in media of pH 3. Extraction of Nb(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 DP. 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.

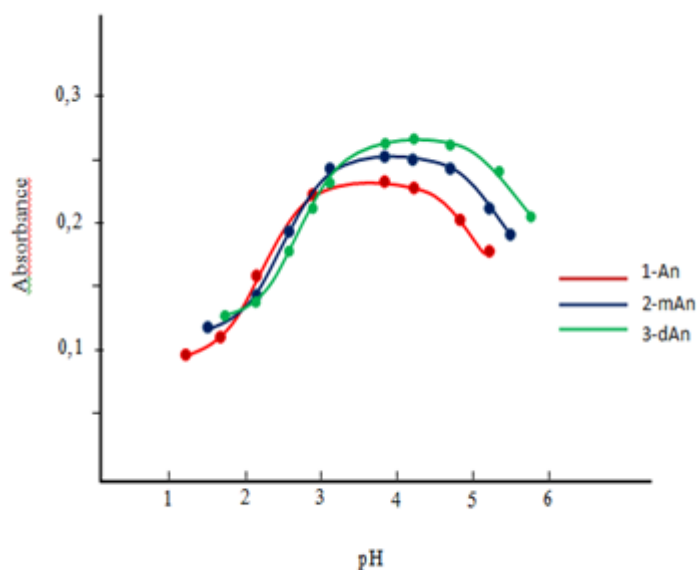


Fig.1. Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase.

1. Nb(V)-DTP-An; 2. Nb(V)-DTP-mAn; 3. Nb(V)-DTP-dAn.

$C_{\text{Nb}}=2.15 \cdot 10^{-5}$ M, $c_{\text{DTP}}=0.88 \cdot 10^{-3}$ M, $c_{\text{Am}}=1.0 \cdot 10^{-3}$ 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 $(1.2-1.4) \times 10^{-3}$ 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 Nb (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 wavelengths. Hence further studies were carried out at 435-440 nm (fig.2). The reagent has minimum absorbance at the maximum absorbance of the complex. Hence further absorbance measurements were made at 440 nm The molar absorptivity of the complex was calculated with Komar method[30] to be $\epsilon = (2.1-2.4) \times 10^4$ L mol⁻¹ cm⁻¹.

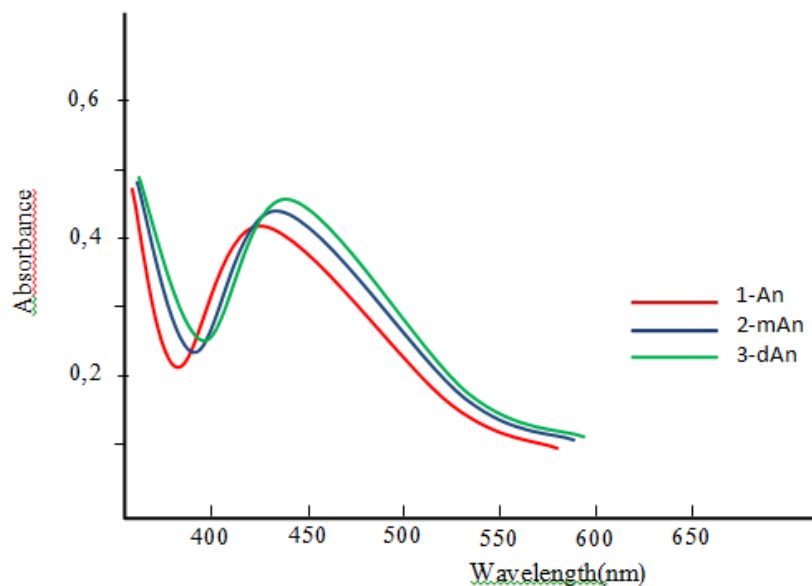


Fig.2. Absorption of mixed-ligand complexes

1. Nb(V)-DTP-An; 2. Nb(V)-DTP-mAn; 3. Nb(V)-DTP-dAn.

$C_{\text{Nb}}=2.15 \cdot 10^{-5}$ M, $C_{\text{DTP}}=0.88 \cdot 10^{-3}$ M, $C_{\text{Am}}=1.0 \cdot 10^{-3}$ M, KFK-2, 440nm, $l=0.5$ cm.

3.5. Stoichiometry of the Complexes and the Mechanism of Complexation

Starik-Barbanel relative yield method, equilibrium shift method, crossed lines method and Asmus' methods were employed to elucidate the composition of the complex [30]. The results suggest the complex composition of 1:2:2 (Nb : DP : Am). The formation of MLC can be presented in the following way. When niobium ion interact with two molecules of DP, they form doubly-charged anionic complexes, which are extracted with two molecules of protonated Am. (Fig. 3). Formed ion-association complex between anionic chelates of niobium (V) with DP and hydrophobic aromatic amines. The stability constant of Nb(V)-DP-Am complexes was calculated and found to be $\lg\beta=7.19-11.25$ at room temperature.

It was found using the Nazarenko method that Nb(V) in the complexes was present in the form of $\text{Nb}(\text{OH})_3^{2+}$. The number of protons replaced by niobium in one DP molecule appeared to be one [31,32].

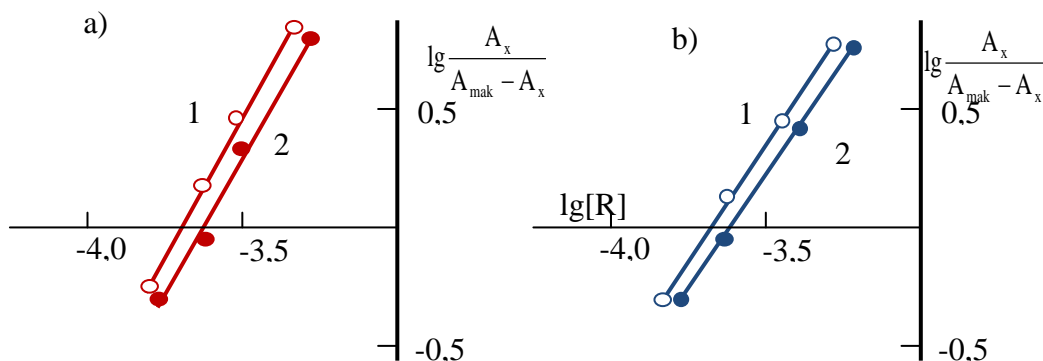


Fig. 3. Determination of the ratio of components by the equilibrium shift method for (a) Nb(V)-DTMP-An and (b) Nb(V)-DTMP-mAn.
 1. Nb:DTPP; 2.Nb : Am.

Fig. 3. Determination of the Two Phase stability Constant by the Crossed Curves Method

$C_{Nb}=2,15 \cdot 10^{-5} \text{ mol L}^{-1}$, $C_{An}=1 \cdot 10^{-3} \text{ mol L}^{-1}$, $\text{pH}=3$. 1- $C_{DTMP}=2,4 \cdot 10^{-4} \text{ mol L}^{-1}$, $C_{comp}=0,98 \cdot 10^{-5} \text{ mol L}^{-1}$; 2- $C_{DTMP}=4,8 \cdot 10^{-4} \text{ mol L}^{-1}$, $C_{comp}=1,94 \cdot 10^{-5} \text{ mol L}^{-1}$

The disappearance of the pronounced absorption bands in the $3200\text{-}3600 \text{ cm}^{-1}$ with a maximum at 3460 cm^{-1} observed in the spectrum of DTPP, 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 2380 cm^{-1} indicates the presence of a protonated aniline [33,34].

Structure extractable complexes can be represented as in Figure 4.

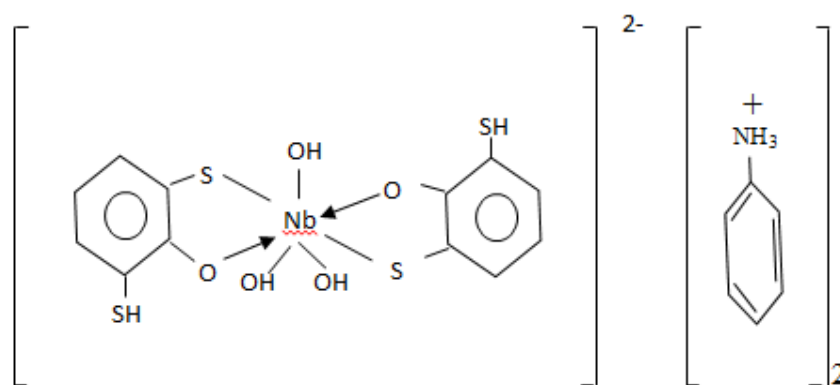


Fig. 4. Structure of complex

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 2.

Calculation of extent of polymerization of complexes was carried out on the equation [35]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma=1,05-1,12$).

3.6. Influence of Interfering Ions

To evaluate the complex applicability for photometric determination of niobium, 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 niobium with DP 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 1.

Table1. Influence of interfering ions on the determination of niobium (V) as MLC with DTP and An (30,0 μg Nb added)

Ion	Molar excess of the ion	Masking agent	Found Nb, μg	RSD,%
Ascorbic acid	120		30.0	3
Tartaric acid	120		30.2	5
Oxalate	8		30.7	4
Fluoride	1,5		29.6	4
Phosphoric acid	30		30.3	3
Thiourea	20		31.2	6
Co(II)	130		29.9	3
Ni(II)	130		30.2	5
Al(III)	190		29.9	4
Fe(II)	80		29.6	4
Fe(III)	80		30.2	4
Cd(II)	180		30.2	5
Zr(IV)	60	NaF	30.5	6
Cu(II)	35	$\text{SC}(\text{NH}_2)_2$	29.7	5
Ti(IV)	5	Ascorbic acid	29.6	5
Mn(II)	50		29.3	4
W(VI)	8		29.8	4
Mo(VI)	15		29.4	5
Cr(III)	30		30.2	2
V(IV)	10		30.6	6
Ta(V)	5	$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	30.2	5
Pt(II)	40		29.3	5
Pd(II)	40		30.4	6
UO_2^{2+}	40	CH_3COO^-	29.7	4

In conclusion the analytical parameters pertaining to the proposed method are given in Table 2.

Table 2. Optical characteristics, precision and accuracy of the spectrophotometric determination of Nb(V) with DP and Am

Compound	The pH range of maximum extraction	R, %	λ_{\max} (nm)	Molar absorptivity ($L \cdot mol^{-1} \cdot cm^{-1}$) $\epsilon \cdot 10^{-4}$	lgK_e	$lg\beta$	lgK_{ex}	Working range / $\mu g \cdot cm^{-3}$
Nb-DTP-An	2,9-3,7	97.5	435	2.1·	5.32	7.19	9.28	0.5-80
Nb- DTP-MAH	3,1-4,0	97.8	438	2.3·	5.46	7.30	9.42	0.5-80
Nb- DTP -dAH	3,3-4,3	98.0	440	2.4·	5.55	7.48	9.46	0.5-85
Nb- DTP -AmPy	3,6-4,8	96.9	450	2.4	5.34	7.16	9.31	0.6-80
Nb-DTP-AP ₁	3,8-5,0	97.9	440	2.9·	5.82	8.40	10.06	0.5-100
Nb-DTP-AP ₂	3,7-4,9	97.8	438	2.8·	5.76	8.31	9.95	0.5-95
Nb-DTP-AP ₃	3,6-4,7	97.6	435	2.6	5.75	8.23	9.82	0.6-95
Nb-DTMP-An	3,2-4,4	97.6	442	2.4·	5.43	10.28	11.08	0.5-85
Nb-DTMP-mAn	3,3-4,6	97.9	445	2.6·	5.75	10.82	11.20	0.5-85
Nb-DTMP-dAn	3,5-4,7	98.1	448	2.7·	5.83	10.93	11.32	0.4-90
Nb-DTMP- AP ₁	3,9-5,3	98.3	450	3.5·	5.93	10.90	11.25	0.4-105
Nb-DTMP- AP ₂	3,8-5,1	98.4	447	3.6·	5.85	10.86	11.05	0.5-100
Nb-DTMP- AP ₃	3,6-5,0	98.4	445	3.8	5.88	10.95	10.83	0.5-95
Nb-DTEP-An	2,9-4,2	97.8	445	2.7·	5.55	9.24	10.33	0.5-85
Nb-DTEP-mAn	3,1-4,4	98.0	448	2.8·	5.86	10.39	10.48	0.5-90
Nb-DTEP-dAn	3,3-4,5	98.2	450	2.9·	5.92	10.50	10.55	0.4-90
Nb-DTEP- AP ₁	3,9-5,3	98.4	450	3.7·	5.88	10.48	10.85	0.4-105
Nb-DTEP- AP ₂	3,8-5,1	98.5	450	3.8·	5.95	10.60	10.75	0.4-100
Nb-DTEP- AP ₃	3,6-5,0	98.6	448	3.9	5.95	10.50	10.63	0.4-95
Nb-DTPP-An	3,1-4,0	98.0	445	3.0	5.65	9.26	10.08	0.5-90
Nb-DTPP-mAn	3,3-4,2	98.0	448	3.2	5.72	9.41	10.26	0.5-90
Nb-DTBP-An	3,3-4,6	98.2	447	3.3·	5.68	11.08	11.60	0.05-85
Nb- DTBP -MAH	3,5-4,8	98.4	450	3.4·	5.92	11.19	11.75	0.05-100
Nb- DTBP -dAH	3,6-4,9	98.5	450	3.6·	5.92	11.22	11.87	0.04-110
Nb- DTBP -AmPy	4.0-5.1	98.2	460	3.5	5.87	11.25	11.90	0.04-110

3.7. Effect of Niobium (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 Nb(V) may be determined in the range 0.03-4.0 $\mu g/ml$. The pertaining calibration graph is shown in the Fig. 5.

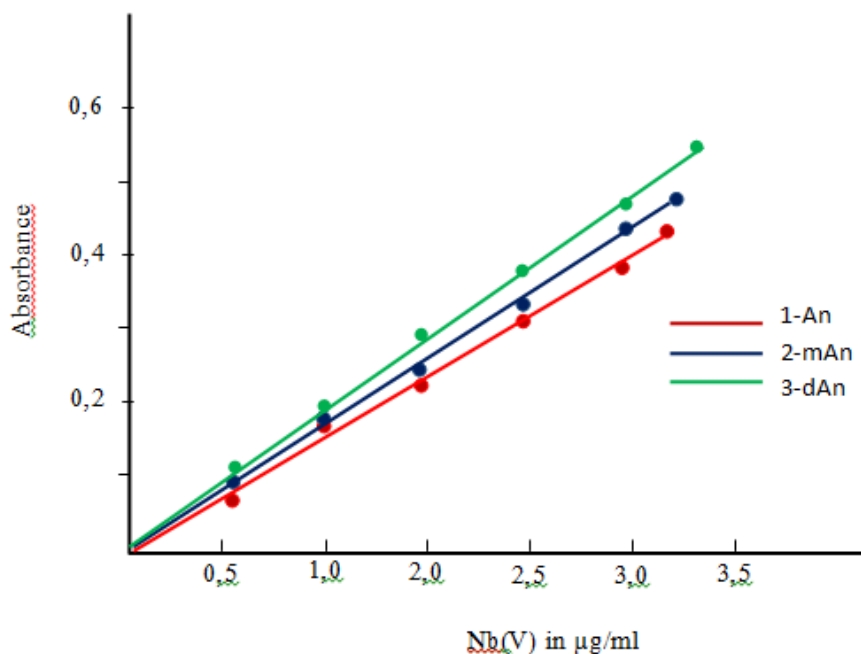


Fig. 5. Analytical determination of Nb (V); $C_{\text{DTMP}} = 1 \times 10^{-3} \text{ M}$; $C_{\text{Am}} = 1.3 \times 10^{-3} \text{ M}$; $\text{pH} = 3$; $\lambda = 440 \text{ nm}$, $l = 0.5 \text{ cm}$.

Table 3. Analytical characteristics of some ternary complexes of Nb 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
Nb-DTP-An	0.0044	0.05-3.2	15	50	$0.020+0.21x$	0.9978
Nb- DTP -mAn	0.0040	0.05-3.2	13	42	$0.024+0.23x$	0.9974
Nb- DTP -dAn	0.0038	0.05-3.4	12	40	$0.015+0.25x$	0.9938
Nb- DTP -AmPy	0.0038	0.05-4.0	12	40	$0.016+0.25x$	0.9978
Nb-DTP-AP ₁	0.0032	0.05-3.8	11	36	$0.023+0.30x$	0.9985
Nb-DTP-AP ₂	0.0033	0.05-3.8	12	40	$0.025+0.29x$	0.9982
Nb-DTP-AP ₃	0.0035	0.05-3.4	14	45	$0.038+0.27x$	0.9975
Nb-DTMP-An	0.0038	0.05-3.4	13	42	$0.038+0.25x$	0.9911
Nb-DTMP-mAn	0.0036	0.04-3.6	12	40	$0.018+0.27x$	0.9838
Nb-DTMP-dAn	0.0034	0.04-4.2	12	40	$0.016+0.27x$	0.9953
Nb-DTMP- AP ₁	0.0026	0.05-4.0	10	33	$0.042+0.35x$	0.9874
Nb-DTMP- AP ₂	0.0025	0.05-3.8	9	29	$0.042+0.36x$	0.9938
Nb-DTMP- AP ₃	0.0023	0.05-3.4	9	29	$0.028+0.39x$	0.9673
Nb-DTEP-An	0.0034	0.05-3.4	11	36	$0.019+0.28x$	0.9871
Nb-DTEP-mAn	0.0033	0.04-3.6	10	33	$0.014+0.29x$	0.9933
Nb-DTEP-dAn	0.0032	0.03-4.2	10	33	$0.021+0.29x$	0.9960
Nb-DTEP- AP ₁	0.0025	0.04-4.0	9	29	$0.043+0.38x$	0.9974
Nb-DTEP- AP ₂	0.0024	0.04-3.8	9	29	$0.046+0.38x$	0.9938
Nb-DTEP- AP ₃	0.0023	0.05-4.2	8	27	$0.028+0.40x$	0.9931

Nb-DTPP-An	0.0031	0.05-3.4	11	36	0.018+0.32x	0.9974
Nb-DTPP-mAn	0.0029	0.05-3.4	9	29	0.028+0.32x	0.9936
Nb-DTBP-An	0.0028	0.04-3.6	10	33	0.031+0.34x	0.9921
Nb- DTBP -mAn	0.0027	0.03-4.2	10	33	0.035+0.35x	0.9974
Nb- DTBP -dAn	0.0026	0.03-4.0	9	29	0.029+0.37x	0.9730
Nb-DTBP-AmPy	0.0026	0.04-3.8	10	33	0.019+0.36x	0.9741

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

The proposed method compares favourably with the existing ones (Table 4) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity [28].

Table 4. Comparative characteristics of the procedures for determining niobium

Reagent	pH (solvent)	λ , nm	$\epsilon \cdot 10^{-4}$	Beer's law range ($\mu\text{g} \cdot \text{ml}^{-1}$)
Pyrocatechol violet	1.6-2.0 2.2-2.3	600	0.93	0.2-6.0
Rodanid	2,5M HCl (water+acetone)	385	3,5	0.08-9.0
4-Nitropyrocatechol +tetrazolium violet	0.7MH ₂ SO ₄ (C ₂ H ₄ Cl ₂)	440	1,59	0.41 - 4.54
Pyrocatechol+ tetrazolium violet	0.4 - 1MH ₂ SO ₄ (CHCl ₃)	390	1,60	1.25 - 11.78
Bromopyrogallol red	5,8-6,6	560	4,75	
DTP+An	2.5-3.4 (CHCl ₃)	435	2.1	0.06-3.2
DTP+mAn	2,7 -3,8 (CHCl ₃)	438	2.3	0,06-3.2
DTEP- AP ₃	3,6-5,0(CHCl ₃)	448	3.9	0.05-4.2
DTBP -dAn	3,6-4,9(CHCl ₃)	450	3.6	0.03-4.0

3.8. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Nb (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 Niobium in steel (n=5, P=0.95)

Prosedure	\bar{X} , %	RSD,%
<i>CBT-2(0,012%Nb)</i>		
<i>Standard method</i>		
Bromopyrogallol red	$(1,29 \pm 0,034) \cdot 10^{-2}$	2.5
Rodanid	$(1,28 \pm 0,029) \cdot 10^{-2}$	2.7
<i>Proposed method</i>		
DTP+An	$(1,24 \pm 0,028) \cdot 10^{-2}$	2.3
DTP+mAn	$(1,23 \pm 0,031) \cdot 10^{-2}$	2.2
DTP+dAn	$(1,24 \pm 0,037) \cdot 10^{-2}$	2.3
<i>CBT-3(0,029%Nb)</i>		
<i>Standard method</i>		

Rodanid	$(3.14 \pm 0,30) \cdot 10^{-2}$	2.8
Bromopyrogallol red	$(3.10 \pm 0,27) \cdot 10^{-2}$	2.7
<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

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 lgK_e) we constructed Fig. 6 and Fig. 7. The pH_{50} values were determined graphically from the dependence $A=f(pH)$ (see Fig. 1) for absorbance of 50% (Tabl. 6). ΔpK_{SH} values in Fig. 3 and Fig. 4 are the differences between pK_{SH} of the unsubstituted reagent (DTP; X=H) and pK_{SH} of its substituted analogues (X=H, CH_3 , C_2H_5 , $-C_3H_7$ and $-C(CH_3)_3$). ΔpH_{50} in Fig. 6. is the corresponding difference between the pH_{50} values for DTP and DTMP, DTEP, DTPP or DTBP ($R^2=0.9985$).

Table 6. Analytical characteristics of some ternary complexes of Nb with DP and An.

H_3R	pK_{SH}	ΔpK_{SH}	pH_{50}	ΔpH_{50}	$lg\beta$	σ_n
H	6.30	0.0	2.21	0.00	7.19	0
$-C_3H_7$	6.72	-0.42	2.62	-0.41	9.26	-0.126
$-C_2H_5$	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

$$\Delta pH_{50} = 0,675 \times \Delta pK_1 - 0,125$$

$$\Delta pK_1 = \frac{\Delta pH_{50} + 0,125}{0,675}$$

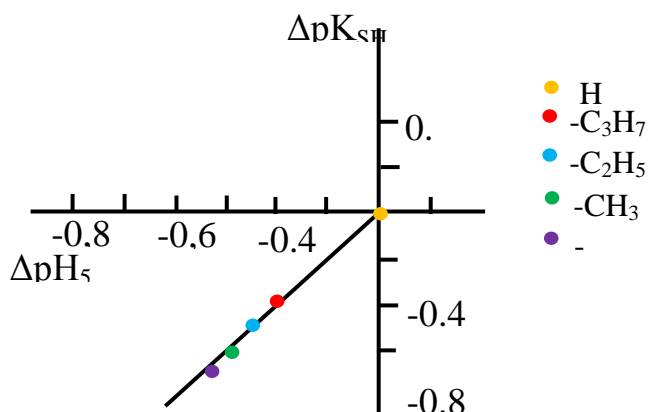
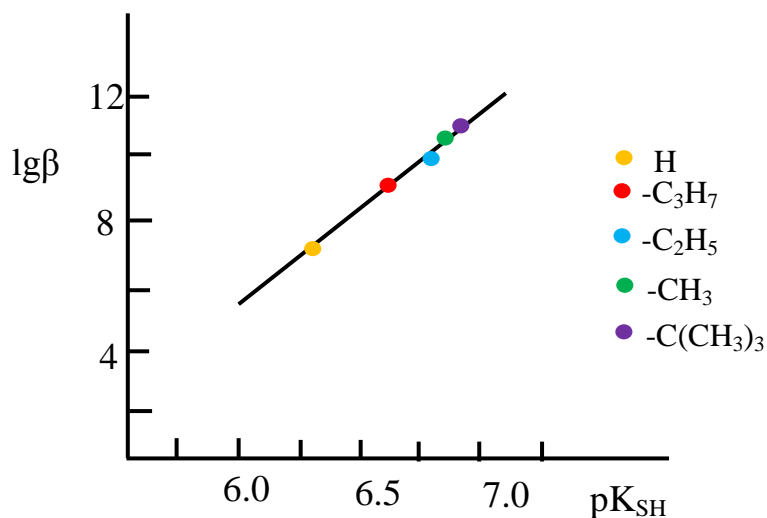


Fig. 6. Correlation between the acidic properties of DP (ΔpK_{SH}) and ΔpH_{50} for the Nb(V)-DP-An complexes

The relationship between pK_{SH} and $lg\beta$ can be described by a linear regression type equation (Fig. 7). ($R^2=0.9985$).



$$pK_{SH}=5,04+0,175 \lg\beta \text{ или } \lg\beta=\frac{pK_{SH}-5.08}{0.175}$$

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

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

$$\varepsilon=2.14 +0.0103M(X)$$

$$R^2 =0.9856$$

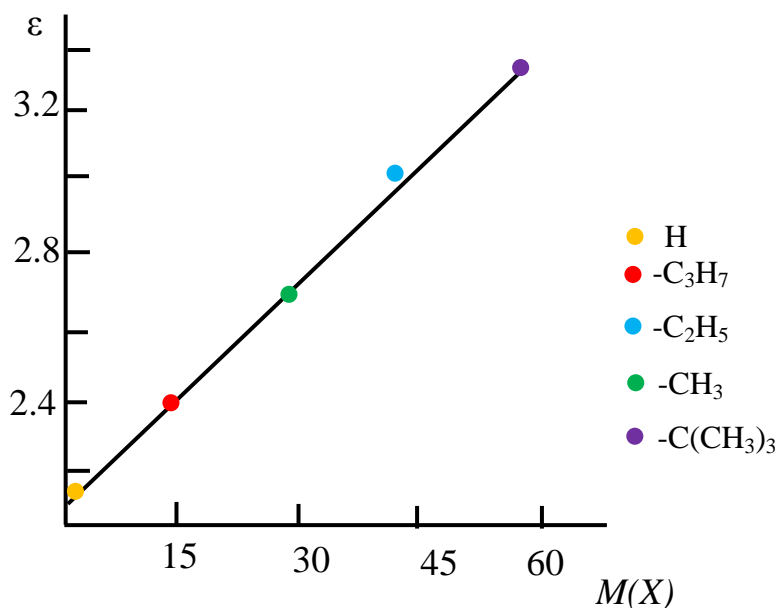


Fig. 8. Correlation between the molar mass ($M(X)$) and molar absorptivity of the Nb(V)-DP-An complexes

Also, there is a correlation between pH_{50} and σ_n , and between pH_{SH} and σ_n . Correlation expressed by the equation:

$$\begin{aligned} \text{pH}_{50} &= 0,045 + 3,38\sigma_n \quad (r=0,98) \\ \text{pH}_{\text{SH}} &= 0,038 + 3,46\sigma_n \quad (r=0,98) \end{aligned}$$

4. CONCLUSION

1. Mixed-ligand complexes of Niobium (V) with DP and Am have been studied by spectrophotometry. Extraction of mixed ligand complexes is maximal at pH 2.9-5.3. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found.
2. The molar ratio of the reacting Nb(V), DP and Am species is 1:2:2. The general formula of the ternary complexes is $[\text{Mb}(\text{OH})_3(\text{DP})_2](\text{AmH})_2$. They can be regarded as ion-associates between doubly charged anionic chelates $[\text{Mb}(\text{OH})_3(\text{DP})_2]^{2-}$ and protonated Am species.
3. The developed method retains specific interaction of niobium(V) with DP and Am to form a colored complex and has good sensitivity at room temperature. The proposed method has significant advantage over the other spectrophotometric methods in terms of simplicity and sensitivity. This proposed method has good precision and accuracy.
4. A procedure has been developed for extraction-spectrophotometric determination Niobium in steels of different brands.
5. 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 Nb (V) complexes can be adequately described by a straight-line equation ($\Delta\text{pH}_{50} = 0,675 \times \Delta\text{pK}_1 - 0,125$). The relationship between $M(X)$ and ε_{max} for the same complexes can be described by a linear regression equation ($\varepsilon = 2.14 + 0.0103M(X)$).

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