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Complex Formation and Liquid-Liquid Extraction in the Niobium(V) – 2,4-Dihydroxythiophenol– Hydrophobic Amines System

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Abstract

The formation and solvent extraction of new ion-association complexes between anionic chelat of niobium(V) with 2,4-dihydroxythiophenol (DHTP) and hydrophobic amines (HAs). The HAs were aniline (An), N-methylaniline (MAn), N,N-dimethylaniline (DAn). The optimum conditions for the extraction of mixed ligand complexes (MLC) (organic solvent, extraction time, acidity of the aqueous phase, concentration of reagents), some key constants {association constant (β), extraction constant (Kex)} and analytical characteristics were determined. The molar absorptivities of MLC were calculated $\varepsilon = (3.5\text{-}3.9) \times 10^4$ L mol^{-1} cm^{-1} . The Beer's law was applicable in the range of 2.2-100 µg/mL.

Keywords: Niobium; Spectrophotometry; Mixed ligand complexes; 2,4-dihydroxythiophenol; Hydrophobic amin; Liquid–liquid extraction

Introduction

Niobium and its compounds have a broad spectrum of applications. They are used for the fabrication of special materials for microelectronics and optics, superconductors, refractory materials, catalysts, and alloys [1-4]. As an important alloy element in steels, niobium can greatly affect the properties of a sample, such as the intensity at high temperature, the ability of tarnish resistance and temper brittleness [5,6]. Niobium steels are valuable constructive materials for the chemical and nuclear industries, jet and rocket engines, gas pipelines and turbines [5]. Unalloyed niobium and some niobium alloys are used for the production of surgical instruments, medical devices (e. g., pacemakers), coins and jewellery. There a son for these applications is niobium's physicological inertness and ability to be coloured by anodisation [2-4,6].

Several analytical methods have been used to determine Nb, including spectrophotometry [2,7-12], high-performance liquid chromatography [5], atomic absorption spectrophotometry (AAS) [13], inductively coupled plasma (ICP) optical emission spectrometry (OES) [14], ICP mass spectrometry (MS)[15], neutron activation analysis (NAA) [16]. The main disadvantage of AAS and OES is low sensitivity (because of spectral interference or high background due to the matrix elements), whilst for ICP-MS and NAA it is high costs. The methods involving spectrophotometry are rather popular due to their simplicity, low-cost instrumentation and easy automation [7]. These methods are often based on ion-association systems composed of intensively coloured anionic chelate and bulky organic cation which makes the complex insoluble in water and easily extractable into organic solvents [2-4,7].

A great variety of photometric reagents is known for the determination of niobium.

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The formation and solvent extraction of new ion-association complexes between anionic-chelates of niobium (V) with nitroderi-vatives of catechol {3,5-dinitrocatechol and 4-nitrocatechol} and tetrazoliumcations {2,3,5-triphenyl-2H-tetrazolium and 3,3’-[3,3’-dimetoxy (1,1’-biphenyl)–4,4’-diyl]-bis[2,5-diphenyl-2H-tetrazolium]} were studied [3].

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 [7].

For determination of niobium in the steel proposed several methods based on the use of complexes of Nb (V) c tetrazolium salts and polyphenols (4-nitropirokatehin, 2,3-dihydroxynaphthalene and pyrocatechol [9].

Oxyphenolate complexes of niobium are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [10, 11].

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

The color 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-xylylhydroxylamine was the most suitable reagent for the spectrophotometric determination of small amounts of niobium [17].

Color reactions studied of niobium and tantalum with certain heterocyclic azoreagent group PAN- PAR: 2- (2-pyridylazo) -5-aminophenol, 2- (3,5-dibromo-2-pyridylazo) -5-aminophenol and 2- (3, 5-dibromo-2-pyridylazo) -5-dietilaminofenol. 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 [18].

Investigated complex formation of niobium fnd tantalum with 2, 3,4-dihydroxyphenyl-azo-5-sulfonaftaline in the presence of cetyltrimethylammonium bromide [8].

Has a high sensitivity method for determination of niobium with sulfonitrofenole M, azoderivatives 8-hydroxyquinoline [19] phenylphluorone, on-nitrofenilphluoron [20], o-nitrophenilphluoron and DAM [21], salitsilfluorona surfactant and SAS [22]. Other organic reagents for determination of niobium include 8-hydroxyquinoline-5-sulfonic acid [23] and thioglycolic acid [24].

However, the studies aiming to find and investigate new photometric reagents with different functional groups are still going on.In this respect, a very promising reagent is 2,4-dihydroxythiophenol (DHTP, H_3R), which contains two hydroxyl and one sulfohydryl groups and is a sulfur-containing analogue of mononuclear polyphenols with one oxygen atom replaced with sulfur atom. The real work is devoted to studying of reaction of a complex formation of Niobium (V) with DHTP and hydrophobic amines (Am). As hydrophobic amine aniline (An), N-methylaniline (MAn) and N, N-dimetilaniline (DAn) were used.

Experimental

Reagents and Instruments

Stock solution of Nb (V) ($1mg^{-1}$) were prepared by fusing 0,1430g Nb_2O_5 with 4 g $K_2S_2O_7$ 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. Working solutions were prepared by appropriate dilution of stock solution 2% solution of tartaric acid [26].The concentration of the niobium solution standardized gravimetrically with phenylarsonic acid [2].

Working solutions ($0.1mg\ mL^{-1}$) were prepared by appropriate dilution of the stock solutions. Chloroform solutions ($1.3\times10^{-2}mol\ L^{-1}$) of there agents DHTF and HAs were used. HAs (97-99% purity) were purchased from Sigma-Aldrich. DHTF were synthesized according to the procedure of Kuliev et al [26]. Their purity was verified by melting point determination and paper chromatography. The acidity was adjusted by adding HCl or 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), equipped with 5 and 10 mm pathlengthcells.

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 2.3 mL portion of a 0.01 M solution of DHTP, and a 2.0 mL portion of a 0.01M solution of HAs 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 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=5mm).

Determination 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 lovapor 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.

Results and Discussion

Determining the sign of the charge is homogeneous ligand complex

The present study is concerned with the investigation of Nb (V) interaction with DHTP, rsulting 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 demonstratedthe anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the blue-green dithiophenolate complexes of Nb (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 HAs were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

The choice of the extractant

The following organic solvents were tested for the extraction of these complexes: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, toluene, xylene, iso-butanol and iso-pentanol. Chloroform was found to be the most effective.
The concentration of niobium in the organic phase was determined with bromopyrogallol red [7] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference.

Extractable complexes evaluated coefficient distribution bution (D) and the extraction ratio (R,%) [3]:

$$D = [Nb]_{org} / [Nb]_{aq};$$

$$R = 100 \cdot D / (D + V_{aq} / V_{org})$$

At the optimum conditions this solvent provides degrees of extraction R=98.3-98.6%.

Influence of the pH of the aqueous phase

Extractable ternary complexes are formed in acidic and weakly acidic medium (pH 3.1-6.2). 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 HAs protonation. At pH values lower than pH_{opt} (4.3-5.0), the concentration of the anionic DHTF species is insufficient for quantitative complex formation.

Influence of Reagent Concentration and Incubation Time

Maximum and constant Nb(V) extraction can be achieved at DHTF and Has concentrations not lower than $(0.95\text{-}1.28)\times10^{-3}$molL^{-1} and $(1.0\text{-}1.2)\times10^{-3}$mol L^{-1}, respectively.

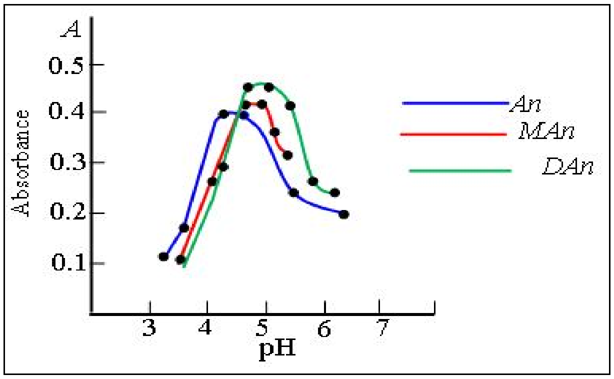


Figure 1. **Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase**
1. Nb(V)-DHTP-An; 2. Nb(V)-DHTP-MAn; 3. Nb(V)-DHTP-DAn. $C_{Nb(V)} = 2.15 \times 10^{-5}$ mol/L, $c_{DHTP}=1.3\times10^{-3}$ mol/L, $c_{Am}=1.2\times10^{-3}$ mol/L, KFK-2, 440nm, ℓ=5 mm.

Fig. 2 illustrate the saturation curves with DHTF and HAs at the optimum of other conditions. One can judge that niobium is extracted to the highest degree with a 440-fold excess of DHTF and a 460-fold excess of An , a 460-fold excess of DHTF and a 490-fold excess of Man, a 590-fold excess of DHTF and a 550-fold excess of Man.

The extraction equilibria establish within 5-10 minutes. The absorbance of the extracts is stable for at least 72 hours.

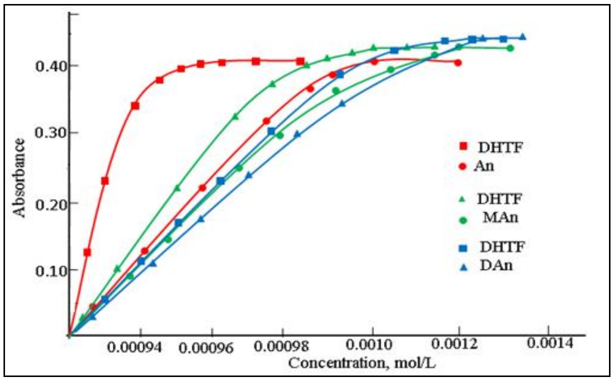


Figure 2. **Absorbance of Nb(V) extracts with DHTF and HAs vs. concentration of the reagent plots. $C_{Nb(V)} = 2.15 \times 10^{-5}$ mol/L, KFK-2, 440nm, ℓ=0.5 mm.**

Absorption spectra and molar absorptivities

The absorption bands in the visible range of the ternary Nb (V)-DHTF-HA complexes are symmetrical and relatively narrow (Fig. 3). They are situated in the range of 420-430 nm. The color reactions are very contrast. The bathochromic shifts Δλ calculated towards λ_{max} DHTF are in the range of 142-152 nm. The Komar-Tolmachev method [28] also allows to calculate the true molar absorptivity of the complex: ε= $(3.5\text{-}3.9)\times10^{4}$L mol^{-1} cm^{-1}.

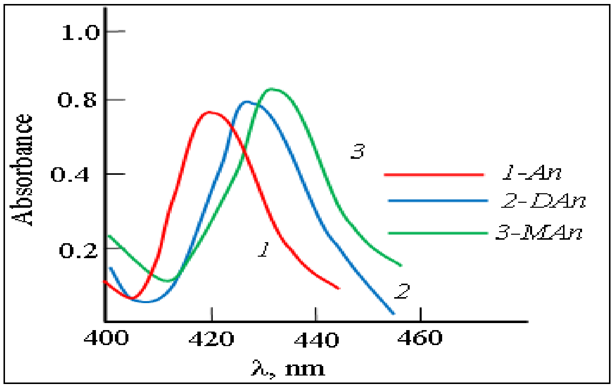


Figure 3. **Absorption of mixed-ligand complexes**
1. Nb(V)-DHTP-An; 2. Nb(V)-DHTP-MAn; 3. Nb(V)-DHTP-DAn. $C_{Nb(V)} = 2.15 \times 10^{-5}$ mol/L, $c_{DHTP}=1.3\times10^{-3}$ mol/L, $c_{Am}=1.2\times10^{-3}$ mol/L, SF-26, ℓ=10 mm.

Stoichiometry of the ternary complexes and general formula

The molar ratios between the components of the ternarycomplex were found by several methods: Starik-Barbanelrelative yield method [28], straight line method [29], equilibrium shift method [27] (Fig. 4) and crossed lines method [30].

The results suggest the complex composition of 1:2:2 (Nb : DHTP : Am). The formation of MLC can be presented in the following way. When niobium ion interact with two molecules of DHTP, they form doubly-charged anionic complexes, which are extracted with two molecules of protonated Am (Fig. 4). Formed ion-association complex between anionic chelates of niobium (V) with DHTP and HAs.

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

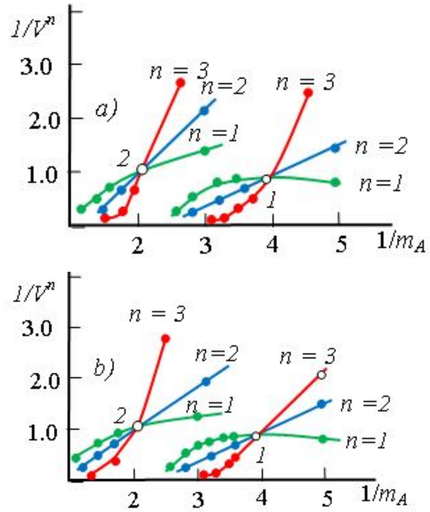
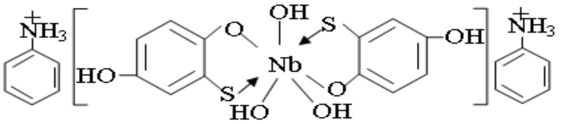


Figure 4. **Determination of the complex Nb (V) -DHTP-An (*a*) and Nb(V) -DHTP-MAn (*b*) by Asmus:**
1-DHTP; 2-Am; $C_{Nb(V)}$ = 2.15 × 10^{-5}mol/L, $c_{DHTP}=1.3\times10^{-3}$mol/L, $c_{Am}=1.2\times10^{-3}$mol/L, SF-26, ℓ=10 mm.

Additional experiments by the Akhmedly’s method [32] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 0.97-1.13).

The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3452 cm^{-1} observed in the spectrum of DHTP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2585cm^{-1} shows that the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1387 cm^{-1} indicates the presence of a protonated aniline (Fig. 5) [33]. Proceeding from the obtainned data, we propose the following structure for the extracted ternary complex (scheme 1).



Scheme 1. **Suggested Structure of the Ternary Complex**

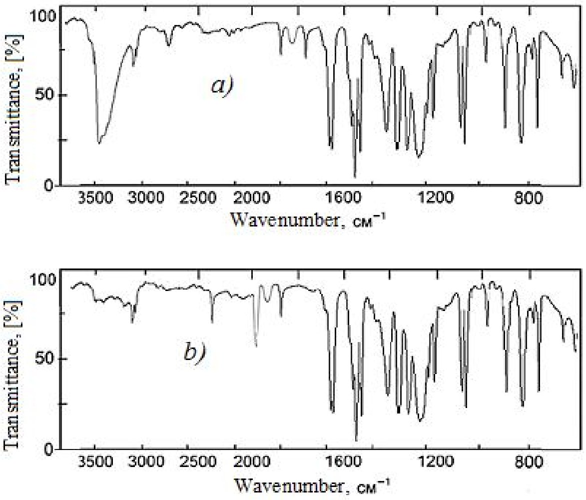


Figure 5. **IR spectrums of DHTP (*a*) and the Nb(V)-DHTP-An(*b*).**

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

$$Nb(OH)_3^{2+} + 2H_3R \leftrightarrow [Nb(OH)_3(HR)_2]^{2-} + 4H^+$$

$$[Nb(OH)_3(HR)_2]^{2-} + 2AmH^+ \leftrightarrow [Nb(OH)_3(HR)_2]_2(AmH)_2$$

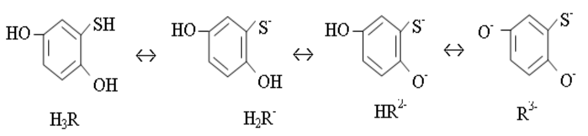
The stability constant determined by crossed lines method. The sizes of equilibrium constant K_e calculated on a formula:

$$\lg K_{eq} = \lg D - 2\lg[AmH^+]$$

were presented in (Table 2).

Dissociation constants of DHTP

DHTP contain two -OH and one -SH groups in their molecules. Depending on the acidity of the medium DHTF can exist in molecular (H_3R) or anionic (H_2R^-, HR^{2-} and R^{3-}) forms. The process of dissociation can be presented by the following scheme 2:



Scheme 2. **Dissociation of DHTP (H_3R) in aqueous solutions**

To determine the corresponding constants of dissociation, K_{SH} and K_{OH}, we used pH-titration with 0.2 mol L^{-1} NaOH [34] (pK_{SH} =6.33; pK_{OH1} =8.96; pK_{OH2}=13.14).

Table 1. **Influence of interfering ions on the determination of Nb(V) as MLC with DHTP and An (30.0 μg Nb added).**

Ion	**Molar excess of the ion**	**Maskingagent**	**Found Nb,μg**	***RSD,%***
Co(II)	120		30.0	1.5
Ni(II)	120		30.2	1.3
Al(III)	190		29.8	2.4
Fe(II)	80		29.6	1.4
Fe(III)	80		30.2	3.4
Cd(II)	200		30.2	1.3
Zr(IV)	75	NaF	30.5	2.5
Cu(II)	35	$SC(NH_2)_2$	29.7	3.5
Ti(IV)	5	Ascorbicacid	29.6	2.5
Mn(II)	50		30.0	2.0
W(VI)	8		29.8	1.4
Mo(VI)	15		29.6	2.5
Cr(III)	30		30.2	2.2
V(IV)	10		30.2	1.6
Ta(V)	5	NaF	30.2	1.5
Pt(II)	50		29.2	2.5
Pd(II)	50		30.4	3.6
UO_2^{2+}	40	CH_3COO^-	29.3	3.4
Ascorbic acid	100		30.0	2.3
Tartaric acid	100		30.2	1.3
Oxalate	5		30.8	3.4
Fluoride	1,5		29.6	2.4
Phosphoric acid	30		30.0	3.3
Thiourea	20		31.2	2.6

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 DHTP and Am. Interference of most cations masked by the addition of complex one III. Tartrate mask the mil-ligram quantities of Ta, Ti, W and Mo. Zr fluorides should mask, and copper-thiourea. The results are summarized in (Table 1).

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 0.44-20μg/ml. The pertaining calibration graph is shown in the (Fig. 6).

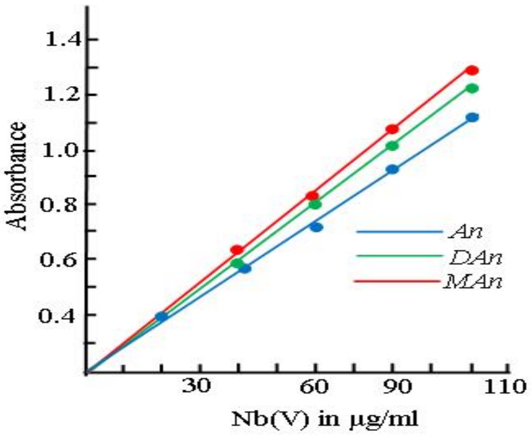


Figure 6. **Analytical determination of Nb (V); [DHTP] =[Am]= 1.2 ×10^{-3} M; pH = 4.5; λ = 440 nm , ℓ=5 mm.**

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

With the increase of the basic amine (pK_a) complexes improved analytical parameters.

The proposed method compares favourably with the existing ones (Table 3) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity [7].

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

Parameter	**An** **pK_a=4.58**	**Man** **pK_a=4.85**	**Dan** **pK_a=5.06**
Color	yellow	yellow	yellow
The pH range of education and extraction	3.1-6.2	3.3-4.5	3.4-6.0
The pH range of maximum extraction	4.3-4.5	4.4-4.8	4.5-5.0
Concentration of DHTP: mol· L^{-1}	0.,95×10^{-3}	1.0×10^{-3}	1.28×10^{-3}
Concentration of Am: mol· L^{-1}	1.0×10^{-3}	1.1×10^{-3}	1.2×10^{-3}
Organic solvent	$CHCl_3$	$CHCl_3$	$CHCl_3$
Extraction time	10 min	8 min	5 min
λmax (nm)	420	425	430
Molar absorptivity (L· mol^{-1} cm^{-1})	3.75×10^{4}	3.80×10^{4}	3.9×10^{4}
Sandell's sensitivity (μg· cm^{-2})	0.025	0.024	0.024
R,%	98.3	98.5	98.6
The equation of calibration curves	0.075+0.068x	0.045+0.076x	0.035+0.049x
lg k_e	9,28	8.82	8.19
Stabilityconstant (β)	9.66	9.73	9.89
Beer's law range (μg· ml^{-1})	0.44-20	0.44-20	0.44-20
Correlationcoefficient	0.9973	0.9975	0.9977
Limit of detection : ng ·mL^{-1}	16	12	10
Limit of quantification : ng ·mL^{-1}	36	32	28

Table 3. **Comparative characteristics of the procedures for determining niobium.**

Reagent	**pH(solvent)**	**λ, nm**	**ε·10^{-4}**	**Beer's law range (μg· ml^{-1}**
Pyrocatecholviolet	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_2SO_4($C_2H_4Cl_2$)	440	1.59	0.41 - 4.54
Pyrocatechol+tetrazolium violet	0.4 - 1MH_2SO_4($CHCl_3$)	390	1.60	1.25 - 11.78
Bromopyrogallolred	5.8-6.6	560	4.75	0.1-1.4
DHTP+An	4.3-4.5 ($CHCl_3$)	420	3.75	0.44-20
DHTP+Man	4.4-4.8 ($CHCl_3$)	425	3.80	0.44-20
DHTP+DAn	4.5-5.0 ($CHCl_3$)	430	3.90	0.44-20

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 4) indicate the successful applicability of the proposed method to real sample analysis.

***Table 4.* Determination of Niobium in steel (*n*=5, *P*=0.95).**

Steel	Prosedure	$\bar{x}$, %	*RSD,%*
CBT-1(0.012%Nb)	DHTP+An	$(1.29\pm0.034)\times10^{-2}$	2.5
	DHTP+MAn	$(1.23\pm0.029)\times10^{-2}$	2.7
	DHTP+DAn	$(1.18\pm0.029)\times10^{-2}$	1.9
CBT-6(0.29%Nb)	DHTP+An	$(1.94\pm0.017)\times10^{-2}$	2.3
	DHTP+MAn	$(1.93\pm0.026)\times10^{-2}$	2.2
	DHTP+DAn	$(2.14\pm0.042)\times10^{-2}$	2.3
CO №158^{a} (1.21 %Nb)	DHTP+An	(1.14 ± 0.030)	2.8
	DHTP+MAn	(1.20 ± 0.027)	2.7
	DHTP+DAn	(1.28 ± 0.029)	2.1
CO№231(0.37%Nb)	DHTP+An	$(3.84\pm0.24)\times10^{-2}$	1.8
	DHTP+MAn	$(3.85\pm0.24)\times10^{-2}$	1.9
	DHTP+DAn	$(3.98\pm0.029)\times10^{-2}$	2.6

Conclusions

Mixed-ligand complexes of Niobium (V) with 2,4-dihydroxythiophenol and hydrofobamins have been studied by spectrophotometry. Extraction of mixed ligand complexes is maximal at pH 3.1-6.0. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found. The molar ratio of the reacting Nb(V), DHTP and HAm species is 1:2:2. The general formula of the ternary complexes is $(HAm^{+})_2[Nb(V)(OH)_3(DHTF^{2-})_2]$. They can be regarded as ionassociates between doubly charged anionic chelates $[Nb(V)(OH)_3(DHTP)_2]^{2-}$ and protonated HAm^{+} species. The molar absorptivities (ε_{max}) belong to the interval $(3.75\text{-}3.9)\times10^{4}$ L mol^{-1} cm^{-1} for the complexes of Nb(V). The highest molar absorptivity can be achieved with the couple DHTP-DAn. A procedure has been developed for extraction-spectrophotometric determination niobium in steels of different brands.

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