

COMPLEX FORMATION AND LIQUID-LIQUID EXTRACTION IN THE NIOBIUM(V) – 4-NITROCATÉCHOL – THIAZOLYL BLUE TETRAZOLIUM SYSTEM

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ABSTRACT

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. Two ion-associated complexes with suggested formulae $(\text{MTT})_2[\text{NbO}(\text{OH})(4\text{-NC})_2]$ (**I**) and $(\text{MTT})_3[\text{NbO}(4\text{-NC})_3]$ (**II**) were detected in the organic phase after shaking at certain conditions. The second one has better analytical characteristics and could compete successfully with many species used for spectrophotometric and extraction-spectrophotometric determination of niobium(V). The optimum conditions for extraction of **II** were found: organic solvent – chloroform, extraction time – 3 min, acidity of the aqueous phase – $0.05\text{-}0.10 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, concentration of 4-NC – $1.4 \times 10^{-3} \text{ mol L}^{-1}$ and concentration of MTT – $2.4 \times 10^{-4} \text{ mol L}^{-1}$. Under the specified conditions Beer's law is obeyed for Nb(V) concentrations ranging from $0.39 \mu\text{g mL}^{-1}$ to $1.7 \mu\text{g mL}^{-1}$ with molar absorptivity coefficient of $\epsilon_{410} = 5.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Some key constants were determined: constant of association ($\text{Log } \beta = 13.2$), constant of distribution ($\text{Log } K_D = 0.82$), constant of extraction ($\text{Log } K_{\text{ex}} = 14.0$), recovery factor ($R = 86.9\%$). The limit of detection (LOD), limit of quantification (LOQ) and Sandell's sensitivity (S) were calculated to be $\text{LOD} = 0.12 \mu\text{g mL}^{-1} \text{ Nb(V)}$, $\text{LOQ} = 0.39 \mu\text{g mL}^{-1} \text{ Nb(V)}$ and $S = 0.0017 \mu\text{g cm}^{-2} \text{ Nb(V)}$.

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

INTRODUCTION

Niobium is widely used for the fabrication of steels and superalloys, special materials for microelectronics and optics, superconductors, refractory materials and

catalysts [1-9]. As an important microalloying element in steels niobium can significantly affect the properties of the sample, such as the intensity at high temperature, the ability of tarnish-resistance and temper brittleness [6,7,9]. Niobium steels are valuable constructive materials for the chemical and nuclear industry, jet and rocket engines, gas pipelines and turbines [6-9]. Unalloyed niobium and some niobium alloys are important for the production of surgical instruments, medical devices (e.g. pacemakers), coins and jewelry. The reason for these applications is niobium's physiologically inertness and ability to be colored by anodisation [9,10].

In nature, niobium almost invariably occurs as complex oxide materials in association with tantalum. Columbite-tantalite minerals are usually found as accessory minerals in pegmatite intrusions, and in alkaline intrusive rocks [11-13]. It should be mentioned that the niobium content in geological samples is of particular interests to geochemists [14-16]. This element remains immobile during post-crystallization rock alternation involving hydrous fluids, and the precise determination of ratios such as Nb/U and Nb/Th can give valuable information for the processes taking place during the generation of continental crust from the mantle [16].

Several analytical methods have been used to determine Nb: spectrophotometry [9,17-37], high-performance liquid chromatography (HPLC) [6,14,15,38], atomic absorption spectrophotometry (AAS) [39], inductively coupled plasma (ICP) optical emission spectrometry (OES) [40], ICP mass spectrometry (MS) [41] and neutron activation analysis (NAA) [42]. The main disadvantage of AAS and OES is low sensitivity because of spectral interference or high background due to the matrix elements. The general disadvantage of ICP-MS and NAA is high cost.

The methods involving spectrophotometry are rather popular due to their simplicity, inexpensive instrumentation and easy automation [29,43]. These methods are often based on ion-association systems composed of intensively colored anionic chelate and bulky organic cation which makes the complex hydrophobic and easily extractable into organic solvents [9,29-36,43-50].

It is known that Nb(V) forms yellow anionic species with 4-nitrocatechol (4-NC) [32,44,45]. The cationic ion-pair reagent 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyltetrazolium bromide (Thiazolyl Blue Tetrazolium, MTT) is considered particularly prospective for liquid-liquid extraction (LLE)-spectrophotometric determination of such species because MTT⁺ absorbs light in the same spectral region. The overlap between the absorption bands of MTT⁺ and Nb(V) – 4-NC anionic chelate is expected to cause a promotion of the intensity of coloration.

In this paper we study the complex formation and LLE in the Nb(V) – (4-NC) – MTT – water – organic solvent system as a first step of its application for LLE-spectrophotometric determination of Nb(V).

EXPERIMENTAL

Reagents and apparatus

✓ A stock Nb(V) solution was prepared by dissolving of 0.2352 g of Nb₂O₅ (Fluka, p.a.) in 10 mL conc. H₂SO₄ in the presence of 5 g (NH₄)₂SO₄ as described in [45,50]. After cooling, the obtained transparent substance was carefully collected into

a 100 mL calibrated flask and diluted to the mark with 10 mol L⁻¹ solution of H₂SO₄ [50]. A 1 mL aliquot of this solution was transferred into a 10 mL calibrated flask and diluted to the mark with 17 mol L⁻¹ solution of H₂SO₄. The concentration of the obtained working solution was 164.4 µg mL⁻¹ Nb(V).

- ✓ 4-NC (Fluka, p.a.), 1.0×10⁻² mol L⁻¹ aqueous solution.
- ✓ MTT, (Loba Feinchemie AG, for microscopy), 3×10⁻³ mol L⁻¹ aqueous solution.
- ✓ Chloroform, redistilled.
- ✓ A Camspec M508 UV/Vis spectrophotometer, equipped with 1 cm path-length cells.
- ✓ A HI 83140 pH meter (Italy) with a combined plastic electrode.

Procedure

The necessary amounts of Nb(V), H₂SO₄ to adjust the acidity of the aqueous medium, 4-NC and MTT were placed in separatory funnels, diluted to 10 mL with distilled water and extracted with 10 mL of organic solvent. The samples were shaken and after phase separation, the organic layer was filtered through a paper filter into a 1 cm cell. The absorbance was measured against a blank prepared in the same way.

For the determination of the distribution constant K_D the absorbance values obtained after single (A_1) and triple (A_3) extractions in the optimum conditions (Table 1) were compared: $K_D = [\text{Nb}]_{\text{org}} / [\text{Nb}]_{\text{aq}} = A_1 / (A_3 - A_1)$. The organic extract (10 mL) after the single extraction was transferred through a paper filter into a 25 mL volumetric flask. It was diluted to volume with chloroform and then the absorbance (A_1) was measured against a blank. Under the same conditions another sample was extracted with three successive portions of chloroform. The volumes of these portions were 10, 7, and 7 mL respectively. The extracts were consecutively transferred through a paper filter into a 25 mL volumetric flask, and after dilution to volume with chloroform, the absorbance (A_3) was measured against a blank.

RESULTS AND DISCUSSION

Spectral characteristic and optimum LLE-spectrophotometric conditions

Preliminary investigations showed that in sulfuric acid solutions Nb(V), 4-NC and MTT form easily extractable into organic solvents (chloroform, 1,2-dichloroethane, benzene, toluene and tetrachloromethane) intensively colored yellow species. Chloroform was chosen for further investigations because of its better performance. The main absorption maximum in this solvent is situated at 400-430 nm. Additional, very sharp maximum is recorded at about 560 nm. This maximum is improper for spectrophotometric measurements.

Other parameters concerning the extraction of Nb(V) were optimized: the acidity of aqueous phase (Fig. 1), the time of extraction (Fig. 2) and the concentrations of the reagents (Fig. 3). The optimum conditions are listed in Table 1.

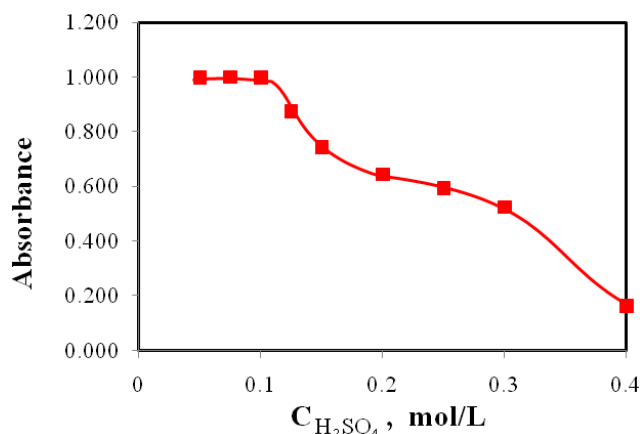


Figure 1. Absorbance of the extracted complex vs. concentration of H_2SO_4 plot.
 $C_{Nb(V)} = 1.77 \times 10^{-5} \text{ mol L}^{-1}$, $C_{4\text{-NC}} = 1.4 \times 10^{-3} \text{ mol L}^{-1}$, $C_{MTT} = 2.4 \times 10^{-4} \text{ mol L}^{-1}$

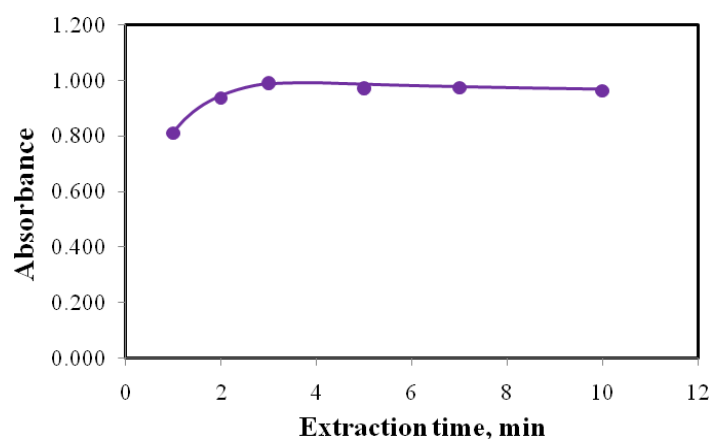


Figure 2. Absorbance of the extracted complex vs. extraction time plot.
 $C_{Nb(V)} = 1.77 \times 10^{-5} \text{ mol L}^{-1}$, $C_{4\text{-NC}} = 1.4 \times 10^{-3} \text{ mol L}^{-1}$, $C_{MTT} = 2.4 \times 10^{-4} \text{ mol L}^{-1}$

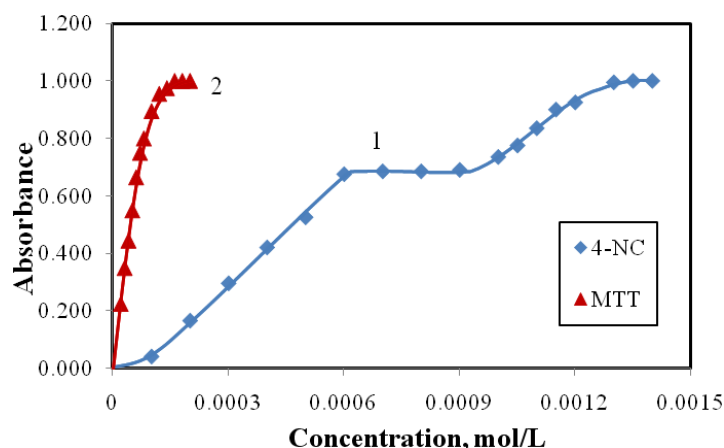


Figure 3. Absorbance of extracts of $Nb(V)$ with 4-NC and MTT vs. concentration of the reagent plots:

(1) 4-NC. $C_{Nb(V)} = 1.77 \times 10^{-5} \text{ mol L}^{-1}$, $C_{MTT} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$;

(2) MTT. $C_{Nb(V)} = 1.77 \times 10^{-5} \text{ mol L}^{-1}$, $C_{4\text{-NC}} = 1.4 \times 10^{-3} \text{ mol L}^{-1}$.

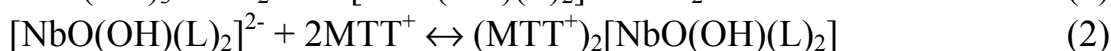
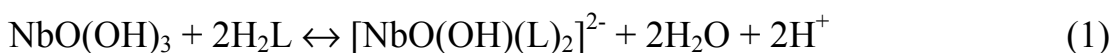
The complicated course of curve 1 is an indication for stepwise complex formation.

Table 1. *Optimum conditions and analytical characteristics of the LLE-spectrophotometric determination of Nb(V) with 4-NC and MTT*

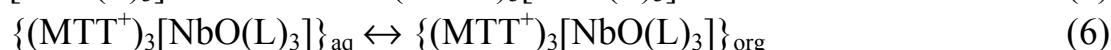
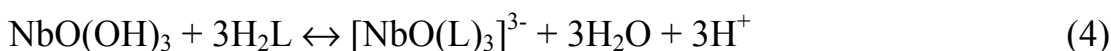
Optimum Conditions	Analytical Characteristics
Organic solvent: Chloroform	Apparent molar absorptivity (ϵ'): $(5.6 \pm 0.2) \times 10^4$ L mol ⁻¹ cm ⁻¹
Absorbance maximum: 410 \pm 5 nm	Adherence to Beer's law: 0.39 – 1.7 μ g mL ⁻¹ Nb(V)
Extraction time: 3 min	Correlation coefficient: 0.9974
Acidity of aqueous phase: 0.05 – 0.10 mol L ⁻¹ H ₂ SO ₄	Sandell's sensitivity: 0.0017 μ g cm ⁻²
Concentration of 4-NC: 1.4×10^{-3} mol L ⁻¹	Limit of detection (LOD): 0.12 μ g mL ⁻¹ Nb(V)
Concentration of MTT: 2.4×10^{-4} mol L ⁻¹	Limit of quantification (LOQ): 0.39 μ g mL ⁻¹ Nb(V)

Suggested formulae and equations

The complicated course of curve 1, Fig. 3 is a strong evidence for stepwise complex formation in the Nb(V) – 4-NC – MTT LLE-system. That is why Nb(V) to 4-NC and Nb(V) to MTT molar ratios were established by the equilibrium shift method [51] (Fig. 4). The results show that at least two different complexes are formed between Nb(V), 4-NC and MTT (with composition of 1:2:2 and 1:3:3, respectively). Suggested equations of complex formation and extraction, based on the mentioned molar ratios, data for the niobium state in sulfuric acid solutions [49,52], and our previous investigations on similar system [45] are presented in Scheme 1 and Scheme 2.



Scheme 1. *Formation and extraction of the ternary complex of Nb(V) with 4-NC (H₂L) and MTT at deficiency of the reagents*



Scheme 2. *Formation and extraction of the ternary complex of Nb(V) with 4-NC (H₂L) and MTT at the optimum extraction-spectrophotometric conditions*

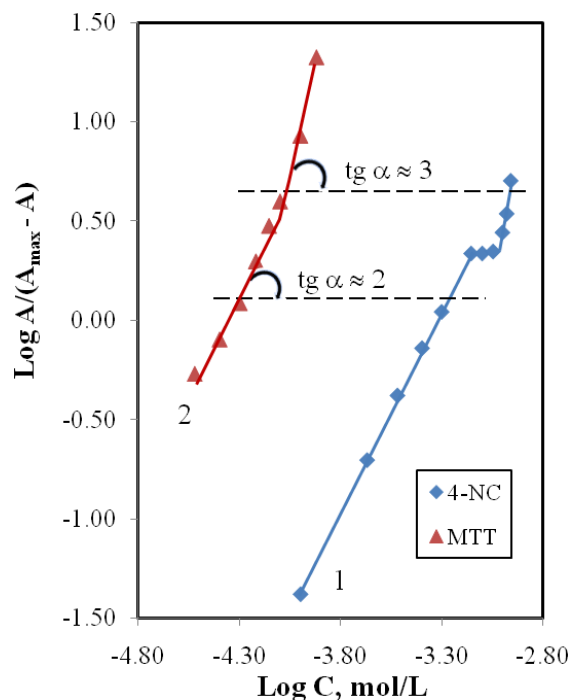


Figure 4. Determination of the 4-NC to Nb(V) molar ratios (curve 1) and MTT to Nb(V) molar ratios (curve 2) according to the equilibrium shift method: (1) $C_{Nb(V)} = 1.77 \times 10^{-5} \text{ mol L}^{-1}$, $C_{MTT} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$; (2) $C_{Nb(V)} = 1.77 \times 10^{-5} \text{ mol L}^{-1}$, $C_{4-NC} = 1.4 \times 10^{-3} \text{ mol L}^{-1}$.

Equilibrium constants and analytical characteristics

The complex with suggested formula $(MTT^+)_3[NbO(4-NC)_3]$ (see Scheme 2), which is formed at the conditions presented in Table 1, has better characteristics. The equilibrium constants characterizing its formation and extraction were calculated as follows: the association constant β (eq. 5) by the method of Komar-Tolmachev [51]; the distribution constant K_D (eq. 6) by comparing the absorption for single extraction at the optimum conditions (A_1) to that for threefold extraction (A_3) in equal volumes (25 mL) $K_D = A_1/(A_3 - A_1)$; and the recovery factor R and extraction constant K_{Ex} from the equations $R\% = K_D 100/(K_D + 1)$ and $\text{Log} K_{Ex} = \text{Log} K_D + \text{Log} \beta$, respectively [46,47,49]. The obtained values are presented in Table 2.

Table 2. Values for the equilibrium constants characterizing LLE of Nb(V) with 4-NC and MTT

Equilibrium Constants	Nb(V) – 4-NC – MTT – Water – Chloroform
Log β	13.2±0.9
Log K_D	0.82±0.01
Log K_{Ex}	14.0±0.9
Recovery	(86.9±0.1)%

The Komar-Tolmachev method [51] also allows to calculate the true molar absorptivity (ϵ) of the complex: $\epsilon = (5.2 \pm 0.5) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. This value agrees well

with that obtained from Beer's law (ϵ') (Table 1) what is an indication for the lack of serious side-reactions [51]. Apparently only $(\text{MTT}^+)_3[\text{NbO}(4\text{-NC})_3]$ is extracted at the specified in Table 1 conditions. The 4-NC to Nb molar ratio in this complex (3:1) is higher than that reported for other complexes with similar reagents (Table 3). This is the first reason for the significantly higher molar absorptivity achieved (Compare rows 3 and 9 in Table 3). The second reason is the ability of MTT^+ to absorb light in the yellow range (Compare rows 7 and 9 in Table 3).

Many others analytical reagents for Nb(V), including 5,7-diiodo-8-hydroxyquinoline ($\epsilon'=4.853 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) [23], p-sulphobenzenoazo-4-(2,3-dihydropyridine) ($\epsilon'=5.218 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) [24], sulphochlorophenol S + laurilamine ($\epsilon'=1.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [25], thiocyanate + promazine hydrochloride ($\epsilon'=2.52 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [34], thiocyanate + tetraphenylarsonium chloride (or tetraphenylphosphonium chloride) ($\epsilon'=3.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [17], Xylenol Orange + 3-hydroxy-2-methyl-1-phenyl-4-pyridone ($\epsilon'=3.72 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [18], PAR ($\epsilon'=3.76 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [19], 3-hydroxyflavone ($\epsilon'=4.088 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [20], tiazolylazo compounds + cetylpyridinium bromide $\{\epsilon'=(2.79\text{-}4.46) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}\}$ [27], 2,3-dihydroxynaphthalene + acetate ($\epsilon'=4.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [37], and N-cinamoyl-N-2,3-xylylhydroxylamine + thiocyanate ($\epsilon'=4.75 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [36] are worse in term of sensitivity than these studied in this work. That is why the couple 4-NC – MTT could be recommended for LLE-spectrophotometric determination of niobium(V) after preliminary investigations on the interfering effect of the matrix components.

Table 3. *Extraction-chromogenic systems for niobium involving ortho-polyphenols and tetrazolium salts.*

No	Reagents	Solvent	Composition Nb:R ₁ :R ₂	Molar abs. (ϵ') [L mol ⁻¹ cm ⁻¹]	Ref.
1	Catechol + Tetrazolium violet	CHCl ₃	1:2:1	0.57×10^4	31
2	Dihydroxynephtalene + Tetrazolium violet	CHCl ₃	1:2:1	1.18×10^4	31
3	4-NC + Tetrazolium violet	C ₂ H ₄ Cl ₂	1:2:1	1.59×10^4	32
4	Pyrogallol + Tetrazolium violet	C ₂ H ₄ Cl ₂	1:2:1	0.649×10^4	32
5	Catechol + Triphenyltetrazolium chloride	CHCl ₃	1:2:1	1.60×10^4	48
6	3,5-dinitrocatechol + Triphenyltetrazolium chloride	CHCl ₃	1:2:2	2.48×10^4	45
7	4-NC + Blue Tetrazolium Chloride	CHCl ₃	1:3:1.5	4.6×10^4	45
8	4-NC + MTT	CHCl ₃	1:2:2	3.9×10^4	This work
9	4-NC + MTT	CHCl ₃	1:3:3	5.6×10^4	This work

CONCLUSION

Nb(V), 4-NC and MTT form well extractable into chloroform ion-association complexes with suggested formulae $(MTT^+)_2[NbO(OH)(4-NC)_2]$ and $(MTT^+)_3[NbO(4-NC)_3]$. The second one has better characteristics and could compete successfully with many species used for spectrophotometric and LLE-spectrophotometric determination of niobium(V).

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