

Extraction and Characterization of Niobium(V) Thiocyanate Complexes

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Extraction of niobium(V) from sulphuric and hydrochloric acid solutions containing an excess of thiocyanate ions with tetraphenylphosphonium (TPP) and tetraphenylarsonium (TPA) chloride into chloroform was investigated. The maximum extraction of niobium from sulphuric acid solutions was about 91% and from hydrochloric acid solutions about 94%. Chloride ions produced a moderate synergistic effect. Niobium(V) was quantitatively extracted (over 99%) from sulphuric and hydrochloric solutions only if chloride ions were also in excess and a lower excess of thiocyanate and extractant was required than in extraction without addition of chloride. The optimal conditions for the quantitative extraction of niobium were 0.2–0.5 M H₂SO₄ or 0.2–4 M HCl, 0.2–0.7 M thiocyanate and more than 4 M chloride in the aqueous phase, and TPP (TPA) concentration in the organic phase higher than 3×10^{-3} M. The extracted complexes in chloroform had an absorption maximum at 390 nm or at 390 and 320 nm, depending on the composition of the aqueous phase. Absorption spectra were studied as a function of H₂SO₄, HCl, thiocyanate and chloride concentrations in the aqueous phase. The optimal conditions for the spectrophotometric determination of niobium by measuring the absorbances of the organic phase at 390 nm were 1–2 M HCl, 0.1–0.5 M thiocyanate and TPP (TPA) chloride in chloroform of at least 5×10^{-3} M. A total chloride concentration lower than 2.2 M had no effect on absorbance. The mechanism of extraction based on the formation of ion-associated compounds between the onium cation and the thiocyanatoniobate(V) or mixed ligand chlorothiocyanatoniobate(V) anion is discussed.

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INTRODUCTION

Various methods have been reported for the spectrophotometric determination of niobium. Thiocyanate methods are perhaps the ones most commonly used for niobium determination. They are applicable for routine analysis but have serious shortcomings. These concern a strong influence of the amounts of tin(II) chloride, thiocyanate and hydrochloric acid on the colour intensity of the complex and the reproducibility of the data, as well as a serious interference by many metal ions.^{1,2} The selectivity, sensitivity and stability of the niobium thiocyanate complex have been enhanced by adding a second ligand, which forms a mixed complex extractable into an organic solvent.²⁻⁷ Extraction of an ion-pair formed between thiocyanatoniobate(V) and an organic cation has been successfully used for the spectrophotometric determination of niobium.⁸⁻¹⁰ Niobium was extracted as an ion-pair with tetraphenylarsonium chloride into chloroform and 9 : 2 chloroform-acetone solution. The composition of the extracted thiocyanatoniobate(V) was $[\text{Nb}(\text{SCN})_2\text{X}]^-$ (X = chloride, oxo or hydroxy ligands) with maximum absorption at 390 nm.⁸ Niobium was also extracted with 1,2,4,6-tetraphenylpyridinium perchlorate into toluene as $[\text{NbOCl}(\text{SCN})_3]^-$ with a maximum absorption at 395 nm⁹ and with ethylene-bis-(triphenylphosphonium) bromide into chloroform as $[\text{NbOCl}_3(\text{SCN})_2]^{2-}$ with maximum absorption at 393 nm.¹⁰

The present paper deals with the extraction of niobium(V) from sulphuric and hydrochloric acid solutions containing an excess of thiocyanate ions with tetraphenylphosphonium (TPP) and tetraphenylarsonium (TPA) chloride into chloroform. Niobium(V) was quantitatively extracted (over 99%) from sulphuric and hydrochloric solutions only if chloride ions were also in excess. Extraction mechanism was based on the formation of ion-associated compounds between the onium cation, on the one hand, and the thiocyanatoniobate(V) or mixed ligand chlorothiocyanatoniobate(V) anion on the other. The extracted complex in chloroform had an absorption maximum at 390 nm, or at 390 and 320 nm, depending on the composition of the aqueous phase. The absorption spectra and the conditions for quantitative extraction and spectrophotometric determination of niobium in the organic phase were investigated in more detail than reported in previous papers,⁸⁻¹⁰ where no mention was made of the existence of two maxima in the absorption spectra of the extracted complex. Furthermore, this investigation helps explain the causes of some shortcomings of the thiocyanate methods for the spectrophotometric determination of niobium.

EXPERIMENTAL

Reagents and Radioactive Tracer

A standard solution of niobium (about 2×10^{-2} M) was prepared in 10 M HCl, or 5 M H₂SO₄. Nb₂O₅ was fused with KHSO₄ in a platinum crucible. The melt was extracted with a hot 10% solution of H₂C₂O₄. The niobium was precipitated with ammonia, centrifuged, and washed three times with a 2% solution of NH₄Cl and once with distilled water. The freshly precipitated niobium hydroxide was then dissolved in 10 M HCl or 5 M H₂SO₄. The solution was filtered and standardized by precipitating niobium with tannin.¹¹ Solutions of lower concentrations were prepared by diluting the standard solution with 10 M HCl or 5 M H₂SO₄. ⁹⁵Nb was supplied from the Radiochemical Centre, Amersham, England, in the form of oxalato complex in a 0.5% solution of oxalic acid. ⁹⁵Nb in chloride and sulphate forms was prepared by dissolving freshly precipitated ⁹⁵Nb hydroxide in 10 M HCl or 5 M H₂SO₄. The freshly precipitated ⁹⁵Nb hydroxide was prepared by the same procedure as inactive niobium hydroxide. Tetraphenylarsonium and tetraphenylphosphonium chloride (analytical grade, Fluka) were dissolved in reagent-grade chloroform. All chemicals used were of analytical purity.

Apparatus

Absorption spectra and absorbance measurements of solutions were made on a Varian Cary 3 spectrometer. Radioactivity measurements (⁹⁵Nb) were performed with a well-type gamma scintillation counter (NaI/Tl) from Ecko Electronic. A Griffin flask shaker with a time switch was used for extraction.

Determination of the Distribution Ratio

The distribution ratio of niobium was determined at room temperature by shaking equal volumes (5 ml) of organic and aqueous phases of a given composition in a 50-ml conical flask with a mechanical shaker for 20 min. After the phases were separated and centrifuged, aliquots (1 ml) were taken for radiochemical analysis using a gamma scintillation counter. Distribution ratios were calculated from counts/100 s of both phases.

Spectrophotometric Determination of Niobium in Chloroform

Equal volumes (10 ml) of organic and aqueous phases of a given composition were shaken in a 50-ml conical flask with a mechanical shaker for 20 min. The phases were separated by gravity and the absorbances of the organic phase were measured at 320 and 390 nm against a reagent blank used as reference.

RESULTS AND DISCUSSION

Optimum Conditions for Extraction

Extraction of niobium(V) from sulphuric and hydrochloric acid solutions containing an excess of thiocyanate ions with TPP and TPA chloride into

chloroform was investigated. The maximum extraction of niobium from sulphuric acid solutions was about 91% and from hydrochloric acid solutions about 94%. Chloride ions showed a moderate synergistic effect. Niobium(V) was quantitatively extracted (over 99%) from sulphuric and hydrochloric solutions only if chloride ions were also in excess and a lower excess of thiocyanate and extractant was required than in extraction with no chloride addition (Figure 1). If chloride ions were not present in excess, quantitative extraction of niobium could not be achieved, regardless of the acidity and thiocyanate concentration in the aqueous phase or the extractant concentration in the organic phase (Figure 1). Niobium(V) could be quantitatively extracted from thiocyanate solutions with TPP or TPA only if the chloride concentration was ≥ 4 M (Figure 2). With increasing sulphuric acid concentration from 0.2 to 0.5 M in solutions without the presence of an excess of chloride the niobium extraction decreased to 60%; it was constant in the acidity range 1.5–4.0 M H_2SO_4 ; at a H_2SO_4 concentration higher than 4.0 M, niobium extraction again decreased and at 8 M H_2SO_4 practically all the niobium remained in the aqueous phase (Figure 3). In the presence of a chloride excess (4 M), niobium was quantitatively extracted in the acidity range 0.2–0.5 M H_2SO_4 or 0.2–4 M HCl. At H_2SO_4 concentration higher than 0.5 M and HCl concentration higher than 4.0 M, the extraction decreased and at 8 M H_2SO_4 or 10 M HCl practically all the niobium remained in the aqueous phase. With an increase in acidity, the decrease in niobium extraction was more marked in the presence of sulphuric acid because the increase in sulphuric acid concentration was accompanied by a simultaneous

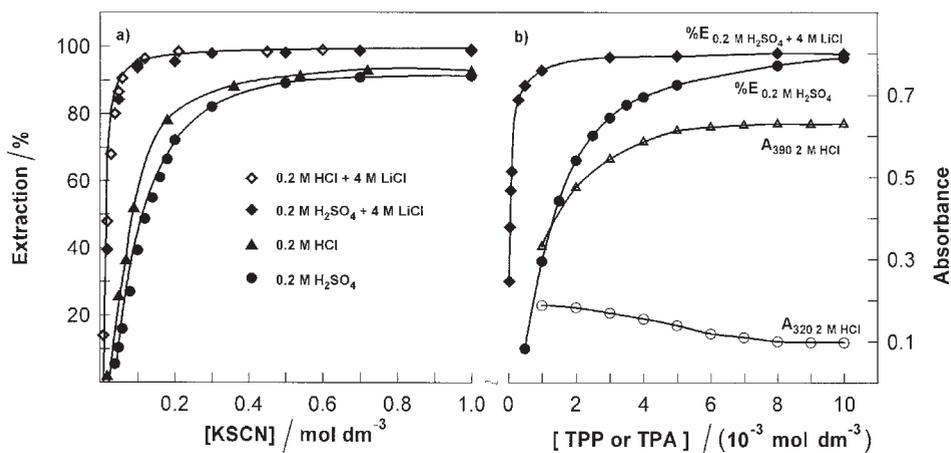


Figure 1. Dependence of the percent of extraction of niobium(V) and the absorbance on thiocyanate (a) and extractant (b) concentration. 2×10^{-5} M Nb^{V} ; (a) 6×10^{-3} M TPP (TPA); (b) 0.2 M KSCN.

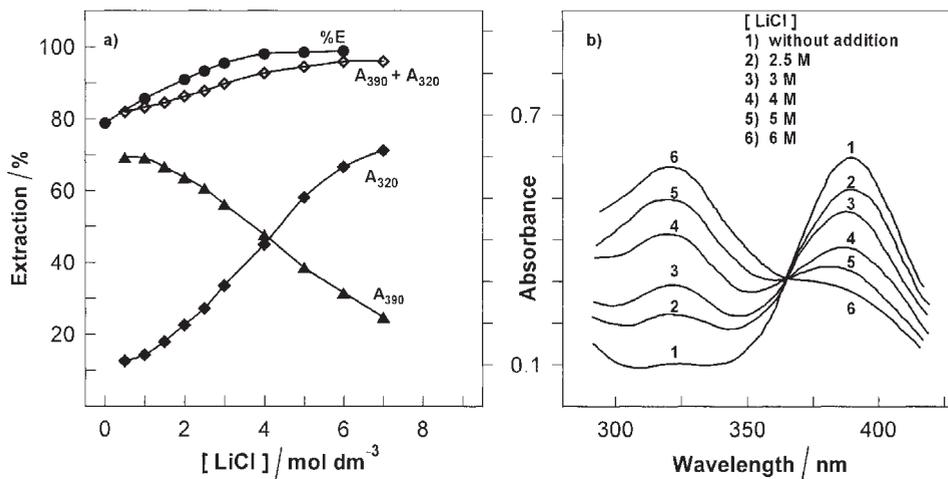


Figure 2. Dependence of the percent of extraction of niobium(V) and the absorbance (a) and absorption spectra (b) on chloride concentration in aqueous phase. 2×10^{-5} M Nb^{V} ; 6×10^{-3} M TPP (TPA); 0.2 M H_2SO_4 ; 0.5 M KSCN.

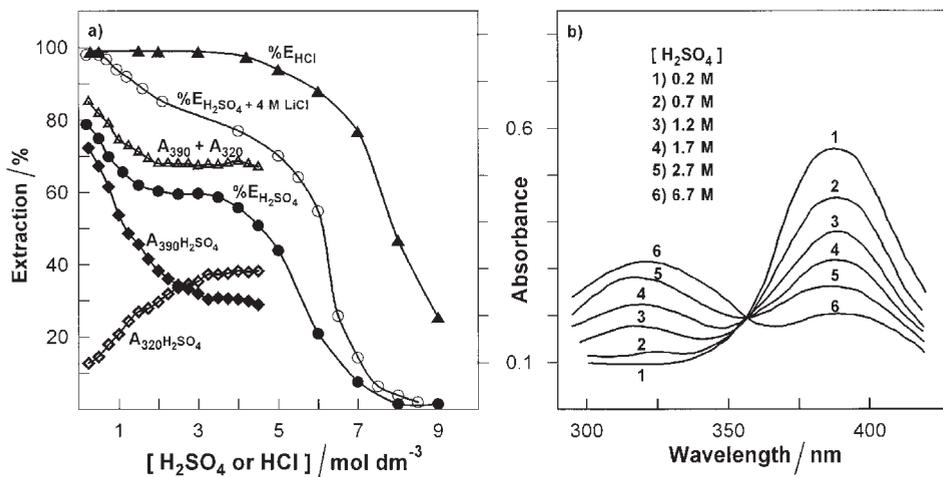


Figure 3. Dependence of the percent of extraction of niobium(V) on sulphuric and hydrochloric acid concentration (a) and the absorbance (a) and the absorption spectra (b) on sulphuric acid concentration. 2×10^{-5} M Nb^{V} ; 6×10^{-3} M TPP (TPA); 0.4 M KSCN.

increase in sulphate ion concentration, which caused the masking of niobium. Namely, contrary to the effect of chloride ions, sulphate ions masked niobium(V) if extraction took place from sulphuric or hydrochloric acid solutions with or without the presence of a chloride excess. The masking effect

of sulphate ions was more pronounced if extraction took place from solutions where no chloride was present.

The optimal conditions for the quantitative extraction of niobium were 0.2–0.5 M H_2SO_4 or 0.2–4 M HCl, 0.2–0.7 M thiocyanate and more than 4 M chloride in the aqueous phase and TPP or TPA concentration in the organic phase higher than 3×10^{-3} M. At these optimal extracting conditions, the anions that could mask niobium(V) did not interfere if present in moderate quantities. Citrate, acetate, perchlorate and sulphate may not have exceeded a 400-fold amount, phosphate and tartarate a 40-fold amount and fluoride and oxalate a 5-fold amount with respect to niobium(V). Distribution equilibrium was attained in less than 10 min. The shaking time of the aqueous and organic phases of 20 min was sufficient to achieve reproducible results. The niobium(V) extracted could be quantitatively stripped with 10 M H_2SO_4 , independently of extraction conditions.

All results of distribution measurements were obtained radiometrically. They pertain to the extraction of niobium(V), regardless of the nature of the extractable complexes involved. To find out the conditions at which the formation of the extracted complex was optimal for the spectrophotometric determination of niobium and for the determination of the compositions of the extracted complexes, the absorption spectra were measured as a function of H_2SO_4 , HCl, thiocyanate, sulphate and chloride concentrations in the aqueous phase and of the TPP or TPA concentration in the organic phase.

Absorption Spectra of the Extracted Complexes

The niobium(V) thiocyanate complex extracted with TPP or TPA had a maximum absorbance at 390 nm only if extraction was carried out from solutions with low concentration of sulphuric acid (0.2 M H_2SO_4), without the presence of chloride. At 0.2 M sulphuric acid, the maximum and constant absorbances at 390 nm were recorded in the thiocyanate concentration range of 0.4–0.8 M. With increasing sulphuric acid concentration at the optimum thiocyanate concentration (0.5 M) without the presence of chloride, as extraction of niobium decreased, so did also the absorbance at 390 nm (Figure 3). At about 0.7 M H_2SO_4 , in addition to this maximum, there was a new shoulder at 320 nm and the intensity of this shoulder increased as the acidity increased. At 1.2 M H_2SO_4 , a new maximum appeared at 320 nm. At this and higher sulphuric acid concentrations, the spectra had maxima at 320 and 390 nm. The increased sulphuric acid concentration intensified the 320 nm maximum and simultaneously decreased the 390 nm maximum, and at about 2–4 M H_2SO_4 , absorbances at 320 and 390 nm had approximately equal values.

A similar effect on absorption spectra was produced by chloride ions. Increase in chloride ion concentration at 0.2 M H_2SO_4 and optimum thiocya-

nate concentration (0.5 M) intensified the 320 nm maximum and simultaneously decreased the absorbance at 390 nm, but the absorption spectra retained both maxima (Figure 2). At about 4 M chloride (quantitative extraction), absorbances at 320 and 390 nm had approximately equal values.

The complex extracted from hydrochloric acid solutions had maximum absorbance always at 390 nm and, depending on hydrochloric acid and chloride ion concentration, also at 320 nm. At a high initial chloride ion concentration, absorbances at 320 nm in the absorption spectra were more strongly marked. The increased chloride ion concentration at constant thiocyanate concentration intensified the 320 nm maximum and simultaneously decreased the absorbance at 390 nm, but the absorption spectra retained both maxima. The increased thiocyanate concentration intensified the absorbance at 390 nm and depending on initial chloride and hydrochloric acid concentration as well as on the thiocyanate concentration range also at 320 nm. In optimum conditions for extraction the absorption spectra retained both maxima.

This investigation indicated a possible presence of a series of thiocyanatoniobates(V) and mixed chlorothiocyanatoniobates(V) in the organic phase. It also showed that chloride ions produced a synergistic effect on niobium extraction from thiocyanate solutions because mixed chlorothiocyanatoniobates(V) had better extraction properties than thiocyanatoniobates(V). It could also be concluded that if extraction was carried out from a concentrated sulphuric acid solution without addition of chloride ions in the aqueous phase, the extracted complex in chloroform had a maximum absorbance at 320 and 390 nm because the distribution of TPP and TPA chloride rapidly decreased at a high acid concentration.^{12,13} Therefore, in high sulphuric acid solutions the concentration of chloride ions in the aqueous phase from TPP or TPA chloride, which were always in great excess with respect to niobium, was sufficient for the formation of a mixed chlorothiocyanatoniobate(V).

Spectrophotometric Determination of Niobium in the Organic Phase

Formation of a mixed ligand chlorothiocyanatoniobate(V) was applicable to the spectrophotometric determination of niobium by measuring the absorbances of the organic phase at 390 nm. The optimal conditions for spectrophotometric determination were 1–2 M HCl, 0.1–0.5 M KSCN, and TPP (TPA) chloride concentration in chloroform of at least 5×10^{-3} M. Total chloride concentration lower than 2.2 M did not have any influence on the absorbance at 390 and 320 nm. The optimal concentration range for niobium was 0.5–5 $\mu\text{g/ml}$. Beer's law was obeyed over this range. The effective molar absorptivity at 390 nm was $3.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and at 320 nm $6.4 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ (Figure 4). The absorbance of the organic phase was stable for

at least one hour. The reproducibility of the method, expressed as relative standard deviation, was 1–5% depending on niobium concentration. The determination of niobium by the proposed spectrophotometric extraction procedure was feasible in the presence of many foreign ions. Acetate, citrate, phosphate, perchlorate, nitrate, cyanide, tartrate, chloride, ammonium, sodium, potassium, magnesium, cadmium, manganese(II), lead, calcium, barium, strontium, chromium(II), nickel and aluminium did not interfere in 1000-fold amounts with respect to niobium. Sulphate, vanadium(V), europium, uranyl and thorium were tolerated in 100-fold amounts and iron, titanium, palladium, osmium and fluoride in a 10-fold molar ratio to niobium. Copper, zinc, tin(II), tungsten(VI), molybdenum(VI) and oxalate were tolerated only in equimolar amounts with respect to niobium.

The optimal conditions for the quantitative extraction of niobium were not applicable to the spectrophotometric determination because of the lower sensitivity of the method and because any change in acidity and/or chloride concentration in the aqueous phase influenced absorbances at 390 and 320 nm. Molar absorptivity at 390 and 320 nm was $1.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ (0.2 M H_2SO_4 and 4 M LiCl) (Figure 4).

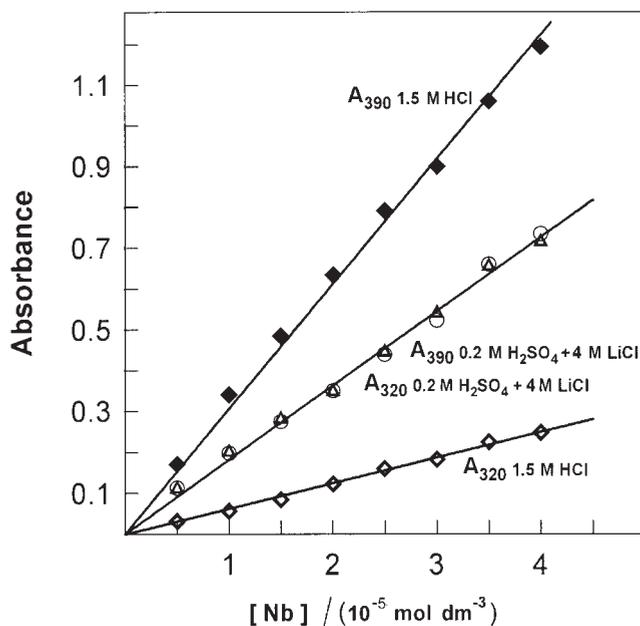


Figure 4. Validity of Beer's law in the extracted system at optimal conditions for spectrophotometric determination (1.5 M HCl) and optimal conditions for quantitative extraction. (0.2 M H_2SO_4 and 4 M LiCl); 0.4 M KSCN; 6×10^{-3} M TPP (TPA).

Identification of Extractable Niobium(V) Complexes

Compositions of the extracted niobium(V) complexes were studied by radiometric and spectrometric methods. The mechanism of extraction was based on the formation of ion-associated compounds between the onium cation on the one hand, and the thiocyanatoniobate(V) or mixed chlorothiocyanatoniobate(V) anion, on the other. At optimal extracting conditions chloride ions were always present in solution and a mixed chlorothiocyanatoniobate(V) was extracted with TPP or TPA. The influence of the extractant concentration in the organic phase on the distribution ratios of niobium was studied to determine the molar ratio of niobium to TPP (TPA) in extractable complexes. This was done by keeping optimum thiocyanate ion concentrations and different hydrochloric or sulphuric acid concentrations constant with an excess of chloride (4 M) and without the presence of chloride in the aqueous phase (Figure 5a). One-power extractant dependence was obtained from a solution with the presence of chloride, independently of the hydrochloric or sulphuric acid concentration. One-power extractant dependence was obtained from solutions without the presence of chloride only at a high sulphuric acid concentration when the concentration of chloride ions in the aqueous phase from TPP or TPA chloride was sufficient for the formation of mixed chlorothiocyanatoniobates,^{12,13} as shown in Figure 3. Decrease in sulphuric acid concentration led to a decrease in the concentration of chloride ions in the aqueous phase from TPP or TPA chloride and therefore positive

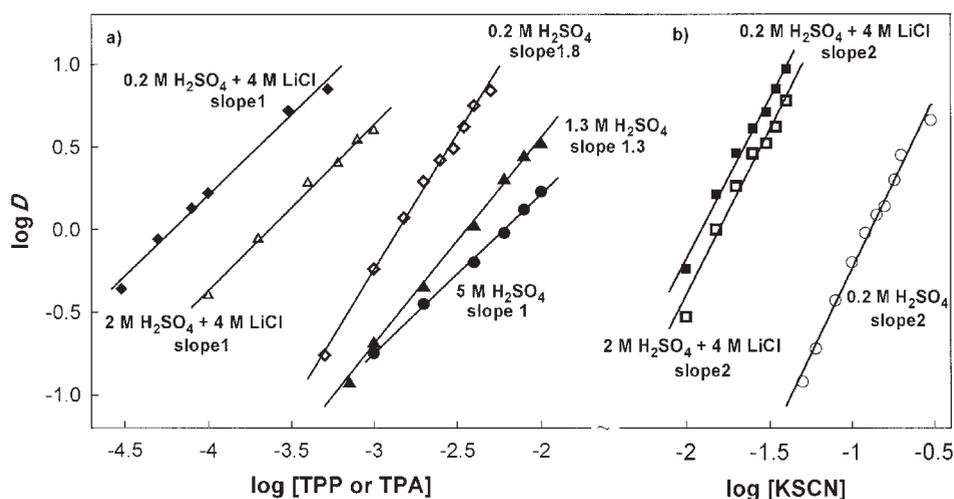


Figure 5. Dependence of the distribution ratio of niobium(V) on the extractant (a) and thiocyanate (b) concentration. 5×10^{-5} M Nb^{V} ; (a) 0.4 M KSCN; (b) 6×10^{-3} M TPP (TPA).

deviations from the slopes were obtained; at 0.2 M H_2SO_4 , the slope was 1.8. The dependence of the distribution ratio on thiocyanate concentration was examined in a similar manner (Figure 5b), and a second-power dependence was obtained. These distribution studies showed that the molar ratio of Nb : NCS : TPP (TPA) in the extracted complex was 1 : 2 : 1. The ratio of niobium(V) to TPP (TPA) in the extracted complex was also determined by studying the dependence of niobium extraction on its initial concentration in the aqueous phase (Figure 6b) and spectrophotometrically by Job's method (Figure 6a). The ratio was found to be equimolar.

The results show that a chlorothiocyanatoniobate(V) bearing one negative charge and one onium ion formed an ion-associated complex that was transferred into the organic phase. All results and the fact that, in an acidic solution, in the presence of chloride ions, niobium(V) probably existed as $[\text{NbOCl}_4]^-$ or $[\text{Nb}(\text{OH})_2\text{Cl}_4]^-$ anions¹⁴⁻¹⁷ suggest that a complex having the formula $[(\text{C}_6\text{H}_5)_4\text{X}][\text{Nb}(\text{NCS})_2\text{Cl}_4]$ (X = P or As) was extracted and spectrophotometrically determined. However, in the extracted chlorothiocyanatoniobate(V), the molar ratio of niobium to chloride could not be determined. Therefore, depending on which ions coordinated on niobium(V) in the aqueous phase were first exchanged with the thiocyanate ligand, the stoichiometry of the extracted complex could also be expressed as $[(\text{C}_6\text{H}_5)_4\text{X}][\text{Nb}(\text{NCS})_2\text{Cl}_m\text{Y}_n]$ (X = P or As; Y = oxo or hydroxy group).

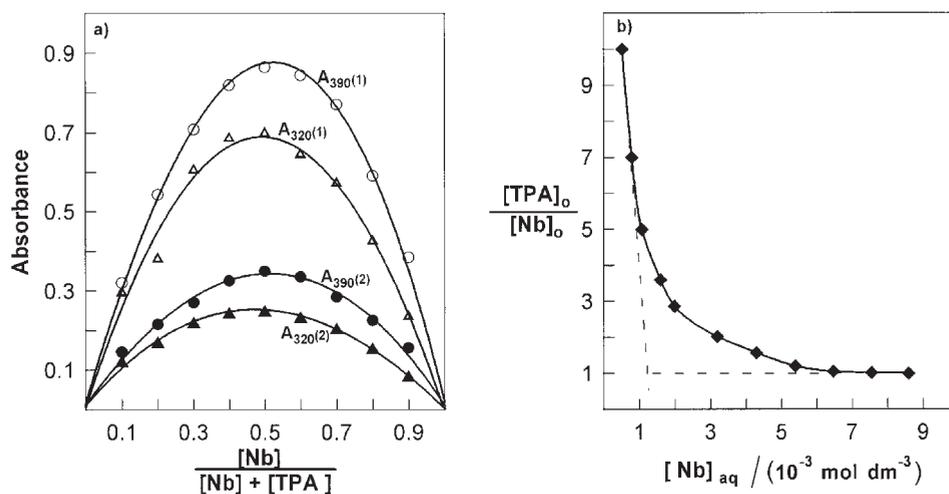


Figure 6. (a) Determination of Nb / TPA ratio by Job's method. 2 M H_2SO_4 ; 0.5 M KSCN; $[\text{Nb}] + [\text{TPA}] = 1 \times 10^{-3}$ M (1) and $[\text{Nb}] + [\text{TPA}] = 6 \times 10^{-4}$ M (2). (b) Determination of Nb / TPA ratio as a function of the initial niobium concentration in the aqueous phase. 2 M H_2SO_4 ; 0.4 M KSCN; 1×10^{-3} M TPA.

It can also be concluded that if the extraction of niobium(V) with TPP or TPA had been carried out under different conditions than depending on thiocyanate, chloride, sulphuric or hydrochloric acid concentrations, niobium could have been extracted in the form of various thiocyanato- and chlorothiocyanatoniobates(V) or as their mixture with a different number of bonded thiocyanato, chloro, oxo or hydroxy ions in the niobate(V) anion. As a consequence, the niobate(V) anion could also bear different negative charges. It was also confirmed that from aqueous solutions and diethyl ether extracts, imitating the conditions for the spectrophotometric determination of niobium complexes $[(C_6H_5)_4X]_2 [NbO(NCS)_5]$ (X = P or As) were isolated in the solid state from sulphuric acid solution. From hydrochloric acid solution, where a series of mixed chlorothiocyanatoniobates(V) were possibly present, no solid pure compounds were obtained.^{18,19}

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SAŽETAK**Ekstrakcija i karakterizacija niobijevih(V) tiocijanato-kompleksa**

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Proučavana je ekstrakcija niobija(V) tetrafenilfosfonijevim (TPP) i tetrafenilarsonijevim (TPA) kloridom u kloroform iz sumporno- i klorovodično-kiselih otopina koje sadržavaju suvišak tiocijanatnih iona. Maksimalna ekstrakcija niobija iz sumporno-kiselih otopina je oko 91% a iz klorovodično kiselih otopina oko 94%. Kloridni ioni imaju umjeren sinergetski efekt. Niobij(V) kvantitativno se ekstrahira (iznad 99%) iz sumporno- i klorovodično-kiselih otopina samo ako su kloridni ioni također u suvišku, a tada je potreban manji suvišak tiocijanata i ekstraktanta nego pri ekstrakciji bez dodatka klorida. Optimalni uvjeti za kvantitativnu ekstrakciju jesu: 0,2–0,5 M H₂SO₄ ili 0,2–4 M HCl, 0,2–0,7 M tiocijanati i više od 4 M klorida u vodenoj fazi i koncentracija TPP (TPA) u organskoj fazi veća od 3×10^{-3} M. Ekstrahirani kompleks u kloroformu ima maksimum apsorpcije pri 390 nm ili pri 390 i 320 nm, ovisno o sastavu vodene faze. Proučavani su apsorpcijski spektri u ovisnosti o koncentraciji H₂SO₄, HCl, tiocijanata i klorida u vodenoj fazi. Optimalni uvjeti za spektrofotometrijsko određivanje niobija mjerenjem apsorpcije organske faze pri 390 nm jesu: 1–2 M HCl, 0,1–0,5 M tiocijanati i TPP (TPA) klorid u kloroformu, najmanje 5×10^{-3} M. Ukupna koncentracija klorida manja od 2,2 M ne utječe na apsorpciju. Proučavan je mehanizam ekstrakcije temeljen nastajanjem ion-asociranih spojeva između onium kationa i tiocijanatoniobata(V) ili mješovitog kompleksa klorotiocijanatoniobata(V).