

Extraction and Separation of Tantalum(V) with 3-Hydroxy-2-methyl-1-(4-tolyl)-4-pyridone

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Extraction of tantalum(V) from aqueous oxalic solution with 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY) dissolved in chloroform has been examined at different acidities and ionic strengths. Tantalum(V) is quantitatively extracted with HY from oxalic solution at pH = 2.3–2.5, probably as a mixed ligand Ta-oxalate-HY complex. Tantalum(V) can be quantitatively extracted even from a more acidic solution in the presence of sulphuric, hydrochloric or perchloric acids, in the acidity range from pH = 2.3 to 3.5 M H₂SO₄ or HCl and from pH = 2.3 to 5.5 M HClO₄. Thiocyanate, perchlorate and chloride ions produce a synergistic effect on the tantalum(V) extraction with HY. In the presence of an excess of thiocyanate, perchlorate or chloride ions, tantalum(V) is quantitatively extracted with HY in the acidity range from pH = 2.3 to 3.5 M H₂SO₄ as a mixed ligand Ta-NCS-HY, Ta-ClO₄-HY or in the form of Ta-Cl-HY complexes. Compositions of the complexes are studied and discussed. Tantalum(V) extraction with HY enables its separation from niobium(V), zirconium(IV) and hafnium(IV).

INTRODUCTION

In our previous papers,^{1,2} the extraction and separation of tantalum(V) with 3-hydroxy-2-methyl-1-phenyl-4-pyridone (HX) were described. We now report the extraction of tantalum(V) with 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY) from different aqueous solutions. The results described here show that the extraction of tantalum(V) with HY is preferable to that with

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HX because it is feasible from a more acidic solution without the presence of strictly controlled sulphate, thiocyanate or perchlorate concentration. For some other metal ions, HY is also a more effective extractant than HX.³⁻⁸ With certain metal ions the tolyl analogue (HY) reacts at higher acid concentration than the phenyl analogue (HX), quantitatively extracted with less excess of extractant, and sometimes causes a change in the composition of extracted complexes. It is well known that niobium(V) and tantalum(V) are characterized by their similar chemical properties and hence it is difficult to carry out their separation. Separation of tantalum(V) from zirconium(IV) and hafnium(IV) is also of large practical importance. In this work we describe the separation of tantalum(V) from niobium(V), zirconium(IV) and hafnium(IV) by extraction with HY. This separation has the advantage over the separation by the HX method because of a larger difference in the extraction properties of these metals.

EXPERIMENTAL

Reagents and Radioactive Tracer

The tantalum-182 radionuclide was used as tracer. It was prepared by irradiation of a metal foil at the »Jožef Štefan« Institute, Ljubljana, Slovenia. After irradiation the metal foil was processed by dissolving the metal in a hydrofluoric-nitric acid mixture.⁹ Tantalum was precipitated with concentrated ammonia, centrifuged and washed three times with distilled water. The freshly formed precipitate was then dissolved in 8% oxalic acid. The standard ¹⁸²Ta solution (1.25×10^{-3} M) was made by dilution with distilled water. The concentration of oxalic acid in standard ¹⁸²Ta solution was about 0.12 M.

HY was synthesized as described previously.¹⁰ Solutions of HY were prepared by dissolving a weighed amount of HY in chloroform (containing 0.5% of ethanol and used without purification or drying). Other chemicals used were of analytical reagent grade. All aqueous solutions were prepared with distilled water.

Distribution Ratio

The distribution ratio of tantalum was determined at room temperature by shaking equal volumes (5 ml) of the organic and aqueous phases of a given composition in a 50-ml conical flask with a mechanical shaker for 20 min. The distribution equilibrium was attained in less than 15 min and a shaking time of 20 min was sufficient to achieve reproducible results. After the phases were separated by centrifugation, aliquots (1 ml) were taken for radiochemical analysis using a gamma scintillation counter. The ratio of counts/100 s of the organic and aqueous phases served to calculate the distribution ratio.

Apparatus

Radioactivity measurements (^{182}Ta) were performed with a well-type gamma scintillation counter (NaI/Tl), LKB-COMPUGAMMA Type 1282-002. A Griffin flask shaker with a time switch was used for the extraction experiments.

RESULTS AND DISCUSSION

Extraction at Low Acidity

Extraction of tantalum(V) from aqueous oxalic solution with HY dissolved in chloroform has been examined at different acidities and ionic strengths. Tantalum(V) is quantitatively extracted with HY from oxalic solution in which tantalum(V) is stable in aqueous solution (about 2×10^{-3} M $\text{H}_2\text{C}_2\text{O}_4$). The extraction takes place at $\text{pH} = 2.3-2.5$ provided the HY concentration is at least 80 times higher than that of tantalum(V). Tantalum(V) forms complexes with different anions and some of these anions like oxalate, citrate and tartarate ions form with tantalum(V) very stable complexes in the aqueous phase.^{11,12} Therefore, we examined the influence of various anions in the aqueous phase on the extraction of tantalum at $\text{pH} = 2.3-2.5$ (Figure 1). With an increase in the initial concentration of some investigated anions, the extraction of tantalum decreases. Depending on the kind of anion present in the aqueous phase, tantalum(V) extraction decreases in the

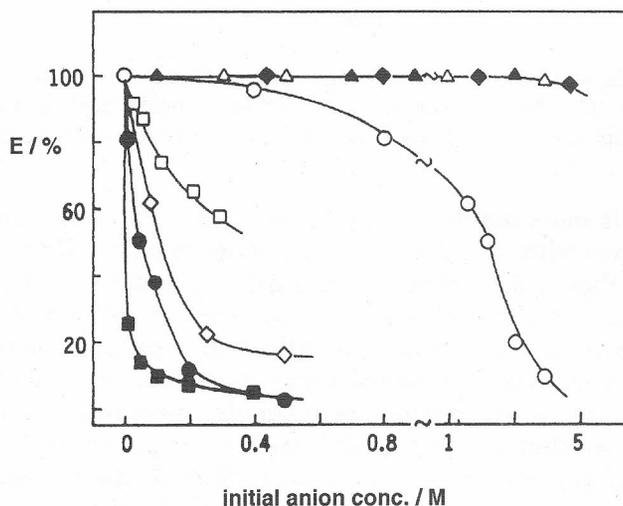


Figure 1. The dependence of the percentage of extraction at $\text{pH} = 2.4$ on the initial anion concentration. Ta(V) conc. 2.5×10^{-5} M; HY conc. 5×10^{-3} M. □, oxalate; ●, tartarate; ■, citrate; ○, sulphate; △, chloride; ◇, phosphate; ▲, perchlorate; ◆, thiocyanate.

order: citrate > tartarate > phosphate > oxalate > sulphate. In contrast to the effect of these anions, the extraction of tantalum at pH = 2.3–2.5 is independent of chloride, perchlorate and thiocyanate ions concentration in the aqueous phase. With an increase in the initial oxalic, phosphoric, citric, tartaric, hydrochloric, sulphuric and perchloric acid concentration, the extraction of tantalum also decreases and at 4 M phosphoric and 9 M sulphuric acid, practically all the tantalum remains in the aqueous phase (Figure 2).

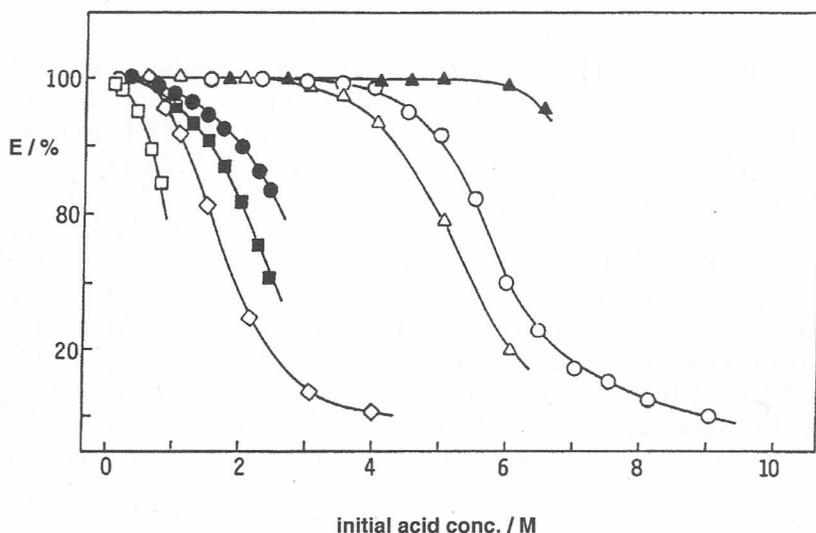


Figure 2. The dependence of the percentage of extraction on the initial acid concentration. Ta(V) conc. 2.5×10^{-5} M; HY conc. 5×10^{-3} M. □, oxalic acid; ●, tartaric acid; ■, citric acid; ○, sulphuric acid; △, hydrochloric acid; ◇, phosphoric acid; ▲, perchloric acid.

The decrease is more marked in the presence of acids whose anions formed stable complexes with tantalum(V) in the aqueous phase. If the acid concentration (from Figure 2) is shown as the pH calculated from K_{a1} (Figure 3), the increase in acidity is followed by a decrease in extraction in the same order as for anions: citric acid > tartaric acid > phosphoric acid > oxalic acid > hydrochloric acid \cong sulphuric acid \cong perchloric acid. The fact that the increase in acidity is accompanied by a simultaneous increase in anion concentration shows that the greater decrease in extraction in the presence of citric, tartaric, phosphoric and oxalic acids than in the presence of hydrochloric, sulphuric and perchloric acids is caused by the masking of tantalum(V) with anions of the acids used. Distribution studies (Figure 4) show that at a low acidity range for citric, tartaric, oxalic or phosphoric acid solutions, tantalum(V) is extracted as a complex with two HY molecules

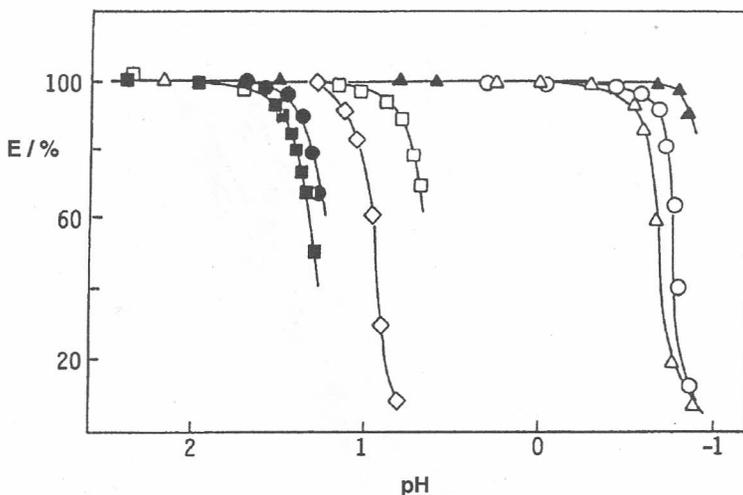


Figure 3. The dependence of the percentage of extraction on pH calculated from K_{a1} in the presence of different acids in the aqueous phase. Ta(V) conc. 2.5×10^{-5} M; HY conc. 5×10^{-3} M. \square , oxalic acid; \bullet , tartaric acid; \blacksquare , citric acid; \circ , sulphuric acid; Δ , hydrochloric acid; \diamond , phosphoric acid; \blacktriangle , perchloric acid.

bonded to a single tantalum atom. These results and the fact that tantalum(V) in an oxalic solution can exist in the form of various hydroxo-oxalate and oxo-oxalate ions and that in an acidic solution hydroxo ions are released before oxalato ions,¹³ the complex extracted at low acidity and formed without the presence of sulphate ions is probably a mixed ligand Ta-oxalate-HY complex.

Extraction at High Acidity

Results in Figures 2 and 3 also show that tantalum(V) can be quantitatively extracted even from a more acidic solution in the presence of sulphuric, hydrochloric or perchloric acids, in the acidity range from pH = 2.3 to 3.5 M H_2SO_4 or HCl and from pH = 2.3 to 5.5 M $HClO_4$.

In the acidity range from pH 2.3 to 1.5 M H_2SO_4 the added sulphate ions decrease tantalum extraction; the influence of sulphate on tantalum extraction decreases with an increase in the initial sulphuric acid concentration and in the range 1.5–3.5 M H_2SO_4 tantalum extraction is independent of sulphate ion concentrations. (Figure 5, Tables I and II). These results and the fact that increase in sulphuric acid concentration is accompanied by a simultaneous increase in sulphate ion concentration show that the composition of the extracted tantalum(V) complex at pH = 2.3–2.5 is different from that extracted at a higher concentration of sulphuric acid. In the presence

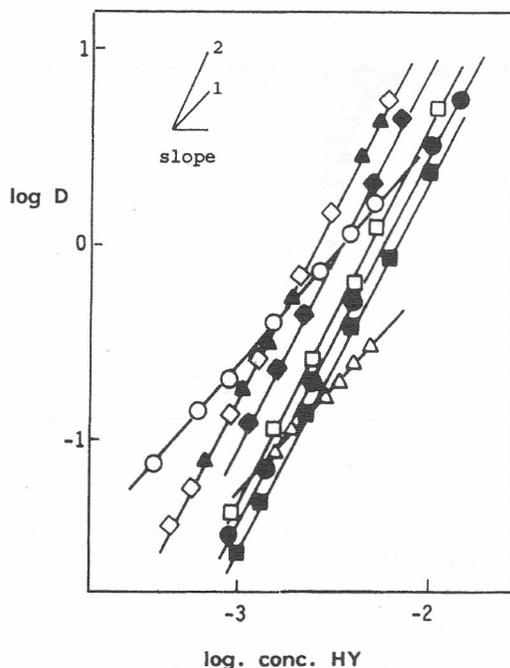


Figure 4. The dependence of the distribution ratio of tantalum(V) on the initial HY concentration. Ta(V) conc. 2.5×10^{-5} M. \diamond , 1.3 M phosphoric acid; \square , 0.78 M oxalic acid; \bullet , 2.9 M tartaric acid; \blacksquare , 2.4 M citric acid; \blacklozenge , 2.0 M H_3PO_4 , 0.02 M KSCN; \blacktriangle , 1.8 M H_3PO_4 , 0.01 M NaClO_4 ; \circ , 4.8 M H_2SO_4 ; \triangle , 5.5 M H_2SO_4 .

TABLE I

The dependence of tantalum extraction on added sulphate ion concentration at different acidity

conc. SO_4^{2-} /M	pH = 2.3–2.5	0.2 M H_2SO_4	2 M H_2SO_4
—	99.9	99.8	99.9
0.4	95.4	98.7	99.8
0.8	81.0	97.5	99.9
1.6	61.4	93.3	99.7
2.4	49.8	67.8	99.9
3.2	19.4	55.2	99.7
4.0	11.0	40.3	99.8

of an excess of sulphate (added as Na_2SO_4 or H_2SO_4) tantalum(V) is extracted as a mixed ligand Ta-sulphate-HY complex which can be quantitatively extracted only at high acidity (1.5–3.5 M H_2SO_4). This is confirmed

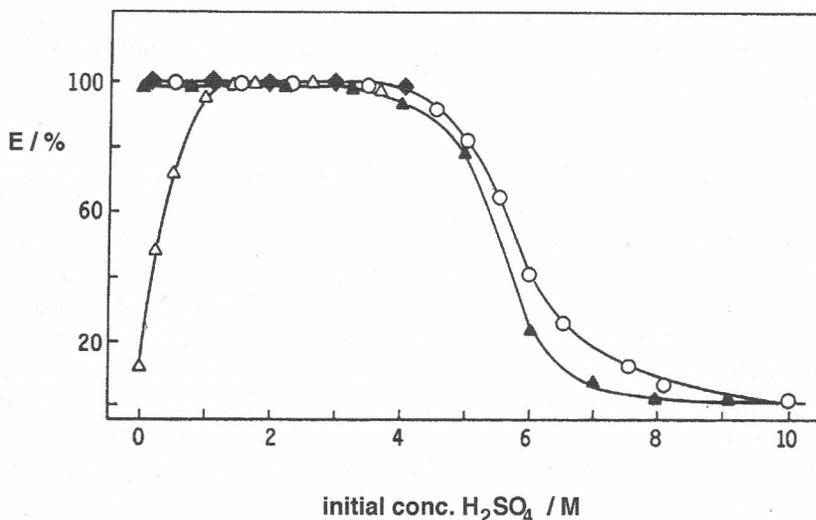


Figure 5. The dependence of the percentage of extraction on the initial sulphuric acid concentration. Ta(V) conc. 2.5×10^{-5} M; HY conc. 5×10^{-3} M. o, without addition of ions; ▲, 0.4 M NaClO₄; ◆, 0.4 M KSCN; Δ, (H, Na)SO₄ = 4.0 M.

TABLE II

The dependence of tantalum extraction on the acidity at a constant concentration of sulphate ions

(H,Na)SO ₄ = 4 M	
acidity	E / %
pH = 2.3–2.5	11.0
0.2 M H ₂ SO ₄	40.1
0.7 M H ₂ SO ₄	78.5
1 M H ₂ SO ₄	95.2
1.5–3 M H ₂ SO ₄	99.9
4 M H ₂ SO ₄	93.5

by the fact that sulphate ions decrease tantalum(V) extraction at a low hydrochloric acid concentration but in the presence of an excess of sulphate ions at a high hydrochloric acid concentration (1.5–3.5 M HCl) tantalum(V) is quantitatively extracted. Distribution studies (Figure 4) show that under these conditions tantalum(V) is extracted as a mixed ligand Ta-sulphate-HY complex with one HY molecule bonded to a single tantalum atom. Moreover, in the acidity range from pH = 2.3 to 1.5 M H₂SO₄, without addition of sulphate ions tantalum(V) is also quantitatively extracted, probably as a mix-

ture of Ta-oxalate-HY and Ta-sulphate-HY complexes. With an increase in sulphuric acid concentration in this acidity range the participation of the Ta-sulphate-HY complex in the extracted mixture increases.

Extraction in the Presence of Chloride, Perchlorate or Thiocyanate Ions

In the presence of an excess of perchlorate, chloride or thiocyanate ions tantalum(V) is quantitatively extracted with HY in the whole acidity range from pH = 2.3 to 3.5 M H₂SO₄ (Figures 1 and 5). This suggests that tantalum(V) can be extracted with HY in the presence of an excess of perchlorate, chloride or thiocyanate ions as mixed ligand Ta-perchlorate-HY, Ta-chloride-HY or Ta-thiocyanate-HY complexes. Those are quantitatively extracted from a wide acidity range, with less excess of HY, and are more stable than the other complexes formed without the presence of thiocyanate, perchlorate or chloride ions. In the presence of an excess of perchlorate or thiocyanate ions, tantalum(V) is quantitatively extracted also from a high concentration of oxalic, tartaric, phosphoric or citric acid or their anions which mask tantalum(V), if extraction takes place without the presence of thiocyanate or perchlorate ions. This is illustrated by Figures 6 and 7 which show tantalum(V) extraction from citric acid solution. Tantalum(V) extraction with HY in the presence of thiocyanate or perchlorate ions is independent of the citric acid concentration (Figure 6). Addition of thiocyanate or perchlorate ions at about pH₅₀% enhances tantalum extraction. From 2.1 M citric acid solution (61% E) tantalum is quantitatively extracted in the presence of thiocyanate or perchlorate concentration higher than the 200-fold molar ratio with respect to tantalum(V) (Figure 7). Distribution studies (Figure 4) show that from citric, tartaric, oxalic or phosphoric acid solutions, in the presence of an excess of thiocyanate or perchlorate ions, tantalum(V) is extracted as a complex with two HY molecules bonded to a single tantalum atom. The influence of the concentration of thiocyanate and perchlorate ions in the aqueous phase on tantalum(V) distribution was also studied to determine the composition of the extractable complex. Curves with the 0.5 slope were obtained independently of the acid used in the aqueous phase. This shows that the mixed ligand Ta-NCS-HY and Ta-ClO₄-HY complexes are probably polymeric complexes with thiocyanate or perchlorate bridges between tantalum atoms and therefore likely to be more stable than the other complexes formed without the presence of thiocyanate or perchlorate ions.

All results suggest that tantalum(V) can be extracted with HY in the form of various mixed ligand complexes depending on the acidity and on the composition of the aqueous phase. They also show that thiocyanate, perchlorate and chloride ions produce a synergistic effect on the tantalum(V) extraction with HY. The extracted tantalum(V) can be quantitatively stripped with 9 M H₂SO₄ or 4 M H₃PO₄, independently of the extractable

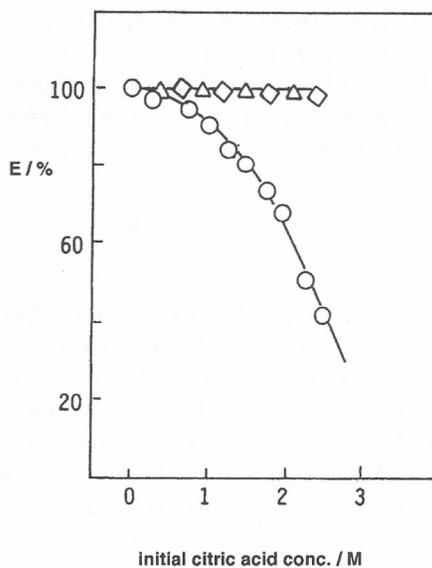


Figure 6. The dependence of the percentage of extraction on the initial citric acid concentration. Ta(V) conc. 2.5×10^{-5} M; HY conc. 5×10^{-3} M. o, without addition of ions; Δ , 0.05 M NaClO_4 ; \diamond , 0.05 M KSCN.

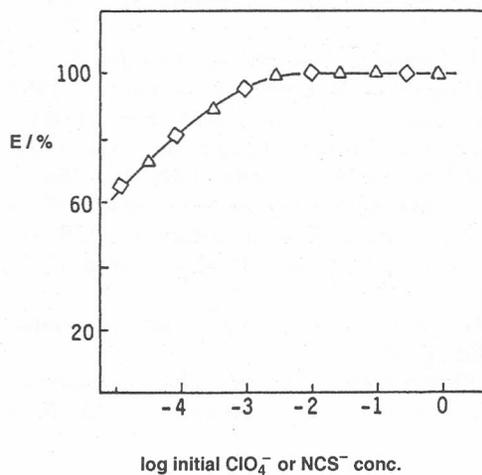


Figure 7. The dependence of the percentage of extraction on the initial thiocyanate and perchlorate concentration. Ta(V) conc. 2.5×10^{-5} M; HY conc. 5×10^{-3} M; citric acid conc. 2.1 M. \diamond , thiocyanate; Δ , perchlorate.

complex composition. At a hydrochloric acid concentration higher than 5 M, and in solutions with the presence of chloride or thiocyanate ions at a sulphuric acid concentration higher than 5 M bring about precipitation in the organic phase. The organic phase must be filtered before measurement and therefore the investigated acidity ranges in these cases are limited.

*Separation of Tantalum(V) from Niobium(V), Zirconium(IV)
and Hafnium(IV)*

The different behaviour of tantalum(V), described here and of niobium(V),⁶ zirconium(IV)⁷ and hafnium(IV)⁷ in extraction with HY can be exploited for their separation. From 1.5 to 3.5 M HCl or H₂SO₄ solutions, tantalum(V) is quantitatively extracted, while zirconium(IV) and hafnium(IV) remain in the aqueous phase. Separation of tantalum from niobium can be carried out from 3.5 M H₂SO₄ or 5.0 M HClO₄ solutions; tantalum(V) is quantitatively extracted while niobium(V) remains in the aqueous phase.

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SAŽETAK**Ekstrakcija i separacija tantala(V)
3-hidroksi-2-metil-1-(4-tolil)-4-piridonom**

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Proučavana je ekstrakcija tantala(V) 3-hidroksi-2-metil-1-(4-tolil)-4-piridonom (HY) iz vodenih oksalatnih otopina u kloroform pri različitim kiselostima i ionskim jakostima. Tantal(V) se kvantitativno ekstrahira s HY iz oksalatnih otopina pri $\text{pH} = 2,3 \dots 2,5$, vjerojatno kao mješoviti kompleks Ta-oksalat-HY. Tantal(V) se može kvantitativno ekstrahirati i iz kiselijih otopina u prisustvu sumporne, klorovodične ili perklorne kiseline u području kiselosti od $\text{pH} = 2,3$ do $3,5$ M H_2SO_4 ili HCl i od $\text{pH} = 2,3$ do $5,5$ M HClO_4 . Tiocijanatni, perkloratni i kloridni ioni imaju sinergetski efekt na ekstrakciju tantala(V) s HY. U prisustvu suviška tiocijanatnih, perkloratnih ili kloridnih iona tantal(V) se kvantitativno ekstrahira s HY u području kiselosti od $\text{pH} = 2,3$ do $3,5$ M H_2SO_4 kao mješoviti ligandni kompleks Ta-NCS-HY, Ta- ClO_4 -HY ili Ta-Cl-HY. Određeni su sastavi tih kompleksa. Opisana ekstrakcija tantala(V) s HY može se primijeniti za separaciju od niobija(V), cirkonija(IV) i hafnija(IV).