5-Hydroxy-1-aryl-4-pyridone-2-carboxylic Acid Esters as Chelating and Extracting Agents. I. Extraction and Separation of Tantalum(V) and Niobium(V) from Oxalate Solutions*

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The extraction of niobium and tantalum from oxalate solution has been studied using the esters of 5-hydroxy-1-aryl-4-pyridone- -2-carboxylic acid as extractants. The influence of the concentration of hydrochloric, sulphuric, hydrofluoric and oxalic acids on the extraction of niobium and tantalum has been investigated. The dependence of the extraction of these metals upon the concentration of the extractant in the organic phase was also studied. A procedure for the separation of niobium from tantalum directly from oxalate solution is described. The radionuclides ^{95}Nb and ^{182}Ta were used for the determination of the distribution coefficients.

INTRODUCTION

The extraction and separation of Nb(V) and Ta(V) by various organic compounds has been the subject of a number of investigations, as previously reported[1,2]. The extraction of Nb(V) and Ta(V) and their separation by organic compounds from the 4-pyridone series is discussed in the present paper. The synthesis of these compounds and their absorption spectra have already been described[3-5]. It has been found that compounds similar to 4-pyridones form with metals very stable chelate compounds[6-9]. The extraction properties of 4-pyridone compounds are investigated with regard to the Ta(V) and Nb(V) metallic ions. The following esters of 5-hydroxy-1-aryl-4-pyridone-2-carboxylic acids were used:
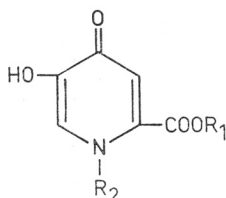
Compound	R_1	R_2
I	CH_3	C_6H_5
II	C_2H_5	C_6H_5
III	C_2H_5	$4\text{-}CH_3 \cdot C_6H_4$
IV	C_2H_5	$4\text{-}Br \cdot C_6H_4$

Tantalum(V) and niobium(V) were extracted from oxalate solutions in the presence or absence of mineral acids. The conditions for a selective extraction of these metals were studied.

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The extraction of metals was performed in Erlenmeyer flasks using equal volumes (2 ml.) of the organic and aqueous phase at approximately 20⁰ C. Shaking time necessary to obtain equilibrium was experimentally determined. After the equilibrium has been attained the systems were centrifuged to speed up the separation of the phases. Radionuclides were used for the determination of the distribution coefficients. The radioactivity of the organic and aqueous phase was measured with a gamma scintillation counter (NaI/Tl). All the measurements were taken after one single extraction.

The radionuclide ^{95}Nb was provided as an oxalate complex with excess of oxalic acid from Radiochemical Centre Amersham. ^{182}Ta was prepared by irradiating a solution of tantalic acid in oxalic acid in the nuclear reactor of the »Boris Kidrič«, Institute, Vinča, Yugoslavia.

The standard solutions of niobium and tantalum were obtained from Nb$_2$O$_5$ and Ta$_2$O$_5$ (Hopkin and Williams), previously fused with KHSO$_4$. The melt was dissolved in oxalic acid. The prepared solutions were then precipitated with ammonia, the precipitate washed with 2⁰/₀ NH$_4$Cl solution, and dissolved in oxalic acid. The concentrations were checked by gravimetric analysis. It is known[10] that simple dilution of solutions of niobic or tantalic acids in oxalic acid may bring about hydrolysis which is made evident by the formation of an opalescence or precipitate on standing. Therefore niobic and tantalic acid in oxalic acid solutions were always freshly prepared. Shaking time of 30 min. was found to be sufficient to obtain reproducible results, the equilibrium being attained after about 15 min.

RESULTS AND DISCUSSION

For the preliminary investigation of the extraction of Nb(V) from oxalate solutions containing different concentrations of hydrochloric acid, 4-pyridone compounds I, II, III and IV were used (Fig. 1). In further investigation, only the compounds II and III were used.

Fig. 1. Distribution ratio D of Nb(V) as a function of HCl concentration in the presence of 8×10⁻³ M oxalic acid in the aqueous phase. Concentration of niobium 1×10⁻⁴ M; concentration of organic compounds 3×10⁻³ M; Compound I (□); compound II (×); compound III (○); Compound IV (△).

*The Influence of the Concentration of HCl, H₂SO₄ and HF on the Extraction
of Nb(V) and Ta(V) from Oxalate Solutions by the Compound III*

The dependence of the distribution coefficient, obtained by the extraction
of niobium from the oxalate solution, on the concentration of mineral acids
is shown in Table I. The concentration of niobium was 1×10^{-4} M and that of

TABLE I

*Dependence of the Extraction of Niobium(V) on the Concentration of HCl, H₂SO₄,
and HF*

Niobium 1×10^{-4} M, oxalic acid 8×10^{-3} M, compound III 3×10^{-3} M.

Concn. HCl (M)	D	Concn. H₂SO₄ (M)	D	Concn. HF (M)	D
0.1	2.28	0.5	7.7	0.003	2.13
0.5	8.10	1.0	10.5	0.01	1.32
1.0	15.0	1.5	14.7	0.03	0.171
1.5	20.95	2.0	14.05	0.05	0.045
2.0	18.75	3.0	9.63	0.1	0.008
3.0	6.62	4.0	2.63	0.3	0.003
4.0	1.43	5.0	0.22	0.5	0.002

oxalic acid 8×10^{-3} M. A 3×10^{-3} M solution of the compound III in chloroform
was used in the extraction. The results indicate that the distribution coefficient
is increasing with the increase of the concentrations of HCl or H₂SO₄ reaching
a maximum at 1.5 M concentrations of these acids; further increase causes the
decrease of the distribution coefficient. By performing similar experiments
with Ta(V) results presented in Table II were obtained.

TABLE II

*Dependence of the Extraction of Tantalum(V) on the Concentration of HCl, H₂SO₄
and HF*

Tantalum(V) 1×10^{-4} M, oxalic acid 8×10^{-3} M, compound III 3×10^{-3} M.

Concn. HCl (M)	D	Concn. H₂SO₄ (M)	D	Concn. HF (M)	D
0.05	1.27	0.05	4.78	0.005	23.25
0.1	0.53	0.1	4.53	0.01	34.7
0.3	1.54	0.3	6.77	0.03	15.9
0.5	1.86	0.5	11.3	0.05	8.33
1.0	3.84	1.0	37.4	0.1	2.22
2.0	25.8	2.0	164	0.3	0.22
3.0	19.7	3.0	175	0.5	0.046
5.0	0.89	5.0	33.8	1.0	0.024

The extraction of niobium and tantalum decreases with the increase of the
concentration of HF and is negligible for niobium at 0.1 M HF and for tantalum
at 1 M HF (Tables I and II).

The Influence of the Oxalic Acid Concentration on the Extraction
of Niobium(V) and Tantalum(V)

Fig. 2 shows the results of the extraction of Nb(V) and Ta(V) from the oxalate solution as a function of the oxalic acid concentration. The concentration of the metal was 5×10^{-5} *M* and that of the organic compounds II and III 5×10^{-3} *M*. The results obtained show that there is a linear dependence of log D on the log concentration of $H_2C_2O_4$ of both Ta(V) and Nb(V) extracted
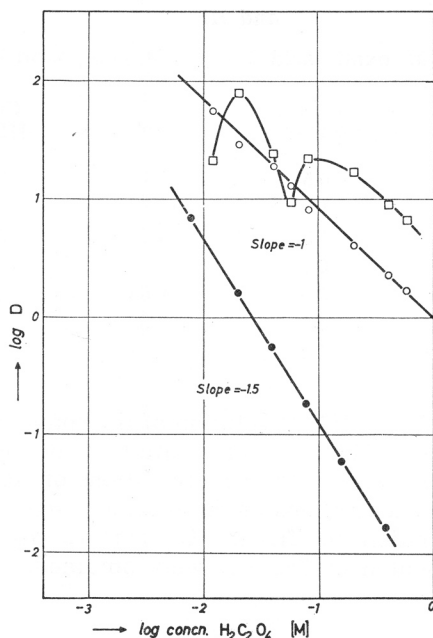

Fig. 2. Distributution ratio D of Ta(V) and Nb(V) as a function of oxalic acid concentration in the aqueous phase. Concentration of tantalum (O☐) : 5×10^{-5} *M*; niobium (●) : 5×10^{-5} *M*; compound II (O●) 5×10^{-3} *M*; compound III (☐) 5×10^{-3} *M*.

with compound II. The slopes for niobium and tantalum were — 1.5 and — 1.0, respectively. The extraction is found to decrease by further increase of the oxalic acid concentration; this being more pronounced for Nb than for Ta. The extraction of tantalum with compound III reveals no linear dependence upon the oxalic acid concentration.

The Dependence of the Extraction of Niobium(V) and Tantalum(V) on
the Concentration of the Ligands

The influence of the concentration of the compound III in the organic phase on the extraction of tantalum is shown in Fig. 3. The total concentration of the compound III used was plotted on the abscissa. When the experiments were performed at oxalic acid concentration of 1.12×10^{-2} *M* a metal-ligand ratio 1 : 2 was obtained while, at higher concentration, this was found to be 1 : 2.5.
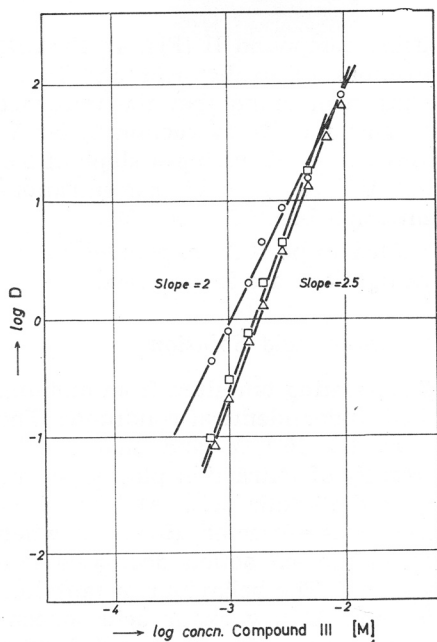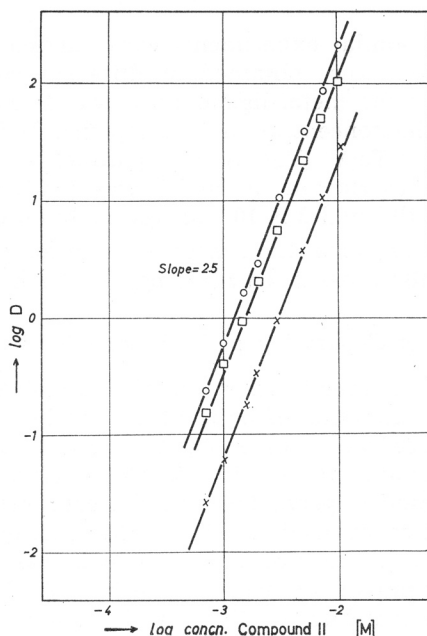
Fig. 3. Distribution ratio D of Ta(V) as a function of the compound III concentration in the organic phase. Concentration of tantalum 5×10^{-5} M and oxalic acid 1.12×10^{-2} M (O); 2×10^{-2} M (□); 2×10^{-1} M (△).

Fig. 4. Distribution ratio of Ta(V) as a function of the compound II concentration in the organic phase. Concentration of tantalum 5×10^{-5} M and oxalic acid 1.12×10^{-2} M (O); 2×10^{-2} M (△); 2×10^{-1} M (×).
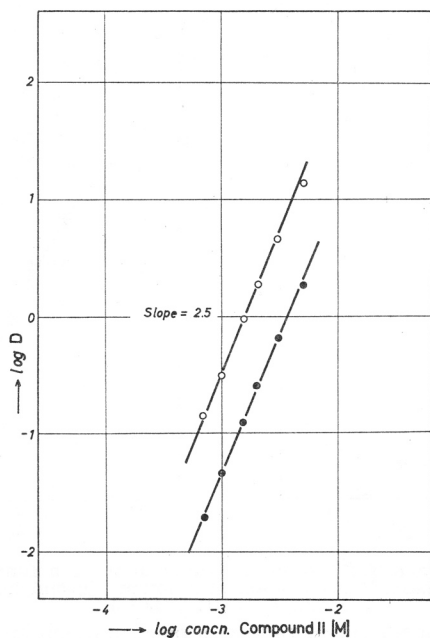

Fig. 5. Distribution ratio D of Nb(V) as a fuction of the compound II concentration in the organic phase. Concentration of niobium 5×10^{-5} M and oxalic acid 8×10^{-3} M (O); 2×10^{-2} M (⬤).

Similar experiments were carried out using compound II (Fig. 4). Parallel curves were obtained at different concentrations of oxalic acid and in all cases the metal-ligand ratio was 1 : 2.5. It has been found that the influence of the concentration of compound II is the same for the extraction of Nb(V) as for Ta(V) (Fig. 5). Two parallel curves were obtained having a slope of 2.5. The extraction of Nb(V) was performed at the oxalic acid concentrations 8×10^{-3} and 2×10^{-2} M, the niobium concentration being 5×10^{-5} M.

The extraction mechanism is too complicated to be fully explained by the results presented in this paper. Further investigations are in progress.

Direct Separation of Ta(V) and Nb(V) from Oxalic Acid Solution

In order to determine the possibilities of separating tantalum from niobium the extraction of both metals has been studied under identical conditions. The concentration of niobium and tantalum was 1×10^{-4} M and that of the compound III 5×10^{-3} M. Fig. 6 gives the results of extraction plotted as the extraction percentage $vs.$ the concentration of the oxalic acid. At low oxalic acid concentrations 93% of the niobium present was extracted. However, when the concentration of oxalic acid was increased the extraction decreased and was practically negligible at 5×10^{-1} M oxalic acid. The behaviour of tantalum was found to be different from that of niobium. At low oxalic acid concentrations up to 98% of the tantalum was extracted. Its extraction was slightly
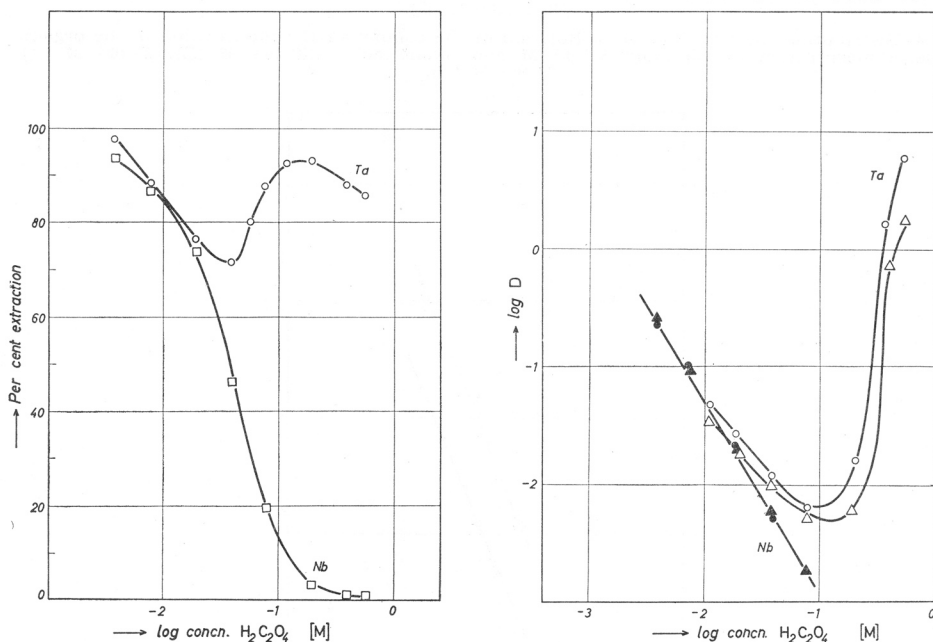

Fig. 6. Extraction of Nb(V) and Ta(V) from oxalate solution as a function of oxalic acid concentration in the aqueous phase. Concentration of niobium (□) and tantalum (○) 1×10^{-4} M and the compound III 5×10^{-3} M.

Fig. 7. Distribution ratio D of Nb(V) and Ta(V) as a function of oxalic acid concentration in the aqueous phase. Oxalate ions (H₂C₂O₄+K₂C₂O₄) were constant 5.6×10^{-1} M. Concentration of tantalum (○△) and niobium (●▲) 5×10^{-5} M. Compound II (○●) and compound III (△▲) 5×10^{-3} M.

reduced by increasing the concentration of oxalic acid up to 5×10^{-2} M; however, further increase of the concentration up to 3×10^{-1} M again increased the extraction. At concentrations of oxalic acid higher than 3×10^{-1} M the extraction of tantalum decreased. In order to find out whether this behaviour is caused by the change of the concentration of oxalate ions or H^+ ions the concentration of $H_2C_2O_4 + K_2C_2O_4 = 5.6 \times 10^{-1}$ M was kept constant. The results (Fig. 7) demonstrate that the extraction of niobium and tantalum strongly depends on the concentration of the H^+ ions, indicating that a good separation of tantalum from niobium is possible when the oxalic acid concentration is higher than 3×10^{-1} M. The separation factor is about 10^4.

The purpose of the experiments described in this paper was to ascertain whether the 4-pyridones would be useful for the extraction of niobium and tantalum. As far as we know these compounds were not as yet used in the extraction of metals. Since the oxalato complexes of niobium and tantalum are soluble in water and easily accessible, the investigation of the extraction from oxalic acid solutions seemed to be of particular importance.

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IZVOD

Ekstrakcija i separacija tantala(V) i niobiuma(V) s esterima 5-hidroksi-1-aril-4-piridon-2-karbonskih kiselina

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Ispitivana je ekstrakcija niobiuma i tantala iz oksalatnih otopina pomoću estera 5-hidroksi-1-aril-4-piridon-2-karbonskih kiselina otopljenih u kloroformu. Koeficijenti ekstrakcije su određivani pomoću radionuklida ⁹⁵Nb i ¹⁸²Ta. Ispitan je utjecaj koncentracije klorovodične, sumporne i fluorovodične kiseline na ekstrakciju niobiuma i tantala iz oksalatno kiselih otopina.

Studirana je ovisnost ekstrakcije niobiuma i tantala o koncentraciji ekstraktanta u organskoj fazi i o koncentraciji oksalne kiseline u vodenoj fazi.

Određeni su uvjeti pod kojima je moguća separacija Ta(V) i Nb(V) direktno iz oksalatno kisele otopine.

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