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Original Scientific Paper

Solvent Extraction of Niobium and Tantalum. II. Extraction and Separation of Zirconium and Niobium with Di-*n*-octyl-methylene-*bis*-phosphonic Acid

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A mehod for separating ^{95}Zr from ^{95}Nb by extraction process with din-n-octyl-methylene-bis-phosphonic acid *(DOMPA)*, of the formula $CH_2[PO(OC_8H_{17})OH]_2$, is given. Extraction behaviour of both metals under different conditions has been studied and extraction from sulphuric, hydrochloric, hydrofluoric and oxalic acid solutions is described. The influence of these acids and reagent conc. on separation of niobium and zirconium is discussed. It has been found that by extraction with DOMPA a quantitative separation is possible from mixed oxalic and sulphuric acid solutions of metal conc. lower than 10^{-5}, as well as separation of radionuclides from carrier free solutions.

Several methods were reported for separation of ^{95}Zr from ^{95}Nb by extraction process. For example separation with theonyltrifluoro-acetone (*TTA*)[1-4], tri-n-butyl-phosphine oxide (*TBPO*)[5], di-n-butyl-phosponic acid (*DBPA*)[6], acetylacetone[7] and tribenzylamine (*TBA*)[8]. Separation with first three reagents proceeds in nitric acid solutions, with acetylacetone in acetate solutions and with *TBA* in hydrochloric acid solutions. Radionuclides ^{95}Zr and ^{95}Nb are frequently used as radioactive indicators for zirconium and niobium, but the commercially available tracer $^{95}Zr/^{95}Nb$ is usually obtained in oxalic solutions (0.5% oxalic acid). In all the methods mentioned above, before separation it is necessary to destroy oxalates by nitric acid or potassium bisulphate. The extraction with *DOMPA*, however, enables the separation directly, in the presence of mineral acids, as shown in Figs. 3—5.

In order to obtain general information on extraction behaviour of these two metals under different conditions, various systems have been investigated using *DOMPA* as extractant. This bis-phosphonic acid proved to be an efficient extracting agent for several metals[9]. A separation of germanium from arsenic has also been reported previously[10]. We have already studied the extraction behaviour of niobium and tantalum[11] with *DOMPA* and have found that this phosphonic acid is an efficient extractant for both metals, which display a very similar behaviour. Separation of niobium and zirconium, in particular on a carrier-free scale is a problem, in which many chemical laboratories are involved. For this reason we have converged our attention to extracting behaviour of zirconium and niobium systems and now report details of this investigation.

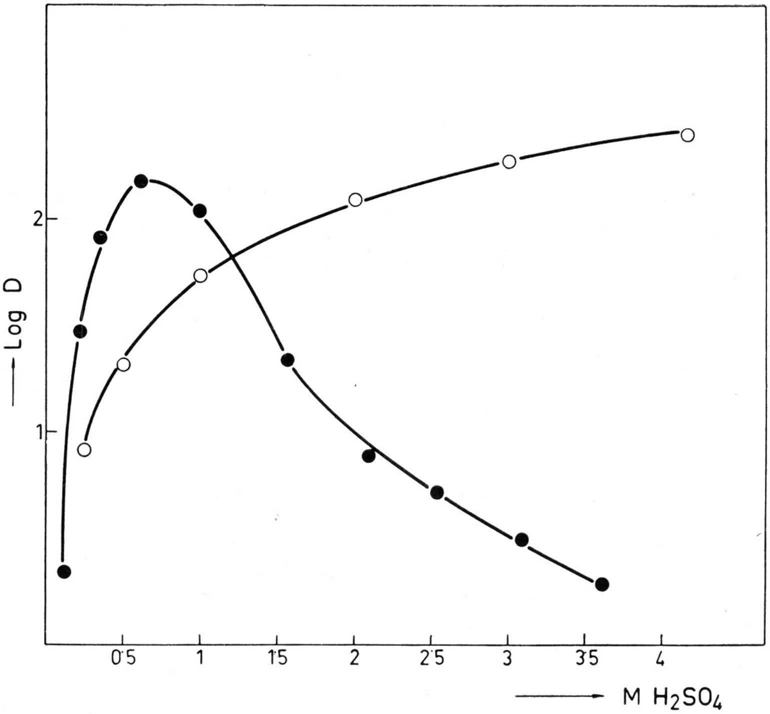

Fig. 1. Extraction of Nb (●) and Zr (○) with 10^{-3} *M DOMPA* from H_2S_4

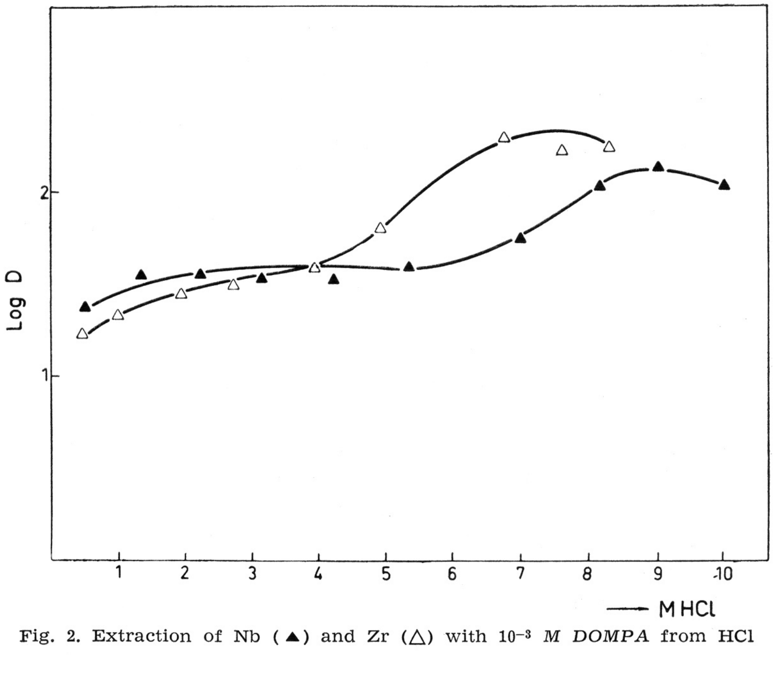

Fig. 2. Extraction of Nb (▲) and Zr (△) with 10^{-3} *M DOMPA* from HCl

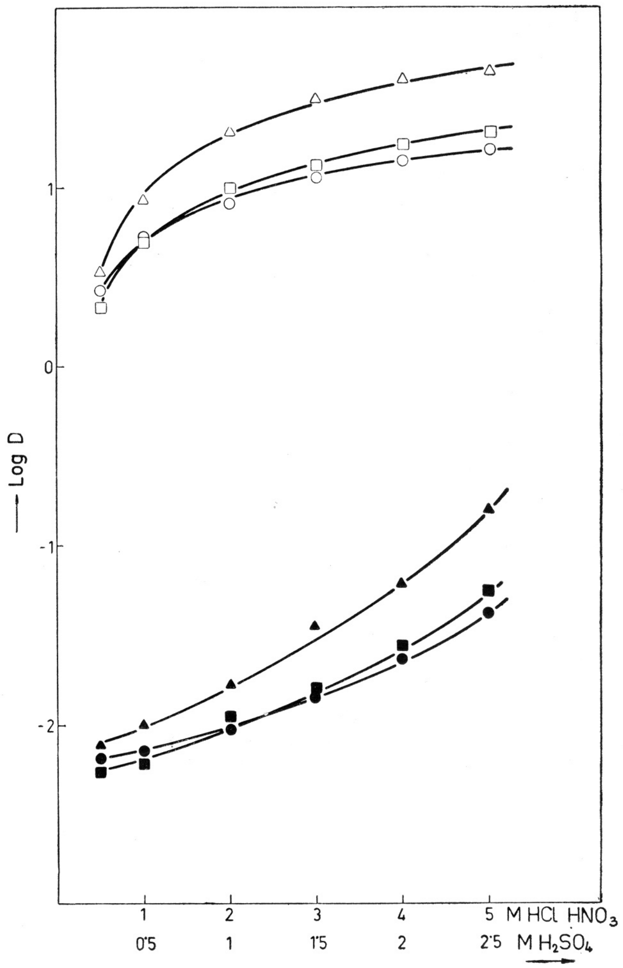

Fig. 3. Extraction of Nb (●■▲) and Zr (○□△) wit 2×10^{-3} *M DOMPA* from 0.1 *M* oxalate solutions in the presence of mineral acids

●	○	Data for H_2SO_4
▲	△	Data for HNO_3
■	□	Data for HCl

EXPERIMENTAL

Radioactive tracers

^{95}Zr/^{95}Nb and ^{95}Nb were obtained from *Radiochemical Centre Amersham* They were dissolved in 0.5% oxalic acid. ^{95}Zr solutions was prepared immediately before use in extraction experiments by removing ^{95}Nb, according to the method of C. J. Hardy and D. Scargill[3] by extraction with *TTA*. After reextraction with HF, zirconium was precipitated with ammonia and transformed into the ionic form needed for extraction purpose. Zirconium precipitate was washed 3—4 times with ammonium chloride solution (2%) and twice with hot water. In this way a satisfactory decontamination of fluoride ions was achieved, because several experiments repeated with freshly prepared tracer solutions gave reproducible results

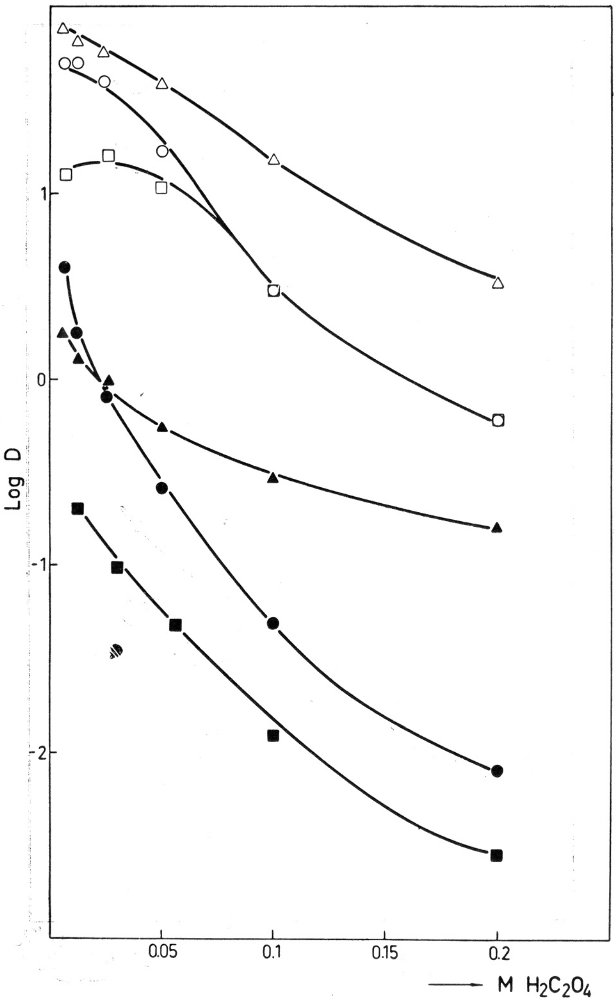

Fig. 4. Extraction of Nb (■●▼) and Zr (□○△) with 2×10^{-3} *M DOMPA* from oxalic acid in the presence of sulphuric acid
■ □ Data for 0.25 *M* H_2SO_4 ● ○ Data for 1.5 *M* H_2SO_4 ▲ △ Data for 3.5 *M* H_2SO_4

Reagents

Di-*n*-octyl-methylene-*bis*-phosponic acid, $CH_2[PO(OC_817_{17})OH]_2$, was prepared as described previously.[12] Pet. ether, 100—120°, Hopkin Williams, was used as solvent of the organic phase. All the acids used were Analar grade, from *Hopkin Williams* or *Merck.*

Extraction coefficient determination

All the experiments were carried out in a thermostatic room at 24° C. Equal volumes (2 ml) of aqueous and organic phase were used. For experiments with hydrofluoric acid polythene containers were employed. Extraction dependence of both metals upon the shaking time was determined. Experiments have shown that the equillibrium is reached for zirconium after 3 minutes, and for niobium after 7 minutes. Shaking time of 10 minutes was then used in the experiments. After centrifugation and separation of the phases gamma activities were measured on a

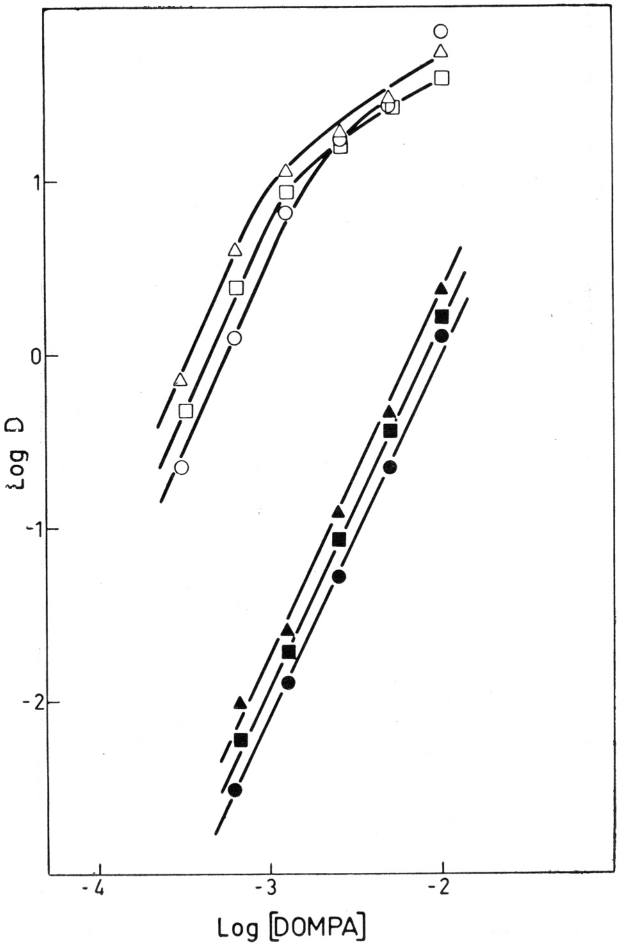

Fig. 5. Extraction dependency of Nb (●■▲) and Zr (○□△) on *DOMPA* conc. in the presence of:

● ○ 0.1 *M* $H_2C_2O_4$ — 0.5 *M* H_2SO_4
■ □ 0.1 *M* $H_2C_2O_4$ — *1* *M* HCl
▲ △ 0.1 *M* $H_2C_2O_4$ — 1 *M* HNO_3

scintillation counter. Reproducible results were obtained. Distribution coefficients for back-extraction were also determined in acid conc. ranges where separation was achieved. Practically the same values of D were obtained, the small differences being of the order of the experimental error.

Separation and preparation of carrier-free tracer ^{95}Zr and ^{95}Nb by extraction with DOMPA.

Solution containing tracer $^{95}Zr/^{95}Nb$ was dissolved in 5 ml containing 0.1 *M* $H_2C_2O_4$ and 0.5 *M* H_2SO_4 and shaken with 5 ml of 2×10^{-3} *M DOMPA* in petrolether. After centrifugation the two phases were separated. The organic phase was washed twice with 5 ml. containing 0.1 *M* $H_2C_2O_4$ and H_2SO_4. Aqueous phase was washed twice with 5 ml. 2×10^{-3} *M DOMPA* petrolether solution. In the organic phase pure ^{95}Zr remains, and can be reextracted with 5 ml. 0.1 *M* HF.

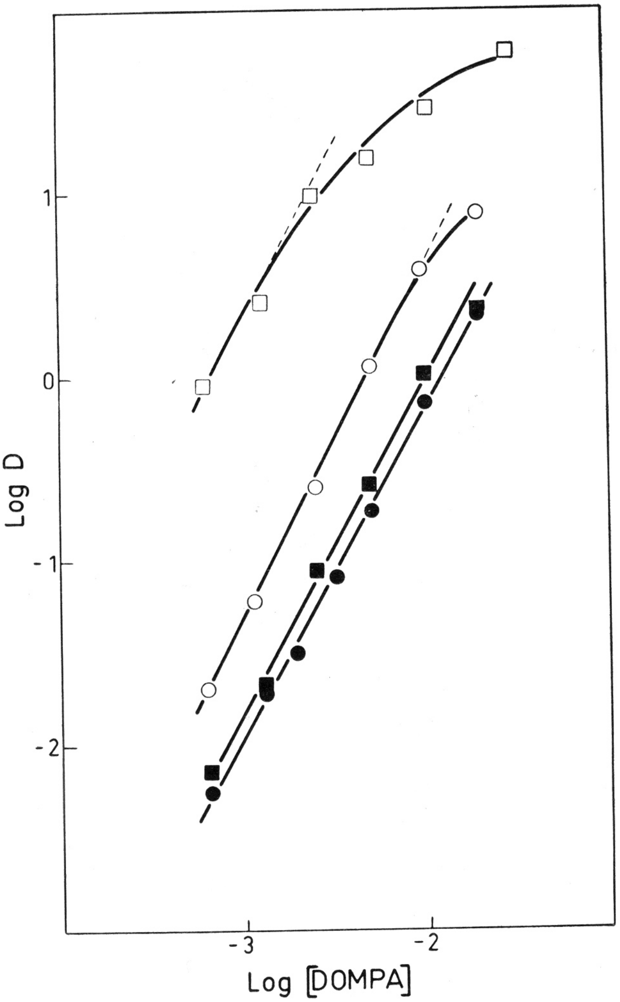

Fig. 6. Extraction dependency of Nb (●■) and Zr (○□) on *DOMPA* conc. in the presence of:
● ○ 0.04 *M* HF
■ □ 0.05 *M* $H_2C_2O_4$

The purity of separated metals was checked by halftime decay measurements and by determining the purity of materials obtained from mixtures of active niobium with inactive zirconium and *vice versa.* The separated metals contain less than 0.1% impurities.

Tracer solutions of the same purity can also be obtained from pure oxalic solutions containing 0.05 *M* $H_2C_2O_4$, but in this case it is better to use lower reagent conc. (1×10^{-3} *M*).

RESULTS

System Nb — Zr — H_2SO_4

On the Fig. 1 the extraction dependence of niobium and zirconium upon sulphuric acid conc. is shown. Extraction was carried out with 1×10^{-3} *M* *DOMPA* and the metal conc. was of the order 10^{-5} *M*. Experiments show that

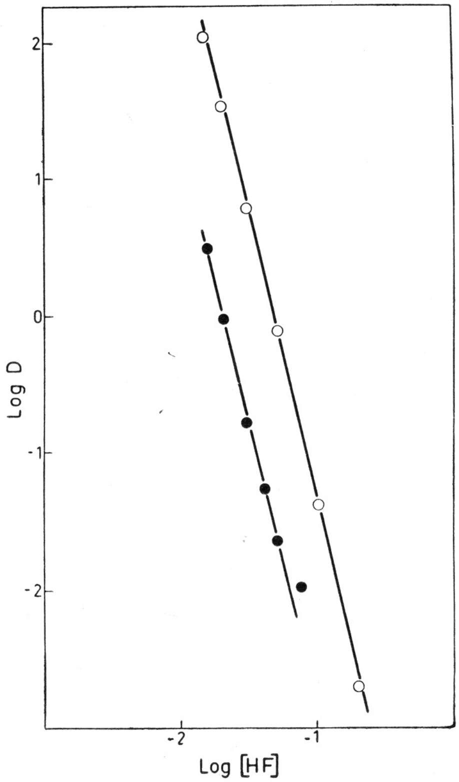

Fig. 7. Hydrofluoric acid dependency of the extraction of Nb (●) and Zr (○) with 10^{-3} *M DOMPA* and 0.5 *M* H_2SO_4

the extraction of zirconium increase steadily with the increase of sulphuric acid conc. Extraction of niobium, however, reaches a maximum between 0.5 and 1 *M* H_2SO_4, and then decreases with further increase of the mineral acid conc. Significant difference therefore exists between these two metals in the range of higher sulphuric acid conc.

System Zr — Nb — HCl

On the Fig. 2 extraction dependence of both metals upon hydrochloric acid conc. is shown. Both metals behave very similarly. Extraction was carried out with 1×10^{-3} *M DOMPA* solutions and 10^{-5} *M* metal solutions. Further increase of the acid conc. above 6 *M* HCl increases extraction of both metals.

System Zr — Nb — HF

Influence of hydrofluoric acid conc. on extraction of both metals is represented in the Fig. 7., where *DOMPA* conc. 1×10^{-3} *M* and metal conc. 10^{-5} *M* in 0.5 *M* H_2SO_4 were used. It has been observed that there is a linear logarithmic dependence of *D* upon the HF conc., with the slope of -4. Extraction decreases sharply with the increase of HF conc. This has been used in further experiments for reextraction of zirconium and the related data are represented in Table I. Extraction dependence upon *DOMPA* conc. for both metals was investigated in

TABLE 1.

Reextracted Zr (%)	*M* HF
0,03	85,7
0,04	92,2
0,06	99,2
0,1	99,8
0,2	99,9
0,4	99,9
0,6	99,1
0,8	97,9

the solutions containing 0.04 *M* HF and 0.05 *M* $H_2C_2O_4$. A metal/ligand ratio of 1 : 2 was observed for zirconium and niobium. However, for zirconium, in higher conc. ranges of *DOMPA* certain deviations occur. Metal conc. in these experiments was 10^{-5} *M*, therefore ligand was in a large excess and total conc. was plotted in the diagrams.

Systems Zr — Nb — Oxalic Acid — Mineral Acids

Extraction dependence of both metals from 0.1 *M* oxalic acid solutions upon the mineral acid conc. is shown on the Fig. 3. Organic phase contained 2×10^{-3} *M DOMPA* and metal conc. was of the order 10^{-5}. Under all the conditions extraction coefficients for zirconium are much higher than the coefficients for niobium. Extraction of both metals increases slowly with mineral acid conc. increase. The highest values of *D* were observed in presence of nitric acid. Significant difference in extraction between niobium and zirconium is therefore observed in these systems, which was used for separation, described in the Experimental.

Extraction dependence of niobium and zirconium upon the oxalic acid conc. is shown in the Fig. 4. This dependence was studied in oxalic solutions containing 0.25, 1.5, and 3.5 *M* H_2SO_4. The diagrams represent dependence of metal extraction upon oxalic acid conc., as well as influence of sulphuric acid conc. on the separation process. Experiments indicate that under these conditions a better prospect for separation is in lower sulphuric acid range. Extraction of both metals decreases with increase of oxalic acid conc., for niobium somewhat faster than for zirconium. Metal conc. 10^{-5} *M* and *DOMPA* conc. 2×10^{-3} *M*.

System Nb — Zr — DOMPA

Extraction, as well as separation dependence upon the reagent conc. is shown on the Fig. 5. Extraction was studied under different circumstances, with the conditions chosen according to previous experiments, where satisfactory separation was expected. The following solutions were examined: 0.1 *M* oxalic acid in 0.5 *M* sulphuric acid; 0.1 *M* $H_2C_2O_4$ in 1 *M* HCl and 0.1 *M* $H_2C_2O_4$ in 1 *M* HNO_3, respectively. It has been found that the extractant conc. has a significant influence on separation of the metals. On changing the conc. from 1×10^{-2} to 1×10^{-3}, percentage of the extracted niobium drops from 54% to 1%. In these systems niobium conc. was carrier-free, and zirconium conc. was lower than 10^{-6}. Extractant conc. ranged from 3×10^{-4} to 10^{-2} *M*. Ligand conc. was therefore in a large excess and total conc. was plotted on the diagrams. For niobium, in all the conc. regions a linear logarithmic dependence of *D* upon *DOMPA* conc.

was observed, with the slope of 2. For zirconium the same dependence was found only at conc. lower than 10^{-3} *M DOMPA.*

Reextraction of zirconium from DOMPA solutions with HF

Dependence of zirconium reextraction upon HF conc. from 2×10^{-3} *M DOMPA* solutions was examined. As shown in the Table I. for quantitative recovery it is sufficient to use 0.06 *M* HF. The best conditions however, are observed between 0.06 and 0.6 *M* HF, where it is possible to recover zirconium with a yield higher than 99%. At HF conc. above 0.6 *M* some loss of zirconium activity occurs and percentage of the reextracted metal is smaller.

DISCUSSION

This investigation was undertaken with an intention to find suitable experimental conditions for an efficient and simple separation of zirconium and niobium. In order to reach this purpose several related studies and examinations were needed and the results are summarized in this paper. One of the most interesting problems in the research of this type is certainly the mechanism of extraction process, as well as the explanation to why is it possible to attain successful separation under certain conditions. Unfortunately, we cannot yet give a straightforward answer to these questions. Mechanism of niobium and zirconium extraction is complex, mainly due to the marked tendency of both metals towards hydrolysis and polynuclear species formation in water solutions[13,14], as well as because the structure of extracting species is not known.

Zirconium and niobium are best extracted (highest *D* values) from sulphuric and hydrochloric acid solutions under certain conditions. It has been observed that extraction of zirconium increases with the increase of sulphuric acid, whereas an opposite course is displayed by niobium. Extraction dependence of zirconium upon the reagent conc. does not show a linear logarithmic dependence in sulphuric acid solutions. This may be caused by some polymeric zirconium species present in water solutions[13], which is difficult to know because of big medium changes. On the other side, extraction studies of niobium and tantalum with *DOMPA*[11] have shown that it is possible to determine Nb/*DOMPA* ratio of 1 : 2 at higher sulphuric acid conc. (3.5 *M*) only. In hydrochloric acid solutions both metals are extracted similarly and in this system it was neither possible to determine the metal/ligand ratio in the solution, which indicates existence of expected complex chloro-metal species in hydrochloric acid solution[8,15].

Extraction of zirconium from hydrofluoric acid solution is analogous to the extraction of niobium and tantalum[11]. With the increase of HF conc. a sharp decrease of distribution ratio is observed. A linear logarithmic dependence of *D* upon HF conc., with the slope of —4, has also been found. Experiments were carried out at low HF conc. and constant sulphuric acid conc. (0.5 *M*). This evidence indicates the presence of some $[ZrOF_4(H_2O)_x]^{2-}$ ionic species in the solutions, similar to niobium and tantalum[11]. It has also been found that two molecules of reagent are bound per one metal ion and based on this evidence, the following tentative extracting mechanism[11] can be proposed for zirconium at low *DOMPA* conc.

$$[ZrOF_4(H_2O)_x]^{2-} + 2\ DOMPA \longrightarrow [ZrO(DOMPA)_2]^{2-} + 4\ HF$$

Separation of niobium and zirconium with *DOMPA* was achieved on basis of different extracting behaviour of these metals in oxalic acid solutions. This method of separation is very efficient at low metal conc., even on the carrier-free scale. It is possible to isolate ^{95}Zr tracer of high purity. Reextraction of zirconium can be successfully performed with hydrofluoric acid. Separation of zirconium and niobium with *DOMPA* has therefore some advantages to the procedures employed earlier. First of all, for the separation, the commercially available solutions can be used without any previous treatment. The purity of the separed radionuclides is satisfactory and it can be also employed on the carrier-free scale. Although the extractant is not commercially available, its preparation is simple. However, mechanism of extraction from these solutions is complex. It has been possible to determine metal/ligand ratio of 1 : 2 at low extractant conc., nevertheless this evidence is not sufficient to assert the related process. We proceed with these investigations with the emphasis put on the study and isolation of extracting species. We believe that characterization of molecular species present in the organic phase, in solution and solid state, is going to bring more understanding of these procedures. However, in case of niobium, tantalum and zirconium, many experimental difficulties are encountered, because of their complex chemistry. We have found that isolated solid extracting species with *DOMPA* of niobium and tantalum have a polymeric character and do not contain oxalates[16]. Apparently, separation of niobium and zirconium from oxalic acid solutions is due to different interaction of metal ionic species with *DOMPA*. An other factor involved is the stability and properties of extracting species formed by the two metals. Knowledge of at least some of these parameters will help in comprehension of chemical processes proceeding in such systems.

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IZVOD

Ekstrakcija niobija i tantala II. Ekstrakcija i separacija cirkonija i niobija sa di-*n*-oktilmetilen-*bis*-fosfonskom kiselinom

H. Goričan i C. Djordjević

Opisana je nova metoda za odijeljivanje ^{95}Zr od ^{95}Nb metodom ekstrakcije sa di-*n*-oktilmetilen-*bis*-fosfonskom kiselinom *(DOMPA)*. Prikazan je studij ekstrakcionog

ponašanja ovih metala pod raznim okolnostima, te opisana ekstrakcija iz sumporno, klorovodično, fluorovodično i oksalno kiselih otopina. Diskutiran je utjecaj ovih kiselina, kao i utjecaj konc. reagensa, na separaciju cirkonija i niobija.

Utvrđeno je da ekstrakcija sa *DOMPA* omogućuje kvantitativnu separaciju iz otopina koje sadrže smjesu oksalne i sumporne kiseline, sa konc. metala manjom od 10^{-4} *M*. Metoda se može primijeniti i na separaciju radionuklida u otopinama cirkonija i niobija bez nosača. Pomoću fluorovodične kiseline kvantitativno je moguće reekstrahirati cirkonij.

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