CYANEX 925 as Potential Extractant for the Extraction and Separation of Zirconium (IV) and Niobium (V) From Nitric Acid Solution

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The potential use of CYANEX 925 in kerosene for the extraction and separation of Zirconium (IV) and Niobium (V) from nitric acid solution was explored. The effects of the different parameters affecting the extraction process as extractant, metal, nitric acid and nitrate concentrations as well as temperature were separately investigated. Stripping investigations on the recovery of Zr(IV) and Nb(V) from their loaded organic solutions were also carried out. The obtained results indicated that the extracted metal species are $Zr(NO_3)_4$.CYANEX 925 and $Nb(OH)_2(NO_3)_3$.CYANEX 925 for Zr(IV) and Nb(V), respectively. The difference in the extraction and stripping behavior of the investigated metals indicated that a good separation between Zr(IV) and Nb(V) could be obtained when carrying out the extraction from low nitric acid concentration at low temperature or when using 1M sulphuric acid for stripping 99% of Zr(IV) with nearly no stripping of Nb(V) from the loaded organic solution. The obtained results indicated that CYANEX 925 is a promising extractant for high extraction and separation of Zr(IV) and Nb(V) from nitric acid solution compared with other organophosphorus extractants.

Keywords: Solid Tumor, Green Tea extract, Simvastatin, Gamma radiation, MRI, Combination Therapy

Introduction

Niobium and zirconium are important strategic materials underlying many of the modern advanced technologies. Since the extraction and processing of rare metal concentrates from their own deposits have diminished abruptly in recent years; it is essential to look into the possibility of extracting these elements from various production wastes, which constitutes an important problem of study [1].

Zirconium is particularly useful for thermal reactors, since this metal has an extremely low thermal neutron cross-section combined with exceptional corrosion resistance under certain conditions. In nuclear countries zirconium has been selected as structural material for the submarine thermal reactors [2].

A major potential for niobium is in nuclear applications. Special tantalum-ferroniobium could be used in stainless steels for nuclear reactors. In cladding or as fuel diluent, niobium has a low thermal neutron cross-section as compared to other materials. Its excellent fatigue resistance, because of its low coefficient of expansion, prevents temperature parts from failing by cyclic stress induced by heating and cooling. Its principle competitor as cladding material is zirconium, which has smaller thermal neutron cross section compared to niobium, therefore, zirconium is being used. Radionuclide niobium-94 and -95 occur in the fission products of uranium-235 as a result of Zr-95 decay [3].

In pressurized water-cooled reactors, zirconium is also used. However, in gas cooled reactors, niobium is more suitable, since its strength is about five times that of zirconium. The competition comes in gas cooled–reactors from alloying with molybdenum and stainless steel. Owing to its low thermal conductivity, low neutron absorption cross-section, and good molten metals, niobium is

more suitable than stainless steel or molybdenum. Zirconium and niobium form an intimate pair is very difficult to separate although the use of some alkyl phosphoric acids for their separation have been reported [4, 5,6].

Hardy and Scargill [7] studied the extraction of zirconium from nitrate solution by di-n-butylphosphoric acid and reported that a maximum distribution ratio was achieved at about 4 M HNO_3 and decreased markedly with increasing HNO_3 concentration above 8 M.

Maya [8] studied the extraction of niobium by butyl lauryl phosphoric acid (HBLP) instead of tributyl phosphate (TBP) in the Purex process. They found that the use of HBLP instead of TBP enhanced niobium extraction above a threefold concentration of 5×10^{-4} M of TBP. The niobium distribution coefficient depended on the HBLP, hydrogen ion and nitrate ion concentration and suggested an extraction mechanism involving neutralization of a hydroxyl group bound to the niobium and no incorporation of nitrate into the extracted species. These results were supported by chemical analysis of the extracted species which showed an empirical formula corresponding to Nb$(OH)_4$BLP.

The Influence of zirconium on the extraction of niobium from nitric acid by phosphate esters was investigated by Healy et al. [9]. They reported that in the case of extraction by di-butyl butylphosphoric acid / solvesso 150, the D_{Nb} was very low and increased with acidity from about 2×10^{-4} at 2M to 4×10^{-3} at 8M HNO_3. Addition of inactive zirconium to the system caused appreciable increase in D_{Nb} at all acidities.

CYANEX reagents are promising extractants for separation and recovery of zirconium from different aqueous media [10].The extraction of zirconium from nitric acid with CYANEX 301, CYANEX 302 and CYANEX 272 were carried out by Taghizadeh et al. [11] who also reported that CYANEX 923 gave good results for the extraction of zirconium [12]. The extraction using octyl (phenyl)-N, N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) and CYANEX 923 (trialkylphosphine oxide, TRPO) was studied by Murali and Mathur [13]. They found that when CMPO was used, the extraction increased with the increase in HNO_3 concentration up to 2 M and then remained constant. In 30 %

TRPO / dodecane system, the extraction coefficient was almost constant in HNO_3 concentration range of 0.5 - 3.0 M and slightly increased up to 6.6 M. From both organic phases, Zr could be stripped with different concentrations of oxalic acid.

In the present work, the potential use of CYANEX 925 for the efficient extraction and separation of zirconium and niobium from nitric acid solution is explored. The effects of the different parameters affecting the extraction and stripping processes of the investigated metal ions were investigated using the slope analysis method of the experimental results. The stoichiometry of the extracted metal species was deduced. Based on the obtained results, the separation feasibility between Zr(IV) and Nb(V) is discussed. Comparison with related systems is presented in order to highlight the advantages of the proposed system.

Experimental
Chemicals and Reagents
Most of the chemicals used were of analytical grade (A.R) and used without further purification. During all experiments, even for washing the glassware, double distilled water was used. CYANEX 925 (Tri (2,4,4-trimethylpentyl) phosphine oxide) which is claimed to be a mixture of trialkylphosphine oxides containing a normal and branched octyl groups with an average molecular weight of 386 [21] was kindly supplied by Cytec Company, Canada and used as received. As stated from the producing company, the reagent is formed from a mixture of only two compounds with the formula R_3PO and $R_2R'PO$ where R = 2, 4, 4- trimethyl pentyl and R' = n-octyl. [14]

Non-aromatic kerosene was used as diluent and obtained from Misr Petrol Ltd., Egypt. Zirconium nitrate, Arsenzo III, 4-(2-Pyridylazo) Resorcinol (PAR) and Sulfuric acid were obtained from Merck, Germany. Niobium pentoxide was supplied by Johnson Matthey Co., London. Nitric acid was an Aldrich (USA) product. Sodium carbonate and sodium nitrate were obtained from Fluka, Switzerland.

Procedure
In batch extraction, niobium (V) solutions were prepared by fusion of 0.143 g of niobium pentoxide, Nb_2O_5, with 4 g of potassium persulfate, $K_2S_2O_7$ in quartz crucible. The melt was dissolved in hot 5% tartaric acid solution then

allowed to cool, diluted with tartaric acid solution to 100 ml in volumetric flask. Finally, a stock solution of Nb (V) (100 ppm) in 3M nitric acid was prepared. Zirconium (IV) solution was prepared by dissolving 0.47 g of zirconium nitrate in 3 M nitric acid to prepare a stock solution of concentration 100 ppm. The organic solution was prepared by dissolving CYANEX 925 in kerosene. In the extraction experiments, the aqueous nitric acid solution containing Zr(IV) or Nb(V) was shaken with an equal volume of the organic solution containing CYANEX 925 in kerosene using a thermostated water bath shaker of the type SW/20C, Germany. After equilibration, a complete separation of the two phases was obtained using a centrifuge of the type Z230, Hermle, Germany.

After equilibration and phase separation, a suitable volume of the aqueous phase was spectrophotometrically measured through their maximum absorbance peaks at λmax 550 for Nb (V) using PAR method and λmax 665 for Zr (IV) using Arsenazo III method with a Shimadzu UV-VIS spectrophotometer, Model160-A, Japan.

The concentration of the metal in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after the extraction. The distribution coefficient (D) was calculated from the relation:

$$D = \frac{C_o - C}{C}$$

Where, C_o is the initial metal concentration before extraction, C is the metal concentration in the aqueous phase after extraction, respectively.

Preliminary experiments on the effect of shaking time on the extraction of the investigated metal ions have shown that 5 and 60 min. were sufficient to reach the extraction equilibrium of Zr (IV) and Nb(V), respectively.

Results and Discussion

Batch studies were carried out to find out the optimum conditions for the extraction of Zr (IV) and Nb(V) with CYANEX 925 in kerosene. The effects of the different parameters affecting the extraction processes were separately investigated. Stripping investigations on the recovery of Zr (IV) from loaded organic phases were also carried out.

Effect of Shaking Time
The effect of shaking time on the extraction of (4.4 x10⁻⁴M) Zr (IV) with 0.012M CYANEX 925 in

kerosene from 3M nitric acid was investigated over the range 1-120 minutes. On the other hand, the extraction of 1.08x10⁻³ M Nb(V) with 0.3M CYANEX 925 in kerosene from 3M nitric acid was also investigated over the range 1-120 minutes at A/O ratio =1 and room temperature. The results illustrated in Fig. (1) indicate that the metal extraction of both metals increased with the increase in the shaking time and the extraction equilibrium was reached after 5 and 60 minutes for Zr (IV) and Nb(V), respectively.

Effect of Extracting Concentration
The effect of CYANEX 925 concentration on the extraction of 4.4 x10⁻⁴ Zr (IV) and 1.08 x10⁻³ M Nb(V) from 3M nitric acid was investigated in the ranges 2x10⁻³ - 1M and 2.5x10⁻³ – 0.3M, respectively. The results showed a linear increase in the extraction of both ions with the increase in the extractant concentration. The plot of the CYANEX 925 concentrations versus the corresponding distribution ratios on a log-log scale gave straight lines with slope 1 in both cases which indicate that one mole of the extractant participates in the extracted Zr (IV) and Nb(V) species, (Fig. 2)

Effect of Nitric Acid Concentration
The effect of nitric acid concentration on the extraction of 4.4 x10-4 Zr (IV) and 1.08 x10-3 M Nb(V) with 1.2x10-3 M CYANEX 925 in kerosene was investigated in the range 0.5-8M. The results shown in Fig.(3) indicate that at low acidity, the extraction decreased probably due to hydrolysis of the metal ions, whereas at high acidity, the extraction of both metal ions increased with the increase in the acid concentration investigated, this may be due to the formation of extractable nitrate complexes [15].

Effect of Nitrate Ion Concentration
The effect of nitrate ion concentration as salting–out agent on the extraction of 4.4 x10⁻⁴ Zr (IV) and 1.08 x10⁻³ M Nb(V) with 1.2x10⁻³ M CYANEX 925 in kerosene from nitric acid solution was studied in the range 3 – 5 M at 3M hydrogen ion concentration. Fig.(4) shows that the distribution ratio of Zr (IV) and Nb(V) decreased slightly from 1.6 to 1.3 and from 0.73 to 0.6, respectively with the increase in nitrate ion concentration from 3 to 5M.
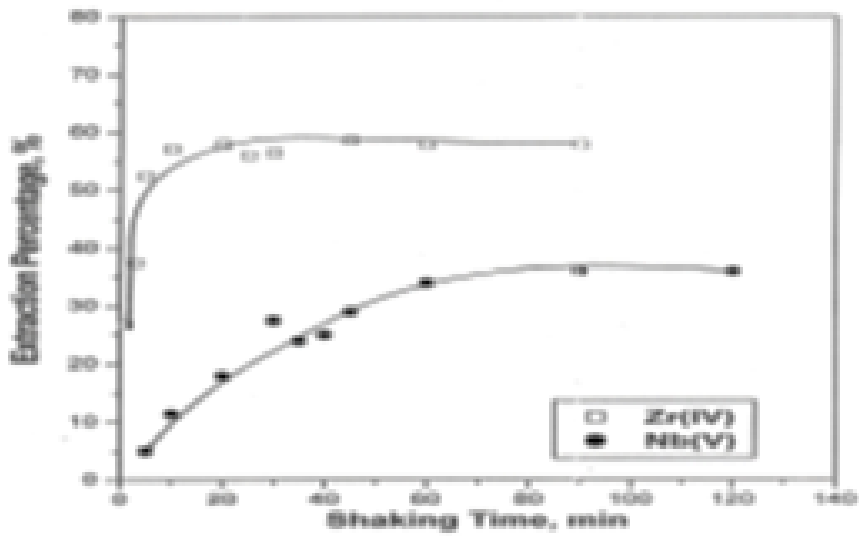
Fig. (1) Effect of Shaking Time on the Extraction of Zr(IV) and Nb(V) by CYANEX 925 from Nitric acid Medium
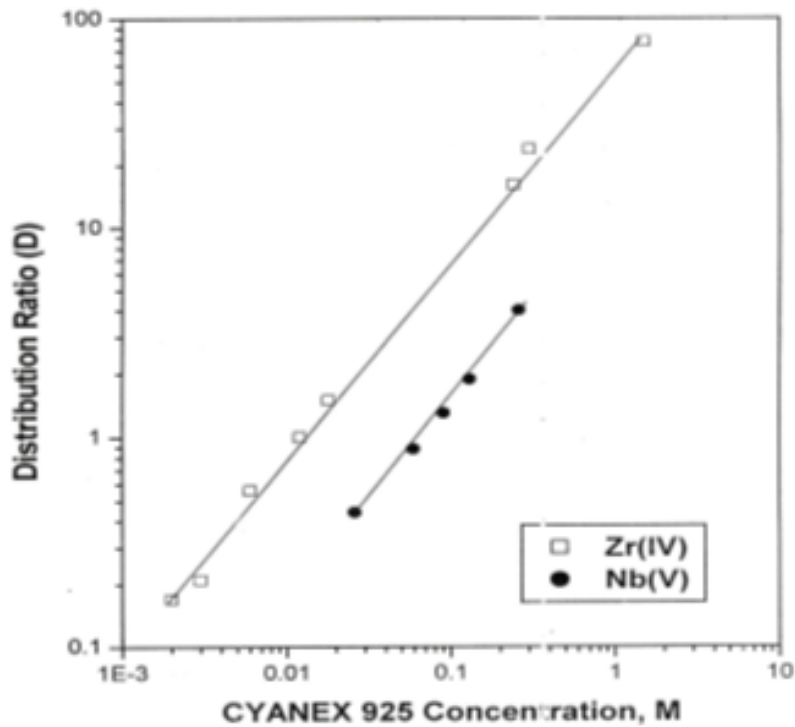

Fig. (2) Effect of CYANEX 925 Concentration on the Extraction of Zr(IV) and Nb(V) from Nitric Acid Medium
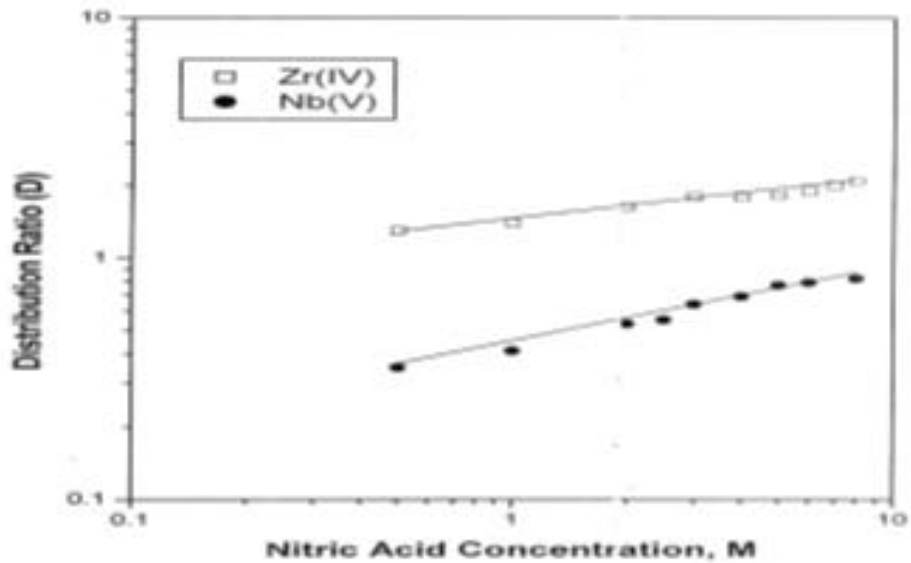
M.M. Zeid et. al

Fig. (3) Effect of Nitric Acid on the Extraction of Zr(IV) and
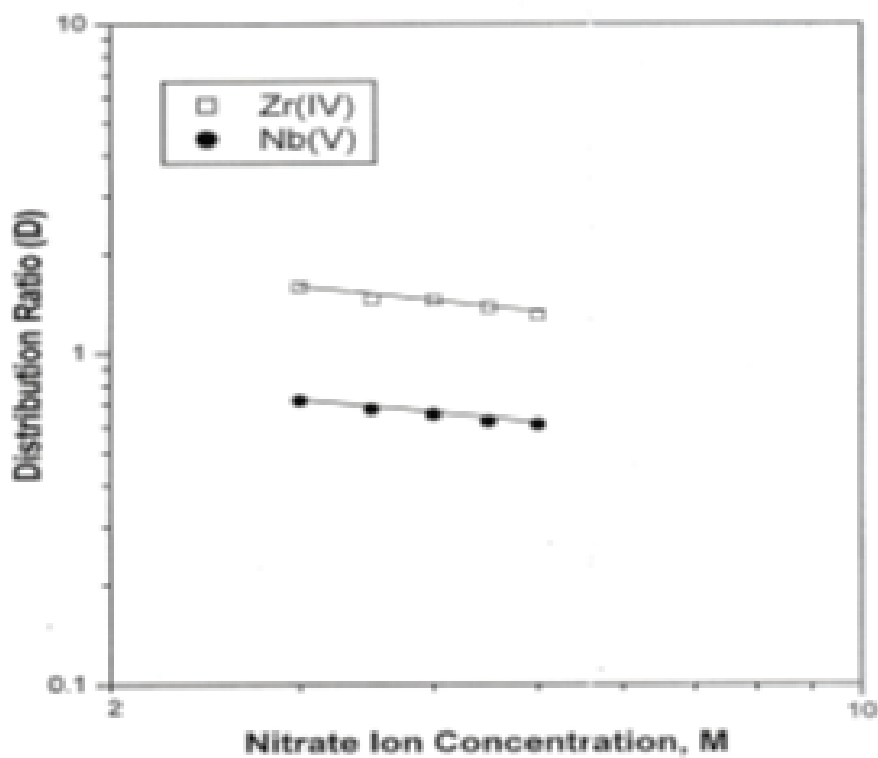Nb(V) by CYANEX 925 from Nitric Acid Medium

Fig. (4) Effect of Nitrate ion Concentration on the Extraction of
Zr(IV) and Nb(V) by CYANEX 925 from Nitric Acid Medium

Effect of Hydrogen Ion Concentration

The influence of hydrogen ion concentration on the extraction of 4.4×10^{-4} Zr(IV) and 1.08×10^{-3} M Nb(V) with 1.2×10^{-3} M CYANEX 925 from nitric acid solution was studied in the range 1-5M at constant nitrate ion concentration of 5M. The results obtained and shown in Fig.(5) indicate that the increase in H^+ concentration from 1 to 5M led to an increase in the value of the distribution ratio from 2 to 2.5 and from 0.38 to 0.67 in case of Zr(IV) and Nb(V) systems, respectively
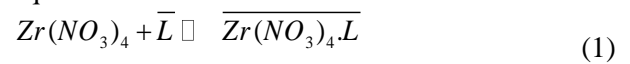
Loading Capacity

The loading capacity of the investigated extractant was determined by two methods. In the first method, 5ml of CYANEX 925 in kerosene (0.012M or 0.3M for zirconium and niobium, respectively) was repeatedly contacted at $25 \pm 1^{\circ}C$ with the same volume of aqueous solution containing 4.4×10^{-4} M of Zr(IV) or 1.08×10^{-3} M Nb(V) and 3M HNO$_3$. The plot of cumulative metal ions concentration in the organic phase versus the contact number shown in Fig .(6) indicates that a maximum loading of 5.3×10^{-4} M Zr(IV) per mole extractant was obtained after 4 extraction stages and 3.18×10^{-4} M Nb(V) per mole extractant was reached after eight stages.

The second method was carried out by contacting aqueous and organic phases at different ratios of 1: 2, 1:1, 2:1, 3:1, 4:1, and 5:1. The results represented in Fig.(7) show that the concentration of the investigated metal ions increased with the increase in the A:O phase ratio and a in maximum loading of 4.02×10^{-4} M and 4×10^{-3} M, was obtained at phase ratio 5:1 for Zr(IV) and Nb(V) , respectively.
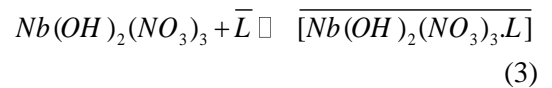
Extraction Equilibrium

Based on the above results and assuming the presence of Zr (IV) as Zr (NO$_3$)$_4$ in 3M HNO$_3$ [16] and Nb(V) as Nb(OH)$_2$(NO$_3$)$_3$, the extraction of Zr (IV) and Nb(V) by CYANEX 925 can be represented at equilibrium by the following equations:

$$Zr(NO_3)_4 + \overline{L} \ \square \ \overline{Zr(NO_3)_4.L} \tag{1}$$

$$K_{ex(L)} = \frac{D_{Zr}}{[L]} \tag{2}$$

and

$$Nb(OH)_2(NO_3)_3 + \overline{L} \ \square \ \overline{[Nb(OH)_2(NO_3)_3.L]} \tag{3}$$

$$K_{ex(L)} = \frac{D_{Nb}}{[L]} \tag{4}$$
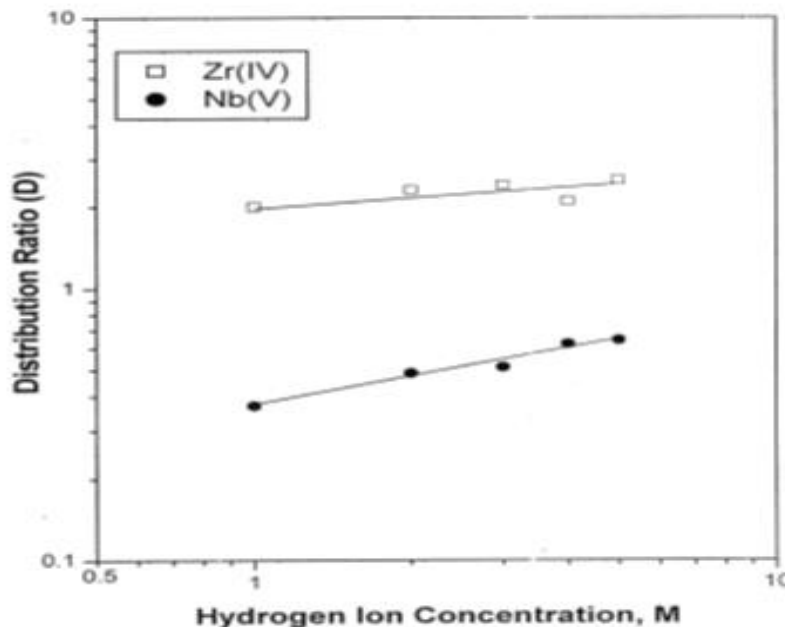

Fig. (5) Effect of Hydrogen Ion Concentration on the Extraction of Zr(IV) and Nb(V) from Nitric Acid Medium

Where, D_{Zr} and D_{Nb} are the distribution ratios of Zr (IV) and Nb(V) between the organic and aqueous phases; L denotes CYANEX 925, K_{ex} is the apparent extraction constant and bars refer to the organic phase. The values of the extraction constants evaluated at different CYANEX 925 concentrations were found to be 81.3 and 15.62 for Zr (IV) and Nb(V), respectively, (Table 1).
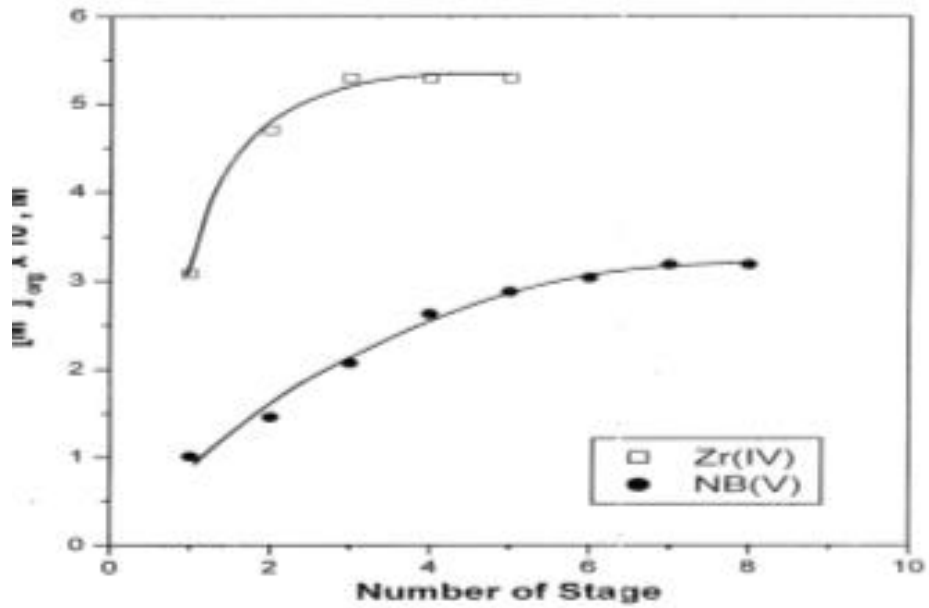
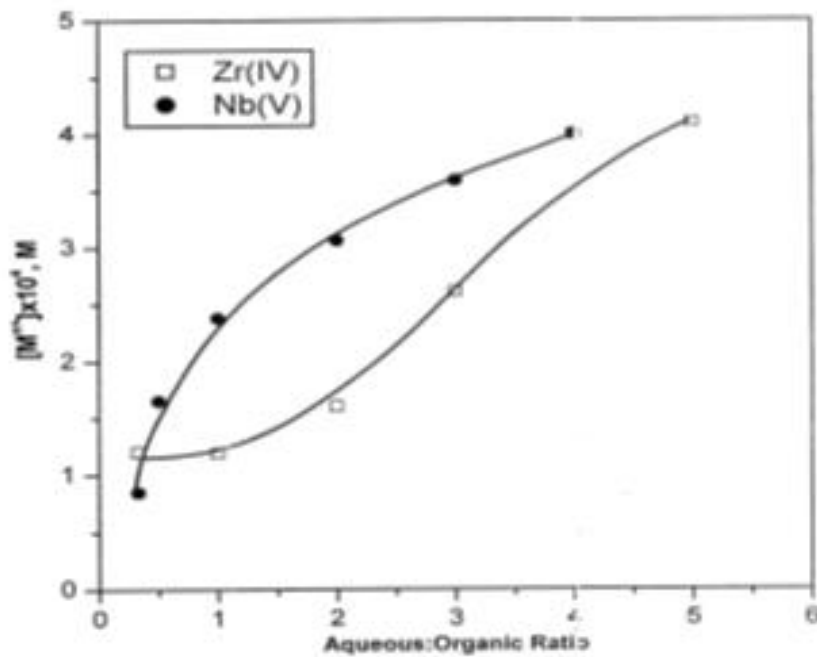(6) Effect of Number of Stage on the Extraction of Zr(IV) and Nb(V) by CYANEX 925 from Nitrate Medium

Fig. (7) Effect of Phase Ratio on the Extraction of Zr(IV) and Nb(V) by CYANEX 925 from Nitric Acid Medium

Effect of Initial Metal Concentration

The effect of initial metal concentration on the extraction of Zr (IV) and Nb(V) from nitric acid solution with CYANEX 925, was carried out by varying the zirconium and niobium concentrations in the aqueous solution in the respective ranges 0.11×10^{-3} -1.1×10^{-3} M and 0.27×10^{-3} – 2.15×10^{-3} M. The results shown in Fig. (8) indicate that the equilibrium concentration of Zr (IV) and Nb(V) in the organic phase increased with the increase in their initial concentrations up to 2.7×10^{-4} M and 1.6×10^{-3} M in for Zr (IV) and Nb(V), respectively , then remained nearly constant with further increase in their initial concentration in the aqueous phase.

The log–log plot between the distribution ratios and the corresponding initial metal concentrations showed a linear decrease in the distribution ratios with the increase in the initial Zr (IV) and Nb(V) concentration, (Fig.9).

Effect of Temperature

The increase in temperature in the range 10-60°C increased the extraction of both metal ions from 52.5 to 86.5% for Zr (IV) and from 13.1 to 80% in case of Nb(V) which indicates that the extraction processes are endothermic, (Table 2). When the corresponding K_{ex} values were plotted versus the variation of 1/T, straight lines were obtained, (Fig. 10). From the slopes of these lines, the enthalpy change (ΔH), the entropy change (ΔS) and the change in the Gibbs free energy ((ΔG) were calculated using **Van't Hoff** equations and are given in Table (3).

Table (1): Extraction Constants, K_{ex}, for the Extraction of 4.4×10^{-4} M Zr (IV) and 1.08×10^{-3} M Nb(V) with CYANEX 925 in Kerosene from Nitric Acid solution

Zr(IV) system		Nb(V) system	
[CY 925]x 10^{+3}, M	K^o_{ex}	[CY 925]x10^{+3}, M	K^o_{ex}
0.002	82.0	0.00026	15.2
0.003	83.3	0.00300	15.5
0.006	81.6	0.04000	15.8
0.012	83.3	0.12600	15.8
0.018	80.6	0.26000	15.8
0.240	80.0		
0.300	80.0		
Mean value	81.3 ± 0.03	Mean value	15.62 ± 0.03

Table (2): Effect of Temperature on Zr (IV) and Nb(V Extraction fom Nitric Acid solution with CYANEX 925

	Extraction Percentage (%)	
Temperature, °C	Zr (IV)	Nb(V
10	52.5	13.5
15	53.2	24.8
30	55.1	70.5
40	64.3	77.4
50	85.8	79.4
60	86.5	80.0

The negative free energy change (ΔG) in case of Zr(IV) extraction indicates that the reaction is spontaneous and the positive value of the enthalpy change (ΔH) indicates the endothermic character of this extraction while the negative value of the entropy change (ΔS) indicates the decrease in the randomness of this system. On the other hand, the positive (ΔG) and (ΔH) values in the case of Nb(V) extraction indicate that the reaction is not spontaneous and has an endothermic character; the high negative value of (ΔS) indicates a higher decrease in the randomness of this system compared to that of Zr(IV).

Stripping Investigations

The stripping investigations were carried out to choose an appropriate stripping agent that can successfully strip Zr (IV) and Nb(V) from the loaded CYANEX 925 organic solution. Among the investigated reagents, 1M sulfuric acid and 1M hydrochloric acid were found to be efficient stripping agents for stripping Zr (IV). On the other hand, 2M hydrofluoric acid was found to be the most efficient agents for stripping Nb(V) , (Table 4).

Increasing the sulfuric acid concentration in the range 0.1- 4M increased the stripping of Zr (IV) up to 1M then the stripping percentage decreased with further increase in the acid concentration, (Fig. 11). It was observed that the maximum stripping percentage of Zr (IV) was 98 % and achieved after 20 minutes with 1M H_2SO_4 and further increase in shaking time decreased the stripping percentage; in the stripping of Nb(V) , the maximum stripping was 64 % and achieved after only one minute with 2M hydrofluoric acid and further increase in the acid concentration decreased the stripping percentage, (Fig.11).

Table (3): Thermodynamic Parameters for the Extraction of of 4.4x10⁻⁴ M Zr (IV) and 1.08 x10⁻³ M Nb(V) with CYANEX 925 in Kerosene from 3M Nitric Acid solution

Extracted Ion	ΔG, kJ/mol.K	ΔH, kJ/mol	ΔS, J/mol.K
Zr (IV)	- 11.20 ±0.17	38.3 ± 0.10	- 10.00 ± 0.03
Nb(V)	7.87 ±0.17	47.9 ± 0.06	-130.00 ±0.18

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Table (4): Stripping of Zr (IV) and Nb(V) from Loaded CYANEX 925 using Different Stripping Agents

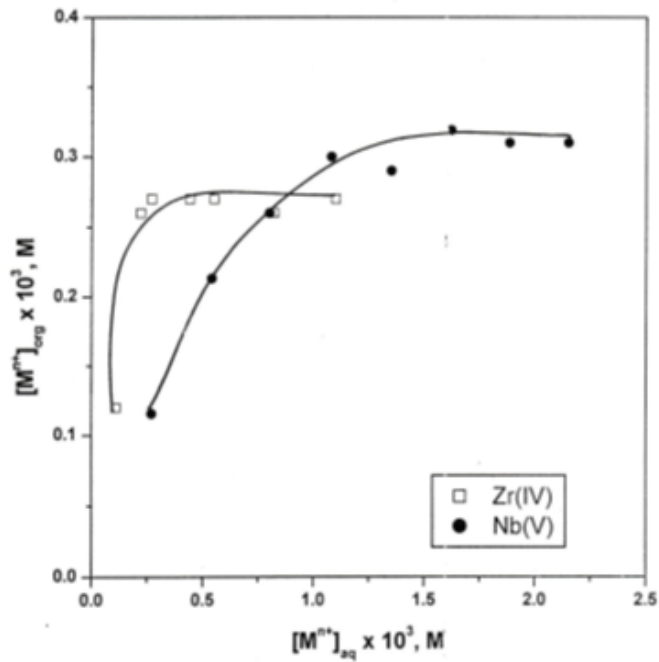| Stripping Agent	Stripping Percentage (%)	
	Zr (IV)	Nb(V
1.0M HCl	75.0	0.00
0.5 M HNO₃	30.0	0.00
1.0 M H₂SO₄	98.0	0.00
2.0 M HF	0.00	64.0
Dist. Water	0.00	0.00

Fig. (8) Effect of Metal Ion Concentration on Its Extraction
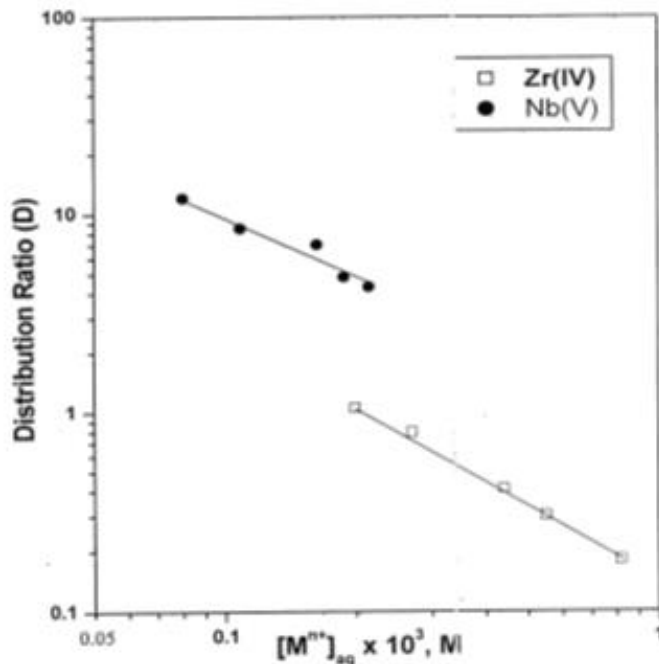with CYANEX 925 from Nitric Acid Medium

Fig. (9) Effect of Metal Ion Concentration on the Distribution
Ratio for the Extraction of Zr(IV) and Nb(V) Using
CYANEX 925 from Nitrate Medium

Separation Feasibility

Separation of two components is possible when the distribution ratio of one component, D_i, differs from that of the other component, D_j. Thus, separation is possible when $D_i / D_j > 1$. The ratio of distribution ratios is a measure of the ease or difficulty of a separation and is known as the separation factor, α. This relation is applied if D_i and D_j are determined under similar conditions.

The effects of temperature and concentrations of nitric, nitrate, and hydrogen ion on the separation factor (**α**) which is defined as the ratio of the distribution ratios of the investigated metal ions (D_{Zr}/D_{Nb}) for CYANEX 925 are shown in Table (5). The listed data indicate that the separation factor decreased markedly with the increase in the nitric acid concentration, temperature and hydrogen ion concentration and with the decrease in shaking time and nitrate ion concentration. Therefore, a good separation of Zr (IV) from Nb(V) could be obtained at low nitric acid concentration, high hydrogen ion concentration and low temperature at shaking time of 10 minutes.
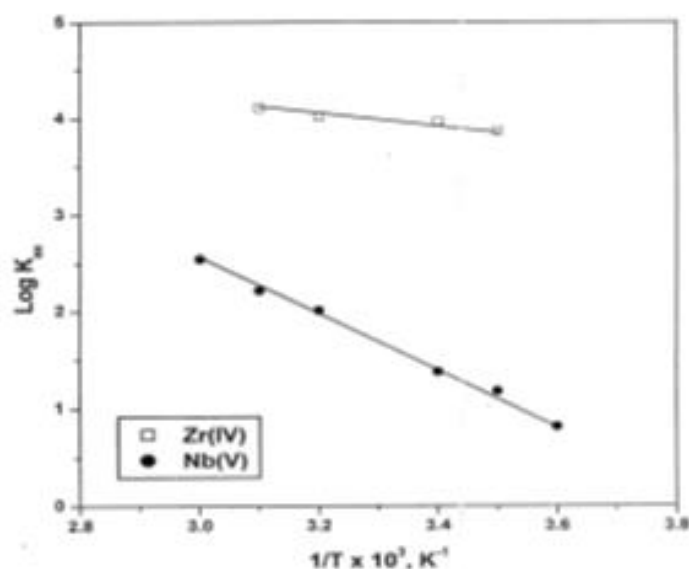

Fig. (10) The Semi-Logarethmic Relation between K$_{ex}$ and 1/T for the Extraction of Zr(IV) and Nb(V) with CYANEX 925 from Nitric Acid Medium

Table (5): Separation Factors (α) of Zr (IV) and Nb (V) at Different Extraction Parameters when Using CYANEX 925 in Kerosene

$[NO_3^-]$, M	α	$[H^+]$, M	α	$[HNO_3]$, M	α	Temp., ^{o}C	α
3.0	1.79	1.0	5.40	1.0	5.00	10	3.31
3.5	2.40	2.0	5.00	2.0	5.18	15	2.12
4.0	2.67	3.0	4.70	3.0	2.06	25	2.01
4.5	3.70	4.0	3.39	4.0	2.61	30	1.56
5.0	4.33	5.0	3.90	5.0	2.20	40	1.95
				6.0	2.13	50	1.22
						60	0.77

The stripping studies of zirconium and niobium indicate that the separation between these ions from loaded CYANEX 925 solution could be also obtained when Zr (IV) is first stripped using 1M H_2SO_4, then Nb (V) is stripped with Hf (2M) . The separation factors of of Zr (IV) from Nb(V) in the investigated system are higher than those obtained when using TBP or CYANEX 921 in a previous publication [17] under the same investigated parameters as shown in Table (6).

Table (6): Separation Factors (α) of Zr (IV) and Nb (V) at Different Extraction Parameters when Using CYANEX 925, CYANEX 921 and TBP in Kerosene

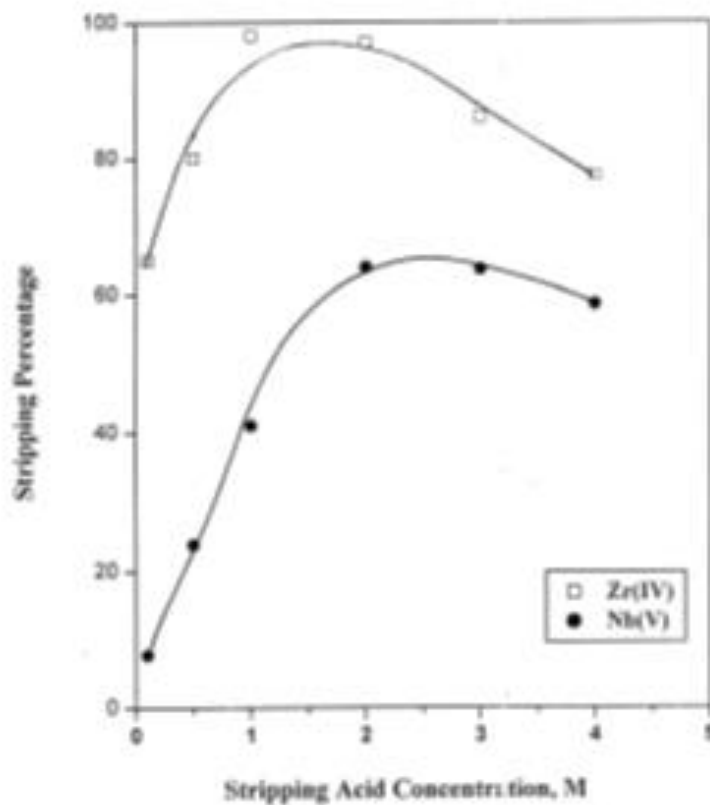|	α_{max}			
Reagent	NO_3^-	H^+	HNO_3	**Temp.**
TBP	0.69 (3M)	0.98 (1)	1.86 (1M)	1.90 (10 °C)
CYANEX 921	2.29 (3M)	0.62 (5M)	1.38 (6M)	1.80 (10 °C)
CYANEX 925	**4.33** (5M)	**5.40** (1M)	**5.00** (1M)	**3.31**(10 °C)

Fig (11) Effect of Acid Concentration on the Stripping of Zr(IV) and Nb(V) from Loaded CYANEX 925 Solution.)

Conclusion

- CYANEX 925 is a potential extractant for the extraction of Zr (IV) and Nb (V) from nitric acid solution .

- The extraction of Zr (IV) and Nb (V) was found to increase with the increase in the concentration of the extractant, nitric acid, hydrogen ion concentration and with the decrease in the nitrate ion concentration.

- Sulfuric acid was found to be efficient for stripping Zr (IV) from loaded CYANEX 925.Increasing sulfuric acid concentration up to 1M H_2SO_4 increased the stripping of zirconium then the stripping decreased with further increase in H_2SO_4 concentration.

- Hydrofluoric acid was found to be a suitable stripping agent for the stripping of Nb (V) from loaded CYANEX 925 in kerosene solution.

- A good separation of Zr (IV) from Nb(V) could be obtained at low nitric acid concentration, high hydrogen ion concentration and low temperature at shaking time of 10 minutes.

- Maximum separation of Zr (IV) from Nb(V) was obtained at 5M NO_3^-, 2M H^+, 2M HNO_3, at 10 ^{o}C and 10 minutes shaking time,

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