Liquid-Liquid Extraction of Tetravalent Zirconium from Acidic Chloride Solutions Using Cyanex 272

B. Ramachandra REDDY,*† J. Rajesh KUMAR,*,** and A. Varada REDDY**

*Inorganic Chemistry Division, Indian Institute of Chemical Technology (CSIR), Hyderabad-500007, India

**Analytical Chemistry Division, Department of Chemistry, SriVenkateswara University, Tirupati-517502, India

The liquid-liquid extraction of zirconium(IV) from acidic chloride solutions was carried out with Cyanex 272 as an extractant diluted in kerosene. An increase of the acid concentration decreased the percentage extraction of metal, which indicates that the extraction follows ion exchange-type mechanism: $\text{MO}^{2+}_{(\text{aq})} + 2(\text{HA})_{2(\text{org})} \leftrightarrow \text{MO}(\text{HA}_2)_{2(\text{org})} + 2\text{H}^{+}_{(\text{aq})}$, where, M = Zr(IV); HA = Cyanex 272. The extraction of Zr(IV) increases with an increase of the extractant concentration. In a plot of $\log D$ vs. $\log[\text{extractant}]$, M is linear with a slope of ~ 2 , indicating the association of two moles of extractant with the extracted metal species. On the other hand, the extraction decreases with an increase of the H^{+} ion concentration. A plot of $\log D$ vs. $\log[\text{H}^{+}]$ gave a straight line with a negative slope of 1.7, indicating the exchange of two moles of hydrogen ions for every mole of Zr(IV). The effect of the Cl^{-} ion concentration at a constant concentration of $[\text{H}^{+}]$ did not show any change in the D values. The addition of sodium salts enhanced the percentage extraction of metal, and followed the order of $\text{NaSCN} > \text{NaNO}_3 > \text{Na}_2\text{SO}_4 > \text{NaCl}$. The stripping of metal from the loaded organic (L.O) with different acids indicated sulfuric acid to be the best stripping agent. An increase of the temperature during the extraction and stripping stages increases the metal transfer, showing that the process is exothermic. The synergism, regeneration and recycling capacity of Cyanex 272; the extraction behavior of associated elements, such as Hf(IV), Ti(IV), Al(III), Fe(III); and IR spectra of the extracted Zr-Cyanex 272 complex were studied.

(Received July 18, 2003; Accepted September 29, 2003)

Zirconium is used in the nuclear industry as a shielding material and as a catalyst in organic reactions in the manufacture of water-repellent textiles; it is also used in dye pigments and ceramics. A survey of the literature showed that a limited number of extractants have been used for the extraction of zirconium. Organophosphorus compounds, namely TBP¹⁻⁵ and D2EHPA,⁶⁻¹¹ have been extensively employed in solvent-extraction studies of zirconium. Amines, such as Aliquat 336 and Alamine 336,¹² have been used for the extraction of zirconium. Also, other extractants studied have been dihexyl *N,N*-diethylmethylcarbamoyl phosphonate,¹³ isopropylphosphonic acid mono(1-hexyl-4-ethyl)octylester (PT-2, HL)¹⁴ and octyl(phenyl)*N,N*-diisobutylcarbamoyl methylphosphineoxide (CMPO).¹⁵

Cyanex 272 is a bis(2,4,4-trimethylpentyl) phosphinic acid. It is a well-known solvent-extraction reagent showing favorable extraction and stripping properties for a range of metals. It has high selectivity for the separation of cobalt(II) and nickel(II),¹⁶⁻¹⁸ and shows an ability to reject calcium(II).¹⁹ The above extractant has the advantage of being a liquid, and is completely miscible with all commonly used hydrocarbons. Despite the large number of studies reporting the solvent extraction of metals with Cyanex 272, it has not been reported for the solvent extraction of zirconium.

The present study reports on the solvent extraction behavior of zirconium(IV) from low acidic chloride solutions with Cyanex 272 in kerosene. Various experimental variables, such as the effect of acid, the effect of $\text{Cl}^{-}/\text{H}^{+}$ at constant $\text{H}^{+}/\text{Cl}^{-}$

concentration, the extractant and the metal concentration, the nature of diluents, the effect of salts, the temperature, the loading capacity, the stripping of metal from a loaded organic, the regeneration and recycling capacity of an extractant, the extraction of associated elements and the infrared spectral data of a metal complex have been studied.

Experimental

Apparatus

The concentrations of Zr(IV) and Hf(IV) in the aqueous phase were determined by the Xylenol Orange (XO) method²⁰ at 535 nm and Ti(IV) by the hydrogen peroxide method²⁰ at 410 nm using a GBC CINTRA 10e UV-VIS-DRS spectrometer. Analyses of Fe(III) and Al(III) were carried out using a Perkin Elmer Model A 300 AAS. The IR spectrum of the solid complex was recorded using a FTIR-Nicolet (USA)-740-spectrophotometer. A Julabo shaker (Temp SW 22 Model) was used for a temperature effect.

Reagents

Cyanex 272 and Cyanex 923, supplied by Cytec, Canada, were used without purification. Tributyl phosphate (TBP), supplied by SRL, Bombay, India was used. Di-*n*-octyl sulfoxide (DOSO) was prepared according to a reported procedure.²¹ As a source of Zr(IV), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Fluka, 98%) was used. Working solutions of Zr(IV) were prepared fresh and used for extraction experiments. Distilled kerosene (160–200°C) was used as a diluent. It was colorless and mostly aliphatic in nature. All other reagents used were of analytical

† To whom correspondence should be addressed.
E-mail: bcreddy_iict@yahoo.com

reagent grade.

Solvent-extraction procedure

Equal volumes (10 ml) of the aqueous phase containing, the desired concentrations of Zr(IV) or other metals, and the organic phase containing the extractant, Cyanex 272, were equilibrated for 30 min in glass stopped bottles using a mechanical shaker. Preliminary experiments on the kinetics of metal extraction showed that equilibrium was achieved within 20 min of contact. After phase disengagement, the aqueous phase was separated and its metal concentrations were estimated by the XO method. The concentration of the metal in the organic phase was calculated from the mass balance. All of the experiments were conducted at room temperature ($30 \pm 1^\circ\text{C}$), except for those involving a temperature effect. The distribution ratio (D) was calculated as the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium. When required, the metal concentration in the organic phase was determined by stripping a suitable aliquot with dilute HCl, followed by an analysis by the XO method.

Preparation of solid complex

A Zr-Cyanex 272 solid complex was prepared by loading 0.005 M Cyanex 272 in chloroform by repeated contact of fresh portions of metal solutions (0.001 M) for 30 min. Finally, the loaded organic (L.O) phase was separated and filtered through a Whatman phase separator (1PS). The diluent from the L.O was removed by a rotavac pump, which resulted in the formation of a semi-solid metal complex. A drop of the Zr(IV) complex was kept on a KBr pellet and placed under an IR lamp to completely evaporate chloroform. The IR spectra of the extracted metal complex and pure Cyanex 272 were recorded for a comparison.

Results and Discussion

Extraction mechanism and species

The extraction equilibrium of zirconium(IV) from hydrochloric acid solutions with Cyanex 272 as an extractant may be represented as

where K_{ex} denotes the equilibrium constant and $(\text{HA})_2$ refers to the dimeric form of the extractant (Cyanex 272). It has been reported elsewhere that these extractants will exist as dimers under the present experimental conditions:^{18,22,23}

$$K_{\text{ex}} = \frac{[\text{ZrO}(\text{HA}_2)_2] [\text{H}^+]^2}{[\text{ZrO}^{2+}] [(\text{HA})_2]^2}, \quad (2)$$

$$K_{\text{ex}} = \frac{D[\text{H}^+]^2}{[(\text{HA})_2]^2}, \quad (3)$$

$$\text{Where } D = \frac{[\text{ZrO}(\text{HA}_2)_2]}{[\text{ZrO}^{2+}]}. \quad (4)$$

Taking the logarithm of Eq. (3) and rearranging,

$$\text{Log } D = \text{log } K_{\text{ex}} + 2\text{log}[(\text{HA})_2] - 2\text{log}[\text{H}^+]. \quad (5)$$

Analyzing the experimental data of the distribution ratio (D) as a function of the H^+ ion and the extractant concentration at a constant value of other parameters allows an estimation of the number of extractant molecules associated with the extracted

Fig. 1 Effect of the hydrochloric acid concentration on the extraction of Zr(IV). Zr(IV), 0.001 M; Cyanex 272, 0.005 M.

Fig. 2 Effect of the hydrogen ion concentration on the distribution ratio of Zr(IV) at constant Cl^- ion. Zr(IV), 0.001 M; $[\text{Cl}^-]$, 0.3 M; Cyanex 272, 0.005 M.

metal complex.

The extraction of zirconium(IV) with Cyanex 272 (0.003, 0.005 and 0.007 M) as a function of the hydrochloric acid concentration showed (Fig. 1) an inverse dependence with the acidity, indicating the release of H^+ ions from the extractant during the extraction process. On the other hand, the effect of the chloride ion concentration in the range of 0.01 – 0.3 M at a constant H^+ ion concentration (0.01 M) was studied for mixtures of HCl and NaCl using a 0.005 M extractant, indicating that the percent extraction of the metal remains constant with an increase of the chloride ion concentration ($D = 1.2 \pm 0.05$). The effect of the hydrogen-ion concentration on the distribution ratio of Zr(IV) was studied in the range of H^+ ions from 0.005 to 0.15 M at a constant Cl^- ion concentration (0.3 M) in the aqueous phase. Log D vs. log $[\text{H}^+]$ plot (Fig. 2) gave a straight line with a negative slope of about 1.7, indicating the exchange of two moles of H^+ for every mole of metal ion during the extraction process.

The effect of the Cyanex 272 concentration (0.001 to 0.015 M) on the extraction of Zr(IV) (0.001 M) from 0.01 M hydrochloric acid solutions was investigated, and the results are depicted in Fig. 3. It is clear from this figure that the extraction of zirconium increases with an increase of the extractant concentrations. A plot of log D versus log $[(\text{HA})_2]$ gave a straight line with a slope 2.2, indicating that two moles of the extractant ($\text{HA} \equiv \text{Cyanex 272}$) were involved in the extracted complexes of Zr(IV). The calculated value of K_{ex} was found to

Fig. 3 Plot of $\log D$ vs. $\log[\text{extractant}]$, M. Zr(IV), 0.001 M; HCl, 0.01 M.

Fig. 4 Effect of the metal concentration on the extraction of Zr(IV). HCl, 0.01 M; Cyanex 272, 0.005 M.

Fig. 5 Effect of sodium salts on the extraction of Zr(IV). Zr(IV), 0.001 M; HCl, 0.01 M; Cyanex 272, 0.005 M.

be 3.4.

The effect of the zirconium concentration on the extraction process was investigated using Cyanex 272 (0.005 M) from hydrochloric acid solutions (0.01 M). The extraction of zirconium(IV) was found to be independent of the metal-ion concentration in the aqueous phase. A log-log plot (Fig. 4) of the equilibrium organic-phase metal concentration against the aqueous-phase metal concentration is linear with a slope of ~ 1.0 , indicating the extraction of the mononuclear species into the organic phase. The species extracted into the organic phase appeared to be $\text{ZrO}(\text{HA}_2)_2$.

Table 1 Effect of temperature on zirconium extraction and stripping

Temperature/ $^{\circ}\text{C}$	Extraction, %	Stripping, %
30	36.3	30.1
40	50.1	47.4
50	64.0	64.5
60	73.7	77.3

Extraction: 0.001 M Zr(IV), 0.01 M HCl, 0.005 M Cyanex 272.

Stripping: Zr(IV) in L.O, 246 mg l^{-1} ; 4 M HCl.

Effect of salts

The effect of salts, such as NaCl, Na_2SO_4 , NaNO_3 or NaSCN, was studied in the concentration range of 0.5 – 2.0 M on the extraction behavior of 0.001 M Zr(IV) from 0.01 M HCl with 0.005 M Cyanex 272. In the case of NaCl, the percentage of extraction steadily increased with increasing the NaCl concentration. The percentage extraction was 39.8% in 0.5 M, and reached 54.8% in 2 M NaCl concentration. In the case of Na_2SO_4 , the percentage of extraction was 40.8% in 0.5 M, salt, and reached 79.6% in 2 M salt concentration. In the case of NaNO_3 , the percentage of extraction started at 60% in 0.5 M salt concentrations and reached 97.3% in 2 M salt concentrations. In the case of NaSCN, the percentage of extraction started at 83.6% in 0.5 M salt concentrations and reaches 100% in 1.0 M salt concentrations, favoring better extraction of Zr(IV) than the other salts (Fig. 5). The enhancement in percent extraction in the presence of added salts may perhaps be due to a common ion effect as well as the presence of mixed metal salt species, that makes the metal more favorable for extraction. At a given concentration of the metal, extractant and acid, the percentage extraction followed in increasing order as $\text{NaSCN} > \text{NaNO}_3 > \text{Na}_2\text{SO}_4 > \text{NaCl}$.

Effect of diluents and temperature

The extraction of Zr(IV) from hydrochloric acid solutions (0.01 M) using Cyanex 272 (0.005 M) in various diluents was investigated. The results clearly demonstrate that the extraction of Zr(IV) varies with the nature of the diluent, and decreases in the following order: toluene ($D = 0.11$) < chloroform ($D = 0.18$) < carbon tetrachloride, xylene ($D = 0.30$ and 0.33) < benzene, nitrobenzene ($D = 0.40$ and 0.43) < *n*-hexane ($D = 0.52$) < kerosene, cyclohexane ($D = 0.57$ and 0.58) < benzonitril ($D = 0.66$). The variation of the temperature in the range of 303 – 333 K ($\pm 1^{\circ}$) on the extraction of metal from an aqueous solution containing 0.001 M Zr(IV) and 0.01 M HCl using 0.005 M Cyanex 272 was studied. An increase in the temperature increased the extraction and the stripping of Zr(IV) from L.O (Table 1). The calculated values of $\Delta^{\circ}H$ from Arrhenius plots were -10.5 and -13.7 kcal mol^{-1} for the extraction and stripping processes, indicating an exothermic reaction.

Loading capacity of the extractant

An aliquot of 10 ml of 0.01 M Cyanex 272 was repeatedly contacted at 303 ± 1 K for 30 min with the same volume of aqueous solutions containing 0.001 M of Zr(IV) and 0.01 M HCl. After equilibration, the phases were analyzed for the zirconium content. The amount of zirconium transferred into the organic phase in each contact was calculated based on the difference and the cumulative concentration of zirconium in the organic phase after each stage of contact was determined. A plot of cumulative $[\text{Zr(IV)}]_{\text{org}}$ of Cyanex 272 versus the contact

Fig. 6 Loading capacity of the extractant. Zr(IV), 0.001 M; HCl, 0.01 M; Cyanex 272, 0.01 M.

Fig. 7 Regeneration and recycling capacity of the extractant. Extraction conditions: Zr(IV), 0.001 M; HCl, 0.01 M; Cyanex 272, 0.007 M. Stripping conditions: H₂SO₄, 0.5 M.

Fig. 8 Extraction of associated metals as a function of acid concentration. Metal, 0.001 M; Cyanex 272, 0.005 M.

number is given in Fig. 6. It is clear that the zirconium existing in the aqueous phase was extracted into the organic phase up to the 7th contact. An analysis of L.O showed that it contained 246 mg l⁻¹ Zr(IV).

Stripping studies

In any commercial extraction process it becomes imperative to back extract the metal from the loaded organic phase.

Table 2 Stripping of Zr(IV) from a loaded organic (246 mg l⁻¹ Zr) phase

Stripping reagent	Zr stripping, %	Stripping reagent	Zr stripping, %
1.0 M HCl	12.3	3.0 M HNO ₃	6.40
2.0 M HCl	16.0	4.0 M HNO ₃	7.80
3.0 M HCl	23.6	1.0 M HCl + 1% H ₂ O ₂	14.5
4.0 M HCl	30.5	3.0 M HCl + 1% H ₂ O ₂	28.8
0.1 M H ₂ SO ₄	30.0	1.0 M HCl + 5% H ₂ O ₂	16.0
0.5 M H ₂ SO ₄	61.3	3.0 M HCl + 5% H ₂ O ₂	30.0
1.0 M H ₂ SO ₄	84.6	1.0 M HNO ₃ + 1% H ₂ O ₂	5.50
2.0 M H ₂ SO ₄	85.1	3.0 M HNO ₃ + 1% H ₂ O ₂	7.80
3.0 M H ₂ SO ₄	88.0	1.0 M HNO ₃ + 5% H ₂ O ₂	10.2
4.0 M H ₂ SO ₄	90.0	3.0 M HNO ₃ + 5% H ₂ O ₂	12.3
1.0 M HNO ₃	3.60	1.0 M H ₂ SO ₄ + 1% H ₂ O ₂	100
2.0 M HNO ₃	5.10	3.0 M H ₂ SO ₄ + 1% H ₂ O ₂	100

Zirconium stripping from a loaded organic solvent system, Cyanex 272 (0.005 M) containing 246 mg zirconium(IV) was investigated using various stripping agents, such as HCl, H₂SO₄ and HNO₃, in the range of 0.1 – 4 M. The results are given in Table 2. In the case of HCl as a stripping agent, the percentage stripping increased with an increase in the acid concentration, and reached 12 – 30% of acid up to 4.0 M. With the addition of 1 – 5% H₂O₂, the percentage stripping was unaffected. In the case of H₂SO₄, the percentage stripping increased with an increase in the acid concentration, and reached ~90% at 4.0 M acid. From these results, it is clear that H₂SO₄ is the best and HNO₃ is the poorest stripping agent.

Recycling capacity of Cyanex 272

Studies on the recycling capacity of 0.007 M Cyanex 272 for the extraction of Zr(IV) were carried out by first loading the extractant with an aqueous phase containing 0.001 M Zr(IV) and 0.01 M HCl. Single-stage extraction gave L.O containing 76.3 mg l⁻¹ zirconium, corresponding to a 99.8% theoretical efficiency. This L.O was stripping with 0.1 M H₂SO₄. The regenerated organic phase was then used for extraction. The results revealed a practically insignificant change in the extraction and stripping efficiency of extractant up to ten cycles of extraction (Fig. 7).

Comparison of the extraction behavior of Zr(IV) with other associated metal ions

The extraction behaviors of hafnium(IV), aluminium(III), titanium(IV) and iron(III) (0.001 M each) were investigated as a function of the hydrochloric acid concentration using 0.005 M Cyanex 272 in kerosene as an extractant. The results are presented in Fig. 8. It is clear from these results that the percentage of extraction of Hf(IV), Zr(IV) and Fe(III) decreased with increasing acid concentration. On the other hand, the extraction of Ti(IV) increased with increasing acid concentration. The percentage extraction of Al(III) was nil.

Synergism

Blake *et al.*²⁵ used the term “synergism” to describe the discovery of a definite enhancement in the extraction of uranium by using mixture of acidic alkyl phosphate and certain neutral organophosphorous esters. The resulting mixture giving a better extraction of uranium than either the acid or the neutral phosphate alone. This effect is understood to be the replacement of one extractant in the extracted complex by the other, and also due to various other factors. This property of the

Table 3 Distribution coefficient values of Zr(IV) using extractant and synergist mixtures

S.No.	D_A , Extractant, 0.005 M	Concentration of synergist/M	D_B	D_{A+B}	ΔD	S.C
1	1.06 (C1)	0.001 (C2)	0.25	2.10	0.79	0.205
2	1.06 (C1)	0.005 (C2)	0.27	2.22	0.89	0.223
3	1.06 (C1)	0.007 (C2)	0.46	3.35	1.83	0.343
4	1.06 (C1)	0.001 (D)	0.06	1.72	0.59	0.185
5	1.06 (C1)	0.005 (D)	0.12	1.80	0.62	0.183
6	1.06 (C1)	0.007 (D)	0.18	2.22	0.98	0.253
7	1.06 (C1)	0.001 (T)	0.01	2.10	1.03	0.292
8	1.06 (C1)	0.005 (T)	0.07	2.22	1.09	0.291
9	1.06 (C1)	0.007 (T)	0.16	4.40	3.22	0.561

C1, Cyanex 272; C2, Cyanex 923; D, DOSO; T, TBP.

D_A , distribution coefficient of Zr(IV) with extractant; D_B , distribution coefficient of Zr(IV) with synergist; D_{A+B} , distribution coefficient of the mixture; ΔD , $D_{A+B} - (D_A + D_B)$; S.C, $\log D_{(A+B)}/(D_A + D_B)$.

mixed-solvent system was utilized to study the extraction behavior of zirconium using a mixture of extractants: Cyanex 272, Cyanex 923, DOSO and TBP.

Synergistic studies were carried out while keeping the concentration of one of the extractant constant at 0.005 M and varying the other (synergist) over the range of 0.001 to 0.007 M. The Zr(IV) and HCl concentrations were kept at 0.001 M and 0.01 M, respectively. The experimental data of the three synergistic systems, *i.e.* Cyanex 272, Cyanex 923, DOSO and TBP, are presented in Table 3. In all three systems, the synergistic coefficient (S.C) values varied marginally with an increase of the synergist concentration. The results show that TBP is the best synergist (S.C = 0.56) and DOSO is the least one (S.C = 0.18). Thus, the extractants can be arranged in the order of their synergism as TBP > Cyanex 923 > DOSO.

IR spectra of a zirconium complex

The IR spectra of a zirconium complex with Cyanex 272 and pure extractant for a comparison were recorded. In the IR spectra of Cyanex 272, the bands in the region 2748–1700 cm^{-1} are due to aggregative P–OH vibrations between intermolecular hydrogen bonding in the dimeric form. The band at 1170 cm^{-1} is due to P=O stretching and the band at 1048 cm^{-1} is assigned to a P–O–H stretch. In the spectra of the Zr–Cyanex 272 complex, bands due to aggregative P–OH vibrations in the region 2748–1700 cm^{-1} are absent. The band due to the P–O–H stretching is also absent. These results suggest that when the dimeric Cyanex 272 molecule forms a complex with zirconium(IV), the hydrogen atom of P–O–H is displaced by Zr, thus confirming the proposed cation-exchange mechanism. Further, the shift in the P=O stretching band from 1171 cm^{-1} to 1000 cm^{-1} is indicative of the participation of oxygen in P=O group in complex formation through coordination.

A survey of literature revealed that Cyanex 272 has not been exploited for the extraction of zirconium. The present study on the liquid-liquid extraction of Zr(IV) from acidic chloride solutions by Cyanex 272 revealed the transfer of metal by a cation-exchange mechanism. The variation of the D values with an increase of the extractant concentration showed a linear plot with a slope of ~ 2 and the IR spectra of the metal complex indicate that the extracted species was $\text{ZrO}(\text{HA}_2)_2$. An increase in the temperature had a positive influence on Zr(IV) extraction

and stripping. Regeneration and recycling of the extractant indicated a greater stability of Cyanex 272.

Acknowledgements

The authors express their sincere thanks to the Ministry of Environment & Forests (MOEF), Government of India, New Delhi, India for the financial support. Thanks are also to Dr. B. M. Choudary, Head, Inorganic & Physical Chemistry Division and Dr. K. V. Raghavan, Director, IICT, Hyderabad for their constant encouragement and permission to publish this work. Thanks are also due to Cytec Canada for providing Cyanex 272 free sample.

References

1. A. Levitt and E. Freund, *J. Am. Chem. Soc.*, **1956**, 78, 1545.
2. K. Alcock, F. C. Bedford, W. H. Hardwick, and H. A. C. Mokay, *J. Inorg. Nucl. Chem.*, **1957**, 4, 100.
3. S. Siekierski, *J. Inorg. Nucl. Chem.*, **1959**, 2, 129.
4. G. F. Egorov, V. V. Fomin, Yu. G. Frolov, and G. A. Yagodin, *Zhur. Neog. Khim.*, **1960**, 5, 1044.
5. S. S. Korovin, E. N. Lebedeva, A. M. Renzik, L. N. Komissarova, and G. P. Kuznetsova, *Khim. I. Khim. Tekhnol.*, **1962**, 5, 231.
6. A. M. Golub and V. N. Sergunkin, *Zh. Prikl. Khim.*, **1970**, 43, 1203.
7. H. Umezawa and R. Hara, *Anal. Chim. Acta*, **1961**, 25, 360.
8. P. H. Tedesco, V. B. De Rumi, and J. A. Gonzalez Quintana, *J. Inorg. Nucl. Chem.*, **1967**, 29, 1307.
9. S. S. Korovin, A. M. Renzik, E. N. Lebedeva, and I. A. Apraksin, *Org. Reagenty Anal. Khim. Tsirkoniya.*, **1970**, 63.
10. G. A. Yagodin and V. V. Tarasov, *Radiokhimiya*, **1970**, 12, 664.
11. R. K. Biswas and M. A. Hayat, *Hydrometallurgy*, **2002**, 63(2), 149.
12. P. K. Mishra, V. Chakravorty, K. C. Dash, N. R. Das, and S. N. Bhattacharyya, *J. Radioanal. Nucl. Chem.*, **1989**, 134(2), 259.
13. D. L. Mcisaac and J. D. Baker, *Solv. Extr. Ion Exch.*, **1983**, 1(1), 27.
14. J. Sun, C. Wang, D. Li, and D. Ye, *Fenxi. Huaxue*, **1995**, 23(9), 998.
15. K. N. Brewer, R. S. Herbst, T. A. Todd, and J. D. Christian, *Solv. Extr. Ion Exch.*, **1998**, 119(3), 1047.
16. W. A. Rickelton, D. S. Flett, and D. W. West, *Solv. Extr. Ion Exch.*, **1984**, 2, 815.
17. B. R. Reddy and P. V. R. Bhaskara Sarma, *Miner. Metall. Process.*, **2001**, 18(3), 172.
18. K. Sarangi, B. R. Reddy, and R. P. Das, *Hydrometallurgy*, **1999**, 52(3), 253.
19. Y. Nagaosa and Y. Binghua, *Talanta*, **1997**, 44, 327.
20. Z. Marczenko, "Spectrophotometric Determination of Elements", **1976**, John Wiley & Sons, 555, 609.
21. S. R. Mohanty and A. S. Reddy, *J. Inorg. Nucl. Chem.*, **1975**, 37, 1791.
22. R. K. Biswas and D. A. Begum, *Hydrometallurgy*, **1998**, 49, 263.
23. K. C. Sole and J. B. Hiskey, *Hydrometallurgy*, **1995**, 37, 129.
24. C. A. Blake, C. F. Baes, K. B. Brown, C. F. Coleman, and J. C. White, Proc. U. N. Intern. Conf. Peaceful uses At. Energy, 2nd ed., **1958**, Vol. 28, Geneva, 289.