



## SOLVENT EXTRACTION AND SEPARATION POSSIBILITIES OF Zr (IV) AND Fe (III)/Al (III) FROM HYDROCHLORIC ACID MEDIA WITH COMMERCIAL EXTRACTANTS

BHIKARI CHARAN BHATTA<sup>1</sup> AND SUJATA MISHRA<sup>\*2</sup>

<sup>1</sup>Department of Chemistry, College of Engineering and Technology, Bhubaneswar -751003, Odisha,

<sup>2</sup>Department of Chemistry, Institute of Technical Education and Research, Siksha'O'Anusandhan Deemed to be University, Bhubaneswar-751030, Odisha, India.

### ABSTRACT

The liquid-liquid extraction and separation of Zr(IV) and Fe(III) / Al(III) from hydrochloric acid solution (4M) using TOA( Tri-octyl amine), Cyanex 921(tri-n-octyl phosphine oxide), Cyanex 923 (a mixture of four trialkyl phosphine oxides) and their binary mixture in kerosene was studied. The extraction of Zr(IV) increased with increase in concentration of Fe(III) or Al(III) in the aqueous phase in all the cases. The separation factors between zirconium (IV) and Fe(III) / Al(III) was maximum when binary mixture of 0.1M TOA and 0.01M Cyanex 923 was used as organic phase extractant. Stripping of Zr(IV) was quantitative using 0.2M HNO<sub>3</sub> and 0.4M Na<sub>2</sub>CO<sub>3</sub> when loaded organic phase contains Fe(III). Whereas 0.25M HNO<sub>3</sub> and 0.55M Na<sub>2</sub>CO<sub>3</sub> were found effective for stripping of Zr(IV) in the presence of Al(III).

**KEYWORDS:** Zirconium, Solvent extraction, Hydrochloric acid, TOA, Cyanex921, Cyanex923 and Kerosene



**SUJATA MISHRA**

Department of Chemistry, Institute of Technical Education and Research,  
Siksha'O'Anusandhan Deemed to be University, Bhubaneswar-751030, Odisha, India.

## INTRODUCTION

Zirconium is very abundant but is typically found in ores combined with other elements. Zirconium is highly active metal and is resistant to corrosion by water, steam, mineral acids, alkalis, salts etc.. Zirconium is mainly produced from two ores i.e, Zirconium silicate(Zircon, $ZrSiO_4$ ) and baddelyite( $ZrO_2$ )<sup>1</sup>. Zirconium is mainly used for cladding nuclear reactor fuels due to its low neutron-capture cross-section<sup>2</sup>. Solvent extraction is one of the most remarkable technologies for the separation of metal ions from aqueous acidic solutions<sup>3-7</sup>. Some of the research efforts have indicated that the separation of Zr from Hf is possible from different sort of acidic aqueous medium using solvent extraction and ion-exchange method<sup>8-11</sup>. Banda et al. developed a process for separation of Zr and Hf from strong hydrochloric acid solution by solvent extraction with TEHA (tri-ethyl hexyl amine)<sup>12</sup>. Many authors have also studied the extraction of Fe(III) using tributyl phosphate (TBP)<sup>13-15</sup>. Satisfactory results have been obtained in separating iron from Al(III) in concentrated HCl solution. The extraction of iron by long- chain amines has been investigated by a number of authors<sup>16-18</sup> and the percentage extraction of iron decreases in the following order: quaternary >tertiary>secondary>primary. Chang et al. reported production of high purity zirconium by removing iron by solvent extraction using D2EPHA, KELEX 100 and TBP and investigated that the percentage extraction of iron increases with increasing hydrochloric acid concentrations. The separation factor of Fe(III) to Zr(IV) is poor for the extractants involving ion association such as Aliquat 336<sup>19</sup>. Taghizadeh et al. proposed a new Zr/Hf separation procedure by solvent extraction using mixture of tri butyl phosphate(TBP) and Cyanex923 varying several parameters TBP/Cyanex 923 volume ratio, extractant concentration in the organic phase, nitric acid and  $NaNO_3$  concentration in aqueous phase have been investigated<sup>20</sup>. Nayal et el investigated that, extraction and separation of Zr(IV) and Hf(IV) from nitrate

medium using some phosphine oxide extractants (Cyanex921, Cyanex923 and Cyanex925) in kerosene. The rate of extraction increases with increase in temperature, suggesting that the reaction is endothermic<sup>21</sup>. Mishra et al reported that appreciable extraction of Zr(IV) by Aliquat 336 from low aqueous HCl acidities i.e, 0.1M to 4.5M. The variation of concentration of HCl, thiocyanate and Aliquat 336 greatly influences the extent of extraction<sup>22</sup>. Manjusha et al reported that Zr(IV) and Hf(IV) were extracted with 0.1M of Aliquat 336 in toluene from 0.005M of ascorbic acid at pH 4.0. The separation of Zr(IV) from Hf(IV) was achieved by stripping Hf(IV) with 9M hydrochloric acid followed by stripping Zr(IV) with 2M hydrochloric acid<sup>23</sup>. Ajsaonkal et el developed a rapid method for the solvent extraction separation of Fe(III) and Al(III) from other elements with Cyanex302 in chloroform as the diluent. Fe (III) and Al (III) were quantitatively extracted at pH 2.0-2.5 and at pH 3.0-4.0, respectively. Both metals were separated from multicomponent mixture<sup>24</sup>. Bhatta et al. investigated the extraction of Zr(IV) from aqueous HCl solution by TOA (tri-octyl amine), Cyanex 921 and their binary mixture using kerosene as the diluent. Kerosene was found to be effective diluents for the extraction of Zr(IV) with binary mixture TOA and Cyanex921<sup>25</sup>. The purpose of this work is to study the extraction and separation of Zr(IV) and Fe(III) / Al(III) from HCl solution using TOA, Cyanex 921, Cyanex 923 and binary mixtures of TOA with Cyanex921/Cyanex923 in kerosene. Stripping investigations has been carried out to recover zirconium from the loaded organic phase in the presence of Fe(III)/Al(III).

## 2. EXPERIMENTAL

### 2.1. Reagents

The stock solution of Zr(IV) (0.01M) was prepared by dissolving its oxychloride in 100ml with double distilled water. One ml of concentrated HCl was added to the stock

solution to avoid further hydrolysis. Synthetic solutions were prepared by dissolving appropriate quantities of ferric chloride and aluminium chloride along with zirconium oxychloride in distilled water. Distilled kerosene was used as organic phase diluents. Organic phase solution was prepared by dissolving the required amount of the extractants in kerosene and then diluting to the required concentration. The commercial extractant, Tri-octyl amine (TOA) (Merck), Cyanex 921 and Cyanex 923, obtained from Cytec Inc. Canada, were used without further purification. All other reagents used were of analytical reagent grade.

## 2.2. PROCEDURE

The extraction process deals with the distribution of a solute in equal aliquots (10ml) between two immiscible solvents, one of which is aqueous and the other an organic solvent. The aqueous phase containing  $ZrOCl_2$  solution (0.001M) in HCl with requisite quantities of ferric chloride and aluminium chloride and the organic phase with TOA, Cyanex921, Cyanex923 and binary mixture of TOA with Cyanex921/ Cyanex923 in kerosene. The above two solutions were shaken for about twenty five minutes using thermostat shaker. The phases were allowed to settle for five minutes and then they were separated. The Zr(IV), Fe(III) and Al(III) concentration in the aqueous phase before and after the extraction was determined by Arsenazo (III) method<sup>26</sup> at 665 nm, 1,10-Phenanthroline method<sup>27</sup> at 510nm, Alizarin Red S method<sup>28</sup> at 510nm, respectively using an ELICO UV-Visible spectrophotometer. The distribution ratio (D) was calculated by taking the ratio of equilibrium concentration of metal ion in organic phase and that in the aqueous phase. The

concentration of the metal ion in the organic phase was calculated by using the mass balance i.e., the difference of metal concentration in the aqueous phase before and after the extraction. From D value, the percentage of extraction was calculated ( $\%E = 100(D/D+1)$ ). Stripping percentage was calculated by using the relation,  $\% \text{ stripping} = \frac{[M]_s}{([M]_o - [M])} \times 100$ , where  $[M]_o$  is the original metal ion concentration in the aqueous phase before extraction,  $[M]$  is the metal ion concentration in the aqueous phase after extraction and  $[M]_s$  is the metal ion concentration in the aqueous phase after stripping. The separation factor ( $\beta$ ) was calculated from the ratio of the respective D values of the metal ions ( $D_{Zr}/D_{Fe}$  or  $D_{Zr}/D_{Al}$ ).

## 3. RESULTS

### 3.1. Extraction of Zirconium (IV) in the presence of Fe (III):

The extraction of Zr(IV) from 4M HCl in the presence of 0.0005 M – 0.2 M Fe(III) has been studied using 0.1M TOA, 0.01M Cyanex 921, 0.01M Cyanex923 and binary mixture of 0.1M TOA and 0.01M Cyanex 921 / 0.01M Cyanex 923 in kerosene. It was observed that the extraction of  $1 \times 10^{-3}$  M Zr(IV) increased from 6.8% to 41.9% in case of 0.1M TOA, 37.6% to 72.4% in case of 0.01M Cyanex 921, 22.5% to 80.9% in the presence of 0.01M Cyanex 923. The extraction percentage varies from 20.4% to 89.6% and 24.5% to 94.9% with binary mixture of 0.1M TOA and 0.01M Cyanex 921 and 0.1M TOA/0.01M Cyanex 923, respectively. The increase in extraction may be due to the competition between two metal ions for the extractant<sup>29</sup>.

The data are presented in Fig 1 and Fig 2.

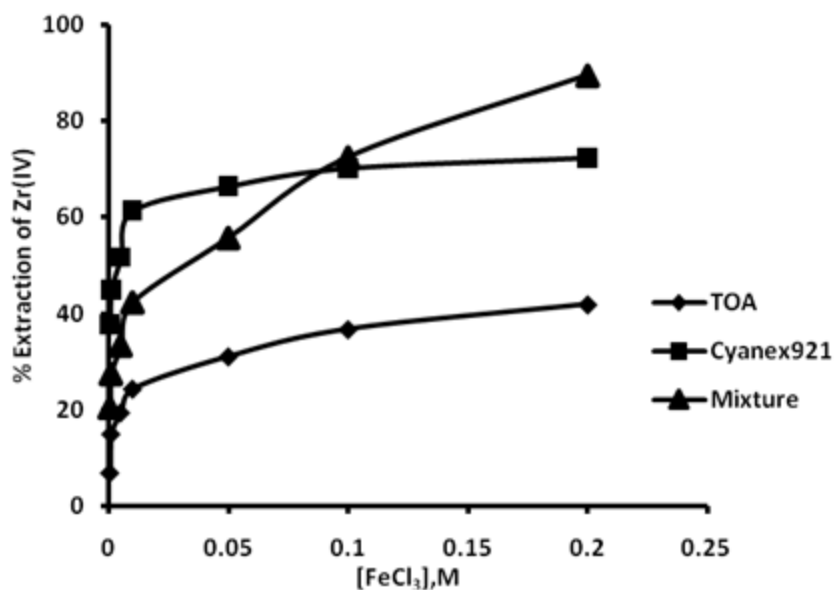


Figure 1

*Plot of %E versus [FeCl<sub>3</sub>], M in the extraction of 0.001M Zr(IV) from 4M HCl using 0.1M TOA, 0.01M Cyanex921 and mixture of 0.1M TOA with 0.01M Cyanex921*

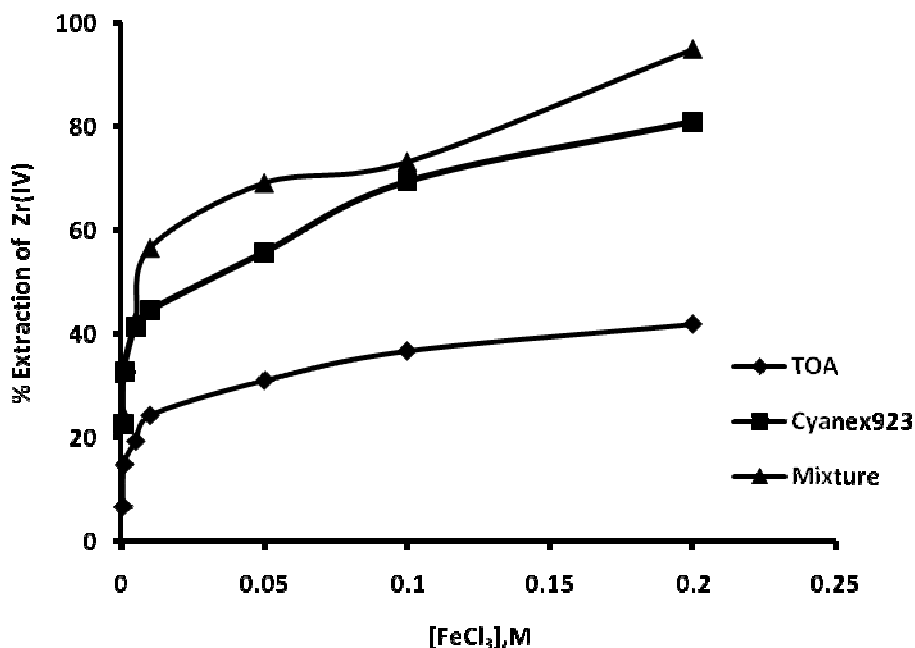


Figure 2

*Plot of %E versus [FeCl<sub>3</sub>], M in the extraction of 0.001M Zr(IV) from 4M HCl using 0.1M TOA, 0.01M Cyanex923 and mixture of 0.1M TOA with 0.01M Cyanex923.*

The separation factor( $\beta$ ) was evaluated by taking into consideration the distribution ratios of Zr(IV) and Fe(III) obtained under the conditions of maximum extraction of Zr(IV) and the data are presented

in (Table 1). It was found that the separation factor increases in the following order: Cyanex 923 < TOA + Cyanex 923 < TOA+Cyanex 921 when 0.1 M FeCl<sub>3</sub> was taken in the aqueous phase but with increase in Fe(III) concentration to 0.2M, order was :TOA + Cyanex 921 < Cyanex 923 < TOA + Cyanex 923. Based on the experimentally obtained  $\beta$ - values there is possibility of separation of Zr(IV) from Fe(III) in 4M HCl using mixture of 0.1M TOA and 0.01M Cyanex 921 ( $\beta$  =19.43) / Cyanex 923( $\beta$  =47.81) in kerosene.

Table 1

Values of distribution ratios (D) and Separation factors ( $\beta$ ) of Zr(IV) and Fe(III) with 4M HCl .

Aqueous phase	Organic phase	D <sub>Zr(IV)</sub>	D <sub>Fe(III)</sub>	$\beta$ (D <sub>Zr</sub> / D <sub>Fe</sub> )
0.001M Zr(IV)+ 0.1M FeCl <sub>3</sub>	0.1M TOA +0.01M Cyanex921	2.643	0.136	19.43
0.001M Zr(IV)+ 0.1M FeCl <sub>3</sub>	0.01M Cyanex923	2.265	0.413	5.48
0.001M Zr(IV)+ 0.1M FeCl <sub>3</sub>	0.1M TOA +0.01M Cyanex923	2.720	0.453	6.00
0.001M Zr(IV)+ 0.2M FeCl <sub>3</sub>	0.1M TOA +0.01M Cyanex921	8.588	0.981	8.75
0.001M Zr(IV)+ 0.2M FeCl <sub>3</sub>	0.01M Cyanex923	4.247	0.240	17.69
0.001M Zr(IV)+ 0.2M FeCl <sub>3</sub>	0.1M TOA +0.01M Cyanex923	18.457	0.386	47.81

### 3.2. Extraction of Zirconium (IV) in the presence of Al (III)

Studies were undertaken to extract and separate Zr(IV) and Al(III) from 4M HCl solution. In this respect 0.1M TOA, 0.01M Cyanex 921, 0.01M Cyanex 923 and binary mixture of TOA and Cyanex 921 / Cyanex 923 in kerosene at fixed organic to aqueous phase ratio of 1:1 were used to extract  $1 \times 10^{-3}$ M Zr(IV) and 0.0005M – 0.2M Al(III) from 4M HCl at a

shaking time of 25 minutes. The results obtained show that extraction of Zr(IV) increases from 12.3% to 49%, 38.3% to 81.4%, 29.7% to 85.5%, 21.7% to 90.3% and 24.5% to 94.9% with 0.1M TOA, 0.01M Cyanex 921, 0.01M Cyanex 923, mixture of 0.1M TOA and 0.01M Cyanex 921 and mixture 0.1M TOA and 0.01M Cyanex 923, respectively, with increase in added Al(III) concentration. The data are presented in Fig 3 and Fig 4.

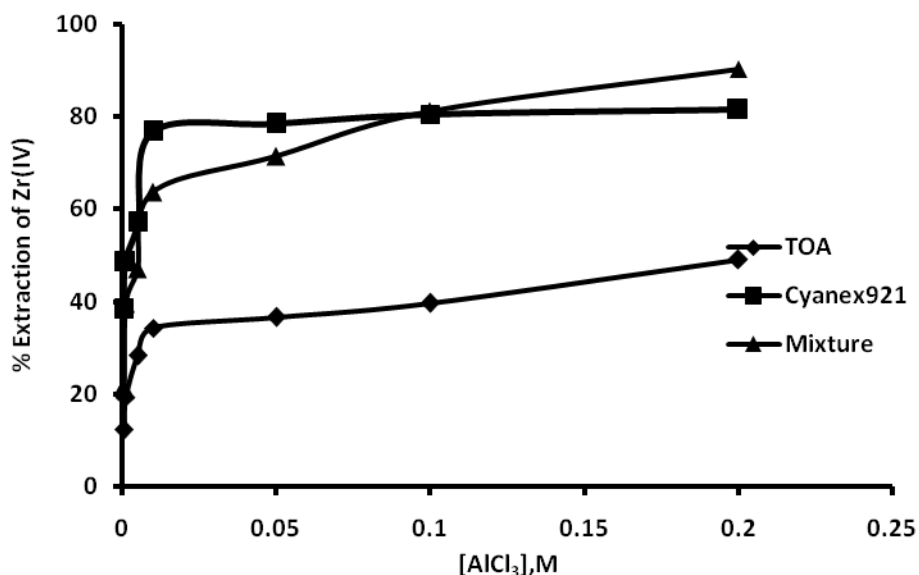


Figure 3

Plot of %E versus [AlCl<sub>3</sub>],M in the extraction of 0.001M Zr(IV) from 4 M HCl using 0.1M TOA,0.01M Cyanex921 and mixture of 0.1M TOA with 0.01M Cyanex 921.

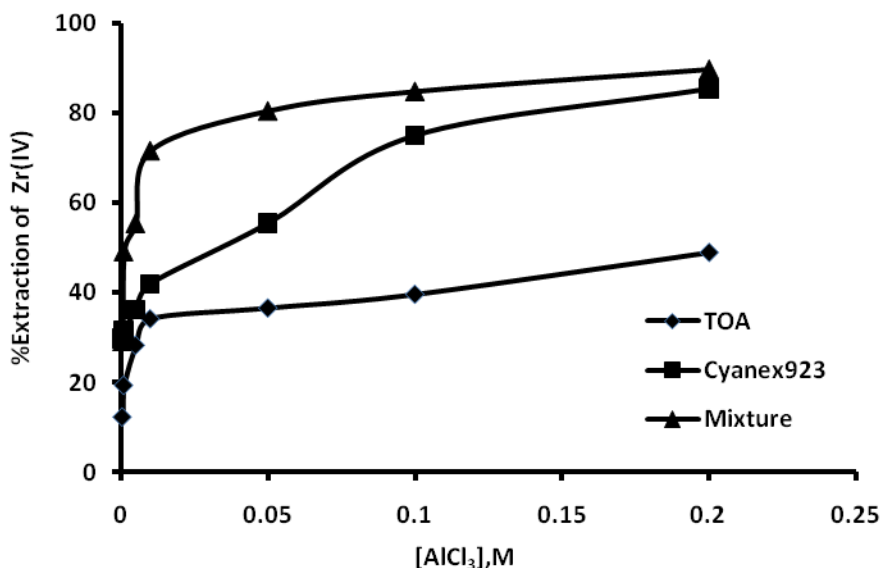


Figure 4

**Plot of %E versus [AlCl<sub>3</sub>], M in the extraction of 0.001M Zr(IV) from 4M HCl using 0.1M TOA, 0.01M Cyanex923 and mixture of 0.1M TOA with 0.01M Cyanex923.**

The separation possibilities were also studied and distribution ratio of Zr(IV) and Al(III) were estimated under the experimental conditions where extraction of Zr(IV) was maximum. From there,  $\beta$  values were calculated and presented in (Table 2). It was concluded that the separation factor ( $\beta = D_{Zr}/D_{Al}$ ) increases in the following order for 0.1M & 0.2M Al (III): TOA + Cyanex 921 < Cyanex 923 < TOA + Cyanex 923.

Table 2

**Values of distribution ratios (D) and Separation factor ( $\beta$ ) of Zr(IV) and Al(III) with 4M HCl .**

Aqueous phase	Organic phase	$D_{Zr}$	$D_{Al(III)}$	$\beta (D_{Zr}/D_{Al})$
0.001M Zr(IV)+ 0.1M AlCl <sub>3</sub>	0.1M TOA +0.01M Cyanex921	4.274	0.859	4.97
0.001M Zr(IV)+ 0.1M AlCl <sub>3</sub>	0.01M Cyanex923	3.00	0.291	10.30
0.001M Zr(IV)+ 0.1M AlCl <sub>3</sub>	0.1M TOA +0.01M Cyanex923	5.561	0.485	11.46
0.001M Zr(IV)+ 0.2M AlCl <sub>3</sub>	0.1M TOA +0.01M Cyanex921	9.348	0.585	15.97
0.001M Zr(IV)+ 0.2M AlCl <sub>3</sub>	0.01M Cyanex923	5.875	0.248	23.68
0.001M Zr(IV)+ 0.2M AlCl <sub>3</sub>	0.1M TOA +0.01M Cyanex923	8.681	0.289	30.03

### 3.4. STRIPPING

The loaded organic phase is stripped off the metal by the back extraction to the aqueous phase which is required for commercial extraction processes. Regeneration of the solvent is achieved by treating the solvent with alkali or acid solutions. The effect of various concentrations of strippants on the stripping of metal ions from the loaded organic solvent was studied at 25 °C and phase ratio 1:1. Zirconium was stripped in the presence of 0.2M FeCl<sub>3</sub> from loaded organic phase of TOA (0.1 M) and Cyanex 923(0.01 M) containing 86.53

mg/L and from TOA (0.1 M) and Cyanex 921(0.01 M) containing 81.70 mg/L of zirconium, respectively, with various stripping agents such as Na<sub>2</sub>CO<sub>3</sub> (0.01M-0.5M) and HNO<sub>3</sub> (0.01-0.25M) (Table-3). Stripping of Zr (IV) was 100% with 0.2M and 0.25M HNO<sub>3</sub> and with 0.4M and 0.50M Na<sub>2</sub>CO<sub>3</sub> in one step. The basic stripping agent like Na<sub>2</sub>CO<sub>3</sub> and low acid concentration compared to that taken for extraction deprotonate the amine salt and in turn helps in increase in stripping. Zirconium was stripped in the presence of 0.2M AlCl<sub>3</sub> from loaded organic phase of TOA (0.1 M) and

Cyanex 923(0.01 M) containing 81.79 mg/L and TOA (0.1 M) and Cyanex 921(0.01 M) containing 82.39 mg/L of zirconium respectively, with various stripping agents such as Na<sub>2</sub>CO<sub>3</sub> (0.01M-0.55M) and HNO<sub>3</sub> (0.01-0.30M) (Table-4). Stripping of Zr (IV) was 100% with 0.25 M

and 0.30 M HNO<sub>3</sub> and with 0.55M and 0.35M Na<sub>2</sub>CO<sub>3</sub> in one step. The tabulated data indicate that the investigated stripping agents could effectively strip Zr(IV) from the loaded organic phase solution, even in the presence of Fe(III) and Al(III).

**Table 3**  
**Percent stripping of the extracted Zr(IV) in presence of Fe(III) with 4M HCl from loaded organic phase.**

Strippant [HNO <sub>3</sub> ], M	%S (0.1M TOA+0.01M Cyanex923)	%S (0.1M TOA+0.01M Cyanex921)	Strippant [Na <sub>2</sub> CO <sub>3</sub> ], M	%S (0.1M TOA+0.01M Cyanex923)	%S (0.1M TOA+0.01M Cyanex921)
0.01	35.9	39.6	0.01	27.1	30.3
0.05	48.3	51.2	0.05	33.0	44.3
0.1	76.2	61.1	0.1	37.9	51.3
0.2	100	83.6	0.2	52.8	60.8
0.25		100	0.25	58.3	68.1
			0.3	77.7	70.5
			0.35	94.7	78.9
			0.40	100	84.4
			0.50		100

**Table 4**  
**Percent stripping of the extracted Zr(IV) in presence of Al(III) with 4M HCl from loaded organic phase.**

Strippant [HNO <sub>3</sub> ], M	%S (0.1M TOA+0.01M Cyanex923)	%S (0.1M TOA+0.01M Cyanex921)	Strippant [Na <sub>2</sub> CO <sub>3</sub> ], M	%S (0.1M TOA+0.01M Cyanex923)	%S (0.1M TOA+0.01M Cyanex921)
0.01	39.4	21.3	0.01	25.7	27.8
0.05	53.0	27.8	0.05	36.0	39.6
0.1	73.8	35.1	0.10	40.9	42.9
0.2	91.5	57.5	0.15	46.0	47.7
0.25	100	73.6	0.20	51.1	51.3
0.30		100	0.25	57.8	68.4
			0.30	64.7	80.6
			0.35	75.0	100
			0.40	82.0	
			0.50	94.8	
			0.55	100	

## 4. CONCLUSION

The separation of Zr(IV) and Fe(III) / Al(III) from 4M HCl is possible using binary mixture of 0.1M TOA and 0.01M Cyanex 923 in kerosene in a single stage. High separation factors ( $D_{Zr}/D_{Fe} = 47.81$  and  $D_{Zr}/D_{Al} = 30.03$ ) were obtained in the above investigations. It was found that stripping efficiency of HNO<sub>3</sub> is stronger than Na<sub>2</sub>CO<sub>3</sub> to recover 100% of Zr(IV) from the loaded organic phase containing binary mixture of 0.1M TOA

and 0.01M Cyanex 923 in the presence of 0.2M Fe(III) / Al (III). The developed method may be applied to recover Zr(IV) from a mixture solution similar in composition to that under consideration. The investigation will be carried out under varying extraction conditions such as temperature, salt concentration, etc. to know its suitability.

## 5. ACKNOWLEDGEMENT

The authors are thankful to Cytec Inc., Canada for providing the gift sample of Cyanex 923. The authors express their sincere thanks to authorities of Siksha'O' Anusandhan deemed to be University for their constant encouragement to carry out this research work. One of the authors (B.C.Bhatta) is grateful to authorities of College of Engineering and Technology, Bhubaneswar for granting permission to do the research work.

## REFERENCES

1. Elvers B, Hawkins S, Ravenscroft M, Rounsaville JF, Sculz G Ulmann's encyclopedia of industrial chemistry, VCH, Weinheim: (1989).
2. Prohit R, Devi S, Determination of nanogram levels of zirconium by chelating ion exchange and on-line preconcentration in flow injection UV-visible spectrophotometry, *Talanta*, 44 : 319-326, (1997).
3. Rajmane MM, Sargar BM, Mahamuni SV, Anuse MA, Solvent extraction of zirconium(IV) from succinate media with N-n-octylaniline, *J.Serb. Chem. Soc.* 71(3): 223-234,(2006).
4. Nandi B, Das NR, Battacharya SN, Solvent extraction of zirconium and hafnium ,*Solvent Extraction Ion Exchange* ,1 :141-202,(1983).
5. Biswas RK, Hayat MA, Solvent extraction of zirconium (IV) from chloride media by D2EHPA in kerosene, *Hydrometallurgy*, 63:149,(2002).
6. Mohammedi Z, Atik F, Impact of solvent extraction type on total polyphenols content and biological activity from tamarix aphylla (l.) karst. *International Journal of Pharma and Bio Sciences*,2(1):609-615
7. Das NR, Lahiri S, Liquid ion exchangers and their uses in the separation of zirconium, niobium, molybdenum, hafnium, tantalum and tungsten, *Solvent Extraction Ion Exchange*, 9 : 337-381, (1991).
8. Hubicki Z, Separation of zirconium (IV) from hafnium (IV) on various types of selective ion-exchangers, *Solvent Extraction Ion Exchange*, 6 : 183-205, (1988).
9. Trubet D, Monroy Guzman F, Le Naour C, Brillard L, Hussonnois M, Constantinescu O, Behaviour of Zr, Hf, Nb, Ta and Pa on macroporous anion exchanger in chloride-fluoride Media, *Analytica Chimica Acta*, 374: 149-158, (1998).
10. Pourreza N, Mouradzadegun A, Mohammadi S, Solid Phase extraction of zirconium as Arsenazo(III) complex on agar and spectrophotometric determination, *J.Iran. Chem. Soc.*, 8 (4): 951-957, (2011).
11. Kraus KA, Moore GE, Separation of zirconium and hafnium with anion exchange resins,*J. Am. Chem. Soc.*, 71 : 3263, (1949).
12. Banda Raju , Lee Hwa Young, Lee Man Seung, Separation of Zr and Hf from strong hydrochloric acid solution by solvent extraction with TEHA, *J Radioanal. Nucl. Chem*,295:1537(2013).
13. Sheng Z, Murtha MJ, Burnet G, The separation of metal chlorides by solvent extraction, *Sep. Sci. Technol.*, 18: 1647-1665, (1983).
14. Muhl P, Gloe K, Fisher C, Ziegenbalg S, Hoffman H, The application of liquid liquid extraction for the separation of iron during the production of alumina, *Hydrometallurgy*, 5 : 161-178, (1980).
15. Colussi I, Kikic I, Preti U, Cocco A, *Proceedings International Solvent Extraction Conference ISEC 83, Denver, CO, 1983, pp. 248.*



16. Mahi P, Bailey NT, Extraction of iron by Alamine 336, Chem. Indl. (London), 1: 18-21, (1985).
17. Cattrall RW, Ilic MZ, Proceedings International Solvent Extraction Conference ISEC 83, Denver, CO, 1983, pp.470.
18. Aue A, Skjutare L, Bjorling G, Reinhardt H, Rydberg, J, Proceedings International Solvent extraction Conference ISEC 71, The Hague, 1971, pp.447.
19. Chang Chih-Chien, Chiu Tai-ming, Hoh Ying-Chu, Wang Wei-Ko, Separation of iron from zirconium in concentrated hydrochloric acid solutions by solvent extraction, Hydrometallurgy, 17 : 1-13, (1986).
20. Taghizadeh M, Ghanadi M, Zolfonoun E, Separation of zirconium and hafnium by solvent extraction using mixture of TBP and Cyanex923, Journal of Nuclear Materials 412: 334-337, (2011).
21. Nayl AA, El-Nadi YA, Daoud JA, Extraction and separation of Zr(IV) and Hf(IV) from Nitrate Medium by some CYANEX Extractants., Separation Science and Technology, 44: 2956-2970, (2009).
22. Mishra PK, Chakravorty V, Dash KC, Das NR, Bhattacharyya SN, Extraction and separation of Zr, Nb and Hf by Aliquat336 and its mixtures with TOPO from acidic thiocyanate media, Journal of Radioanalytical and Nuclear Chemistry, Articles, 162 (2): 289-298, (1992).
23. Karve Manjusha A, Khopkar Shripad M, Application of liquid Anion Exchangers for the separation of zirconium and Hafnium, Analytical Sciences, 8 : 237-241(1992).
24. Ajaonkar HS, Dhadke PM, Solvent extraction separation of iron(III) and aluminium(III) from other elements with Cyanex302, Talanta, 44: 563-570, (1997).
25. Bhatta BC, Panda N, Mishra S, Extraction of Zr(IV) from hydrochloric acid with tri- octyl amine and Cyanex 921 in kerosene, International Journal of Minerals, Metallurgy and Materials, 20 (9): 823-828 (2013).
26. Onishi H, Sekine K, Spectrophotometric determination of zirconium, uranium, thorium and rare earths with arsenazo III after extractions with thenoyltrifluoroacetone and tri-n-octylamine, Talanta, 19 (4): 473-478, (1972).
27. Niazi A, Simultaneous Spectrophotometric Determination of Fe<sup>II</sup> and Fe<sup>III</sup> in Pharmaceuticals by Partial Least Squares with Chromogenic Mixed Reagents, Croatica Chemica Acta, 79 (4): 573-579, (2006).
28. Supian SM, Ling TL, Heng LY, Chong KF, Determination of Al(III) ion by using Alizarin Red S including its microspheres optical sensing material, Analytical Methods, 5 : 2602-2609, (2013).
29. Fathi Habashi, A text book of Hydrometallurgy, 2<sup>nd</sup> Edn, 458-464, (1993).