CHAPTER-4
CHAPTER 4

SYNTHESIS, CHARACTERIZATION AND ION EXCHANGE PROPERTIES OF THREE COMPONENT ION EXCHANGER-ZIRCONIUM (IV) IODO ARSENATE

IV-1 INTRODUCTION

Now a days, an ion exchange technology has versatile applications in numerous fields. The ion exchange materials have been the essential constituents for a number of processes attaining to analysis pre concentration and recovery of a number of precious metals, rare earth chemicals from aqueous as well as non-aqueous system. During the last decades an active research has been undertaken in different laboratories in order to find new selective ion exchangers and absorbents. As a result of the intensive work done, a wide variety of synthetic in organic compounds exhibiting ion exchange properties were found, specifically, metal hydrous-oxides hetero poly acids metal ferrocyanides\[^{[1-5]}\]. Some of these compound due to their high thermal stability, resistance to the oxidization and radiation and good selectivity to certain ions, appear as promising material
capable of operating in extreme conditions (high radiation, temperature, pressure, presence of oxidants, organic solvents and high concentration of background electrolyte etc.) in which organic ion exchange resins fail to work efficiently.

Ion exchangers have played a prominent role in water processing and in the chemical industry. Meeting the stringent coolant purity requirement of nuclear industry is solely attributable to ion exchangers. In the last decade, ion exchangers have been used extensively in the chemical decontamination process for metal ion recovery, regeneration of decontaminants and removal of the formulation chemicals from the coolant [6]. Therefore there is a continuing need to find new inorganic ion exchangers, which are capable of removing toxic substances from an aqueous effluent [7]. As they have good stability toward temperature ionizing radiation and oxidizing solutions.

Synthetic inorganic ion exchangers based on tetravalent metals have been objects of considerable study in recent years because of their selectivity and intercalation properties [8-16]. Zirconium based ion exchangers have received attention because of their excellent ion exchange properties and some important chemical applications in the field of ion exchange, ion exchange membrane and solid state electrochemistry.
Various number of hetero poly acid salts based on tin (IV),
titanium (IV) and Zirconium (IV) etc, have been studied and
reported in earlier literature as good ion exchange material
exhibiting improved properties over the simple salts of metals\textsuperscript{[17-20]}. Inorganic ion exchangers of the class of TMA salts have been
extensively studied in the field of separation science and catalysis.
However attempts have been made to study the transport
properties of these materials\textsuperscript{[21-23]}. The mechanism of diffusion and
ionic transport in crystalline $\alpha$-Zirconium phosphate has been
studied in detail\textsuperscript{[24]}. The number of water molecules depends upon
the method of preparation, drying condition etc. They possess
structural hydroxyl protons, which are responsible for their ion
exchange behavior. When these-OH groups are hydrated, the
protons can easily move on the surface, thus accounting for their
conductivities which depend strongly on relative humidity, the
surface area and the degree of crystallinity\textsuperscript{[25]}.

A wide range of materials is available for the ion exchange
treatment of radioactive liquids. These materials are available in a
variety of forms, have widely differing chemical and physical
properties and can be naturally occurring.

Ion exchange materials can be categorized according to their
suitability for different applications, nuclear grade organic ion
exchange resins are normally used when liquids from primary
circuits or fuel pools are purified. The type of material to be used is selected based on its ability to remove impurities and ions and to control pH. Nuclear grade ion exchangers are similar to commercial grade resins but have a tighter specification for particle size and composition. Organic resins are often used for a number of treatment cycles by eluting the absorbed radioisotopes with suitable solutions and then restoring the ion exchanger to its original ionic form before its reuse.

Inorganic materials are commonly used for the treatment of liquid waste streams for which very high chemical cleanliness is not required; for example, inorganic ion exchange media can be used in systems in which contaminated liquid concentration in the liquid to allow its reclassification. Highly selective inorganic materials also make it possible to utilize ion exchange in the event that very high concentrations of competing ions are present. Inorganic ion exchangers are almost entirely used on an once through basis only.

Even if an inorganic ion exchanger is highly selective for a certain radionuclide, it needs to meet several other requirements to become a product that can be used in industrial scale separation process. Some inorganic ion exchangers can be produced in a granular form, but the granules are often of a low mechanical
strength and when in contact with aqueous solutions, they break down and may peptize to produce colloidal particles.

To overcome the problem of poor physical strength of the intrinsic exchanger granules, methods for incorporating inorganic ion exchangers into supporting binder materials, both inorganic and organic, have been developed.

IV-2 Experimental Section-

IV-2.1 Reagent and Chemicals-

Zirconium (IV) oxy chloride, Sodium arsenate and potassium iodate were obtained from CDH (India) and all other reagents and chemicals were of analytical grade.

IV-2.2 Instrumentation-

pH measurements was performed using an Elico (India) L1-10 model pH meter. FTIR model shimadzu 820 PC, Philips X-ray unit, Duprot 900 and 950 thermal analyser and an electric shaking machine were used for IR studies, X-ray diffraction, thermal analysis and shaking respectively. SEM images were obtained by using a JEOL JSM 840 A electron microscope.
IV-2.3 Synthesis of ion exchange materials-

The ion exchange material was synthesized by mixing 0.10 M Zirconium oxy chloride solution gradually to a mixture of potassium iodate and sodium arsenate solution with continuous stirring in various mixing volume ratios and is given in Table-4.1. The gelatinous precipitate so obtained was allowed to settle down for 24 h at room temperature. The supernatant liquid was removed and the precipitate was washed with distilled water and finally filtered under pressure. The product was dried at 40± 1°C in an electric oven. The material was broken down into small granules by placing in distilled water. The granules were converted into H⁺ form by treating with 1M HNO₃ solution for 24h. The material was then washed several times with distilled water to remove excess of acid and finally dried at 40±1°C. Six samples are prepared by using above same method.
Table 4.1

Conditions of Synthesis and Few Properties of Different samples of Zirconium (IV) iodo arsenate.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Molar Concentration</th>
<th>Mixing Ratio (v/v/v)</th>
<th>pH</th>
<th>Appearance of beads after drying at 40°C</th>
<th>I.E.C. Meq/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zr(M)</td>
<td>IO₃(M)</td>
<td>As₂O₃(M)</td>
<td>1:1:1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1:1:1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1:2:1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2:1:2</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2:2:1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1:3:2</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2:3:2</td>
<td>1</td>
</tr>
</tbody>
</table>
IV.3- CHARACTERIZATION

IV-3.1 Determination of ion exchange capacity-

The ion exchange capacity of an exchanger is a measure of its total content of exchangeable ions, and is conventionally expressed in terms of the total number of equivalents of ion per kilogram (milli-equivalents per gram) of the exchanger in its dry state and in a given univalent ionic form. Ion exchanger capacity of the synthesized compound sample was determined by column process\textsuperscript{[261]}. The ion exchanger in H\textsuperscript{+} form was placed in a glass column containing a cotton support. Different salt solutions were used as eluants. 200 ml of each electrolyte was passed through the ion-exchanger column made from 0.5 gram of the exchanger. Hydrogen ions eluted from the column were determined titrimetrically. Ion exchange capacity of the material was determined for some uni and bivalent cations.

The ion exchange capacity (IEC) was calculated using the following equation:

\[
IEC = \frac{V \times M}{W_{dry}}
\]

Where, IEC is the ion exchange capacity (Meq g\textsuperscript{-1}), V is the added titrant volume at the equivalent point (ml), M is the Molar
The concentration of the titrant and \( W_{\text{dry}} \) is the dry mass of the sample (g). The results are summarized in Table-4.2.

**IV-3.2 pH Titration**

The pH titration of material was performed by the method of toppe and pepper. In this method 0.50 gram of exchanger was equilibrated with varying amounts of 0.1M NaCl and NaOH solutions. pH titration curve is shown in figure 4.1.

**IV-3.3 Thermal Stability**

The ion exchanger sample was dried at different temperature from 40\(^{0}\)C to 600\(^{0}\)C in a muffle furnace. Thermal stability of the material was evaluated by heating it at various temperatures for one hour in a muffle furnace and the Na\(^{+}\) ion exchange capacity in meq g\(^{-1}\) dry exchanger was determined. Results are summarized in Table-4.3.
Figure 4.1 pH Titration Curve of Zirconium (IV) Iodo Arsenate
IV-3.4 Chemical Composition and chemical stability

For the determination of chemical composition of the sample ZIA-6, 0.1 gram of exchanger was dissolved in minimum amount of hot concentrated sulphuric acid. The solution was diluted to 100ml with DMW. The amounts of Zirconium and iodate were determined spectrophotometrically using alizarin red-S and pyrogallol as colouring reagents respectively. Arsenate was determined titrametrically using the standard method\textsuperscript{[28]}.

500mg of the sample ZIA-6 was shaken with 50ml of the various solution at 30±2\textdegree C for 6 hours. The amounts of Zirconium iodate and arsenate released in the solutions were determined spectrophotometrically\textsuperscript{[29]}. The material is found to be quite stable in lower concentration of mineral acid, such as HCl, H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3}. The sample is quite stable in organic acids.

Chemical stability, especially low solubility, is important for the use fullness of inorganic ion exchange materials. Most Zeolites for example, only work over a limited pH range (4-9), since they are soluble both in acidic and alkaline media. Of the inorganic ion exchange materials developed so far, those based on pure or mixed Zirconium or titanium oxides have been shown to be the most stable.
IV-3.5 Distribution Studies-

The distribution studies of various metal ions in distilled water and nitric acid were carried out by the batch equilibrium technique for this purpose, 0.50 gram of the exchanger in H\(^+\) form was equilibrated with 25.0 ml of 0.01 M solutions of different metal ions.

The mixture was shaken for 6 hours to attain equilibrium. The amount of metal ions left in the solutions was then determined by titrating against 0.01M EDTA solution using appropriate indicators.

The Kd values, were calculated using the following equation

\[
K_D = \frac{(1-F)V}{F \times M}
\]

where, I and F denote the volume of EDTA solution required before and after equilibrium respectively, V is the solution volume in ml and M is the mass of the exchanger in gram.

IV-3.6 Metal ion Separation-

For binary separations, 5 gram of the ion exchangers in H\(^+\) form was taken in glass column (30x1.1cm dia). The column was washed thoroughly with deionized water and the mixture to be separated was loaded on it maintaining a flow rate of 0.5ml min\(^{-1}\) in
all the separations, the cation concentration was maintained at 0.01M concentration; 5ml of each metal ion solution was taken.

IV-3.7 X-Ray Study

X-ray studies were carried out using a Philips pw-1730 high angle diffracto meter (Poland) Cu-Ka (Ni Filter) radiation and it was found that material shows amorphous in character.

IV-3.8 FTIR Spectrum-

FTIR spectrum of sample ZIA-6 was obtained by KBr disc method. FTIR spectrum of the prepared sample was obtained by using a FTIR model shimadzu 820 PC.

IV 3.9 Scanning electron micrographs-(SEM)-

Surface morphology of the dried exchanger was investigated using SEM. Figure-4.5 shows the scanning electron micrographs of the exchanger.

IV-4 Result and Discussion-

The results from the study of the ion exchange capacity of various samples of Zirconium (IV) iodo arsenate are presented in Table 4.1. The improvement in the ion exchange capacity and
chemical stability seemed to be much higher for sample ZIA-6 and therefore this sample was selected for detailed studies.

The ion exchange capacities for mono- and bivalent metal ions are shown in Table 4.2 these results indicate that ion exchange selectivity of the material is different for different cations. The ion exchange capacities in meq g⁻¹ dry exchanger for various metal ions follow the order:

\[ \text{Li}^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{Ca}^{2+} > \text{Sr}^{2+} . \]
Table 4.2

Ion Exchange Capacity (Meq g⁻¹ dry exchangers) of Zirconium (IV) iodo arsenate (Sample ZIA-6 for various metal ions).

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Cation</th>
<th>Salt Used</th>
<th>I.E.C. (Meq g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li⁺</td>
<td>LiCl</td>
<td>2.45</td>
</tr>
<tr>
<td>2</td>
<td>Na⁺</td>
<td>NaCl</td>
<td>2.30</td>
</tr>
<tr>
<td>3</td>
<td>K⁺</td>
<td>KCl</td>
<td>1.40</td>
</tr>
<tr>
<td>4</td>
<td>Mg²⁺</td>
<td>Mg(NO₃)₂</td>
<td>1.58</td>
</tr>
<tr>
<td>5</td>
<td>Sr²⁺</td>
<td>Sr(NO₃)₂</td>
<td>1.36</td>
</tr>
<tr>
<td>6</td>
<td>Ca²⁺</td>
<td>Ca(NO₃)₂</td>
<td>1.26</td>
</tr>
</tbody>
</table>
The pH titration curve [figure 4.1] of ZIA-6 performed in NaCl-NaOH system shows one inflexion point indicating that the exchanger in nonfunctional.

In order to examine the effect of heating temperature on the ion exchange capacity. The material was heated at 40, 100, 200, 300, 400, 500 and 600°C and ion exchange capacity for Na⁺ ion was found to be 2.30, 2.05, 1.50, 0.70, 8.30, 0.20 and ~0 meq g⁻¹ dry exchanger respectively. The results are summarized in Table 4.3.

These observations reveal that IEC decreases with increasing temperature. Varshney et al [30] reported similar results while studying the Zirconium (IV) alumino phosphate. The material was found to be fairly stable in lower concentration of mineral acids such as HCl, H₂SO₄, HNO₃ and acetic acid. The ion exchanger completely dissolved in 2M H₂SO₄ and 2M NaOH solution. The results are shown in Table 4.4.
**Table 4.3**

Effect of heating temperature on the ion exchanger capacity of Zirconium (IV) iodo arsenate

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Heating Temperature</th>
<th>Colour of beads after drying</th>
<th>Ion exchanger Capacity Meq g⁻¹ dry exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>White</td>
<td>2.30</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>White</td>
<td>2.05</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>Brown</td>
<td>1.50</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>Brown</td>
<td>0.70</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>Brown</td>
<td>0.30</td>
</tr>
<tr>
<td>6</td>
<td>500</td>
<td>Black</td>
<td>0.20</td>
</tr>
<tr>
<td>7</td>
<td>600</td>
<td>Not Stable</td>
<td>0.00</td>
</tr>
</tbody>
</table>
### Table 4.4

**Chemical Stability of Zirconium (IV) iodo arsenate in different Solutions**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Solution</th>
<th>Zr(IV) Released (mg/50ml)</th>
<th>IO₃ released (mg/50ml)</th>
<th>As₂O₃ Released (mg/50ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.1M HClO₄</td>
<td>0.00</td>
<td>0.34</td>
<td>0.41</td>
</tr>
<tr>
<td>3</td>
<td>1.0M HClO₄</td>
<td>0.46</td>
<td>0.89</td>
<td>0.93</td>
</tr>
<tr>
<td>4</td>
<td>0.1M HNO₃</td>
<td>0.00</td>
<td>0.13</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>1.0M HNO₃</td>
<td>0.36</td>
<td>0.82</td>
<td>0.21</td>
</tr>
<tr>
<td>6</td>
<td>0.1M HCl</td>
<td>0.00</td>
<td>0.00</td>
<td>0.14</td>
</tr>
<tr>
<td>7</td>
<td>1.0 M HCl</td>
<td>1.26</td>
<td>0.67</td>
<td>0.50</td>
</tr>
<tr>
<td>8</td>
<td>1.0M CH₃COOH</td>
<td>0.00</td>
<td>0.21</td>
<td>0.32</td>
</tr>
<tr>
<td>9</td>
<td>0.1M NaOH</td>
<td>0.91</td>
<td>2.95</td>
<td>3.05</td>
</tr>
<tr>
<td>10</td>
<td>2.0 M NaOH</td>
<td>Completely</td>
<td>Dissolved</td>
<td></td>
</tr>
</tbody>
</table>
The chemical composition data of material suggests the molar ratio of Zr (IV), IO₃ and As₂O₃ as 2:1:3 which may point to the following tentative formula.

\[ [(ZrO)_2 \cdot (IO_3) \cdot (As_2O_3)_3 \cdot nH_2O] \]

On the basis of thermal stability measurements it was observed that the weight due to presence of water molecules in the gel in 9.2% of the total weight. The number of such molecules per mole of the exchanger can be determined on the basis of Alberti's equation \(^{[31]}\).

\[ 18n = \frac{n(M + 18n)}{100} \]

Where \( n \) is the present water content and \( (m+18n) \), the molecular weight of the material.

**Calculation for \( n \):**

Molecular weight of \( \{ZrO\}_2 \cdot (IO_3) \cdot (As_2O_3)_3 \)

\[ \Rightarrow (ZrO)_2 = (91.22+15.99)_2 = 214.42 \]

\[ (IO_3) = (126.90+15.99\times3) = 174.07 \]
\[
(\text{As}_2\text{O}_3)_3 = (74.92 \times 2 + 15.99 \times 3)_3 = 593.43
\]

Molecular weight of the material

\[
= 214.42 + 174.87 + 593.43
\]

\[
= 982.72
\]

\[
18n = \frac{n(m + 18n)}{100}
\]

\[
1800n = n(m + 18n)
\]

\[
1800n - 9.2 \times 982.72 + 10n \times 9.2
\]

\[
1800n = 9041.024 + 165.6n
\]

\[
1634.4n = 9041.024
\]

\[
n = \frac{9041.024}{1634.4} = 5.53
\]

The FTIR of Zirconium (IV) iodo arsenate shows broad bands in the 3400 cm\(^{-1}\) region characteristic of asymmetric and symmetric hydroxo-OH and aqua-OH stretching frequency. A sharp medium band at 1620 cm\(^{-1}\) is attributed to the aqua (H-OH) bending. The spectrum also shows weak band in the region 1000-
500 cm\(^{-1}\) indicating the presence of iodate and metal oxide. The FTIR spectrum is shown in figure 4.3.

Absence of sharp peaks in the X-ray diffraction pattern of Zirconium (IV) iodo arsenate indicates that the material is amorphous in nature. Graph of X-ray diffraction is shown in figure 4.4.

Surface morphology of the dried exchanger was investigated using SEM. It is shown in figure 4.5. This figure shows the scanning electron micrographs of 10% ZIA. The distribution of inorganic particles is relatively uniform in the organic matrix. Exchanger is compact with low degree of prosily. In this figure no phase separation was observed, suggesting that the synthesized exchanger was homogeneous in nature.
Figure 4.3 I.R Spectrum of Zirconium (IV) Iodo Arsenate
Figure 4.4 X-ray diffraction pattern of Zirconium (IV) Iodo Arsenate.
Figure 4.5 SEM images of a sample of Zirconium (IV) lodo Arsenate
In order to explore the potential of this cation exchange material in the separation of metal ions, distribution studies for 10 metal ions were performed. The presence of other electrolytes in metal ion solution strongly affects the $K_D$ value of the metal ion $K_d$ values change depending on the ionic strength and pH of the electrolyte. The degree of ionization of the ionic groups of the exchanger depends on the acid or base strength of the groups i.e. on their $pK$ value. The acid groups become predominantly nonionic, and the apartment capacity, and hence the $K_d$ values thus fall off based on such a study a proper electrolyte can be selected for the elution of a particular metal ion from the column of the exchanger when a metal ion pair is to be separated using a column of the exchanger, the $K_d$ value of particular metal ion in a particular further gives us a guideline to separate out distribution coefficient ($K_D$) calculated for several metal ions in aqueous and various electrolyte media. The distribution studies showed that the material was found to possess exceptional high $K_D$ values for Pb(II). Pb(II) has been considered as a major polluting material in water.

The Table 4.5 reveals that all the metal ions except Ca$^{2+}$, Al$^{3+}$, Ba$^{2+}$ exhibit exceptionally higher $K_D$ values in 0.02M CH$_3$COOH media than in distilled water. Similar observation have been made by others.$^{[32]}$
Table 4.5

$K_0$ values of Metal ions on Zirconium (IV) iodo arsenate in different Solvent.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Metal ions</th>
<th>DMW</th>
<th>0.01M HNO$_3$</th>
<th>0.1M HNO$_3$</th>
<th>1M HNO$_3$</th>
<th>0.01M HCl</th>
<th>0.1M HCl</th>
<th>1M HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al$^{3+}$</td>
<td>9300</td>
<td>4600</td>
<td>3300</td>
<td>2250</td>
<td>3200</td>
<td>1820</td>
<td>1600</td>
</tr>
<tr>
<td>2</td>
<td>Ba$^{2+}$</td>
<td>3016</td>
<td>1100</td>
<td>932</td>
<td>750</td>
<td>1740</td>
<td>1220</td>
<td>700</td>
</tr>
<tr>
<td>3</td>
<td>Ca$^{2+}$</td>
<td>1755</td>
<td>1200</td>
<td>660</td>
<td>640</td>
<td>1050</td>
<td>510</td>
<td>450</td>
</tr>
<tr>
<td>4</td>
<td>Cu$^{2+}$</td>
<td>7950</td>
<td>3800</td>
<td>1540</td>
<td>1050</td>
<td>2100</td>
<td>880</td>
<td>810</td>
</tr>
<tr>
<td>5</td>
<td>Co$^{2+}$</td>
<td>3700</td>
<td>1650</td>
<td>880</td>
<td>800</td>
<td>1210</td>
<td>820</td>
<td>790</td>
</tr>
<tr>
<td>6</td>
<td>Cd$^{2+}$</td>
<td>4500</td>
<td>1224</td>
<td>904</td>
<td>750</td>
<td>1350</td>
<td>1000</td>
<td>900</td>
</tr>
<tr>
<td>7</td>
<td>Hg$^{2+}$</td>
<td>4200</td>
<td>2800</td>
<td>1604</td>
<td>1066</td>
<td>2033</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>8</td>
<td>Mg$^{2+}$</td>
<td>1600</td>
<td>1332</td>
<td>900</td>
<td>750</td>
<td>1500</td>
<td>840</td>
<td>700</td>
</tr>
<tr>
<td>9</td>
<td>Pb$^{2+}$</td>
<td>8600</td>
<td>8700</td>
<td>7200</td>
<td>1150</td>
<td>7700</td>
<td>200</td>
<td>1250</td>
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<tr>
<td>10</td>
<td>Sr$^{2+}$</td>
<td>2150</td>
<td>1050</td>
<td>850</td>
<td>520</td>
<td>1220</td>
<td>800</td>
<td>620</td>
</tr>
</tbody>
</table>
A study of the distribution behavior of metal ions in aqueous as well as in various electrolyte media gives an indication of the possible binary metal separations as well as the eluants that could be used for separation $K_D$ values suggest the possibilities for many important binary separations. Based have been carried out four sets of metal ions: Pb(II)-Mg(II), Pb(II)-Cd(II), Pb(II)-Cu(II) and Pb(II)-Th(IV). The details of these separation studies are presented in Table 4.6. To elute Pb(II), 0.02M CH$_3$COOH is used to elute Th(IV). ZIA exhibits a 65-98% separation efficiency for these metal ions in the following order: Pb(II)(81.3)-Th(IV) (98.0) > Pb(II)(73.2) - Cu(II)(90.4) > Pb(II)(72.2) – Cd(II)(94.3) > Pb (II) (64.9) - Mg(II)(95.0). Through the separation factor is very low for Pb(II)-Cu(II). The separation is never these found to be quite efficient.

Load Selective TMA salts have been reported by Varshney and Coworkers for tin(IV), antimonate and polyacrylonitrile thorium(IV) phosphate$^{[23]}$. 
### Table 4.6

Binary Separation of Metal ions Using ZIA.

<table>
<thead>
<tr>
<th>No.</th>
<th>Separation achieved</th>
<th>$\alpha = \frac{K_{d1}}{K_{d2}}$</th>
<th>Eluant Used</th>
<th>Metal ion (mg)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pb(II)-Mg(II)</td>
<td>26.46</td>
<td>0.02M HClO$_4$, Pb(II) &amp; 0.02M NH$_4$NO$_3$, (Mg)</td>
<td>Loaded: 0.9177, Eluted: 0.5956</td>
<td>64.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2027, 0.1926</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pb(II)-Cd(II)</td>
<td>9.55</td>
<td>0.02M HClO$_4$, Pb(II) &amp; 0.02M NH$_4$NO$_3$, (Cd)</td>
<td>Loaded: 0.1829, Eluted: 0.1725</td>
<td>94.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.7333, 0.5295</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pb(II)-Cu(II)</td>
<td>9.05</td>
<td>0.02M HClO$_4$, (Pb) &amp; 0.02M Ni$_4$NO$_3$, (Cu)</td>
<td>Loaded: 0.6631, Eluted: 0.5995</td>
<td>90.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8176, 0.5905</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Pb(II)-Th(IV)</td>
<td>40.95</td>
<td>0.02M HClO$_4$, (Pb) &amp; 0.02M CH$_3$COOH, (Th)</td>
<td>Loaded: 0.6951, Eluted: 0.6812</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8087, 0.6795</td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES


