CHAPTER-5
CHAPTER-5

NEW METHOD OF SYNTHESIS OF TITANIUM (IV)

CHLORO TUNGSTATE AND ITS CHARACTERIZATION

AS AN INORGANIC EXCHANGER

5.1 INTRODUCTION

Heteropolyacid salts of tin (IV) and zirconium (IV) are reported in literature having better ion exchange properties than their single salts\textsuperscript{1-7}. Synthetic inorganic ion exchangers are generally produced as gelatinous precipitates rapidly by mixing the elements of group III A to IV A of the periodic table usually at room temperature.

The early ion exchangers were largely inorganic in origin. In the recent years, the interest in the inorganic ion exchangers has been revived with the need for high temperature separation of ionic components in radioactive wastes. In order to accomplish such operations, high selective exchangers are required which are not only stable at high temperature but also have ion exchange properties unaffected by the acidity at high radiation levels. Organic ion exchange resins are not suitable for such applications, as changes in capacity and selectively take place on exposure to radiation. Also the degradation takes place at the high temperature.
A large number of inorganic ion exchangers were prepared by mixing phosphoric, arsenic, molybdic, antimonie and vanadic acids with Zirconium, Tin, Titanium, Cerium, Bismuth, and Tantalum etc. Alberti\textsuperscript{[5]} and Clearfield\textsuperscript{[8]} devoted their studies mainly on the crystalline materials with a view to evaluate their structures based on X-ray studies. The analytical studies were initiated and exhaustively made by the research group of Qureshi\textsuperscript{[11-16]} who mainly concentrated on the amorphous materials. It was based on the observation that in general the gel type materials from good granules or pallets suitable for column operation and thus column chromatographic separation are easily achieved with these materials as compared to the crystalline ones\textsuperscript{[17]}.

Ion exchange materials with higher selectivity are continuously being investigated.\textsuperscript{[18]} Amongst the most important inorganic ion exchangers studied are synthetic clay minerals, heteropoly acid salts, hydrous oxides and tetravalent metal acid salts.

Amongst these, TMA salts have been the most widely, studied due their excellent thermal stability and chemical resistivity. In this respect, TMA salts have proved to be superior to many organic resins\textsuperscript{[19-21]}. TMA salts have the general formula, M (IV)(H\textsubscript{XO\textsubscript{4}}\textsubscript{n}H\textsubscript{2}O, where M = Zr, Ti, Ce,
Th, Ti etc. and X=P, Mo, W, As, Sb etc. The protons present in the structural hydroxyl groups of these cations and thus act as cation exchangers.

5.2 EXPERIMENTAL SECTION

5.2.1 REAGENTS AND CHEMICALS

Ti(IV) chloride, sodium tungstate and Potassium chlorate were obtained from CDH (India) and all other reagents and chemicals were of analytical grade.

5.2.2 INSTRUMENTATION

pH measurements were performed using an Elico (India) LI-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, an electron microscope. An electric thermostat oven (Microsil, India) was used for drying the samples.

5.2.3 SYNTHESIS OF ION EXCHANGE MATERIALS

The ion exchange material was synthesized by mixing 1.0 M Ti(IV) chloride solution gradually to a mixture of sodium tungstate in the presence of sulphuric acid (5N), H₂O₂ (0.3%) and potassium chlorate (5N).
Flocculating agent was added to reaction mixture. The whole process of synthesis is carried out at pH 1. Reaction time is of 1 hr. 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 suction 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 were prepared by using above same method. Results are summarized in table 5.1.
Table 5.1: Condition of Synthesis and Properties of different samples of Titanium(IV) Chloro Tungstate

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Molar Concentration</th>
<th>Mixing Ratio</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>Ti(M)</td>
<td>ClO₃(M)</td>
<td>W₂O₇(M)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1:1:1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1:2:1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2:1:2</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2:2:1</td>
<td>1</td>
</tr>
<tr>
<td>5*</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3:2:1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3:1:2</td>
<td>1</td>
</tr>
</tbody>
</table>
5.3 CHARACTERIZATION

5.3.1 DETERMINATION OF ION EXCHANGE CAPACITY

Ion exchanger capacity of the synthesized compound sample was determined by column process\textsuperscript{[22]}. The ion exchanger in H\textsuperscript{+} form was placed in a glass column containing a cotton support. Different salt solutions were used as eluents. 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 mono and bivalent cations.

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

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

where, IEC is the ion exchange capacity (Meq g\textsuperscript{-1}), \(V\) the added titrant volume at the equivalent point (ml), \(M\) the molar concentration of the titrant and \(W_{\text{dry}}\) is the dry mass of the sample (g). The results are given in Table 5.2.
Table 5.2: Ion Exchange Capacity (Meg g⁻¹ dry exchangers) of Titanium Chloro Tungstate (Sample TiCT-5 for various metal ions)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Cation</th>
<th>Salt Used</th>
<th>I.E.C. (Meg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li⁺</td>
<td>LiCl</td>
<td>1.40</td>
</tr>
<tr>
<td>2</td>
<td>Na⁺</td>
<td>NaCl</td>
<td>1.32</td>
</tr>
<tr>
<td>3</td>
<td>K⁺</td>
<td>KCl</td>
<td>1.38</td>
</tr>
<tr>
<td>4</td>
<td>Mg²⁺</td>
<td>Mg(NO₃)₂</td>
<td>1.45</td>
</tr>
<tr>
<td>5</td>
<td>Sr²⁺</td>
<td>Sr(NO₃)₂</td>
<td>1.44</td>
</tr>
<tr>
<td>6</td>
<td>Ca²⁺</td>
<td>Ca(NO₃)₂</td>
<td>1.24</td>
</tr>
</tbody>
</table>

5.3.2 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 5.1
Figure – 5.1

pH titration curve of Ti(IV) Chlorotungstate

Volume of NaOH added (ml)
5.3.3 **THERMAL STABILITY**

The ion exchanger sample was dried at different temperature from 40\(^{\circ}\)C to 600\(^{\circ}\)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.

**Table-5.3: Effect of heating temperature on the ion exchanger capacity of Titanium (IV) Chloro Tungstate.**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Heating Temperature</th>
<th>Color 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>1.35</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>White</td>
<td>1.05</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>Brown</td>
<td>0.90</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>
5.3.4 CHEMICAL COMPOSITION AND STABILITY

For the determination of chemical composition of the sample TiCT-5, 0.1 gram of exchanger was dissolved in minimum amount of hot concentrated sulphuric acid. The solution was diluted to 100 ml with DMW. The amounts of Titanium and chlorate were determined spectrophotometrically using Alizarin red-S and pyrogallol as colouring reagent respectively. Tungstate was determined titrametrically using the standard method[23].

500 mg of the sample TiCT-5 was shaken with 50 ml of the various solutions at 30±2°C for 8 hours. The amounts of Titanium, Chlorate and Tungstate released in the solutions were determined spectrophotometrically[24]. The material is found to be quite stable in lower concentration of mineral acid, such as HCl, H₂SO₄ and HNO₃. The sample is quite stable in organic acids.

Chemical stability, especially low solubility, is important for the usefulness 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. The results are shown in Table 5.4.
Table 5.4: Chemical Stability of Titanium (IV) Chloro Tungstate in different Solvents

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Solution</th>
<th>Ti Released (Mg/50ml)</th>
<th>ClO$_3^-$ released (Mg/50ml)</th>
<th>W$_2$O$_5$ Released (Mg/50ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$O</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>0.1 MHClO$_4$</td>
<td>0.00</td>
<td>0.24</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>1.0 MHClO$_4$</td>
<td>0.46</td>
<td>0.79</td>
<td>0.90</td>
</tr>
<tr>
<td>4</td>
<td>0.1 MHNO$_3$</td>
<td>0.00</td>
<td>0.12</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>1.0 MHNO$_3$</td>
<td>0.36</td>
<td>0.72</td>
<td>0.26</td>
</tr>
<tr>
<td>6</td>
<td>0.1 M HCl</td>
<td>0.00</td>
<td>0.00</td>
<td>0.12</td>
</tr>
<tr>
<td>7</td>
<td>1.0 M HCl</td>
<td>1.26</td>
<td>0.57</td>
<td>0.54</td>
</tr>
<tr>
<td>8</td>
<td>1.0 M CH$_3$COOH</td>
<td>0.00</td>
<td>0.20</td>
<td>0.22</td>
</tr>
<tr>
<td>9</td>
<td>0.1 M NaOH</td>
<td>0.91</td>
<td>2.90</td>
<td>2.05</td>
</tr>
<tr>
<td>10</td>
<td>2.0 M NaOH</td>
<td>Completely Dissolved</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.3.5 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 20.0 ml of 0.1M 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 $K_d$ values, were calculated using the following equation

$$K_d = \frac{(I - F)V}{F \times M} \text{ Meq/g}$$

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.

5.3.6 X-RAY STUDY

X-ray studies were carried out using a Philips pw-1730 high angle diffractometer (Poland) Cu-Kα (Ni Filter) radiation and it was found that material shows amorphous nature. The XRD has shown in figure 5.2.
5.3.7 **FTIR SPECTRUM**

FTIR spectrum of sample TiCT–5 was obtained by KBr disc method. FTIR spectrum of the prepared sample was obtained by using a FTIR model shimadzu 820 PC. The FTIR spectrum has shown in figure 5.3.

5.3.8 **SCANNING ELECTRON MICROGRAPHS-(SEM)**

Surface morphology of the dried exchanger was investigated using SEM. It is shown is figure 5.4. This figure shows the scanning electron micrographs of 10% TiCT. 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.
Fig 5.2

X-ray Graph of Titanium Chloro Tungstate
Fig 5.3

F.T.I.R Spectrum of Titanium Chloro Tungstate
5.4 RESULTS AND DISCUSSION

The results from the study of the ion exchange capacity of various samples of Titanium (IV) Chloro Tungstate are presented in Table 5.1. The improvement in the ion exchange capacity and chemical stability seem to be much higher for sample TiCT-5 and therefore this sample was selected for detailed studies.

The ion exchange capacities for mono- and bivalent metal ions are shown in Table 5.2. These results indicate that ion exchange capacity 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:

\[ \text{Li}^+ > \text{K}^+ > \text{Na}^+ , \quad \text{Mg}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} \]

The pH titration curve [figure 5.1] of TiCT-5 performed in NaCl-NaOH system shows one inflexion point indicating that the exchanger is monofunctional.

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 1.35, 1.05, 0.90, 0.70, 0.30, 0.20 and ~0 meq g⁻¹ dry exchanger, respectively. The results are summarized in Table 5.3.
These observations reveal that IEC decreases with increasing temperature. Varshney et al.\textsuperscript{[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, H\textsubscript{2}SO\textsubscript{4}, HNO\textsubscript{3}, and acetic acid. The ion exchanger completely dissolved in 2M H\textsubscript{2}SO\textsubscript{4} and 2M NaOH solution. The chemical composition data of material suggests the molar ratio of Ti (IV), ClO\textsubscript{3} and W\textsubscript{2}O\textsubscript{3} as 2:1:3 which may point to the following tentative formula.

\[ [(\text{TiO}_2)_2 \cdot (\text{ClO}_3) \cdot (\text{W}_2\text{O}_3)_3 \cdot n\text{H}_2\text{O}] \]

On the basis of thermal stability measurements if we assume the weight due to presence of water molecules in the gel is 90\% of the total weight. The number of such molecules per mole of the exchanger can be determined on the basis of Alberti's equation\textsuperscript{[31]}.

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

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

**CALCULATION FOR \( n \)**

Molecular weight of \( \{\text{TiO}_2\}_2 \cdot (\text{ClO}_3) \cdot (\text{W}_2\text{O}_3)_3 \)

\[ \Rightarrow (\text{TiO}_2)_2 = (47.9 + 32)_2 = 159.8 \]

\[ \text{ClO}_3 = 35.5 + 47.7 = 83.2 \]
\[ W_2O_3 = 183.8 \times 2 + 47.7 = 418.3 \times 3 = 1245.9 \]

Molecular weight of the material

\[ = 159.8 + 83.2 + 1245.9 \]

\[ = 1488.9 \]

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

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

\[ 1800n = 9.2 \times 658.3 + 18n \times 9.2 \]

\[ 1800n = 13697.88 + 165.6n \]

\[ 1634.4n = 13697.88 \]

\[ n = 13697.88 / 1634.4 \]

\[ n = 8.38 \]

The FTIR of Titanium (IV) Chloro Tungstate shows broad bands in the 3180 cm\(^{-1}\) region characteristic of asymmetric and symmetric hydroxoxo-OH and aqua-OH stretching frequency. A sharp medium band at 1680 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 chlorate and metal oxide. The FTIR spectrum has shown in figure 5.2.
Absence of sharp peaks in the X-ray diffraction pattern of Titanium (IV) Chloro tungstate indicates that the material is amorphous in nature. Graph of X-ray diffraction is shown in figure 5.3.

Surface morphology of the dried exchanger was investigated using SEM. It is shown in figure 5.4. This figure shows the scanning electron micrographs of 10% TiCT. 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 5.4: SEM images of a sample of Titanium Chloro Tungstate
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 $K_d$ value of the groups, 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 electrolytic 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 5.5 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 has been made by others.$^{[32]}$
Table 5.5: $K_{d}$ values of Metal ions on Titanium Chloro Tungstate 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>
<th>0.2M CH$_3$COOH</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>
<td>9500</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>
<td>3200</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>
<td>1890</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>
<td>7100</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>
<td>310</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>
<td>400</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>
<td>1610</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>
<td>800</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>
<td>160</td>
</tr>
<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>
<td>1050</td>
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References:


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