

## CHAPTER VI

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*Synthesis, characterization and analytical applications  
of aluminium tungstate ion exchangers*

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**Abstract**

A novel inorganic ion exchanger aluminium tungstate was prepared and characterized by Fourier transform infrared spectrometer and elemental analysis. The compound is stable in thermal, radiation and diverse chemical environments. This material exhibits an excellent adsorption of parent-daughter  $^{137}\text{Cs}$ - $^{137\text{m}}\text{Ba}$ . The newly synthesized crystalline inorganic ion exchanger was employed to separate carrier-free  $^{137\text{m}}\text{Ba}$  from  $^{137}\text{Cs}$ , using  $0.0426 \text{ mol. L}^{-1}$  ascorbic acid solution as eluting agent. Trend in elution is encouraging to apply the system as radionuclide generator.

## VI.1. Introduction

Solid phase extraction is a well-established sample pretreatment technique in pharmaceutical and environmental, biomedical and environmental field because it demands less organic solvents and can remove interferences and preconcentrate the objective simultaneously [1, 2]. In general, sorbent materials are the key points for solid-phase extraction as similar to stationary phase for high performance liquid chromatography; therefore, there are considerable interests in developing new selective sorbents for extracting and isolating components from complicated matrices. Solid-phase extraction is one of the fastest, economic and clean preconcentration methods to separate and concentrate trace metals by using this ion exchangers.

Polyoxometalates, in addition to their importance in catalysis, biochemical separation, medicinal chemistry [3-11] and in the design of new materials with novel electronic, magnetic and topological properties [12] have received significant attention in the field of radio analytical chemistry as synthetic inorganic ion exchangers for trace level separations of cations due to the excellent stability of these materials towards thermal and radiation dose. Exchangers like stannic silicomolybdate and zirconium antimonate for the separation of  $^{134}\text{Cs}$  -  $^{134}\text{Ba}$  [13], but in all cases, the preparation and evaluation of both poorly crystalline and amorphous compounds of polyoxometalates have been reported, with zirconium phosphate being the most widely studied [14, 15].

However, no attention has been paid to the structure-property relationships between the polyoxometalates and sorption behavior though the chemistry of such materials is of considerable interest because of their fascinating structural diversities [16-19]. Here, we report a exchanger based on aluminium tungstate, synthesis and spectroscopic characterization of which has been investigated. The exchange capacities of this exchanger for several cations of different oxidation states have been reported. The time of equilibration and the maximum weight of the exchanger for uptake of a fixed amount of radionuclide were also determined. The study of the extraction behavior and the mutual separation of cesium and barium radionuclides are of interest and importance to fulfill the increasing demand for the radioactive waste management for environmental

protection. The results have revealed that this new compound is suitable for the separation of the carrier-free daughter nuclide ( $^{137\text{m}}\text{Ba}$ ) from its parent ( $^{137}\text{Cs}$ ).

## VI.2. Experimental

### VI.2.1. Synthesis of aluminium tungstate

The aluminium tungstate compound was synthesized by dissolving  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (4.77 g, 14.46 mmol) and ammonium nitrate (0.185 g, 2.31 mmol) in water (300.0 mL) followed by the addition of glacial acetic acid (40.0 mL) and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  (6.0 g, 24.84 mmol). The pH of the resulting solution was adjusted to 2.60 with nitric acid and stirred for 2 h. The mixture was filtered and the filtrate was kept for overnight to precipitate out the material. The residue obtained after filtration was washed several times with de-ionized water and then finally the precipitate was dried in vacuum for 24 h.

### VI.2.2. Elemental analysis

For elemental analysis the compound was analyzed for its aluminium and tungstate content. For this purpose a weighed amount of the solid material was fused in a nickel crucible with caustic soda. The fused mass was poured into 200.0 mL hot water and then filtered. The precipitate was dissolved in hot 2.0 mol.  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  and analyzed for aluminium by complexometric titration with ethylenediaminetetraacetate (EDTA) and the filtrate was analyzed for tungstate by gravimetric method [20].

### VI.2.3. Stability of aluminium tungstate exchanger

The stability of the exchanger was determined in different chemical, thermal and radiation environments. Chemical stability was determined by taking a 0.5 g portion of the exchanger in 50.0 mL of acid or alkaline solution of various strengths. This mixture was then shaken for 24 h; the solid-exchanger was filtered off and washed with water. The exchange capacity of the compound for  $\text{Na}^+$  was checked after this acid or alkali treatment. Thermal stability of the resins was studied employing a thermo-gravimetric

analysis technique. Radiation stability was checked by measuring the exchange capacity of the exchanger, before and after  $\gamma$ -irradiation dose rate of 4.0 kGy/h by a  $^{60}\text{Co}$  radiation source.

#### ***VI.2.4. Determination of ion exchange capacity (IEC) of the exchanger***

Hydrogen ion capacity was determined by batch method. An accurately weighed (0.5 g) exchanger was treated with 2.0 mol. L<sup>-1</sup> HCl and then filtered off, washed with distilled water and dried at 50°C for 2-3 h to remove free HCl. The acidic form of the exchanger was equilibrated with 20.0 mL 0.1 mol. L<sup>-1</sup> NaOH solution for 1 h at room temperature at stirring condition and then the excess alkali was titrated with 0.1 mol. L<sup>-1</sup> hydrochloric acid solution to determine the total acidic hydrogen content.

The exchange capacities of the exchanger for different alkali and alkaline metal ions were determined by batch method. To a glass-stoppered centrifuge tube (diameter 2.0 cm) containing 0.5 g of the dry solid-exchanger, 50.0 mL of 2.0 mol. L<sup>-1</sup> solutions of different alkali and alkaline metal ions was added to the tube in each case; then the mixture was shaken for a period of 1 h. The exchanger was subsequently filtered and washed with doubly distilled water to remove the adhering H<sup>+</sup> ions. The exchange capacities for the metal ions were determined by measuring the liberated acid by titration with standard alkali solution.

#### ***VI.2.5. pH-metric titration***

pH-metric titration of the exchanger was studied by taking 0.1 g of aluminium tungstate exchanger and immersed in 50.0 mL of mixed solution of varying ratio of NaCl and NaOH with intermittent shaking at room temperature. Equilibration was maintained in 0.1 mol.L<sup>-1</sup> of NaOH solution. After the equilibration time of 24 h, the pH of the supernatant solution was measured by pH-meter. The variations of pH against the amount of alkali added are displayed in **Fig.VI.3**.

### ***VI.2.6. Studies of radiochemical separation***

In column method, the glass column of 5.0 cm length and 1.0 cm inner diameter was packed with the exchanger (1.0 g). The column bed was first conditioned with 0.01 mol.L<sup>-1</sup> HCl solution. A sample volume of 2.0 mL solution of measured radioactivity of cesium and barium radionuclides where <sup>137</sup>Cs ( $t_{1/2} = 30\text{y}$ ) is in secular equilibrium with its daughter element <sup>137m</sup>Ba ( $t_{1/2} = 2.55\text{ min.}$ ) was passed through the column at a flow rate of 1.0 mL/min. After absorption of the mixture, 10.0 mL of 0.01 mol. L<sup>-1</sup> HCl solution was passed through the column to ensure the total absorption of the mixture. Finally, the daughter fraction was eluted with 0.0284 mol. L<sup>-1</sup> ascorbic acid, which was followed by collecting the effluent in ten successive counting tubes (1.0 mL each). The  $\gamma$ -activity in each tube was measured with the help of NaI (TI)  $\gamma$ -ray spectrometer several times with a time gap of 30 sec.

## **VI.3. Results and discussion**

### ***VI.3.1. Synthesis and characterization***

The compound was prepared by stirring the mixture of sodium tungstate and aluminium chloride in presence of ammonium nitrate at ambient temperature adjusting the pH of the mixture at 2.60. The compound was found to be insoluble in water, alcohol, moderately concentrated acid and alkali and other common organic solvents. For elemental analysis, the compound was dried and then analyzed for the determination of aluminium and tungstate present in the exchanger. Aluminium can be analysed for by complexometric and gravimetric method can be applied for the estimation of tungstate. The exchanger was found to contains 20.1 % W and 2.9 % Al, which nearly corresponds to the molar ratio of Al:W = 1:1

The IR spectrum (**Fig.VI.1**) of the compound shows the characteristic peaks at 1623, 1381 and 832 cm<sup>-1</sup> assignable to the characteristic stretching of the tungstate [21, 22].

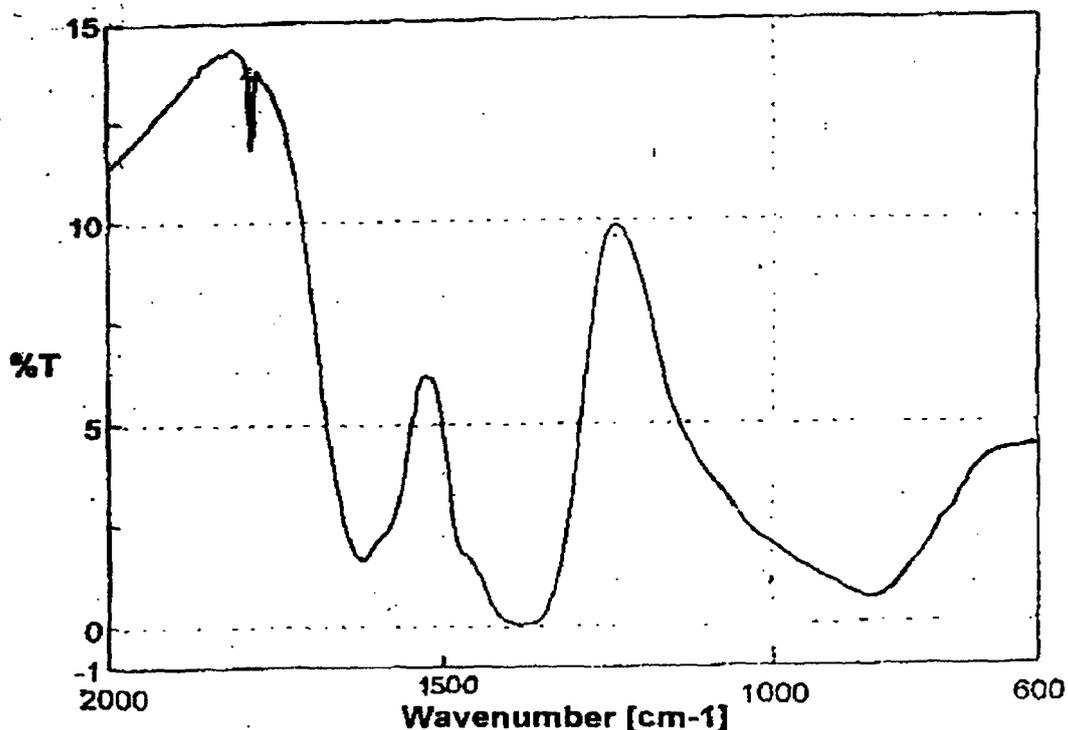


Fig.VI.1: IR-spectrum of the aluminium tungstate ion exchanger

### VI.3.1a. Chemical, thermal, and radiation stability

The compound was found to be insoluble in water, alcohol, moderately concentrated acid and alkali and other common organic solvents. By comparing the exchange capacity of sodium ion, the chemical stability of the exchanger in different acid and alkali media has been checked. The exchanger is quite stable in normal chemical environment. In thermal analyses of the exchanger, a big endothermic peak **Fig. VI.2** appears near 100 °C, indicating loss of water molecules, otherwise the compound is stable upto 150 °C. The radiation stability of the exchanger was measured by determining the ion exchange capacity of the exchanger before and after  $\gamma$ -irradiation at a dose rate of 4.0 kGy/h in dry condition. The exchanger was found to retain its ion exchange capacity up to a total dose of 96.0 kGy/h, which is quite an appreciable amount of radiation dose (**Table VI.1**).

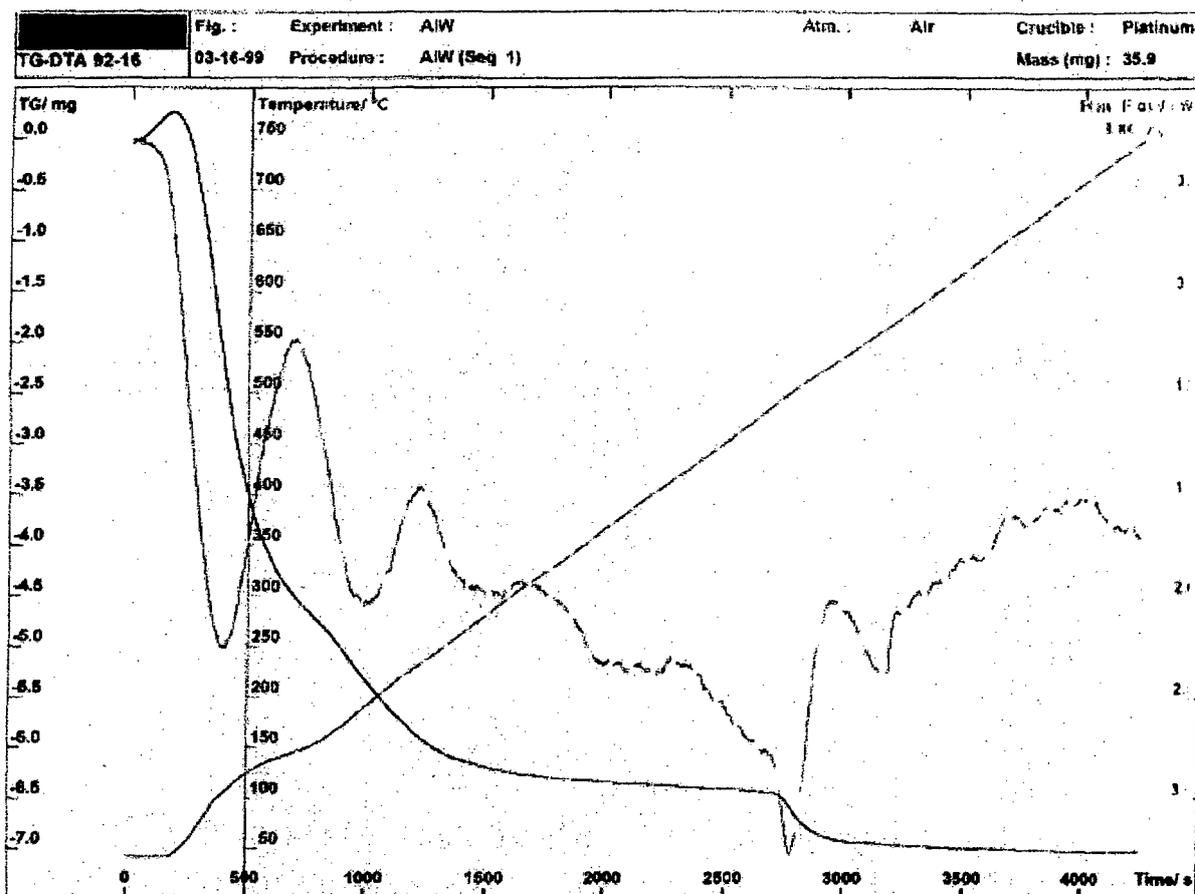


Fig.VI.2: TGA curve of aluminium tungstate

Table VI.1: Ion exchange capacity with radiation dose

Radiation dose (kGy)	Ion exchange capacity (meq/g)	Radiation dose (kGy)	Ion exchange capacity (meq/g)
96	2.37	768	1.59
192	2.13	864	1.41
288	1.82	960	1.35
576	1.72	1248	1.09
672	1.59	1344	0.92

### VI.3.1a. pH metric titration curve

The variation of pH against the amount of alkali added is shown in Fig.VI.3. which clearly indicates that there is only one inflection point. The ion exchange capacity corresponding to inflection point was also calculated from the curve and found to be 2.30 meq/g.

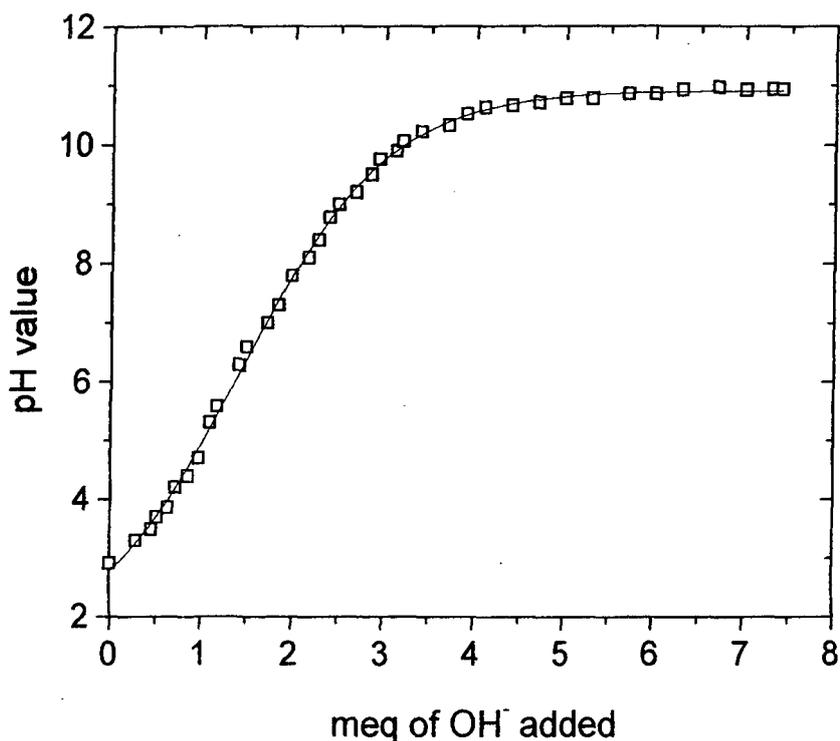


Fig.VI.3: pH metric titration curve of aluminum tungstate

### VI.3.2. Sorption behavior of metal ions

The exchange capacities of different alkali and alkaline metal ions are tabulated in Table VI.2. The data show that the compound can be employed as an exchanger. The exchange capacity for sodium ion is the highest and the exchange capacities are in the order of  $\text{NH}_4^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ . The exchange capacity for alkaline metal ions is higher than that for the alkaline earth metal ions.

**Table VI.2:** Ion exchange capacity of the exchanger

Ions	Exchange capacity (meq/g)	Ions	Exchange capacity (meq/g)
Li <sup>+</sup>	2.3173	Mg <sup>2+</sup>	1.9280
Na <sup>+</sup>	2.3088	Ca <sup>2+</sup>	1.9004
K <sup>+</sup>	2.2497	Sr <sup>2+</sup>	1.8602
Cs <sup>+</sup>	1.9730	Ba <sup>2+</sup>	1.8335
NH <sub>4</sub> <sup>+</sup>	2.8746		

## VI.4. Application of the exchanger in radiochemical separation

### VI.4.1. Separation of <sup>137m</sup>Ba from <sup>137</sup>Cs radionuclides

For the studies on separation of <sup>137</sup>Cs- <sup>137</sup>Ba parent daughter pair, a glass column of was packed with amorphous aluminium tungstate and thoroughly washed with 0.01 mol·L<sup>-1</sup> HCl solution to remove any tracers of adhered activity and preconditioned with 0.01 mol·L<sup>-1</sup> HCl solution. Equilibrated mixture of <sup>137</sup>Cs- <sup>137</sup>Ba was loaded over the column. After absorption of both the radionuclides, the daughter activity was successfully removed from exchanger by using 0.0426 mol·L<sup>-1</sup> ascorbic acid solution. As Ba(II) forms stronger complex with ascorbic acid solution, it elutes out of the column matrix but Cs(I) remains absorbed on the column. It was found that when 0.0426 mol·L<sup>-1</sup> ascorbic acid was passed through the column, only the Ba(II) ions was eluted, leaving the Cs(I) on the column. The eluted sample was collected and counts of the some fraction were taken at different time intervals to plot the decay curve (Fig. VI.4). From the decay curve it is found that the half -life of the daughter is 2.61 min, which matches perfectly with the half-life of <sup>137</sup>Ba (t<sub>1/2</sub> = 2.55 min). As Ba(II) forms a stronger complex with 0.0426 mol·L<sup>-1</sup> ascorbic solution, only 4.0-5.0 mL ascorbic acid solution was sufficient for removal of <sup>137</sup>Ba completely at a given moment. When all the <sup>137</sup>Ba was eluted from

the  $^{137}\text{Cs}$  generator, the  $^{137}\text{Ba}$  was allowed to grow until secular equilibrium was re-established so that the subsequent fractions of daughter could be recovered from the parent adsorbed on column by again eluting with  $0.0426 \text{ mol. L}^{-1}$  ascorbic acid solution, so that overall system can be prescribed as a radionuclide generator. The elution pattern of  $^{137}\text{Ba}$  has been plotted in Fig. VI. 5.

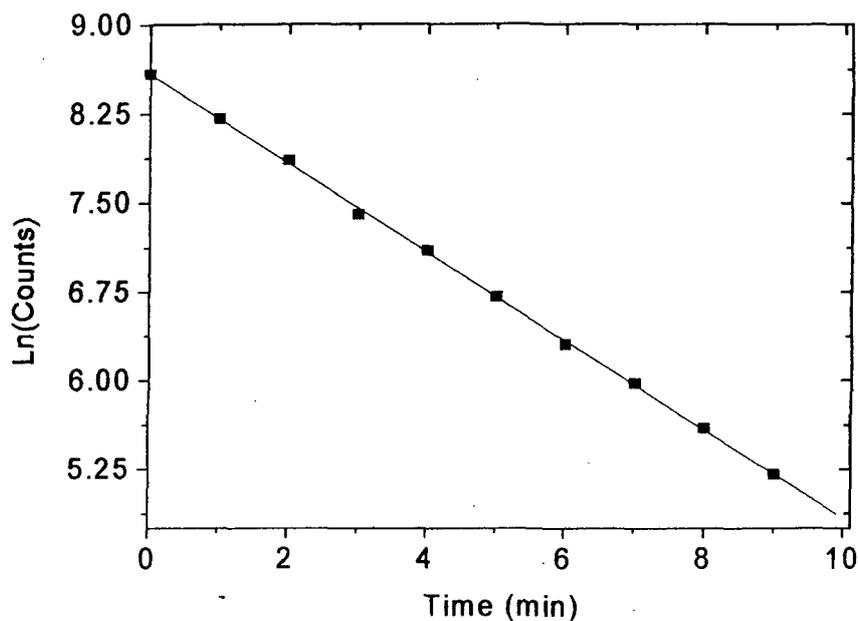


Fig.VI. 4: Decay curve of eluant  $^{137\text{m}}\text{Ba}$  of aluminium tungstate ion exchanger (eluent  $0.0426 \text{ mol. L}^{-1}$  ascorbic acid)  $t_{1/2}=2.61 \text{ min}$

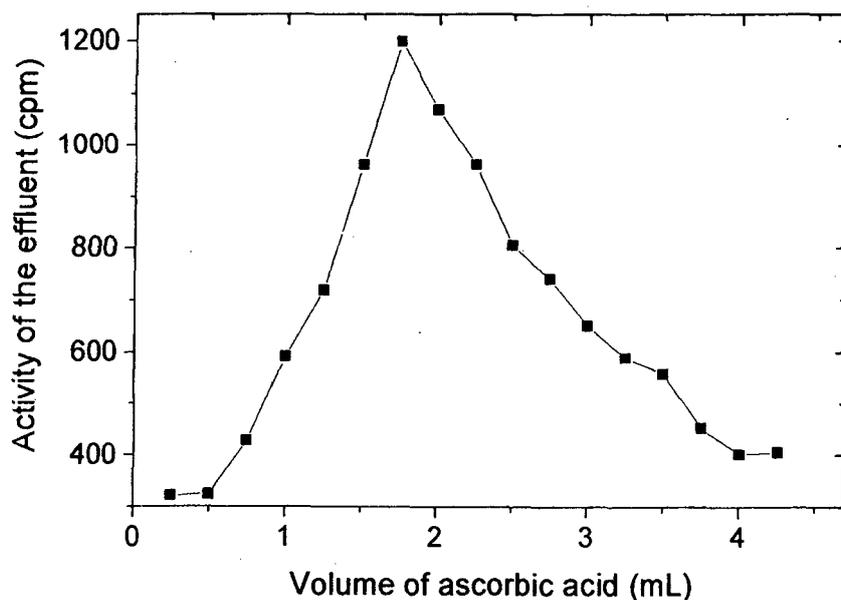


Fig.VI.5: Elution curve of  $^{137\text{m}}\text{Ba}$  (aluminium tungstate)

### ***VI.5. Epilogue***

In summary, a novel new inorganic aluminium tungstate ion exchanger has been synthesized, structurally characterized and successfully applied for the separation of  $^{137m}\text{Ba}$  in no-carrier added state from  $^{137}\text{Cs}$ , from their equilibrium mixture. The material possesses great potential for its application in the field of separation due to its good adsorption properties and the low cost. This new material can be used as an exchanger in a generator system to have the carrier-free short-lived  $\gamma$ -active daughter product  $^{137m}\text{Ba}$  from the long-lived  $^{137}\text{Cs}$ . This is obvious because the daughter fraction was preferentially eluted out of the column by the use of ascorbic acid at a mild concentration so that the parent was still retained on the exchanger. After 15-20 minutes interval, which was sufficient for growth of daughter from parent decay, the exchanger was eluted with same ascorbic acid in order to check the generator formation and of course the systems accorded with the expectation.

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