CHAPTER V

Synthesis, characterization and analytical applications of quinolinephosphomolybdate ion exchanger

Synthesis, characterization and analytical applications of quinolinephosphomolybdate ion exchanger

Abstract

The quinolinephosphomolybdate ion exchanger was prepared by mixing potassium dihydrogen phosphate and sodium molybdate in aqueous quinoline hydrochloride solution. This inorganic ion exchanger is highly stable towards thermal, chemical and radiation dose. The adsorbents exhibit an excellent ion exchange capacity for many metal ions. It has been employed in the separation of carrier free ^{90}Y from its parent ^{90}Sr from an equilibrium mixture. The absorbed daughter was recovered by using 0.0284 mol. L^{-1} ascorbic acid solutions at pH 5 as eluting agent.

V.1. Introduction

Nowadays, the use of positron emission tomography (PET) has gained considerable significance in diagnostic and therapeutic nuclear medicine, and for metabolic studies and drug evaluation-using cyclotron produced positron-emitting (β^+) radioisotopes [1-6]. ^{86}Y ($t_{1/2}$ = 14.7 h, 66% EC, 34% β^+, $E_{\beta+ max}$ = 3.2 Mev) is a promising positron emitting radionuclide capable of serving as a PET imaging surrogate to ^{90}Y, allowing for seamless integration into existing ^{90}Y labeled pharmaceuticals [7-15].

For the therapeutic purposes ^{90}Y can be used successfully. Many successful studies of site-specific monoclonal antibody labeling involving ^{90}Y have been applied in radioimmuno-therapy [1, 5, 16-20]. Several methods for the separation of pure ^{90}Y from ^{90}Sr have been reported, which include precipitation, solvent extraction [21, 22] and ion exchange chromatography [23, 25]. Amongst these, ion exchange chromatography is used most frequently in ^{90}Y- ^{90}Sr generator system [26]. The use of inorganic ion exchangers for the separation of metal ions is of wide interest, particularly in the field of radio analytical chemistry due to the excellent stability of these materials towards thermal and radiation dose. Insoluble oxides, crystalline silicates, salts of polybasic acids and multivalent metals have been thoroughly studied. Preparation and evaluation of both poorly crystalline and amorphous compounds have been reported with zirconium phosphate being the most widely studied [27-30]. However no attention has been paid to quinolinephosphomolybdate until now and we have synthesized this compound as an amorphous material for column operation. The exchange capacity of this exchanger for several metal ions was determined. The results suggested that this exchanger might be suitable as a decontaminant for different hazardous radionuclides. The time of equilibration and the maximum weight of the exchanger for uptake of a fixed amount of radionuclides were also pre-determined.

In this present investigation a radiochemical technique is being reported that could be applied for the routine production of no carrier added ^{90}Y from enriched ^{90}Sr parents by using quinoline phosphomolybdate ion exchanger.

V.2. Experimental

V.2.1. Synthesis of quinolinephosphomolybdate

To a 50.0 mL solution of KH_2PO_4 (1.36 g, 10.0 mmol) 40.0 mL concentrated hydrochloric acid was added in a 500 mL beaker. In another beaker 40.0 mL of quinoline (30.0 mmol) immersed in 50.0 mL of water and also added required amount of concentrated hydrochloric acid solution for complete dissolved in water. The KH_2PO_4 solution was heated to boiling and added with quinoline reagent drop by drop with constant stirring. To the mixture 50.0 mL solution of Na_2MoO_4, $2H_2O$ (250.0 mmol) was added dropwise and then the suspension was allowed to stand in boiling water both for 15 minutes. Then it was cooled to room temperature. The mixture was filtered and the filtrate was kept for overnight to precipitate out the material. Decant to clear solution through the filter and the precipitate was washed twice by decantation with about 20.0 mL of HCl (1:9) this removes most of the excess of quinoline and of molybdate. The residue obtained after filtration was also washed several times with de-ionized water and then finally the precipitate was dried in vacuum for 24 h.

V.2.2. Elemental analysis

For elemental analysis, the compound was analyzed for its molybdate and phosphate 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. L^{-1} H_2SO_4 and analyzed for molybdate by gravimetric method, and the filtrate was analyzed for phosphate also by gravimetric method using ammonium molybdate [31].

II.2.3. Stability of the 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 25.0 mL of acid or alkaline solution of various strengths. This mixture was then shaken for 48 h the solid-exchanger was filtered off and washed with water.

The exchange capacity of the compound for 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 γ-irradiation dose rate of 4.0 kGy/h by a ^{60}Co radiation source, IUC, Kolkata.

V.2.4. Determination of ion exchange capacity (IEC)

The exchange capacities of the exchanger for different alkali and alkaline metal ions were determined by batch method [32]. 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^{-1} solutions of each of the different alkali and alkaline metal ions was added to the tube in each case; then the mixture was shaken for a period of 2 h. The exchanger was subsequently filtered and washed with doubly distilled water to remove the adhering H^+ ions. The exchange capacities for the metal ions were determined by measuring the liberated acid by titration with standard sodium hydroxide solution. Resulted are presented in **Table V.1.**

$$\text{Capacity} = \frac{(\text{Titrate of alkali} \times \text{Strength of alkali})}{\text{Weight of exchanger}}$$

V.2.5. pH metric Titration

The pH titration was performed with a mixture of NaCl and NaOH. In different sample containers, accurately weighed amount of the exchanger (~0.1 g each) were immersed in 25.0 mL of mixed solution of varying ratio of NaOH and NaCl with constant shaking. Equilibration was done at room temperature and for a period of 24 h. The total strength of sodium ion in each was maintained at 0.1 mol. L^{-1}. After equilibration the pH of the supernatant solutions were measured by a systronics pH meter. The variation of pH against the amount of alkali added is shown in **Fig. V.4.**

V.2.6 Studies of radiochemical separation

The equilibrium mixture containing ^{90}Sr-^{90}Y in nitrate form was repeatedly evaporated to dryness [33-39] leached with dilute pH 5 buffer solution of sodium acetate-acetic acid and finally loaded into the column of size 40 mm into 4 mm containing 1.0 gm of quinolinephosphomolybdate, pretreated at pH 5. For the studies on separation of ^{90}Sr- ^{90}Y parent daughter pair, a glass column of length 40 mm into 4 mm internal diameter was packed with amorphous quinoline phosphor molybdate and thoroughly washed with pH 5 buffer solution to remove any traces of adhered acid and preconditioned at pH 5. Equilibrated mixture of ^{90}Sr- ^{90}Y (100 μL) maintaining pH 5 was loaded over the column. About 10.0 mL pH 5 solution was passed through the column and no activity came out from the column. Then ^{90}Y was eluted with 0.0284 mol. L^{-1} ascorbic acid solution. The rate of the elution adjusted to 1.0 drop/min. Each 5 drops fraction was collected and measured for its radioactivity in a GM counting system after definite time of intervals. Purity of the eluted solution was checked by its decay curve **(Fig.V.5)**.This indicates that the daughter is radiochemically free from its parent. The adsorbed ^{90}Y was eluted with 0.0284 mol. L^{-1} ascorbic acid solution, and the elution profile of ^{90}Y has been displayed in **Fig.V.6**.

V.3. Results and discussion

V.3.1. Synthesis and characterization

The quinolinephosphomolybdate exchanger has been prepared by mixing potassium dihydrogen phosphate and sodium molybdate in aqueous quinoline hydrochloride solution in water medium. This greenish yellow colored exchanger is highly insoluble in water and organic solvents. The air dried compound was used for the the determination of molybdate and phosphate content in it. Both the molybdate and phosphate has been estimated by gravimetric method. The exchanger was found to contain 21.6 % Mo and 26.2% PO_4^{3-} which nearly corresponds to the molar ratio of Mo: PO_4^{3-}= 1:2.

This inorganic material is not amorphous but the crystalinity of this substance is poor. The efforts of several times to get the single crystals of this material produced

crystals having weak diffused spot. The broad reflections along with several sharp reflections on the powder XRD pattern (**Fig.V.1**) suggest that the synthesized compound is weak crystalline in nature but not ampoorphous, as the spectrum showed the characteristic feature of poor crystalline nature of almost 50-55 % and characteristic peaks for crystalline amorphous nature of 45-50 %.

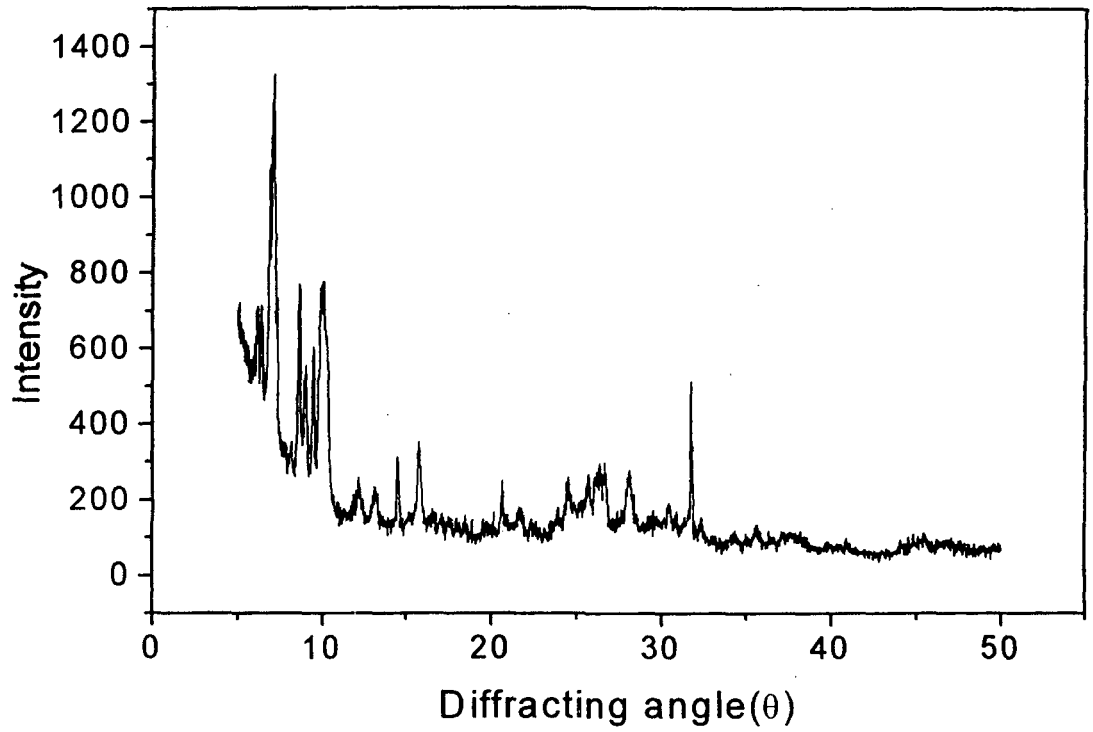

Fig.V.1: Powder XRD patterns of quinoline phosphomolybdate

The IR spectrum (**Fig.V.2**) of the dried material has been obtained using KBr pellet and the spectral analysis shows the different characteristic peaks at 2931 cm^{-1}, 1488 cm^{-1} and 707 cm^{-1} for aromatic $\nu_{(C=C)}$; and 1636 cm^{-1}, 1596 cm^{-1} and 1555 cm^{-1} for quinoline ring present in the material [40-42]. The characteristic peaks at 961 cm^{-1}, 875 cm^{-1} and 795 cm^{-1} in the infrared spectrum are assignable to the $\nu_{(Mo-O)}$, $\nu_{(Mo-O-Mo)}$ and $\nu_{(Mo-O-Mo)}$ stretches, respectively [43, 44].

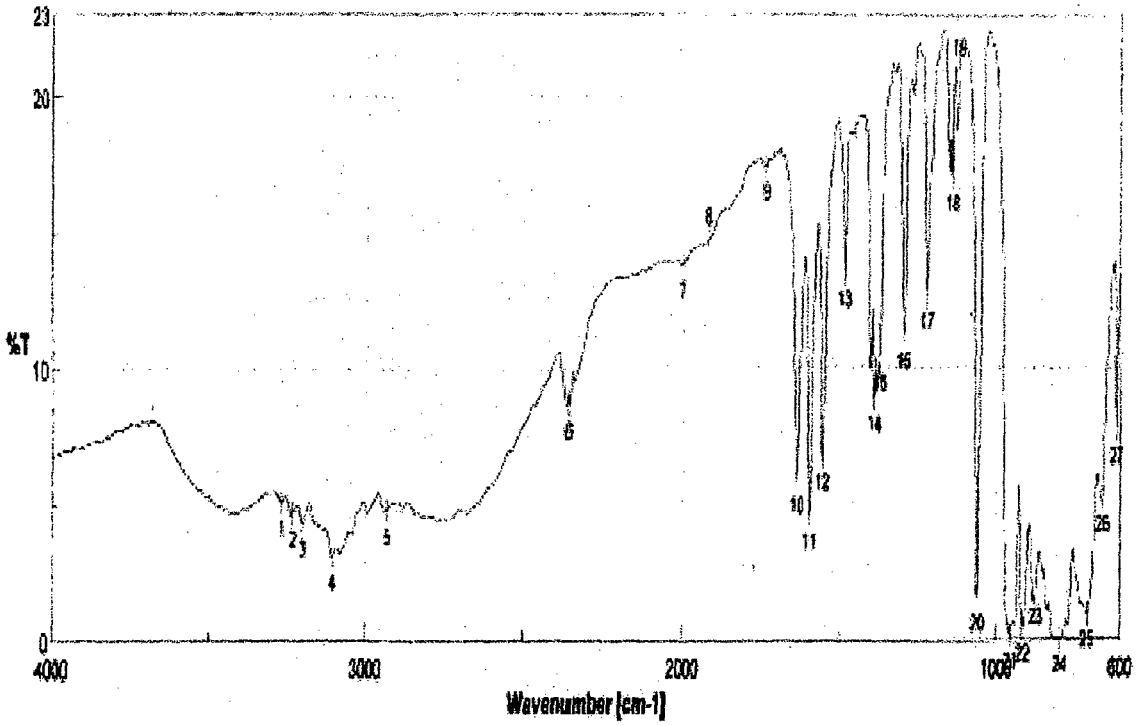

Fig.V.2: IR-spectra of quinolinephosphomolybdate

V.3.2. Chemical, thermal and radiation stability

By comparing the exchange capacity of sodium ion, the chemical stability of exchanger in different acid and alkali media has been checked. The exchanger is quite stable in normal chemical environment. The compound was quite stable in normal chemical environment. However use of, 4.0 mol.L^{-1} H_2SO_4, and 1.0 mol.L^{-1} alkali solution slightly decomposes the solid exchanger.

From thermal analyses a big endothermic peak appears near 100 °C, indicating loss of water molecules, otherwise the compound is stable upto 150 °C (**Fig.V.3**). Radiation stability of the exchanger was studied by determining the exchanging capacity of the exchanger before and after γ-irradiation at a dose rate of 4.0 kGy/h in dry condition. The exchanger was found to retain the exchange capacity for the metal ions up to a total dose of 40.0 kGy.

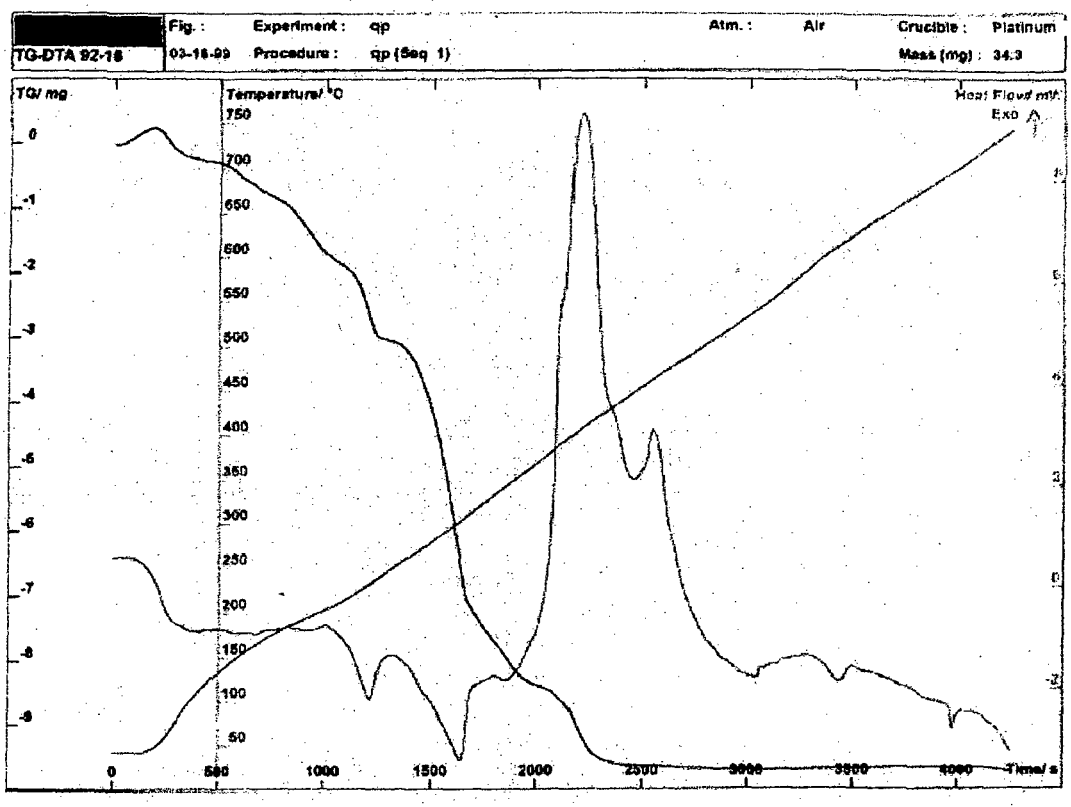

Fig.V.3: Thermo gravimetric and differential thermal analysis curve of the compound

V.3.2. pH metric titration curve

From the curve it is clearly indicated that only one inflexion point and subsequently one exchangeable hydrogen ion is present per molecule in the exchanger matrix. The adsorption of Na^+ is also reflected from pH titration curve **Fig. V.4.** It is also observed from the curve that the exchange capacity of the sodium metal ion is nearly 1.1 meq/g of the exchanger.

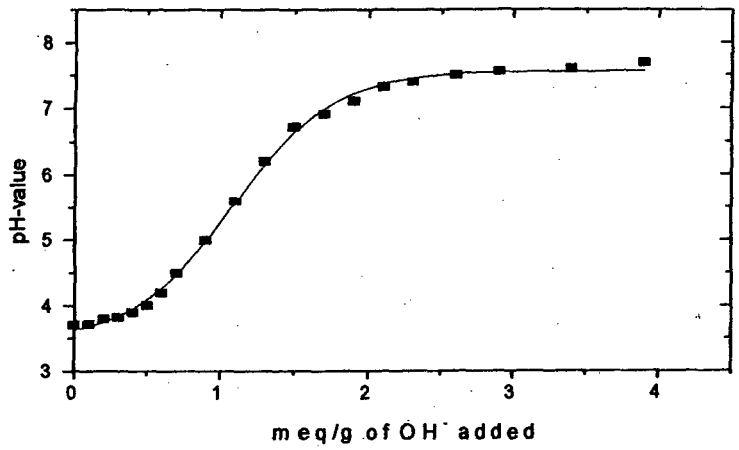

Fig.V.4: pH metric titration curve of the exchanger

V.3.2.Sorption behavior of the metal ions

The exchange capacities of different alkali and alkaline metal ions are tabulated in **Table V.1.** From the table it is clearly shows that the ion exchange capacity are in the order $Mg^{2+} > Ca^{2+} > NH^{4+} > K^{+} > Li^{+} > Cs^{+} > Na^{+} > Sr^{+} > Ba^{2+}$.

Table V.1. Ion exchange Capacity (IEC) of different metals

Cations	Exchange capacity (meq/g)
Li^{+}	1.18657
Na^{+}	1.1516
K^{+}	1.2332
Cs^{+}	1.173
NH_4^{+}	1.5766
Mg^{2+}	1.846
Ca^{2+}	1.7685
Sr^{+}	1.1006
Ba^{2+}	0.9673

V.4. Application of the exchanger in radiochemical separation

V.4.1. *Separation of yttrium from strontium radionuclides*

^{90}Y can be separated from its long lived ^{90}Sr. For the column chromatographic separation of ^{90}Y from the equilibrium mixture of ^{90}Sr -^{90}Y, a 100 µL radionuclide mixture was absorbed on quinoline phosphor molybdate bed from top of the column. After adsorption, about 10.0 mL pH 5 solution passed through the column. However, no activity was found in the eluate. Then, ascorbic acid solution was used as eluting agent. It was found that 0.0284 $mol.L^{-1}$ ascorbic acid solution helps to elute ^{90}Y preferentially while ^{90}Sr remains absorbed in the column in this condition. The activity of the eluted solution was checked with GM counter at different time intervals. From the decay curve (**Fig.V.5**) it was found that the half- life of the eluant 63.45 h, which is very close to the half-life of the pure ^{90}Y ($t_{1/2}$ = 63.5 h). Thus, it is concluded that eluted solution contains

radiochemically pure ^{90}Y. The trend in separation of ^{90}Sr- ^{90}Y is quite satisfactory. As Y(III) forms a stronger complex than Sr(II), it is desorbed from the column preferentially. For removal of ^{90}Y at a given moment 10.0 mL of ascorbic acid (0.0284 mol. L^{-1}) was sufficient. As the parent ^{90}Sr remains absorbed in the column, it would produce ^{90}Y again after a considerable time and the same method can be repeated for milking ^{90}Y from ^{90}Sr after some days from the same column.

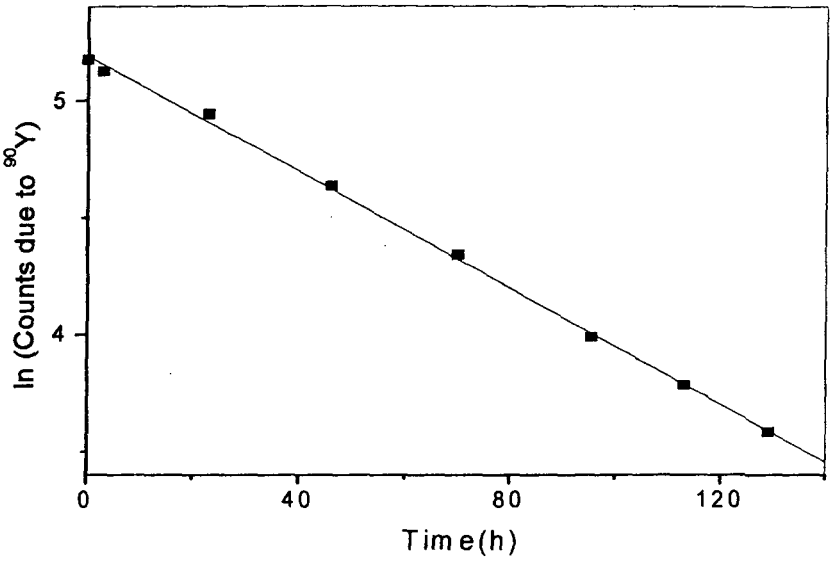

Fig.V.5: Decay curve of ^{90}Y

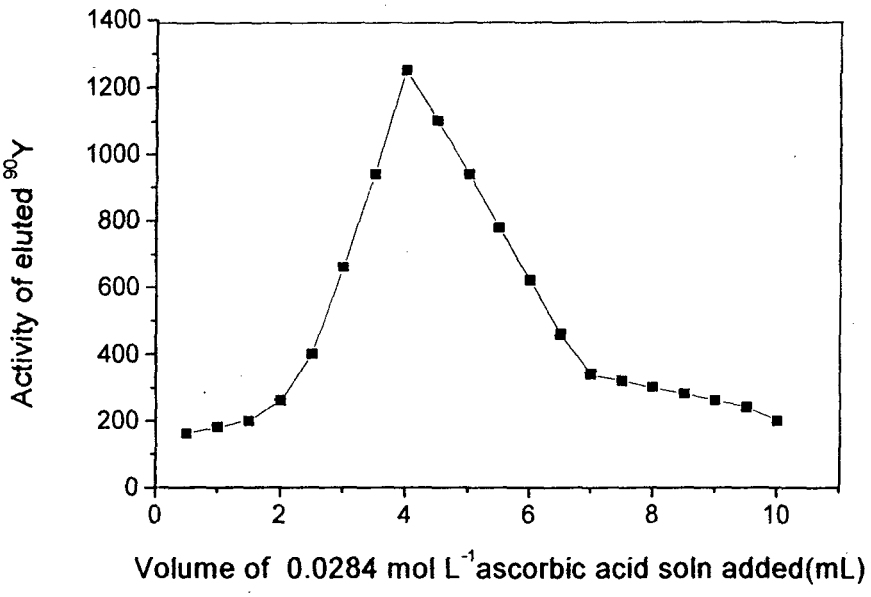

Fig.V.6: *Elution curve of ^{90}Y over quinolinephosphomolybdate*

V.6. Epilogue

A new inorganic material, quinolinephosphomolybdate has been synthesized and characterized. The new material can be used as an exchanger to have the carrier free short-lived β-active daughter product ^{90}Y from the long-lived ^{90}Sr. Elution of trivalent yttrium takes place due to the formation of ascorbate complex of the metal. An optimum concentration of the ligand (0.0284 mol. L^{-1} ascorbic acid) was found to be sufficient for the desorbtion of the Y(III)-chelate from the exchanger surface. However, the solid phase exchanger remains practically unchanged under this condition. It is also predicted that this exchanger might be useful for the separation of alkali metals from selective alkaline earth metal ions.

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