

CHAPTER IV

*Synthesis, characterization and analytical applications
of aluminiumvanadate ion exchanger*

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Abstract

A newly designed inorganic ion exchanger, based on aluminiumvanadate has been synthesized and characterized by elemental analysis, spectroscopic tools and powdered X-ray diffraction. The insoluble poorly polycrystalline material is highly stable towards thermal and radiation doses and in various chemical environments. The data of exchange capacities of the solid material for the different alkali and alkaline metal ions determined by batch technique show that the compound can be employed as an ion exchanger. The successful radiochemical separations of the no-carrier added daughter nuclides, ^{137m}Ba and ^{115m}In from their respective parents present in equilibrium mixtures have been carried out using this material. Elutions of ^{137m}Ba and ^{115m}In were performed using $0.0426 \text{ mol. L}^{-1}$ ascorbic acid solution and 4.0 mol. L^{-1} HCl respectively after sorption of the mixtures ^{137}Cs - ^{137m}Ba at 0.01 mol. L^{-1} HCl medium and ^{115}Cd - ^{115m}In at pH 7.0 respectively. In another column operation, it has been observed that the separation of gold and silver is possible with the help of the eluents, 0.01 % alcoholic solution of rhodamine-B for gold and 0.5 % thiourea solution in 0.1 mol. L^{-1} HClO_4 for silver respectively, after the sorption of ^{198}Au and ^{110m}Ag onto this material at pH 2.0 at a no-carrier added level.

IV.1. Introduction

The synthetic inorganic ion exchangers, due to their resistance to radiation and chemical attack and their compatibility with potential immobilization matrices, find wide applications in industries, including waste treatment, hydrometallurgy, preparation of high purity materials, water purification and several environmental applications. Amongst these materials, hydrous oxides, salts of hetero poly acids, insoluble ferocyanides are of worth to mention. Besides, salts of polyacids with multivalent metals have gained increased importance because of their ease of synthesis and subsequent utilization in column separation. They provide exchangeable hydrogen ions when immersed in aqueous solution, thus exhibiting cation exchange properties. Preparations of both poorly crystalline and amorphous compounds of polyoxometalates have been reported earlier, amongst which stannic silicomolybdate and zirconium antimonate for the separation of ^{134}Cs - ^{134}Ba [1]; ammonium phosphomolybdate and zirconium vanadate for parent-daughter separation between ^{90}Sr and ^{90}Y [2, 3]; and the compounds like antimonate, molybdate, tungstate and silicate salts of zirconium and analogous compounds of titanium and thorium have been investigated [4, 5].

Due to the growing concern for environmental protection, radioactive waste management has emerged as one of the most challenging areas of present day research. The man made of green chemistry is to reduce the use of such carcinogenic materials. Separation with an inorganic ion exchanger does not involve organic solvents and in that way is clear than a conventional liquid-liquid extraction (LLX) process. The advantage of solid phase extractants to be used for practical purposes like 'water purification' and 'decontamination' lies in the fact that the extractants does not require further treatment after taking up the desired element from its matrix. For an effective applicaton, the inorganic ion exchangers are supposed to contain ions that are exchangeable with others present in a solution in which it is considered to be insoluble. During the past few years, a wide applications of inorganic ion exchangers in nuclear waste treatment has been investigated for fission and activation product elimination [5, 6]. In this regard, the separation of long lived radionuclides such as ^{134}Cs (2.06 y) ^{137}Cs (30 y), or ^{133}Ba (10.54 y) from the high level waste is essential, as it reduces the volume of disposed

wastes. Hence, the study of the extraction behavior and mutual separation of cesium and barium radionuclides is of interest and importance. The uses of In(III) complexes in the development of target-specific radiopharmaceuticals for tumor imaging and therapeutic purposes are the main impetus of separation of carrier free radioisotopes of indium [7-11]. The separation of gold and silver in trace level is also an important topic from analytical point of view [12-15] and nowadays the no carrier added ^{198}Au radionuclide has got considerable interest in the field of nuclear medicine e.g. ^{198}Au -metallic gold colloid is being used for radionuclide synovectomy in intracavitary treatment [16].

In this chapter, we have designed a new exchanger based on aluminium vanadate matrix for the separation of $^{137\text{m}}\text{Ba}$ from the ^{137}Cs - $^{137\text{m}}\text{Ba}$, $^{115\text{m}}\text{In}$ from the ^{115}Cd - $^{115\text{m}}\text{In}$ radio-equilibrium mixture and separation a synthetic binary mixture of ^{198}Au - $^{110\text{m}}\text{Ag}$. In all cases, the activity of the radionuclides and the purity of the daughter fractions were measured by a γ -ray spectrometer equipped with a well type NaI(Tl) detector.

IV. 2 Experimental

IV.2.1. Synthesis of the aluminium vanadate exchanger

A solution of ammonium nitrate (2.31 mmol) in 100 mL double distilled water was acidified with acetic acid (15.0 mL, 100 %) followed by the addition of sodium metavanadate (14.46 mmol) and aluminium chloride (6.21mmol). The pH of the resulting solution was adjusted to 2.60 with nitric acid and then the mixture was stirred for 2 h and allowed to settle for 24 h. It was then filtered, the filtrate being kept in an open flask at room temperature for crystallization. The compounds so obtained were dried over desiccators and then the dried solid was analyzed for its aluminium and vanadium content.

IV.2.2 .Elemental analysis

The dried solid was analyzed for its aluminium and vanadium content. For this purpose a weighed amount of the dried solid material was fused with NaOH. The fused mass was poured into hot water and then filtered. The precipitate was dissolved in

2.0 mol. L⁻¹ hot H₂SO₄ and analyzed for aluminium by complexometric titration with EDTA and the filtrate was analyzed for vanadium by gravimetric method [17].

IV. 2.3. Stability of the exchanger

The exchanger is quite stable in normal chemical environment. The chemical stability of the exchanger in different acid and alkali media of different concentration has been checked by comparing the exchange capacity of sodium ion. From this experiment it has been found that the material is stable in mineral acid. In strongly oxidizing acids the material degrades as the results shows that the exchange capacity reduces on and from 10.0 mol. L⁻¹ hydrochloric acid, 6.0 mol. L⁻¹ nitric acid, and 6.0 mol. L⁻¹ sulphuric acid. Thermal analysis of the material shows that the compound is thermally stable up to 150 °C. Radiation stability of the exchanger was studied by determining the exchanging capacity of the solid material as 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 35.0 kGy.

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

The exchange capacities of the compound for different alkali and alkaline metal ions were determined by batch method. For this purpose, 50.0 mL of 2.0 mol. L⁻¹ solutions of each of the different alkali and alkaline metal ions was added to the glass-stoppered centrifuge tube (diameter 2.0 cm) containing accurately weighed 0.5 g of the dried solid-exchanger. Then the mixture was equilibrated for a period of 1 h, the solid was subsequently filtered and washed with doubly distilled water to remove the adhering H⁺ ions. The exchange capacities for the different metal ions were then calculated by titrating the liberated acid with standard NaOH solution and the the data have been tabulated in (Table IV. 1).

IV.2.5. pH metric titration

The pH-metric titration was performed taking an accurately weighed amount of the exchanger (0.1 g) immersed in 25.0 mL of mixed solution of NaCl and NaOH and

stirred for 1 h at ambient temperature. The equilibrium was achieved by allowing the mixture kept aside for a period of 24 h. The strength of sodium ion was maintained at 0.1 mol. L⁻¹. After equilibration, the pH of the supernatant solution was measured by systronics digital pH meter. A curve was obtained by plotting the variation of pH against the amount of alkali added.

IV.2.6. Studies of radiochemical separation

In column operation, chromatographic separation of the daughter fraction from two parent/daughter mixtures in equilibrium (¹³⁷Cs - ^{137m}Ba pair and ¹¹⁵Cd - ^{115m}In pair) and two precious metal ions (gold and silver) of binary synthetic mixture by tracer technique using ¹⁹⁸Au- ^{110m}Ag radiotracers have been carried out using this exchanger. In the study of separation of barium from cesium as ¹³⁷Cs tracer solution in the column packed with this exchanger, it has been observed that complete sorption of activity of both the radionuclides of the radioactive solution having the radioisotope ¹³⁷Cs was taken place onto the bed of the exchanger conditioned with 0.01 mol. L⁻¹ HCl solution. When the 0.0426 mol. L⁻¹ ascorbic acid solution as eluent was passed through the column, only the daughter radionuclide, ^{137m}Ba was found in the various fractions collected at 1.0 min intervals without any trace of ¹³⁷Cs in any fraction of the eluate. This fact was confirmed by the characteristic half-life period ($t_{1/2} = 2.54$ min) of ^{137m}Ba shown in **Fig.IV.5** with no growth of the activity due to the presence of long-lived ¹³⁷Cs. This observation is due to the preference of the exchanger site of the exchanger towards the unipositive alkali metals. The elution profile of ^{137m}Ba by 0.0426 mol. L⁻¹ ascorbic acid solution shown in **Fig.IV.6** suggests that 7.0-9.0 mL of 0.0426 mol. L⁻¹ ascorbic acid solution is sufficient for removal of ^{137m}Ba at a given moment and the trend of the separation of daughter radionuclide (^{137m}Ba) from the mixture of ¹³⁷Cs-^{137m}Ba is quite satisfactory.

Separation of short lived daughter radionuclide, ^{115m}In from the equilibrium mixture of ¹¹⁵Cd-^{115m}In tracer solution has been carried out onto the column packed with this exchanger. In this study, it has been observed that no activity was obtained when pure distilled water was passed through the bed of the exchanger after absorption of equilibrium mixture solution at pH 7.0. The activity in the fraction eluted by

4.0 mol. L⁻¹ HCl solution due to the presence of the only ^{115m}In ion was observed and the purity of this eluate was checked by the characteristic half-life period ($t_{1/2} = 4.5$ h) of ^{115m}In (Fig.IV.8) and no growth of the activity due to the presence of relatively long-lived parent, ¹¹⁵Cd was observed. This observation has also been confirmed by the γ -spectra of the mixture of ¹¹⁵Cd-^{115m}In before separation (Fig.IV.7a) and the γ -spectra of the eluate after separation of the mixture (Fig.IV.7b). From these two γ -spectra it is observed that the eluate is devoid of the activity due to ¹¹⁵Cd as the characteristic energy peak at 528 KeV is absent.

Chromatographic separation of no-carrier-added gold and silver from the synthetic binary mixture of short-lived ¹⁹⁸Au and long-lived ^{110m}Ag has been carried using this exchanger. Complete sorption of both gold and silver ions was done onto this material in the column conditioned with nitric acid solution of pH 2.0. The elution of gold was carried out by alcoholic solution of 0.01 % rhodamine B and then the silver was eluted by 0.5 % thiourea solution in 0.1 mol. L⁻¹ HClO₄. The exponential decay curve (Fig.IV.9) of the activity of the eluate of alcoholic solution of 0.01 % rhodamine-B follows the first order kinetics of the half-life period ($t_{1/2} = 2.70$ days) which is very close to the characteristic half-life period of ¹⁹⁸Au radionuclide ($t_{1/2} = 2.69$ days). The activity of the eluted solution by 0.5 % thiourea solution in 0.1 mol. L⁻¹ HClO₄ has been checked and its nature in accordance with the activity of ^{110m}Ag with corresponding photopeak observed at 667 k.

IV.3. Results and discussion

IV.3.1. Synthesis and characterization of the exchanger

The exchanger was prepared by stirring the mixture of sodium metavanadate and aluminium chloride in presence of ammonium nitrate at ambient temperature adjusting the pH of the mixture at 2.6 using nitric acid. The compound was found to be insoluble in water, alcohol, moderately concentrated acid and alkali and other common organic solvents. The dried solid was analyzed for its aluminium and vanadium content. The exchanger on chemical analysis was found to contain 17.1 % Al and 28.9 % V, which

nearly corresponds to the ratio of Al: V = 1:1. The broad reflections observed in the XRD spectrum (Fig. IV.1) exhibits the poor crystallinity of the material [18].

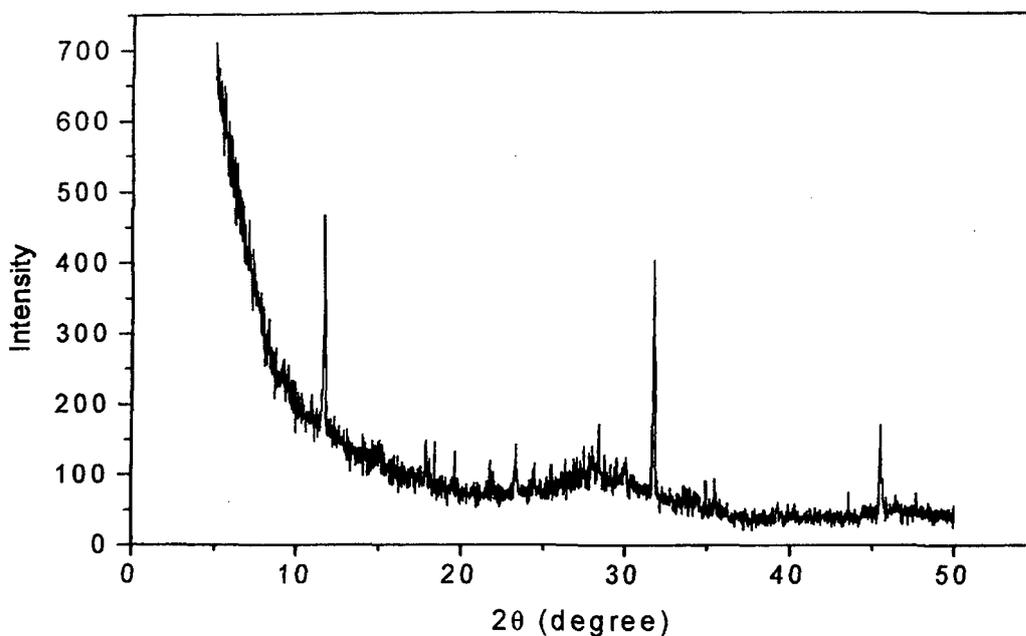


Fig.IV.1: Powder XRD of aluminium vanadate

The IR-spectrum of the compound (Fig. IV.2) shows the characteristic peaks at 986 cm^{-1} , 860 cm^{-1} and 814 cm^{-1} and 682 cm^{-1} assignable to the $\nu_{(V=O)}$ modes of the cyclic vanadate ion [19].

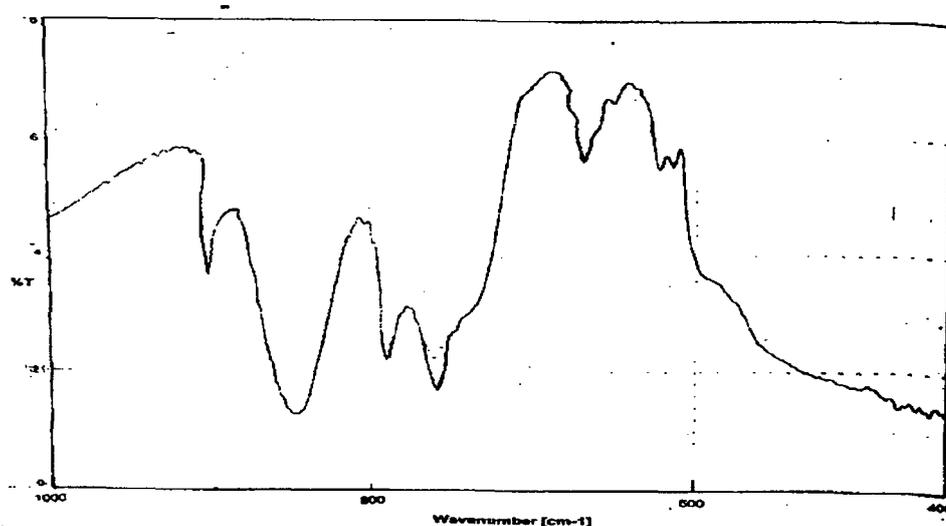


Fig. IV.2: IR Spectrum of the aluminiumvanadate exchanger

IV.3.1.a. Thermal stability, radiation and chemical stability

Thermal stability of the exchanger was studied by differential thermo gravimetric analysis (TGA). Thermal analysis of the material shows that the compound is thermally stable up to 150 °C (Fig. IV.3) though there is an endothermic peak near 100 °C, the indication of loss of water molecules at 100 °C.

Radiation stability was checked by determining the ion exchange capacity (IEC) of the solid before and after irradiation with ^{60}Co gamma-rays at a dose rate of 4.0 kGy/h. Radiation stability of the exchanger was studied by determining the exchanging capacity of the solid material as 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 35.0 kGy. However, the ion exchange capacity decreases when exposed to still higher doses.

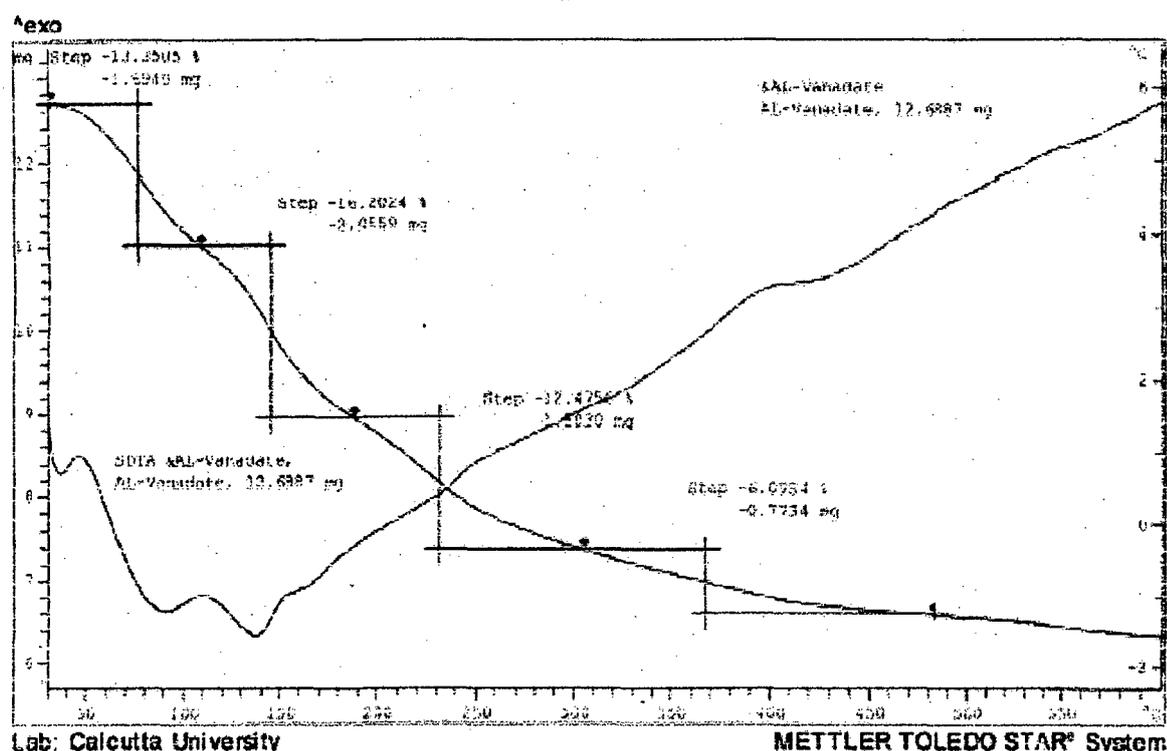


Fig. IV.3: Thermal analysis curve of aluminiumvanadate ion exchanger

Chemical stability was determined by immersing about 0.5 g of the exchanger in 50.0 mL of different mineral acids and solvents for periods of 16 h and after chemical

treatment, recovered exchanger was dried and checked for its IEC with Na^+ ion. The exchanger is quite stable in normal chemical environment. The chemical stability of the exchanger in different acid and alkali media of different concentration has been checked by comparing the exchange capacity of sodium ion. From this experiment it has found that the material is stable in mineral acid. In strongly oxidizing acids the material degrades as the results shows that the exchange capacity reduces on and from 10.0 mol. L^{-1} hydrochloric acid, 6.0 mol. L^{-1} nitric acid, and 6.0 mol. L^{-1} sulphuric acid. The compound was quite stable in normal chemical environment. The compound was found to be insoluble in water, alcohol, moderately concentrated acid and alkali and other common organic solvents.

IV.3.1.b. pH metric titration curve

The pH metric titration curve shown in (Fig.IV.4) where the observed variation of pH was plotted against the amount of alkali added. The graph clearly indicates that there is only one inflection point in the curve, which corresponds to the exchange capacity of this material for Na^+ of more than 3.0 meq/g of the exchanger.

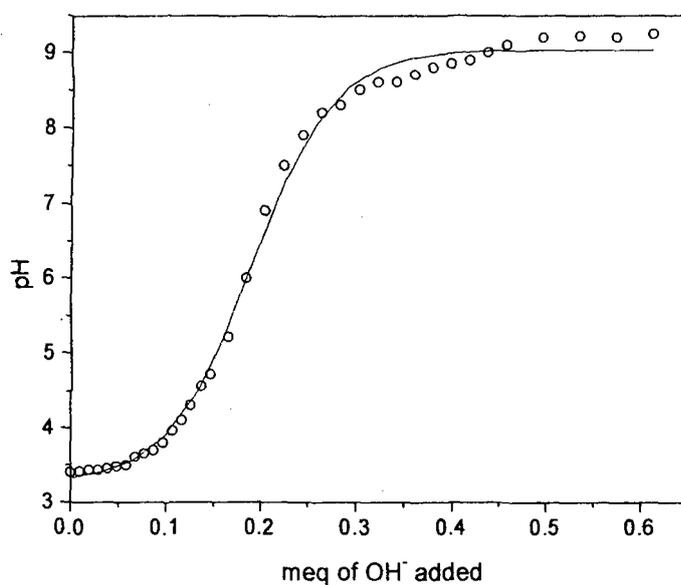


Fig.IV.4: pH-metric titration curve of the ion exchanger (Exchanger: 0.1 g and the strength of NaOH: 0.099 mol. L^{-1})

IV.3.1.c. Sorption behavior of metal ions

The sorption behavior of different alkali and alkaline metal ions onto this compound has been determined by batch technique. The evaluated values of the exchange capacities of the metal ions are tabulated in (Table IV. 1) and these data show that the compound can be employed as an exchanger. The ion exchange capacity has decreased with increase of atomic number within a group with increase of ionic radius of the corresponding cation as the exchange capacities and the ionic radii are in the same order of Li^+ (90 pm) > Na^+ (116 pm) > K^+ (152 pm) > Cs^+ (181 pm) and Mg^{2+} (86 pm) > Ca^{2+} (114 pm) > Sr^{2+} (132 pm) > Ba^{2+} (149 pm). Again, the exchange capacity of the material for ammonium ion is the highest and the ion exchange capacities for the alkali metal ions are relatively higher than those for the alkaline earth metal ions.

Table IV .1. Ion exchange capacity for different cations

Metal ions	Exchange capacity (meq/g)	Metal ions	Exchange capacity (meq/g)
Li^+	3.095 ± 0.003	Mg^{2+}	1.537 ± 0.002
Na^+	3.050 ± 0.004	Ca^{2+}	1.310 ± 0.004
K^+	2.987 ± 0.002	Sr^{2+}	1.059 ± 0.003
Cs^+	2.702 ± 0.005	Ba^{2+}	0.923 ± 0.002
NH_4^+	3.602 ± 0.006		

IV.4. Application of the exchanger

IV.4.1. Application of exchanger in radiochemical separations

The studies of radiochemical separation were carried out in column method taking a glass column of 5.0 cm length and 1.0 cm inner diameter packed with the exchanger (1.0 g) in each case.

IV.4.1a. Separation of ^{137}Cs - $^{137\text{m}}\text{Ba}$ pair

For the separation of $^{137\text{m}}\text{Ba}$ ($t_{1/2} = 2.55$ min.) from its parent ^{137}Cs ($t_{1/2} = 30\text{y}$), the column bed was first conditioned with 0.01 mol. L^{-1} HCl solution. A sample volume of 2.0 mL solution of measured radioactivity of cesium and barium radionuclides was passed through the column at 1.0 mL/min flow rate. The adhered activity was washed out by passing 10.0 mL of 0.01 mol. L^{-1} HCl solutions through the column. Then, the fraction of $^{137\text{m}}\text{Ba}$ was eluted with $0.0426\text{ mol. L}^{-1}$ ascorbic acid solution and it was followed by collecting the eluate in ten successive counting tubes (1.0 mL each). The γ -activity of the each tube was recorded with the help of NaI(Tl) γ -ray spectrometer several times with a time gap of 30 sec . The purity of the daughter fraction was checked by its decay curve (Fig.IV.5).

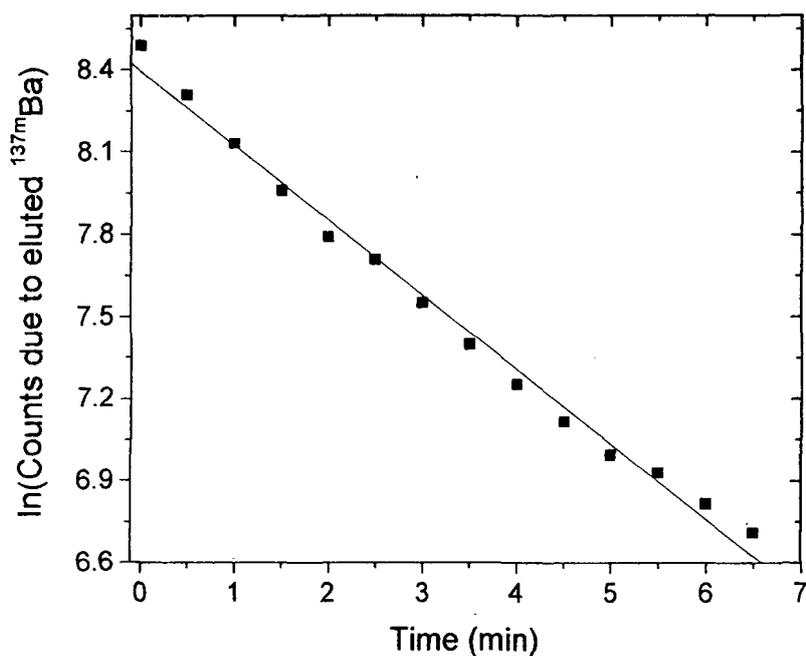


Fig.IV.5: Decay curve (Slope = -0.27256 ± 0.00739) of $^{137\text{m}}\text{Ba}$ ($t_{1/2} = 2.55$ min) taking the count of the eluate (eluent: $0.0426\text{ mol. L}^{-1}$ ascorbic acid solution) by NaI(Tl) detector

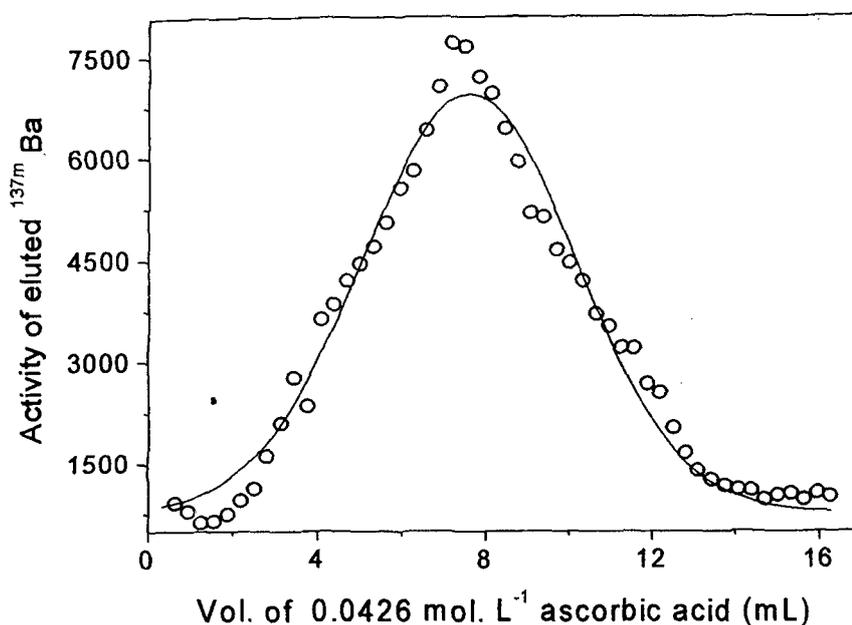


Fig IV.6: Elution curve of ^{137m}Ba daughter by 0.0426 mol. L⁻¹ ascorbic acid solution

IV.4.1b. Separation of ¹¹⁵Cd-^{115m}In pair

The column bed was equilibrated at pH = 7.0 by passing pure d.d. water for the separation of ^{115m}In ($t_{1/2} = 4.5$ h) from its parent ¹¹⁵Cd. The equilibrium mixture was evaporated to dryness and then the dried mass was dissolved in water. The solution was then directly fed into the column containing the exchanger at 1.0 mL/min flow rate. After absorption of the mixture, 5.0 mL d.d. water was passed through the column to ensure the total absorption of the mixture. The activity due to the daughter ^{115m}In was eluted with 4.0 mol. L⁻¹ HCl solutions and it was followed as above. Here, the γ -activity of the each tube was measured several times with a time gap of 1 h. The γ -spectra of the mixture of ¹¹⁵Cd-^{115m}In in water before separation and the γ -spectra of the eluate after separation were also recorded (Fig.IV.7).

Not only from the elution curve but also from the decay measurement from the graph (Fig. IV.8) of the eluent, it is clearly shows that the half life of the eluent is 4.51 h,

which is very close to the half life of ^{115m}In . So it is concluded that ^{115m}In could be eluted ^{115}Cd from the column by using $4.0 \text{ mol. L}^{-1} \text{ HCl}$ solution.

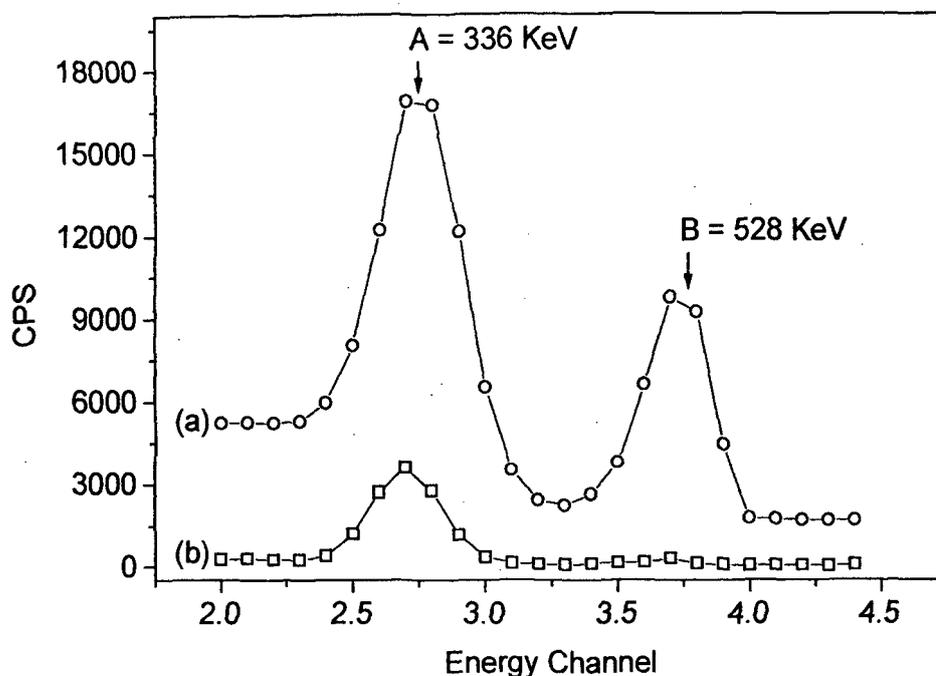


Fig.IV.7: γ -spectra of (a) the mixture of $^{115}\text{Cd} - ^{115m}\text{In}$ before separation and (b) the eluate after separation; peak A for ^{115m}In and peak B for ^{115}Cd ; [336 KeV of ^{115m}In and 528 KeV for ^{115}Cd ; eluent : $4.0 \text{ mol. L}^{-1} \text{ HCl}$]

IV.4.1c. Separation of $^{198}\text{Au} - ^{110m}\text{Ag}$ pair

For the separation of ^{198}Au ($t_{1/2} = 2.69$ days) from the synthetic mixture of ^{198}Au and ^{110m}Ag , the exchanger (1.0 g) in another column was equilibrated at $\text{pH} = 2.0$ by passing nitric acid solution. A sample volume of 1.0 mL solution containing 0.5 mL each of ^{198}Au and ^{110m}Ag radiotracers was passed through the column at 1.0 mL/min flow rate followed by the passing of 5.0 mL solution of $\text{pH} 2.0$ through the column bed to wash out the adhered activity. At first the activity due to ^{198}Au was eluted out with alcoholic solution of 0.01 % rhodamine-B and then the ^{110m}Ag activity was eluted with 0.5 % thiourea solution in $0.1 \text{ mol. L}^{-1} \text{ HClO}_4$. The purities of both of the fractions were checked by γ -spectra in which absence of other component indicated the success of the separation procedure.

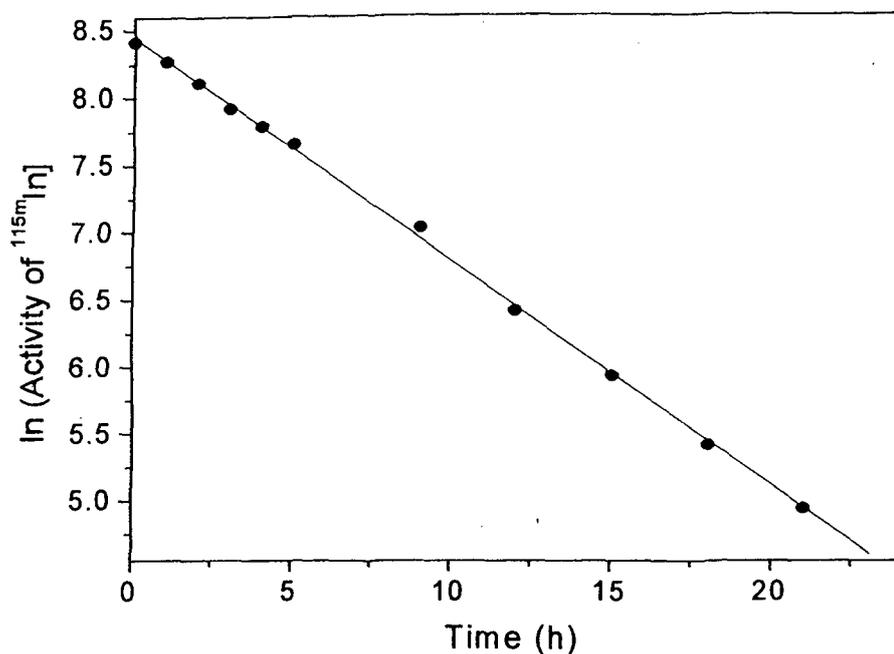


Fig. IV.8: Decay curve (Slope = -0.16642 ± 0.00182) of ^{115m}In ($t_{1/2} = 4.51$ h) taking the count of the eluate (eluent : 4.0 mol. L^{-1} HCl solution) by NaI(Tl) detector

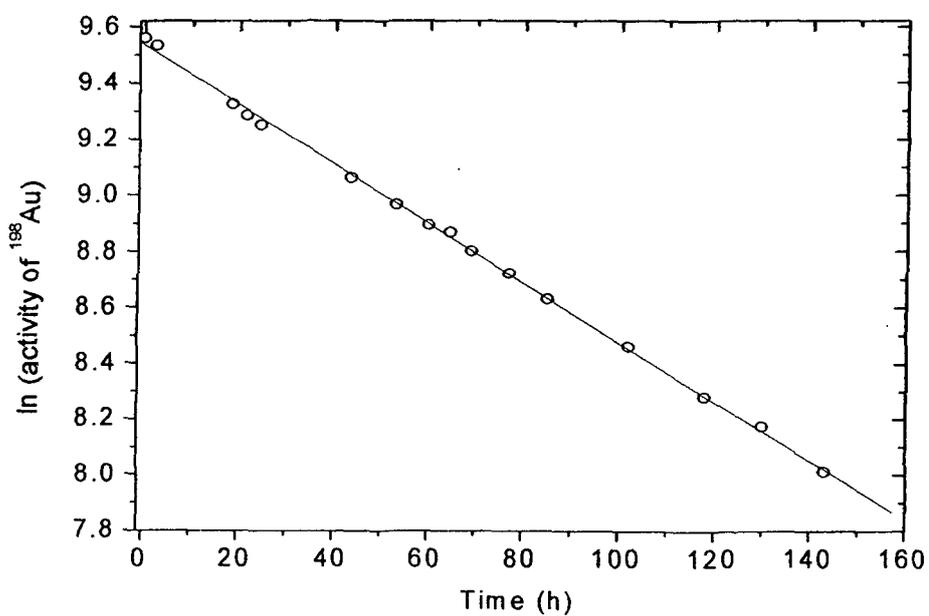


Fig. IV.9: Decay curve (Slope = -0.0106 ± 0.0001) of ^{198}Au by plotting $\ln(\text{counts})$ vs. time; eluent : 0.01% rhodium B in ethanol; $t_{1/2} = 2.70$ days.

IV.4. Epilogue

A new polyoxometallate has been synthesized and characterized spectroscopically. This material has been applied in successful separation of the short-lived daughter radionuclides and confinement of long-lived parent radionuclides. This material could be used as a potent solid exchanger in radionuclide generators of inexpensive and convenient alternative of in-house radioisotope production facilities from where carrier-free daughter activity ($^{137m}\text{Ba}/^{115m}\text{In}$) may be milked out after a definite time of interval from their respective radioactive long-lived parent radionuclides. Such generator system might be used for a long period of time. From the experimental results of the separation of ^{115m}In from ^{115}Cd , it is revealed that this exchanger can also be safely employed in the separation of cyclotron produced ^{111}In ($t_{1/2} = 67.9$ h) from ^{111}Cd (p, n) nuclear reaction as ^{111}In is a promising radionuclide to produce radiopharmaceuticals [8-10]. In another column operation, it has been found that the sorption of both gold and silver onto this material at pH 2.0 and this solid exchanger material is also useful in the successful separation of the two precious metal ions, gold and silver at trace level.

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