

PREFACE

In his closing remarks to the international conference on Ion Exchange (IEX' 88) held at Cambridge in 1988, Dr. Robert Kunin expressed the firm opinion that had he the opportunity to start his scientific life again, he would devote his career to the inorganic ion exchange materials.

This comment, coming from one of the most eminent pioneers of resin technology, was an acknowledgement of the potential offered by inorganic materials to provide robust, highly selective exchange media, at the costs competitive to the relatively unselective and less stable resins.

The last few decades have seen a clear revival in inorganic ion exchange studies a major area has been in the study of zeolites. So far as non zeolitic inorganic ion exchangers are concerned, the acidic salt of multivalent metals with polybasic acids deserved special mention due to the immense potentiality offered by them during the manifestation of ion exchange behavior. A wide range of compounds of this type has been described in early literatures. Among the materials studied are the cations zirconium(IV), thorium(IV), titanium(IV), cerium(IV), tin(IV), chromium(III), etc. and the anion employed included phosphate, molybdate, arsenate, antimonite, vanadate, tungstate, tellurate etc. These salts acting mostly as cationic exchangers with gel like or microcrystalline materials, with the composition and properties depending upon the method of preparation and possess a high chemical, radiation and thermal stability. The cation exchange properties arise from the presence of readily exchangeable hydrogen ions. Besides possible application of these exchangers in chemical processing of radioactive materials and in treatment of contaminated moderator and cooling water in nuclear reactors working at high temperatures and pressure, new applications have recently been found such as in water desalination process and in fuel cells employing ion exchange membranes for transport of hydrogen ions. The present dissertation is the result of the investigations carried out mainly with this background.

The research work embodied in this thesis entitled “**synthesis and applications of inorganic ion exchangers in radioanalytical separations**” was initiated in the year of 2003. The thesis contains seven chapters of which five chapters include the experimental part describing the synthesis, characterization and applications of the exchangers.

Inorganic ion exchangers are now currently used in separation chemistry and these are now widely employed in most of the analytical works such as preconcentration, separation, determination and speciation of different metal ions due to high selectivity, low cost, low consumption of organic solvent (i.e. ecofriendly) over all other separation techniques and also greater simplicity in chemical procedure.

Chapter I contains a general introductory discussion about different inorganic ion exchangers, radiochemical separation techniques by using inorganic ion exchangers, cause and its advantages over other techniques. Here, we also review the synthesis of some inorganic ion exchanges and their applications in different analytical fields, radioanalytical separations in particular. At the end of this chapter, we have briefly described the aim of the present investigation and also materials used in experimental part.

Chapter II deals with the synthesis of a new polyoxometalate of chemical formula, $\text{Na}_2(\text{H}_2\text{O})_4(\text{H}_3\text{O})[\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ containing Anderson type large anion. Its synthesis and characterization by single-crystal X-ray structure determination and IR-spectroscopic studies are described. The compound behaves as an ion exchanger and is stable in thermal, radiation and chemical environments. Radiochemical separation of ^{137}Cs - $^{137\text{m}}\text{Ba}$ using this new ion exchanger has been reported.

Chapter III describes the synthesis of another new inorganic ion exchanger, cerium(IV)iodotungstate. The material has been synthesized and characterized by elemental analysis and IR-spectroscopy. This inorganic compound is highly stable towards thermal, chemical and radiation dose. It has appreciable ion exchange capacity for many metal ions and has been employed in the separation of ^{90}Y from its parent ^{90}Sr from an equilibrium mixture. The adsorbed daughter was recovered using $0.0063 \text{ mol. L}^{-1}$ EDTA at pH 6.

Chapter IV describes the synthesis of a new inorganic ion exchanger aluminiumvanadate. The exchanger is characterized by elemental analysis, spectroscopic tools and powdered X-ray diffraction. The 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 metal ions are very high compare to alkaline earth metal ions. The successful radiochemical separation of ^{137}Cs - $^{137\text{m}}\text{Ba}$, ^{115}Cd - $^{115\text{m}}\text{In}$ and ^{198}Au - $^{110\text{m}}\text{Ag}$ can be performed over this new ion exchangers. Elutions of $^{137\text{m}}\text{Ba}$ and $^{115\text{m}}\text{In}$ were performed using $0.0426 \text{ mol. L}^{-1}$ ascorbic acid solution and 4.0 mol. L^{-1} HCl respectively after sorption of the equilibrated mixtures ^{137}Cs - $^{137\text{m}}\text{Ba}$ at 0.01 mol. L^{-1} HCl medium and ^{115}Cd - $^{115\text{m}}\text{In}$ at pH 7.0 respectively. ^{198}Au - $^{110\text{m}}\text{Ag}$ mixtures were absorbed at pH 2.0. (nitric acid medium) and elution of gold by 0.01 % alcoholic solution of rhodamine-B and 0.5 % thiourea solution in 0.1 mol. L^{-1} HClO_4 for silver was achieved without any change in exchanger matrix.

Chapter V presents the preparation of a new solid phase ion exchanger quinolinephosphomolybdate. The exchanger was characterized by elemental analysis and IR-spectroscopy. This material is highly stable towards thermal, chemical and radiation dose. This absorbant exhibits an excellent ion exchange capacity for many metal ions. The exchanger can be employed in the separation of ^{90}Y from its parent ^{90}Sr from an equilibrium mixture. The absorbed daughter was recovered by using $0.0284 \text{ mol. L}^{-1}$ ascorbic acid solution buffered at pH-5.

Chapter VI describes the synthesis of a novel inorganic ion exchanger aluminium tungstate and characterisation 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}Cs - $^{137\text{m}}\text{Ba}$. The newly synthesized crystalline inorganic ion exchanger was employed to separate $^{137\text{m}}\text{Ba}$ in no-carrier added state from ^{137}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. This is specially true as the half-life of the daughter is very low.

Finally we have established these systems as potent ion exchanger to be used for further development of the subject in a conclusive way. In keeping with the general practice of reporting scientific observations, due acknowledgements have been made whenever the work has been described on the basis of other investigators. I must take responsibility of any unintentional oversight and error which might have been incorporated in spite of due precautions.

**Department of Chemistry
The University of Burdwan
Burdwan -713104
W.B., India**

(Sanjoy Dhara)