



# Ammonium molybdophosphate impregnated alumina microspheres as a new generation sorbent for chromatographic $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$ generator

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## ABSTRACT

Barium-137m availed from a  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator is an attractive industrial radiotracer for liquid flow rate measurement owing to its short half-life ( $T_{1/2} = 2.5$  min) and emission of highly energetic gamma radiation ( $E_\gamma = 661.7$  keV). Ammonium molybdophosphate (AMP) impregnated alumina microspheres (AMP- $\text{Al}_2\text{O}_3$ ), an engineered form of sorbent material was synthesized by Gel Entrapment Technique (GET). The utility of the material in the preparation of  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator was evaluated. Various experimental parameters were optimized for efficient retention of  $^{137}\text{Cs}$  and selective elution of  $^{137\text{m}}\text{Ba}$ . A chromatographic 0.74 GBq (20 mCi)  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator was developed using this material and its performance was evaluated for 6 months. Barium-137m could be eluted from the generator using 0.1 M  $\text{NH}_4\text{NO}_3 + 0.5$  M  $\text{HNO}_3$  solution with >80% yield and with acceptable radionuclidic purity suitable for industrial radiotracer investigations.

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## 1. Introduction

The technical, economic and environmental benefits of the radiotracer technology have been well demonstrated and recognized by the industrial sectors. The use of short-lived gamma-emitting radiotracer can be valuable for numerous industrial applications [1]. Ensuring timely availability of short-lived radiotracers at the industrial site is the main hurdle towards use of radiotracer techniques in industries. A convenient availability of short-lived radiotracer, without the expense of an on-site cyclotron or reactor facilities lies in the utilization of a radioisotope generator. The generator can also be used in tracer studies in emergency situations, routine inspections and process control, especially in remote areas as well as for repeated tracer studies in pilot plants and laboratories.

There is a great deal of interest in the use of  $^{137\text{m}}\text{Ba}$  ( $T_{1/2} = 2.5$  min) as an industrial radiotracer due to its energetic gamma emission ( $E_\gamma = 661.7$  keV, 85.12%) [2]. The short half-life of the  $^{137\text{m}}\text{Ba}$  has been cited as an advantage, leading to multiple elutions from a single generator and facilitating repeated studies on the same subject within a short time interval. It eliminates concerns about site contamination, environmental persistence, and waste disposal issues. The  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator has emerged as the most popular source for availing  $^{137\text{m}}\text{Ba}$ . The long half-life

( $T_{1/2} = 30$  y) of the parent radionuclide  $^{137}\text{Cs}$  ensures convenient availability of  $^{137\text{m}}\text{Ba}$  for long periods of time. Barium-137m is a very useful radiotracer for liquid flow rate measurement [3,4] because of its highly energetic gamma ray which can be easily detected outside the pipes. It is also possible to install the generator into an industrial assembly to provide continuous supply of  $^{137\text{m}}\text{Ba}$  tracer into the process stream for flow rate measurement.

The  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generators available commercially are of very low activity (typically 370 kBq), intended for the demonstration purposes in academic institutions. The current demand for the  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator of durable construction, amenable for industrial applications is perceived to be rather small to make its commercial production economically attractive. Concerted efforts are therefore necessary to undertake the development of  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generators in order to realize the scope of accessing  $^{137\text{m}}\text{Ba}$  in several MBq quantities for industrial radiotracer studies.

Several column chromatographic  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator systems using variety of inorganic exchangers have been reported over the past several years [5–15]. Out of these ion-exchangers, ammonium molybdophosphate (AMP) received the maximum attention owing to its high specificity towards  $\text{Cs}^+$  ion and stability in the radioactive media [16]. However, AMP has a microcrystalline structure having particle size in the range of 1–5  $\mu\text{m}$  [17–25] which is impervious to liquid, thereby rendering it unsuitable for use in column application in pure form. In order to overcome the problems associated with fine particle size, the AMP particles must be engineered into an acceptable granular form. During the last two decades, several techniques to fix AMP on different

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supporting matrices such as asbestos [18], silica gel [26], Amberlite XAD-7 [27], polyacrylonitrile (PAN) [28,29], calcium alginate [30], cenospheres [31] and  $\text{Al}_2\text{O}_3$  [32,33] have been developed to make engineered forms of materials suitable for column operations. Out of these, AMP–PAN has been extensively studied and used for the removal of  $^{137}\text{Cs}$  from high level acidic radioactive waste at Idaho National Engineering and Environmental Laboratory (INEEL), USA [34–36]. Although granulated AMP containing organic materials as supporting matrices provides excellent flow characteristics, issues regarding the potential radiation degradation of the polyacrylonitrile (PAN) binder under long-term use are yet to be addressed. The degradation of organic materials would result in  $^{137}\text{Cs}$  breakthrough in the  $^{137\text{m}}\text{Ba}$  eluate, which in turn would interfere in radiotracer investigations. In view of the above described drawbacks, use of inorganic matrix to make an engineered form of AMP is ideally suited for such type of applications.

In this context, the use of AMP– $\text{Al}_2\text{O}_3$  microspheres developed by our group [32] using Gel Entrapment Technique (GET), as a column matrix for chromatographic  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator deemed worthy of consideration. The inorganic back bone of the microsphere could be of valuable attribute towards the preparation of a chromatographic  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator suitable for industrial radiotracer applications. In this communication, we describe the overall synthesis procedure, structural characterization, sorption properties assessment, development of AMP– $\text{Al}_2\text{O}_3$  based  $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$  generator, evaluation of long-term operation and assessment of the quality of the separated  $^{137\text{m}}\text{Ba}$  for industrial radiotracer applications.

## 2. Materials and methods

### 2.1. Materials

Reagents including nitric acid, ammonium hydroxide, etc. were of analytical grade and were procured from S.D. Fine Chemicals, Mumbai, India. Ammonium nitrate, aluminum nitrate, ammonium molybdate, hexamethylenetetramine (HMTA), urea, and citric acid were of analytical grade and obtained from E. Merck, Mumbai, India. Radioisotopes such as  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$  and  $^{133}\text{Ba}$  were available in the Radiopharmaceuticals Division, BARC.

### 2.2. Equipments

A mechanical wrist-action shaker (Secor, India) was used for batch equilibrium studies. An HPGe Multichannel analyzer (coaxial photon detector system, Canberra Eurisys, France) with a 0.5 keV resolution and range from 1.8 keV to 2 MeV was used for gamma spectrometric analysis and also for quantitative estimation. The trace level of metal contaminations was estimated using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-ES JY-238, Emission Horiba Group, France). Standard  $^{152}\text{Eu}$  source of known strength was used for efficiency calibration of the detector. The activity of  $^{133}\text{Ba}$  and  $^{134}\text{Cs}$  were measured by  $\gamma$ -spectrometry by the quantification of 356 keV and 605 keV photo peaks, respectively. All samples were counted at the same geometry.

### 2.3. Synthesis of AMP

Ammonium molybdophosphate (AMP) used in this work was synthesized adopting the reported citromolybdate procedure [20]. A solution containing a mixture of citric acid (81 g), ammonium nitrate (81 g) and ammonium paramolybdate (102 g) in 2 L of distilled water was poured into 2 L nitric acid solution (7 M) in a 5 L capacity beaker with constant stirring. Then, 10 mL of 5% solution of diammonium hydrogen phosphate was added slowly to this reaction mixture and the mixture was heated to boiling. The precipitate

thus formed was allowed to settle down and subsequently it was filtered and dried under infrared lamp at  $\sim 60^\circ\text{C}$ .

### 2.4. Synthesis of the gel spheres (AMP– $\text{Al}_2\text{O}_3$ )

A broth solution was prepared by mixing AMP powder with a solution containing 1.4 M aluminum nitrate, 1.54 M urea and 1.54 M hexamethylenetetramine at a temperature of  $5^\circ\text{C}$ . The droplets of this broth were passed through hot silicone oil at  $95^\circ\text{C}$  during which they gelled [37]. The spheres were separated from the oil, degreased with carbon tetrachloride ( $\text{CCl}_4$ ) and then washed thoroughly with 0.1 M  $\text{NH}_4\text{OH}$  solution followed by washing with deionized water to remove the chemical impurities that might have percolated inside the spheres. The washed gels were then calcined at  $200^\circ\text{C}$ ,  $300^\circ\text{C}$  and  $380^\circ\text{C}$  for 10 h. After thermal treatment, the prepared gel particles were cured in ambient temperature for 24 h under vacuum.

In order to estimate the AMP content in the gel, 1 g of the material was crushed in an agate mortar using a pestle. The powder obtained was treated with 2 M NaOH solution in which AMP got dissolved. This solution was filtered and the filtrate was acidified. On acidification, AMP got precipitated and the amount of precipitate was estimated gravimetrically.

### 2.5. Chemical stability of AMP– $\text{Al}_2\text{O}_3$ microspheres

The chemical stability of the AMP– $\text{Al}_2\text{O}_3$  sorbent prepared was assessed in  $\text{HNO}_3$  and  $\text{NH}_4\text{NO}_3$  solution of strength 0.1–6 M. A weighed amount of the sorbent material (1 g) was placed in 50 mL solvent of interest and kept for 24 h with continuous shaking at room temperature. Subsequently it was filtered and the level of Al and Mo metal ions in the filtrate was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

### 2.6. Determination of the distribution ratios ( $K_d$ ) of $\text{Cs}^+$ and $\text{Ba}^{2+}$ ions

The distribution ratios ( $K_d$ ) of  $\text{Cs}^+$  and  $\text{Ba}^{2+}$  ions for the AMP– $\text{Al}_2\text{O}_3$  matrix were measured at different acid concentrations, using  $^{134}\text{Cs}$  and  $^{133}\text{Ba}$  as radiotracers. In each experiment, 200 mg of sorbent was suspended in 20 mL solution containing the radioactive metal ions, in a 50 mL stoppered conical flask. The flasks were shaken in a wrist arm mechanical shaker for 1 h at  $25^\circ\text{C}$  and then filtered. An aliquot of the solution before and after equilibration were measured in a well type NaI(Tl) counter using appropriate window ranges (300–400 keV for  $^{133}\text{Ba}$  and 600–650 keV for  $^{134}\text{Cs}$ ). The distribution ratios were calculated using the following expression:

$$K_d = \frac{(A_i - A_{eq})V}{A_{eq}m} \text{ L g}^{-1}$$

where  $A_i$  is the initial total radioactivity of 1 mL of the solution,  $A_{eq}$  is the unadsorbed activity in 1 mL of the solution at equilibrium,  $V$  is the solution volume ( $\text{cm}^3$ ) and  $m$  is the mass (g) of the sorbent. All measurements were carried out at  $25^\circ\text{C}$  in triplicate.

### 2.7. Determination of sorption capacity of AMP– $\text{Al}_2\text{O}_3$

#### 2.7.1. Static sorption capacity

The static sorption capacity of the sorbent (AMP– $\text{Al}_2\text{O}_3$ ) for  $\text{Cs}^+$  ions was determined by batch equilibration method. For this, 50 mL of cesium nitrate solution ( $1 \text{ mg Cs mL}^{-1}$ ) prepared in double distilled water was taken in a flask. The solution was then spiked with  $\sim 10 \mu\text{Ci}$  (370 kBq) of  $^{134}\text{Cs}$ . A known amount of sorbent material (here 0.5 g of AMP– $\text{Al}_2\text{O}_3$ ) was added to the flask and the mixture was kept in a shaker for  $\sim 1$  h at room temperature. The activity of

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