Separation and Purification Technology 124 (2014) 179–185

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

# Perchloric acid: A promising medium for the chromatographic separation of $^{90}$Y from $^{90}$Sr

Chirag K. Vyas [a], Pranav M. Joshirao [a], Vijay K. Manchanda [a,b,*]

[a] Department of Energy Science, Sungkyunkwan University, Suwon 440746, South Korea
[b] School of Electronics and Electrical Engineering, Sungkyunkwan University, Suwon 440746, South Korea

ARTICLE INFO

*Article history:*
Received 7 August 2013
Received in revised form 9 January 2014
Accepted 16 January 2014
Available online 28 January 2014

*Keywords:*
Yittrium-90
Strontium selective resin
Tetraoctyldiglycolamide resin
Distribution coefficient
Extraction chromatography

ABSTRACT

There is growing demand to develop efficient separation methods to produce high purity $^{90}$Y (required for radiopharmaceutical applications) from the secular equilibrium mixture of $^{90}$Sr–$^{90}$Y. Studies for the chromatographic separation of $^{90}$Y from $^{90}$Sr using ditertiarybutyl dicyclohexano 18-crown-6 (Sr-selective resin) and N,N,N′,N′-tetraoctyldiglycolamide (Y-selective resin) sequentially were performed in $HNO_3$, HCl and $HClO_4$ media. Batch studies for distribution coefficient data and column studies for chemical separation were carried out under conditions of varying acidity and varying metal ion concentration. Experiments were carried out on tracers (radioactive/stable) in a wide range of acidity (pH 2–5 M). Distribution coefficient values of Sr(II) in Sr-selective resin and of Y(III) in Y-selective resin were distinctly larger and of Sr(II) in DGA-resin were distinctly lower in perchloric acid medium as compared to those in nitric acid/hydrochloric acid media suggesting that former is distinctly a better medium for the production of high purity $^{90}$Y. The mechanism of extraction changes with the nature and concentration of acid as well as with the metal ion concentration.



## 1. Introduction

$^{90}$Y is a pure beta emitter ($E_{\beta max.}$ = 2.28 MeV) with moderate half life ($t_{½}$ = 64 h), a stable daughter product $^{90}$Zr and continual supply from its long lived mother radionuclide, $^{90}$Sr ($t_{1/2}$ = 28.8 y) as shown in the following radiochemical equilibrium [1,2].

$$^{90}\mathrm{Sr} \xrightarrow[28.8\ \mathrm{y}]{\beta^- (0.54\ \mathrm{MeV})} {}^{90}\mathrm{Y} \xrightarrow[64\ \mathrm{h}]{\beta^- (2.28\ \mathrm{MeV})} {}^{90}\mathrm{Zr}\ (\mathrm{stable})$$

$^{90}$Y is therefore one of the best therapeutic radionuclide candidates for radiolabeling of pharmaceuticals for cancer treatment, radiation synovectomy, bone palliation, rheumatoid arthritis and plays a topical role in tumor therapy when chelated with tumor-targeted antibodies in nuclear medicine [3–8]. Unlike external beam radiation source, $^{90}$Y bearing microspheres have been proved to be more precise and specific in dose delivery to the targeted tumor [9–11]. Due to the low activation cross-section of $^{89}$Y (0.001 b) and presence of large amount of carrier, production of $^{90}$Y via neutron activation is not an acceptable route for its applications in radiopharmaceuticals. On the other hand high specific activity (carrier free) $^{90}$Y production can be achieved from $^{90}$Sr, which is a high yield fission product and is readily available in multi curies concentration in spent nuclear fuel of a power reactor. Cumulative yield of $^{90}$Sr with fast neutrons is particularly high for Th based reactors (7.3% in case of $^{232}$Th and 6.4% in case of $^{233}$U) suggesting spent fuels of future Th based reactors as a rich source of $^{90}$Y [12]. $^{90}$Sr(II), a pure beta emitter is chemically similar to Ca(II) and is a bone seeker, and hence is a potential hazard if present as a contaminant in $^{90}$Y. Maximum permissible body burden (MPBB) of $^{90}$Sr is 74 KBq (2 μCi) and the desired D.F values of $^{90}$Y with respect to $^{90}$Sr is >$10^5$ [13,14].

Separation and purification method of $^{90}$Y should meet following requirements: (a) Decontamination Factors (D.F.), defined as the ratio of concentration of $^{90}$Y/concentration of impurity or impurities in the product stream to that in the feed solution, with respect to critical impurities should be above threshold value specified by the radiopharmacist; (b) duration of purification cycle should be as low as possible to minimize the losses of $^{90}$Y, due to nuclear decay, (c) volume of the final eluted product should be as low as possible to conform to the specific activity requirements, (d) volume of the liquid waste should be as low as possible and (e) chemical composition of the final purified radionuclide with respect to acidity and complexing agent should conform to the specifications laid by the radiopharmacist. It is particularly important to ensure that the metal ions having large chelate formation constants with 1,4,7,10-tetraazacyclododecane-N,N′,N″,N‴-tetraacetic acid (DOTA),

* Corresponding author at: Department of Energy Science, Sungkyunkwan University, Suwon 440746, South Korea. Tel.: +82 31 299 6272; fax: +82 31 299 4279.
*E-mail addresses:* vkm49@skku.edu, vkm25749@gmail.com (V.K. Manchanda).

http://dx.doi.org/10.1016/j.seppur.2014.01.026
1383-5866/

a promising bifunctional chelating agent candidate for use in radioimmunotherapy with $^{90}$Y, are below the threshold concentrations to avoid any competition with the binding of $^{90}$Y(III). Similarly, the eluting complexing molecules should not compete with complexation of DOTA with $^{90}$Y(III). However, most of the existing methods suffer from drawbacks of poor $^{90}$Y recovery and multiple steps/large waste volumes to achieve desired D.F. [15–27]. Further work is needed to develop a $^{90}$Sr–$^{90}$Y generator which is radiation/acid resistant, simple in operation, economic and meets the criterion mentioned above. Radiochemical separation methods like precipitation, ion exchange, solvent extraction, extraction chromatography and liquid membrane, have been reported in literature for effective separation of $^{90}$Y from $^{90}$Sr using selective extractants. Extraction chromatography due to its favorable features like low volume of volatile organic solvents as well as low volume of waste and of product aqueous stream is the most suitable technique for separation of radionuclides and has been investigated for setting up $^{90}$Sr–$^{90}$Y generator [28–30].

Dhami et al. have reported separation of carrier-free $^{90}$Y from high-level liquid waste by extraction chromatographic technique using 2-ethyl hexyl-2-ethyl hexyl phosphonic acid (KSM-17), a two-stage Supported Liquid Membrane (SLM) based generator system principally based on the solvent extraction properties of KSM-17 and octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) [24]. Strontium selective resin (using ditertiarybutyl dicyclohexano 18-crown-6 (Fig. 1) in octanol as the stationary phase) has been used extensively for the separation, purification, isolation and concentration of strontium from high-level liquid waste as well as from environmental samples [31–39]. This resin is capable of purifying $^{90}$Sr(II) from large number of possible metal ion contaminants (including Ba(II), Hg(II), Pb(II), lanthanides and actinides in different oxidation states at 3 M $HNO_3$. DTBCH18C6 is also reported to withstand beta/gamma radiation at curie level.

Nature and concentration of the acid influences the separation behavior significantly [40]. It was demonstrated in our laboratory that perchloric acid offers a promising medium for the preferential leaching of $^{90}$Sr from irradiated $^{232}$Th and for its subsequent purification (by Sr selective resin) from fission/activation products as well as from thorium [41,42].

N,N,N′,N′-tetraoctyldiglycolamide (TODGA, Fig. 2) is a widely used extractant for the partitioning of the trivalent lanthanides and actinides from the high level radioactive liquid waste (HLW) by solvent extraction technique and as a stationary phase in extraction chromatography (EXC) studies [43–48]. Horwitz et al. have developed the DGA (diglycolamide, common name for N,N,N′,N′-tetraoctyldiglycolamide) based EXC resin and have shown its promising application as an efficient extractant for the uptake of different trivalent lanthanides and actinides using the DGA resin in $HNO_3$ and HCl medium. It was recommended for the final purification of $^{90}$Y(III) from $^{90}$Sr(II) where D.F. of $10^3$ is expected at 3 M acid [49]. Datta et al. have studied $^{90}$Sr–$^{90}$Y separation using TODGA in solvent extraction, extraction chromatography and liquid membrane studies, and they have

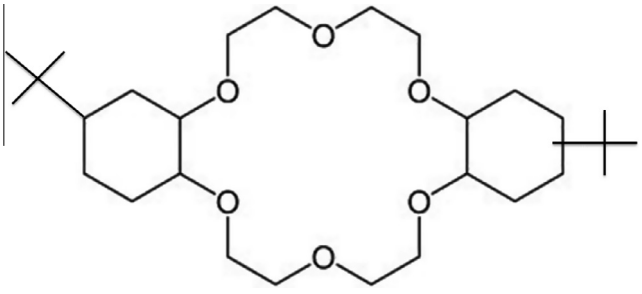

**Fig. 1.** 4,4′(5′)-Di-tert-butyldicyclohexano18-crown-6 (DTBCH18C6).

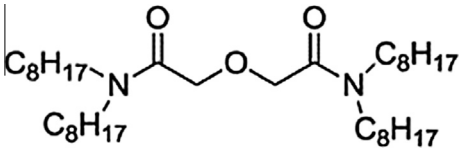

**Fig. 2.** Tetraoctyldiglycolamide (TODGA).

recommended separating $^{90}$Y from $^{90}$Sr using DGA extraction chromatography resin [50–54]. All the publications appeared so far on separation of $^{90}$Y from $^{90}$Sr using DGA resin have employed either $HNO_3$ or HCl medium and no work has been reported in $HClO_4$ medium.

Attempt has been made for the first time in the present work to optimize the extraction and purification of $^{90}$Y from $^{90}$Sr in perchloric acid medium using strontium selective and DGA resin sequentially. Distribution coefficient values for $^{90}$Sr(II) as well as $^{90}$Y(III) were obtained in both EXC resins in $HNO_3$, HCl and $HClO_4$ media. Column studies were also carried out in all the three media and the % recovery as well as D.F. values obtained were compared. The final elution of $^{90}$Y was done in 0.01 M EDTA at pH 4.0 which can be used for clinical applications after radiochemical processing.

## 2. Experimental

### 2.1. Reagents

Sr-selective resin, Sr-selective pre packed columns, DGA resin, DGA pre packed columns (Eichrom Tech. Inc. USA), Nitric acid 65% (Acros, USA), hydrochloric acid 36.5–38% (Acros, US), perchloric acid 70% (Showa, Japan), EDTA (Sigma Aldrich), liquid cocktail ULTIMA Gold (Perkin Elmer, USA) and 0.45 μl PTFE syringe filter (Whatman, USA) were used as procured. Radiotracers $^{90}$Sr–$^{90}$Y, were obtained from Eckert & Ziegler USA and $^{85}$Sr from Perkin Elmer USA.

### 2.2. Apparatus

$^{90}$Y and $^{90}$Sr were assayed using Perkin Elmer Quanta Smart automatic liquid scintillation counter whereas a well type NaI(Tl) Perkin Elmer (1480 WIZARD) automatic gamma detector was used to measure $^{85}$Sr activity. Measurement of Sr and Y concentration in inactive experiments (with stable isotopes) was carried out using either ICP-OES (Varian 720-ES) or ICP-MS (Agilent 7500 series). DGA column needs a special vacuum setup due to its particle size and hydrophobic nature and therefore DGA columns were operated using a vacuum box system procured from Eichrom Tech. Inc., USA.

### 2.3. $^{90}$Sr–$^{90}$Y separation

Separation of $^{90}$Y from $^{90}$Sr was achieved by using Sr-selective column [38,40]. The $^{90}$Sr–$^{90}$Y solution in secular equilibrium in 3 M $HNO_3$ was loaded on the column and washed with 7 free column volumes. This solution was then passed through two more columns sequentially to confirm the complete removal of $^{90}$Sr from $^{90}$Y. Purity of $^{90}$Y was ascertained by half life method [50]. $^{90}$Y thus obtained was further used for $K_d$ determination and extraction chromatographic studies.

### 2.4. Distribution coefficient studies

$^{90}$Y and $^{85}$Sr were used as radiotracers in the batch uptake studies. Distribution coefficient studies were carried out in plastic tubes with desired amounts of resin, volumes of acidic solution